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Effects of organic binders on the sintering of isostatically compacted zirconia powders

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Certain processing-related flaws in cold isostatically pressed ceramic powder compacts may arise from the delayed burn-out of organic binders until the sintering temperature is approached, although the isostatic compaction technique usually gives a higher and much more uniform green density than the conventional die compaction technique. For the 3 mol% Y_2O_3-doped zirconia powder in which 3 wt% PEG 1500 was introduced, the sintered density and sintering shrinkage were found to decrease in a near linear manner with increasing isostatic compaction pressure. The processing-related defects were identified as intergranular pores (1–5 μm). It is considered that these processing-related defects are a consequence of incomplete organic burn-out at low and intermediate temperatures in the heating-up period and the swelling of intergranular pores associated with the burn-out of residual organic binders at temperatures close to the sintering temperature. A higher calcination temperature and an extended calcination dwell time may be required to eliminate the organic residuals in the isostatically pressed ceramic powder compacts than in the conventional die-pressed samples.

1. Introduction

The mechanical properties of engineering ceramics are largely dependent on their microstructures which are, in turn, determined by the specific processing routes employed to fabricate these materials [1, 2]. Both in laboratory research and in industrial production, an organic binder is often used either in preparing ceramic powders or in forming ceramic powder compacts prior to sintering, to enhance the fracture strength of ceramic green compacts [3, 4]. It is very important to control the heating rate in sintering ceramic compacts in order to avoid any microstructural defects caused by the sudden burn-out of organic residuals, which could result in a large reduction in the sintered density and the formation of cracks at grain boundaries [5]. An appropriate dwell period at low or intermediate temperatures is required to eliminate the organic binders before any significant densification occurs close to and at sintering temperatures. The dwell temperature and time (usually at 300–800 °C for a few hours) will be dependent on the characteristics of the green compacts such as density and structural uniformity, and on the type and amount of the organic residuals. It has been demonstrated that a considerable increase in fracture strength can be achieved by means of careful selection of the dwell temperature and time in many ceramic systems.

The conventional uniaxial die pressing [6, 7] is the powder-forming technique most widely used both in research laboratories and industry for the production of advanced engineering ceramics. It offers the advantages of simplicity, low cost and high production efficiency. However, its application is largely limited in that it is unsuitable for making sophisticated shapes and the likelihood of potential compaction defects, such as non-uniform stress and density distributions and structural laminations. In contrast, cold isostatic pressing (CIP) [8, 9] of ceramic powders offers several advantages over the conventional die compaction, including higher and more uniform green density and, therefore, green strength, and the ability to make much more complex shapes. The burn-out of organic residuals (mostly as binders in ceramic processing) requires well interconnected channels to eliminate the gaseous components formed. It is therefore apparent that a cold isostatically pressed ceramic compact may require a higher calcination temperature and longer dwell period to complete the burn-out of a given volume fraction of organic binder without causing any greater structural degradation than would occur in a conventional die-pressed compact. This is a consequence of the more closely compacted and uniform green microstructure. The objective of the present work was to investigate the effects of organic binders on the microstructural development during sintering for isostatically pressed ceramic compacts, and to compare the results with those for the conventional die-pressed samples.

