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Characteristics and effect of thermal treatment on surface texture of ultrafine zirconia powders

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Yttria-stabilized zirconia ultrafine powders were prepared by the hydrolysis of their hydroxides at 200° C. The powders obtained were investigated for their crystal structure and degree of fineness. The surface characteristics of the prepared powders were determined by nitrogen gas adsorption. The effect of calcination conditions on the powder characteristics were thoroughly investigated and the results discussed in relation to their surface textures and degree of crystallinity.

1. Introduction

Stabilized zirconia is one of the most interesting refractory oxides for its versatile high temperature applications. Zirconia is stabilized in the cubic fluorite structure by alloying pure zirconia with enough of another oxide e.g. CaO, MgO, Y_2O_3, and rare earth oxides at sufficiently high temperatures [1–3]. Traditional ceramic fabrication methods require temperatures as high as 1800 to 2000° C to attain dense stabilized bodies. To avoid this requirement there are several possible approaches. Among these the employment of the compositionally homogeneous and ultrafine powders prepared by wet chemical methods has proved to be suitable [4–6]. However, the hard agglomerates that may develop during the calcination step usually cause microstructural inhomogeneities and poor sintering behaviour [7, 8]. Suitable attention must be given to both the precise preparation conditions and to the subsequent handling in order that fine powders sinterable at moderate temperatures can be attained [9].

The large surface areas of zirconia powders obtained by chemical methods mean that a sensitivity of powder behaviour to atmosphere [10] and to residual chemical species [11] is to be expected and the need for adequate surface characterization of these powders is evident. Although the surface properties of monoclinic and metastable tetragonal zirconia, obtained by pyrolysis of zirconia gels, have been investigated [12–14], stabilized zirconia has not yet received the attention it deserves.

In the present work yttria-stabilized zirconia powders were prepared by the high-temperature hydrolysis technique. The obtained powders, after being characterized by their composition, structure and particle size, were investigated for their surface texture, which was studied as a function of both calcination temperature and isothermal heating.

2. Experimental procedures and results

2.1. Preparation and characterization of yttria–zirconia powders

The yttria-stabilized zirconia powders were prepared by the hydrolysis method developed by Burkin *et al.* [15] with rather simple laboratory equipment. The preparation was carried out as follows.

Solutions of analytically pure (more than 99.80% pure according to the supplier, BDH chemicals, Poole, England) zirconium oxychloride and yttrium chloride were separately prepared and then mixed according to the required ratios. Concentrated ammonia solution was added dropwise to the well stirred solution mixture until a white precipitate was formed and then excess ammonia was added [16, 17]. The white precipitate was transferred to a stainless steel autoclave (250 cm^3) with its mother liquor. The autoclave was placed in a manually controlled electrically heated oven and the temperature was raised gradually to 200° C at which temperature the hydrolysis process was carried out for 2 h. The settled white precipitate obtained was filtered after each preparation and washed with distilled water until free from chlorine ions. The precipitates were dried after filtration in an oven for 24 h at 110° C after which a fine powder was obtained. The supernatant liquids were chemically analysed for any traces of yttrium ions but none were detected. Four yttria–zirconia mixtures were prepared with yttria content of 4, 6, 8 and 10 mol % of the mixture.

Qualitative analysis of the dried precipitates was done using an X-ray diffraction technique. A Siemens diffractometer (D 500) was used. Sample portions of each dried powder were used for X-ray analysis. The samples were exposed to nickel-filtered Cu$K\alpha$ radiation at 30 kV and 15mA and with a scanning speed of 2° in $2\theta\,\mathrm{min}^{-1}$.

The X-ray diffraction patterns of the prepared powders are shown in Fig. 1. All the powders displayed the diffraction lines of the cubic ZrO_2 structure. No

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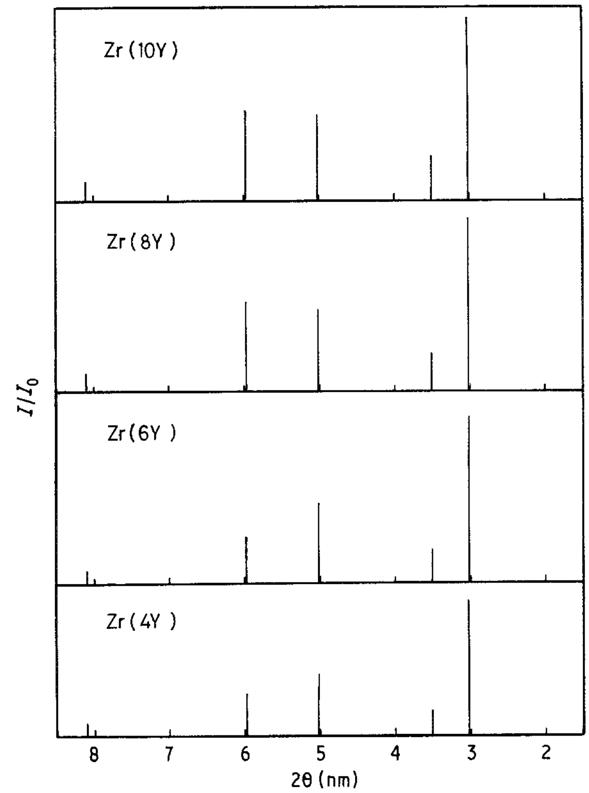


