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The Relation Between Preparation, Microstructure and Mechanical Properties of Spherical Yttria–Zirconia Powders

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Abstract

The effect of preparation procedure on the behaviour of spherical yttria–zirconia powders during heat treatment and also on their resultant properties has been studied. The powders were prepared from coprecipitated hydrous zirconia gels and also from precalcined material using a spray drying technique. The powders were characterised by determining the changes in morphology, specific surface area, pore size distribution, porosity and compressive strength that occurred due to heat treatment.

It has been found that the characteristics of the powders were affected greatly by the following steps of the preparation procedure: (i) washing the original gels with organic liquid, (ii) drying and milling of the gels, and (iii) precalcination. The enlargement of the modal pore size of the granules observed during heat treatment was dependent on the width of the pore size distribution and on the ratio between pore size and grain size. The compressive strength of the granules was dependent on the porosity, particle size and flaws present in the sintered granules. © 1996 Elsevier Science Limited.

1 Introduction

Interest is still growing in the use of porous zirconia as catalyst supports, filters and biochemical applications.[1–6] Its amphoteric nature develops a unique surface chemistry involving both redox and acid-base functions. Zirconia for catalytic applications must have both high surface area and porosity at elevated temperatures. The excellent chemical stability of porous zirconia at high pH (>13) is utilised in high-performance liquid chromatography (HPLC). In this case, a balance of high porosity and high compressive strength of the spherical particles packed into the chromatography columns is required.

Generally, two approaches are being used to obtain microporous ceramics with specific pore characteristics. The first one combines the original particles in assemblies of controlled packing density and shape. The sol-gel methods,[3–4] precipitation combined with calcination,[4] spray pyrolysis,[7,8] and glycothermal treatment[9] are examples of this approach. The second removes some fraction of the material by chemical leaching[10] or by burning out organic additives.[11] Both approaches require a step of heat treatment which affects both surface area and porosity of the resultant porous material.

In this work, yttria–zirconia granules of spherical shape were prepared by using yttria–zirconia hydroxides treated in different ways to develop various pore characteristics. The effect of the original microstructure of the granules on the evolution of porosity during heat treatment was studied. The compaction behaviour and mechanical properties of the granules were also characterised.

2 Experimental

Three zirconia powders stabilised with 8 mol% yttria were prepared by coprecipitation and spray drying using zirconium tetrachloride and yttrium oxide as starting materials in the manner described in detail elsewhere.[12,13] The powder W was derived from the slurry of a hydrous yttria–zirconia gel washed only with distilled water. The powder E was prepared from the slurry of the gel washed additionally with ethyl alcohol. The dried and attrition milled agglomerates of the water washed gel were used to produce the powder G. Spray drying of the powders W and G was performed from the water slurries and the powder E from ethanol slurry. The fourth powder (powder C) was a spray dried zirconia–2·85 mol% yttria powder produced by ICI Advanced Ceramics using a co-precipitation technique followed by calcination at 1000°C. The powders were heat treated at temperatures ranging from 500 to 1400°C for 2 h.

Transmission electron microscopy (Philips EM420) was used for measurements of agglomerate and aggregate size distributions. The morphology and microstructure of the granules were observed with scanning electron microscopy (Jeol JSM-840). This method was also used to determine the granule size distributions. The BET surface areas were measured by nitrogen adsorption at –196°C with Micromeritics Gemini 2360 equipment. Samples were outgassed for 2 h at 150°C before making measurements.

The evolution of the granule porosity during heat treatment was studied using mercury porosimetry. A Micromeritics Porsizer 9310 was used. Pores of diameters of >7·5 nm were intruded under the maximum applied pressure (205 MPa). Pore size distributions of granules with pores smaller than 7·5 nm were calculated from the nitrogen adsorption isotherms that were measured on a Micromeritics ASAP 2000 instrument.