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2. Experimental procedure

High-purity 3 mol % Y_2O_3-doped zirconia powder, is a material sinterable at temperatures of 1450–1650 °C (sintered density >99% theoretical density). As indicated by the technical information on the ignition loss (0.9 wt %) given by the manufacturer, the as-received powder was considered to contain a low level of organic residuals, which were introduced during the powder preparation process in order to facilitate the spray drying of the chemically prepared powder. Polyethylene glycol (PEG 1500) 3 wt %, was added to the as-received powder in the following steps: (i) dissolving the desired amount of PEG 1500 in a small amount of distilled water; (ii) mixing the PEG–water solution with the ball milled zirconia powder–methanol suspension (using zirconia milling media, milled for 24 h to eliminate the spherical agglomerates formed as a result of spray drying); (iii) drying the mixed suspension using a heating lamp and hot plate. The dried powder was calcined at temperatures of 200, 400, 600, 800 and 1000 °C (for 5 h), respectively, to reduce the content of PEG 1500 in the powder. The dried and calcined powders were then compacted in a steel die of 12.5 mm diameter at various pressures from 30–300 MPa (thickness/diameter ratio 0.45), followed by an isostatic pressing in the pressure range 50–300 MPa at room temperature. The compacted samples were then sintered at 1500 °C for 2 h in an electric furnace using 3 °C min^{-1} for both heating and cooling rates. The sintered density was measured using the water-displacement method. Phase analysis was made using standard powder X-ray diffraction (XRD) technique. Scanning electron microscopy (SEM) was used to characterize the fracture surface of the samples.

3. Results and discussion

Fig. 1 shows the dimensional shrinkage for the 150 MPa die-pressed samples due to isostatic pressing in the die press axis direction and a direction perpendicular to the die press axis. Isostatic pressing shrinkage was not observed in the die press axis direction until the isostatic pressure was above the die compaction pressure (150 MPa). Above this compaction pressure, the isostatic pressing shrinkage increased almost linearly with increasing pressure in the pressure range investigated (up to 300 MPa). The total shrinkage at 300 MPa isostatic pressure was ~ 2%. In contrast, some isostatic pressing shrinkage was observed in the direction perpendicular to die press axis even when the isostatic pressure was below the initial die compaction pressure. The isostatic pressing shrinkage increased sharply on increasing the isostatic pressure from 80 MPa to 250 MPa, followed by a reduced rate of increase with a further increase in the isostatic pressure. The total linear shrinkage at 300 MPa in the direction perpendicular to die press axis was ~ 5.5%, almost three times that in the die press axis direction.

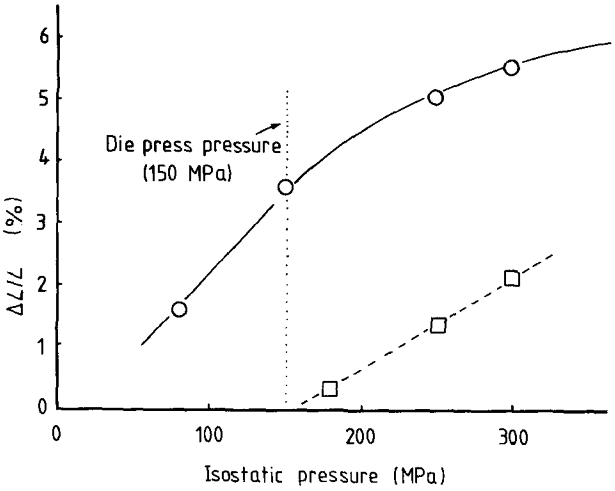


Figure 1 The dimensional shrinkages for the 150 MPa die-pressed samples due to isostatic pressing in (□) the die press axis direction and (○) in a direction perpendicular to die press axis.

The dependence of isostatic pressing shrinkage on applied pressure for the initially die-pressed samples is related to the non-uniform stress and density distributions in the die-pressed powder compacts [6, 7]. Both residual stress and density gradients are expected to occur in the die-pressed compacts, depending on the specimen dimensions (in particular, the aspect ratio, 0.45 in the present work), powder characteristics (including binders if present), and the lubrication between the powder and the die wall [10]. In general, pressing defects (usually laminations) occur in the direction perpendicular to the punch travel axis on ejecting the sample after compaction, due to the friction between die wall and powder. The average compacted density in this direction may be slightly lower than that in the punch travel axis. On application of an isostatic pressure, further compaction shrinkage is therefore expected to occur in the direction perpendicular to die press axis. The occurrence of isostatic pressing shrinkage in this direction at pressures below the die compaction pressure, shown in Fig. 1, indicates the non-uniform density distribution in the conventional die-pressed samples. Some regions may be subjected to a much lower stress (pressure) level than that of the externally applied pressure.