Figure 1 X-ray diffraction pattern of the prepared yttria–zirconia powders. Zr(4Y) indicates zirconia containing 4 mol % yttria, etc.

other phases of ZrO_2 were detected in the patterns. From the patterns it is clear that the intensity of the diffraction lines gradually increases as the yttria content is increased in the solid solution. Such increase in intensity reflects the development of better crystallinity as the amount of the stabilizer increases.

Infrared spectra were obtained for the dried powders with a Backman Spectrometer IR 4250. In-line transmission was measured on thin sections (1.0 mm thick) using a glass standard. Powder absorption spectra were taken using KBr pellets. In Fig. 2 infrared spectra of the powders containing 4 and 10 mol % Y_2O_3 in the medium infrared region are shown. Spectra of the powders containing 6 and 8 mol % Y_2O_3 are similar and are not shown. The presence of the broad absorption band at 600 to 400 cm^{-1} peaking at 480 cm^{-1} with its weak shoulder at 620 cm^{-1} shows that full stabilization of zirconia in the cubic phase is obtained [15]. The absence of the sharp bands corresponding to the monoclinic ZrO_2 even in the sample containing 4 mol % Y_2O_3 confirms this result [18].

Particle size and shape were studied by an E 10 Zeiss transmission electron microscope (TEM). Copper grids of 0.2 cm diameter coated with carbon film were used as the sample support. Each sample of the investigated powders was dispersed in ethyl alcohol using an ultrasonic bath for 15 min, ethyl alcohol producing a better spread of particles on the grid than water or acetone [5]. The powders were not tumbled before dispersion in the alcohol. The particles were then studied by the microscope at various magnifications and electron micrographs were taken (Fig. 3). It is clear that the samples consist of small rounded crystallites agglomerated together. The mean particle size of the powder containing 4 mol % Y_2O_3 was determined and found from the electron micrographs to be 25 ± 2 nm [19]. The mean particle size was increased for the powder containing 10 mol % Y_2O_3 to 29 ± 2 nm. Such increase in particle size confirms the results obtained by X-ray analysis shown in Fig. 1.

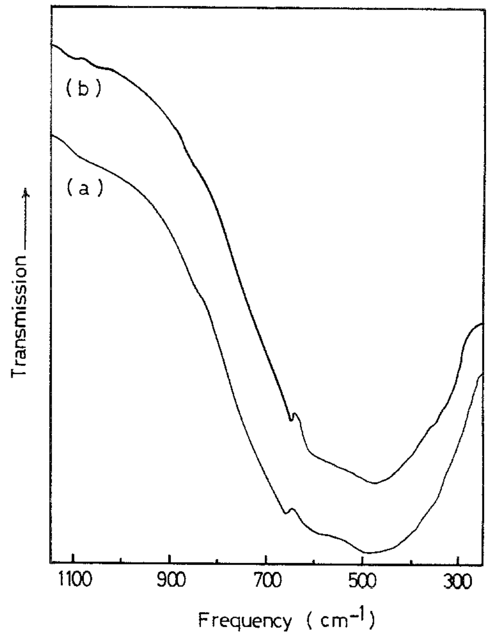


Figure 2 Powder transmission spectra of; (a) 4 mol % yttria zirconia and (b) 10 mol % yttria–zirconia prepared powders.