The compaction behaviour of the powders was studied by determining the densification curves using an Instron 4505 testing machine. Uniaxial pressing of the powders was performed in a 10 mm diameter steel mould. The loading rate was 1 mm/min and the maximum load used was 31·5 kN. The calculated compact density was corrected for elastic deformation of the mould and the powder. The critical nominal pressure p_c estimated from points of inflexion in the relative density of the compact *vs* logarithm of compaction pressure curves gave a measure of the compressive strength of the granules.

3 Result and Discussion

3.1 Characteristics of original granules

The microstructures of the spray dried granules used in the experiments are shown schematically in Fig. 1. The granules of W and E were composed of the primary particles of the hydrous yttria–zirconia gel of 5–7 nm in size. The granules of G were composed of porous, high specific surface area agglomerates which made up the primary particles (5–7 nm) of the amorphous gel. The granules of C were composed of the aggregates of fine (D_{111} = 31 ± 2 nm), dense particles of crystalline yttria–zirconia solid solution which contained 48·9 vol% tetragonal phase. The balance was the monoclinic phase. The particle size distributions shown in Fig. 2 indicate a smaller aggregate size and narrower aggregate size distribution of the powder C when compared to the agglomerates of the powder G.

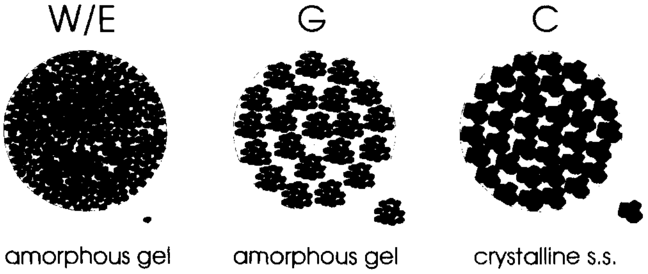

Fig. 1. Scheme of granule microstructures studied. Elementary particles of the powders that were used to form the granules and their crystallinity are indicated.

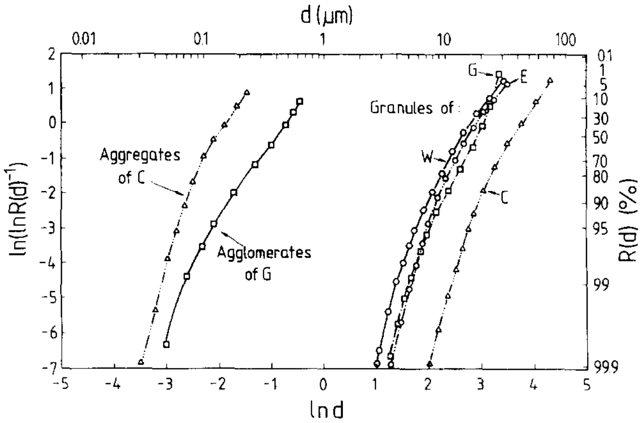

Fig. 2. Agglomerate, aggregate and granule size distribution drown in the Rosin–Rammler coordinates.

Characteristics of the spray dried granules are summarised in Table 1 and in Figs 2 and 3.

The pore size distributions of the powders are shown in Fig. 4. The microstructural similarity between G and C and between W and E is evident. Distinct pore populations were observed within the granules of the powders G and C. They were formed from inter-agglomerate (Powder G) and inter-aggregate (Powder C) pores. The nitrogen adsorption measurements for sample G indicated that 25·5±1·5% (0·151 cc/g) of the total amount of pores was not penetrated by mercury. The granules prepared from the gels directly dispersed with water or ethanol showed much smaller pores and broad pore size distributions. As many as 84·3% (0·151 cc/g) and only 20·7±3·5% (0·174 cc/g) of the total amount of pores were smaller than 7·5 nm within the granules of W and E, respectively, as was measured by nitrogen adsorption.

3.2 Heat treatment behaviour

A reduction of granule size was observed as a result of heat treatment. The linear shrinkage of the powders E, G and W was closely linked with the porosity of the original granules (see Table 1), namely 41, 36·1±2·6 and 16·2±1·7% at 1400°C, respectively. The granules of C composed of crystalline material showed the smallest shrinkage of 15·8±2·1%, even though the original porosity was high. This was due to the fact that calcination of the powders to 1000°C prior to milling and spray drying had already densified the aggregates.