Fig. 2 shows the sintered density as a function of compaction pressure for the die and the subsequently isostatically compacted samples. All the die-pressed specimens exhibit similar sintered density on sintering at 1500 °C for 2 h, 6.10 g cm^{-3}, which is very close to the theoretical density of Y_2O_3-stabilized tetragonal zirconia polycrystals (Y–TZP), regardless of the initially applied die compaction pressure (from 30–300 MPa). In comparison, an application of isostatic pressure to the die-pressed specimens results in a reduction in the sintered density, although their green density is further increased. The sintered density decreases almost linearly with increasing isostatic pressure in the pressure range investigated in this work (up to 300 MPa). For a given isostatic pressure, the sintered density also depends on the initial die compaction pressure, decreasing with decreasing die compaction pressure. Fig. 3 further indicates that the final sintered density decreases with increasing difference between the isostatic pressure and the die compaction pressure.

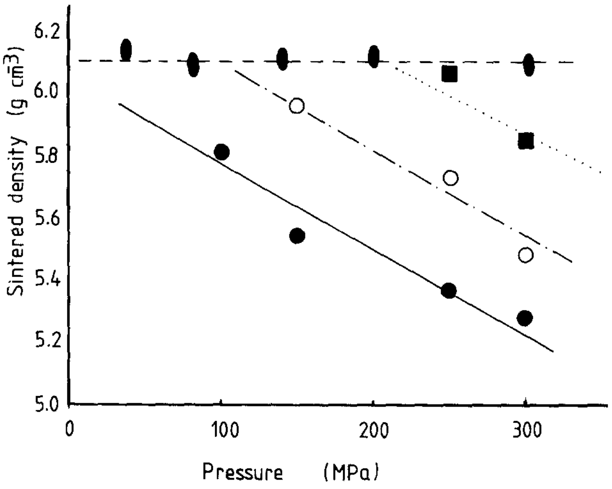


Figure 2 The sintered density as a function of pressure for the die and subsequently isostatically compacted samples. The conventional die compacted samples show the high sintered density which is close to the theoretical density. In contrast, a further application of isostatic pressure resulted in a large reduction in the sintered density. (⬮) Die press only, (●) die press (35 MPa) + isostatic press, (○) die press (100 MPa) + isostatic press, (■) die press (250 MPa) + isostatic press.

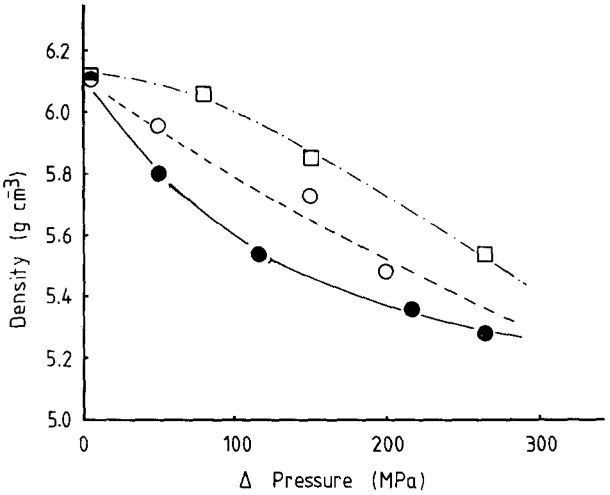


Figure 3 A plot showing that the sintered density decreases with increasing difference between the isostatic compaction pressure and the die compaction pressure. Die pressing pressure: (●) 35 MPa, (○) 100 MPa, (□) 150 MPa.