In all cases a reduction of the specific surface area accompanied the shrinkage of the granules.

Table 1. Properties of the spray dried powders

Property	*Powder W*	*Powder E*	*Powder G*	*Powder C*
Granule size D_{mode}(μm)	5.6	7.3	6.4	16.0
Specific surface area (m^2/g)	143.0±5.7	295.1±10.9	93.5±2.9	14.4±0.5
Porosity of the granules (vol%)	33.0±0.8	79.1±1.0	66.0±1.4	63.9±1.2

± denotes the confidence interval at confidence level 0.95 in the entire work.

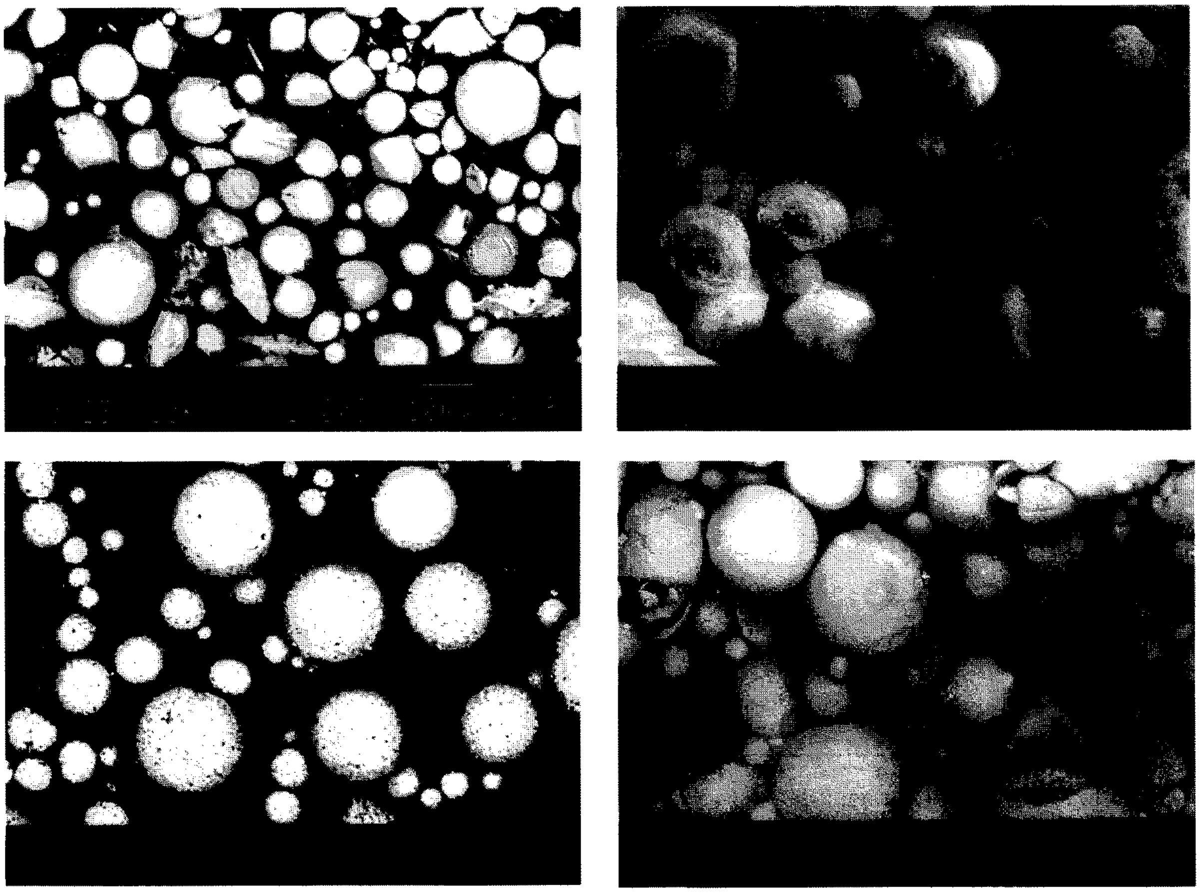

Fig. 3. SEM micrographs of the 'as spray dried' granules: (a) powder W (back scattered), (b) powder E (SEI), (c) powder G (back scattered), (d) powder C (SEI, fractured surface of a compact pressed to p_c).

It was found that at temperatures below 800°C the specific surface area measured for the granules of W, E and G was controlled by the crystallite size whereas in the powder C it was the aggregate size which was the controlling factor. The powder prepared from the ethanol washed gel exhibited the highest values of the specific surface area at temperatures below 1000°C (from S=88·1±3·4 m^2/g at 500°C to S=13·9±0·5 m^2/g at 1000°C). At higher temperatures the powder C was more stable (3·9±0·2 m^2/g at 1200°C) whilst the powders G, E and W exhibited 2·2±0·2, 0·9±0·1 and 0·4±0·1m^2/g, respectively. These figures are consistent with the changes in the porosity of the granules shown in Fig. 5. Detailed information about the pore size distributions of the granules studied is given in Refs 12 and 13.

The changes of modal pore diameter and of modal pore diameter relative to the pore diameter at 500°C as a function of the temperature of heat treatment are shown in Fig. 6. Maximum pore growth is observed in the granules prepared from the ethanol washed gel (E). The pores of W show much smaller growth and there is only a slight pore enlargement within the granules of G and C.

The differences in pore growth can be explained if the maximum increase of the modal pore diameter is correlated with the width of the original pore size distributions. The constant n in the Rosin–Rammler equation[14] is a good measure of the width of the particle size distribution. In this work, the pore size distributions have been expressed in terms of the Rossin–Rammler equation. Table 2 contains the values of n together with the correlation coefficients r of the linear regressions that were used to determine each n. The linear regression of each pore size distribution was statistically valid to a confidence level of

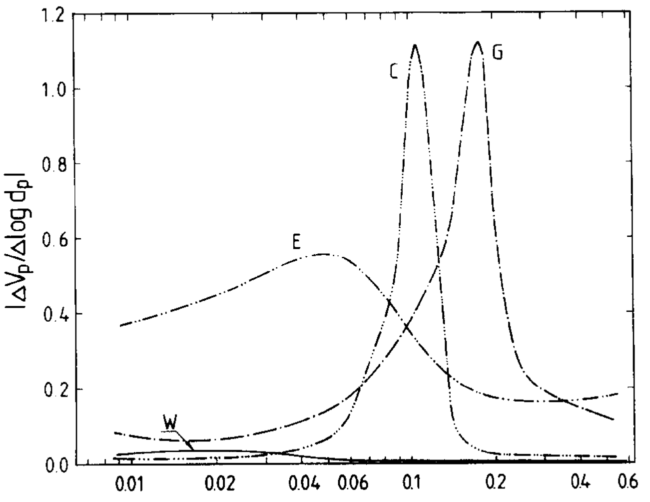

Fig. 4. Pore size distribution curves of the 'as spray dried' granules.

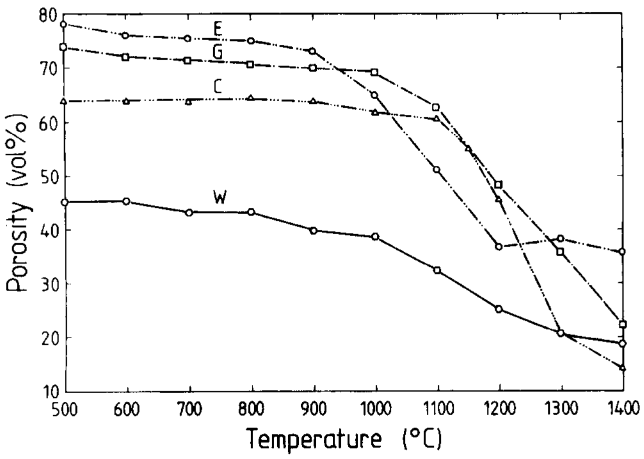

Fig. 5. Porosity of the granules *vs* temperature of heat treatment.