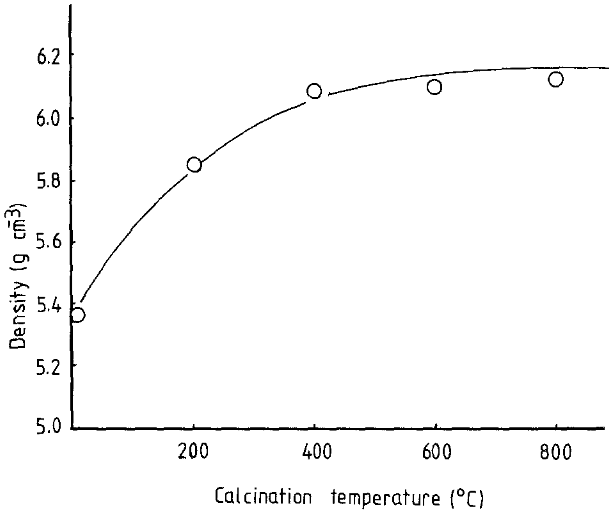


Figure 4 The dependence of sintered density on the calcination temperature (5 h) for the specimens compacted at 30 MPa die pressure and subsequently at 300 MPa isostatic pressure, indicating that the elimination of 3 wt % PEG 1500 can be effectively achieved by calcining the powder at temperatures above 600 °C for 5 h.

Several investigators have demonstrated that the elimination of residual organic binders is an important step in sintering advanced ceramics [1, 5, 11, 12]. Large processing defects, and therefore a degradation in the mechanical properties, such as fracture strength and fracture toughness, will occur if the organic binders are not properly eliminated at the low and intermediate temperature stages in the heating-up period. It is believed that the reduction in sintering shrinkage and sintered density for the isostatically compacted specimens in this work was due to the delayed burn-out of PEG 1500 in the powder, until relatively high temperatures are approached during sintering. An experiment was thus carried out to burn off the organic binders by calcining the powder at low and intermediate temperatures from 200–1000 °C (5 h). The calcined powders were then subjected to the identical compaction and sintering procedures as those for the uncalcined powder. Fig. 4 shows the sintered density as a function of calcination temperature for the ceramic compacts formed using a 30 MPa die pressing followed by a 300 MPa of isostatic pressing. The uncalcined powder shows the remarkably low sintered density (86.3% theoretical density). The sintered density increases significantly when the powder was calcined at 200 and 400 °C, respectively. A high sintered density (> 99% theoretical) was obtained when the calcination temperature was above 600 °C, indicating that the residual PEG 1500 was almost completely eliminated.

The effectiveness of eliminating organic residuals by calcination at low and intermediate temperatures can be influenced, to a large extent, by the characteristics of powder compacts. As is indicated by the sintered density data shown in Fig. 2, the organic binders in the die-pressed compacts can be effectively eliminated by heating the samples at a rate of 3 °C min^{-1}, regardless of the die compaction pressure. In contrast, an isostatic compaction at pressures higher than the die-pressing pressures will result in the retention of some organic binders in the compacts until a relatively high temperature is attained, if the same heating rate is used. Thus, an isostatically compacted specimen requires a much slower heating rate than the die-pressed sample in order to achieve the desired elimination of organic residuals. The non-uniform distribution of compact density in the die-pressed samples is responsible for the increased effectiveness in eliminating organic residuals over the isostatically pressed specimens. It is therefore sensible to consider an extended dwell period at low or intermediate temperatures for the isostatically compacted materials if organic binders are present in the starting powder.

Using scanning electron microscopy (SEM), it was observed that the materials with different sintered densities exhibit considerably different microstructures. The sintered samples formed using the conventional die compaction technique show the densely