0·999. The pore size distributions of the granules heat treated at 500°C were taken as the original ones in order to analyse the crystalline samples only. However, the conclusions are the same for the pore size distributions of the originally amorphous granules.

The data from Table 2 suggest a distinct relationship between pore growth and the width of the pore size distribution. Since larger *n* reflects a narrower pore size distribution, one can state that pore growth is promoted by the broader pore size distribution of the starting sample. This is associated with an increase of the average grain size as is shown in the SEM micrographs of the granules sintered at 1400°C (Fig. 7). The fine grained microstructure of the granules of C was due to a smaller amount of yttria added as a stabiliser.[15]

X-Ray measurements of the changes of the crystallite size (D_{111}) with temperature of heat treatment together with the SEM measurements of the grain size of the granules sintered above 1100°C revealed the relationship between relative pore diameter and the temperature of heat treatment of the powders (Fig. 8). The relative pore diameter is defined as the ratio between modal pore diameter and grain diameter. At 500°C, the crystallites of the powders E, W, G and C had the D_{111} size of 23, 29, 36 and 35 nm, respectively. The average grain size of the samples sintered at 1400°C reached the values of 1·43, 0·84, 0·70 and 0·35 μm for the powders E, W, G and C, respectively.

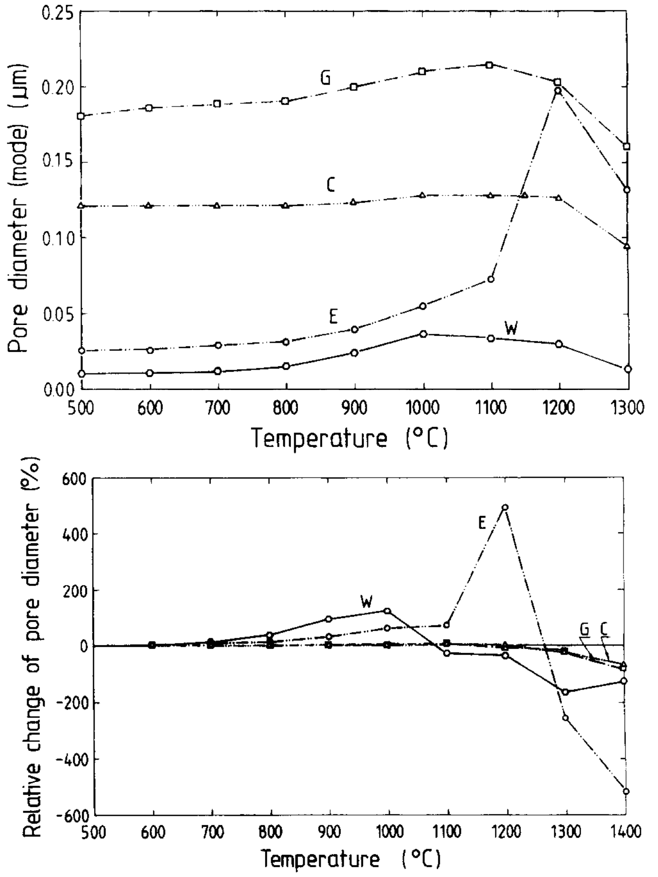

Fig. 6. Modal pore diameter (a) and relative change of modal pore diameter (b) *vs* temperature of heat treatment.

3.3 Mechanical strength of the granules

The compaction curves shown in Fig. 9 show a large difference in compaction behaviour of the powders. This arises from the large difference in apparent densities of the granules and in the size of the particles within the granules. All the curves do not exhibit the existence of well defined breakpoints over the whole range of the pressures; this may arise from a distribution in agglomerate strength[16] or from more than one failure mechanism. It can be seen from Fig. 9 that the granules of W had the highest compressive strengths at temperatures below 1200°C. Above this temperature both W and E exhibited a relatively small increase in compressive strength. The granules of C and G increased significantly their compressive strengths after sintering above 1200°C.

Table 2. Maximum increase of modal pore diameter d_{mode} during heat treatment and n values of the pore size distributions of the granules heat treated at 500°C.

	Powder W	*Powder E*	*Powder G*	*Powder C*
n value	2.2	2.6	3.7	5.0
Maximum increase of d_{mode}(%)	124	491	5.2	4.0
Correlation coefficient r	0.967	0.879	0.987	0.974

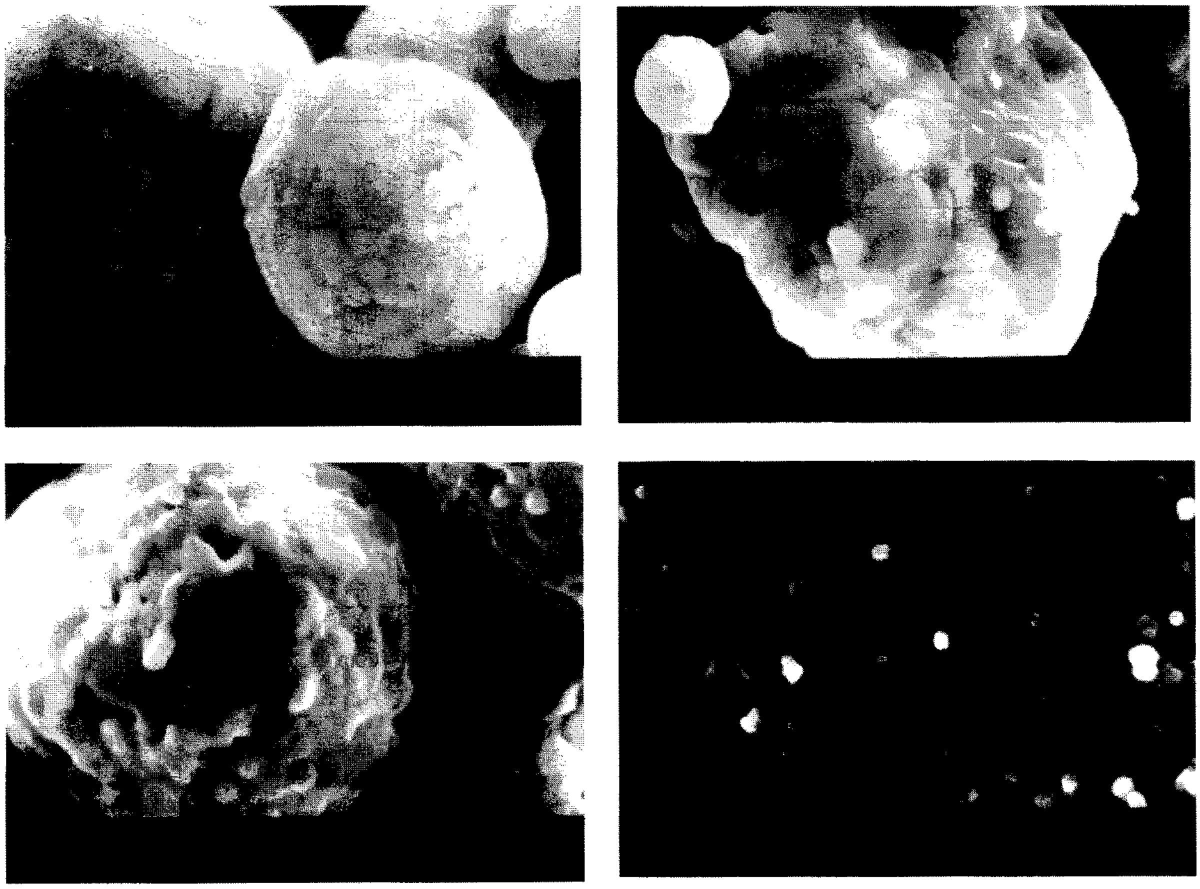

Fig. 7. SEM micrographs of the powders sintered at 1400°C: (a) powder W, (b) powder E, (c) powder G, (d) powder C.