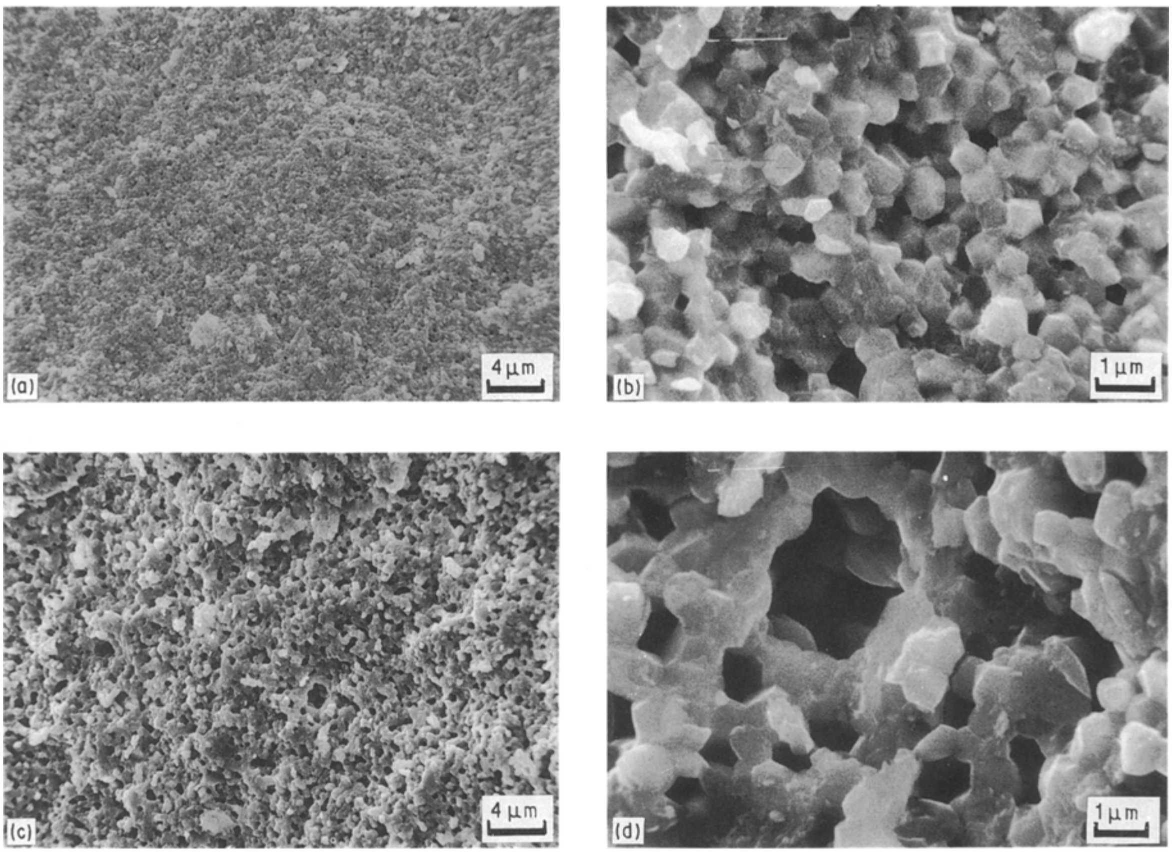
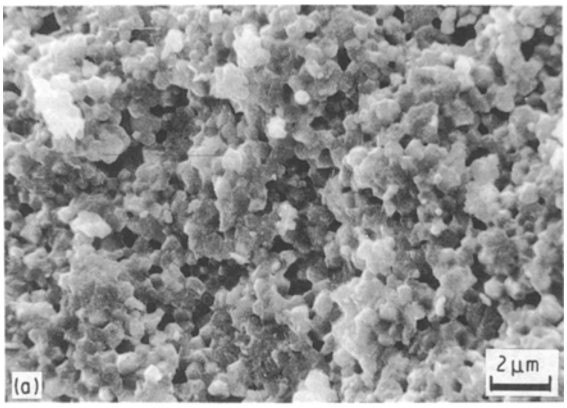
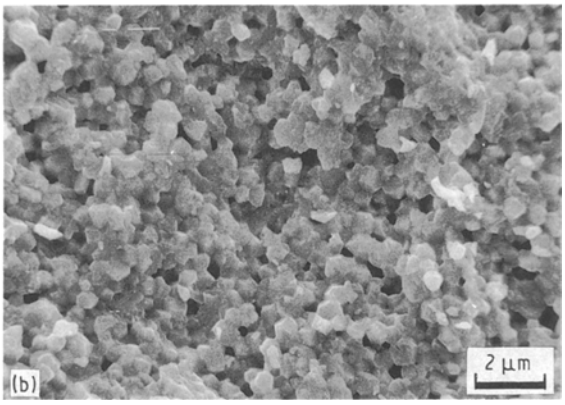