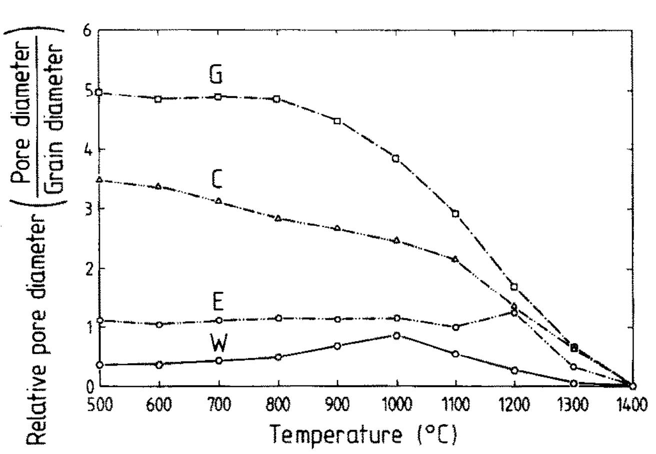

Fig. 8. Relative pore diameter *vs* temperature of heat treatment.

On the basis of fracture mechanics, Kendall[17] has proposed the following equation for the strength σ^* of an agglomerate (granule) formed from clean smooth spherical particles:

$$\sigma^* = 15{\cdot}6\phi^4\Gamma/(Dc)^{0{\cdot}5}$$

where ϕ is the packing volume fraction, Γ is the work of adhesion, D is the particle size and c is the notch (flaw) length. This equation is consistent with the present experimental findings in showing the strong influence of the packing fraction (Fig. 10), the weaker influence of particle diameter and the influence of packing defects.

4 Conclusions

Four yttria–zirconia powders (W, E, G and C) with different microstructures were characterised with respect to their behaviour during heat treatment in order to study the relation between preparation, microstructure and mechanical properties. The ratios between the pore size and particle size for the original granules were 0·34, 1·11, 4·95

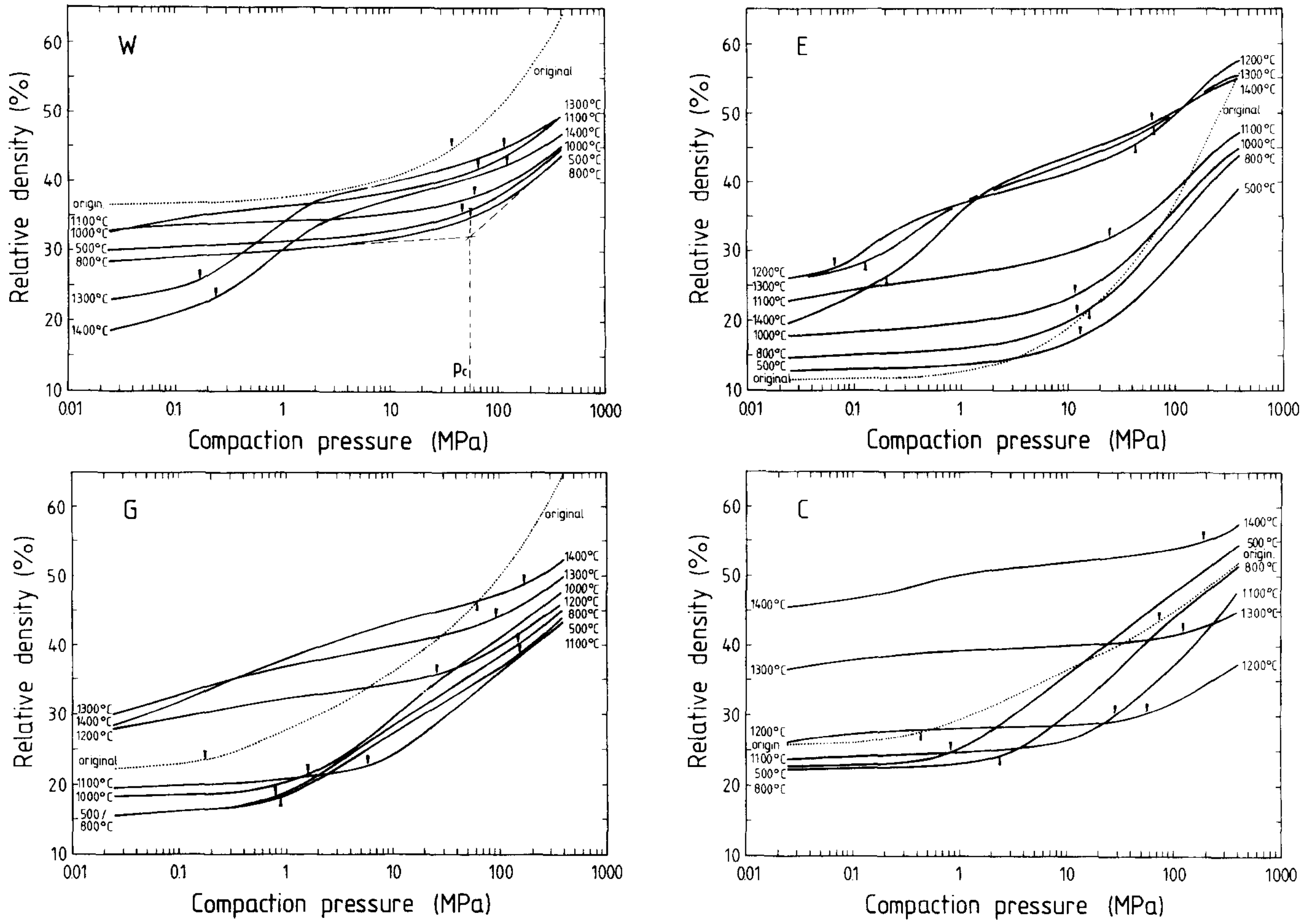

Fig. 9. Compaction curves of the powders: (a) powder W, (b) powder E , (c) powder G, (d) powder C.

and 3·47 for granules of W, E, G and C, respectively. The granules of W and E were composed of primary particles of hydrous yttria–zirconia gel. The granules of G consisted of agglomerates of these particles and C was composed of crystalline particles of yttria–zirconia solid solution.

The original granules of W spray dried from a water slurry of hydrous zirconia gels had the highest density, the finest pores and a broad pore size distribution. The spray drying of an ethanol slurry of zirconia gels results in granules with increased porosity, pore size and a broad pore size distribution. Both G and C had large and comparable porosities and pore size distributions narrower than W and E.

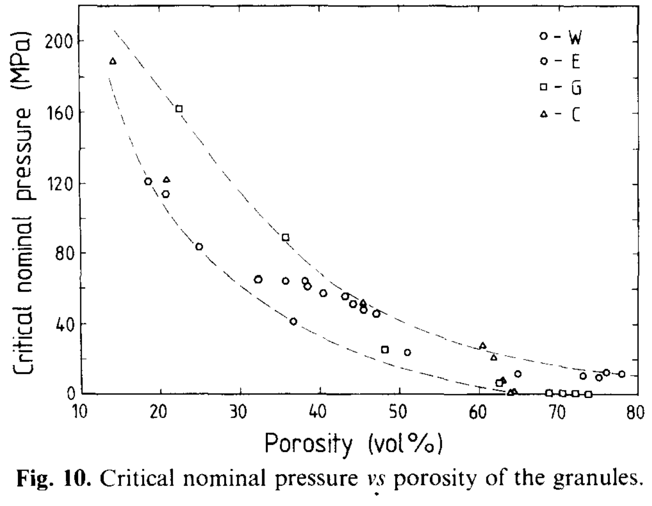

Fig. 10. Critical nominal pressure *vs* porosity of the granules.

Enlargement of the modal pore size of W, E and G is observed during heat treatment of the powders due to local densification by shrinkage in the dense regions of the gel. It was found that an increase in the width of the pore size distribution promoted pore enlargement. The granules with a narrow pore size distribution do not exhibit pore growth during the early stage of sintering.

The compaction behaviour of the powders is affected by the morphology and strength of the granules. The compressive strength of the granules is controlled by their porosity, particle size and flaw size.

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