Figure 5 Scanning electron micrographs showing the fracture surfaces for the sintered samples at 1500 °C/2 h formed using (a, b) 30 MPa die pressure, (c, d) 30 MPa die pressure + 300 MPa isostatic pressure. The die-pressed sample exhibits a densely packed structure and the isostatically pressed sample a porous structure.

packed and uniformly distributed tetragonal zirconia grains (average grain size 0.70 µm according to the standard linear interception measurement), Fig. 5a,b. X-ray diffraction (XRD) phase analysis on the polished surface indicated that these materials consisted of > 95% tetragonal phase and a minor amount of monoclinic phase. In comparison, the materials formed using the conventional die compaction and the subsequent isostatic compaction show a more porous microstructure, Fig. 5c and d. Their grain sizes are slightly larger than that for the material shown in Fig. 5a and b (average grain size 0.95 µm, according to the standard linear interception measurement). It is further observed from Fig. 5c and d that the processing defects associated with the burn-out of re-





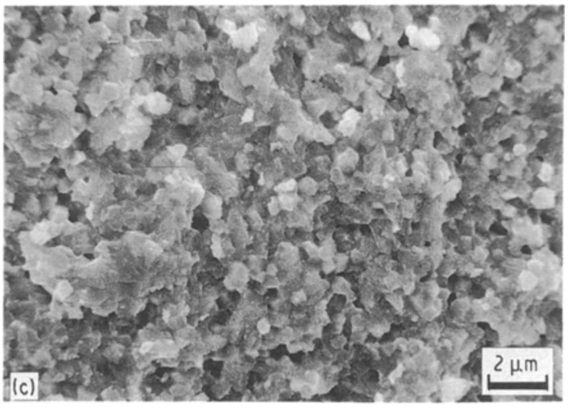


Figure 6 Scanning electron micrographs showing the fracture surfaces for the sintered samples formed using 30 MPa die pressure + 300 MPa isostatic pressure. (a) Powder calcined at 200 °C for 5 h; (b) Powder calcined at 400 °C for 5 h; (c) powder calcined at 600 °C for 5 h. It is seen that both the number and size of pores associated with the burn-out of PEG 1500 decrease with increasing calcination temperature.

sidual organic binders (mostly PEG 1500) in the isostatically compacted specimens were pores of intermediate sizes (1–5 µm) which are almost uniformly distributed in the fracture surface. The internal surface of large pores shows the appearance of a sintered surface. Both the number and size of the processing defects decrease with increasing calcination temperature, Fig. 6a–c.

4. Conclusions

A brief study has been made of the effects of organic binders on the sintered density and sintering shrinkage in isostatically pressed ceramic powder compacts. Certain processing-related flaws may arise from the delayed burn-out of organic residuals, although cold isostatic compaction gives a higher and much more uniform green density than the conventional die compaction. For the 3 mol % Y_2O_3-doped zirconia powder in which 3 wt % PEG 1500 was introduced, the sintered density and sintering shrinkage were found to decrease almost linearly with increasing isostatic compaction pressure. The processing-related defects were identified as intermediate size pores (1–5 µm). The occurrence of these processing defects was due to the incomplete organic burn-out at low and intermediate temperatures in the heating-up period during sintering, which results in the swelling of intergranular pores at relatively high temperatures. The elimination of the residual PEG 1500 can be accomplished by calcining the powder at temperatures above 600 °C. It is further suggested that the completion of organic burn-out in the isostatically pressed compacts may need a higher calcination temperature and/or a more extended dwell period than the conventionally die-pressed compacts.

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