2.2. Measurement of surface properties

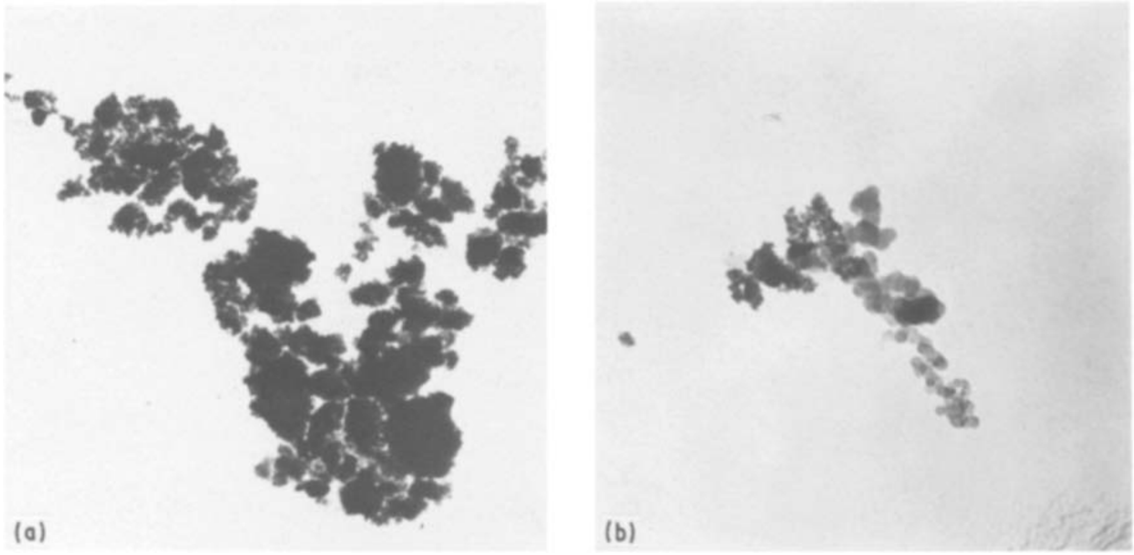
The surface properties were investigated by the adsorption of nitrogen gas at liquid nitrogen temperature using a BET volumetric apparatus of the conventional type. Before each adsorption run the powder was outgassed at 200° C for 3 h.

Full adsorption–desorption isotherms of nitrogen gas at liquid nitrogen temperature (– 195.8° C) were obtained for the prepared yttria–zirconia powders and are shown in Fig. 4. All the isotherms show the common characteristics and are similar in shape to type II of Brunauer's classification. They are characterized by the presence of closed hysteresis loops indicating the presence of mesopores as a part of the total pore system.

Specific surface areas were derived from the adsorption isotherms by the Brunauer–Emmett–Teller (BET) method in the conventional range of relative pressure, adopting a value of 0.162 nm^2 for the molecular area of nitrogen. The total pore volumes were calculated from the amount of nitrogen molecules adsorbed at the saturation vapour pressure of the adsorbate and expressed in millilitres of liquid nitrogen per one gram of the adsorbent (V_p; ml g^{-1}). The hydraulic radii of the total pore system in nm,

$$\bar{r}_h = \frac{V_p}{S_{BET}} 10^3$$

The obtained values of the BET surface areas, the total pore volumes, and the hydraulic radii of the pore systems are given in Table I. It is evident from the obtained data that the specific surface areas and the total pore volumes decrease gradually with the



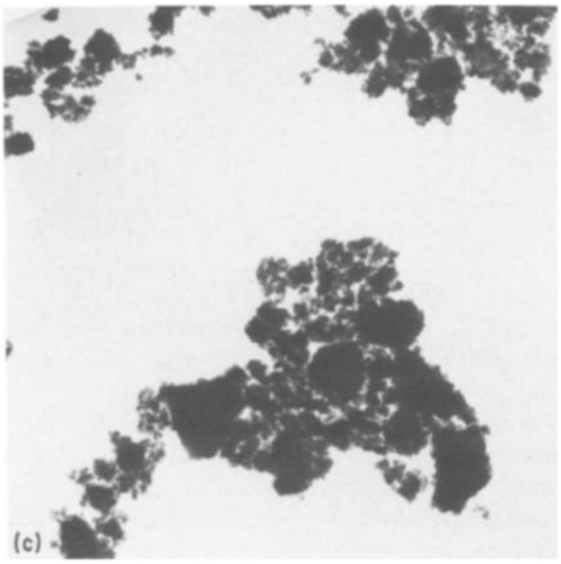


Figure 3 TEM photomicrographs of as-prepared powders, (a) and (b) 4 mol % Y_2O_3-stabilized ZrO_2 and (c) 10 mol % Y_2O_3-stabilized ZrO_2. (a) and (c) × 12 500, (b) × 40 000.

increase of yttria content in the zirconia–yttria solid solutions. The hydraulic radius, $\bar{r}_h$, displays a slight decrease with increasing Y_2O_3 content in the powders; this result is mainly associated with the increased accessibility of nitrogen molecules to a major part of the total pore system as a consequence of the increased crystallinity of the powders as indicated in the X-ray reflections of Fig. 1.

The plots of the volume of liquid adsorbate absorbed, expressed in millilitres per gram of the absorbent (V_l; ml g^{-1}), versus the statistical multilayer thickness of the adsorbed layer (t; nm) are shown in Fig. 5. The values of t reported here are as those obtained by Mikhail *et al.* [20] for the low-heat adsorbent adsorbate interactions. Pronounced upward deviations from the initial straight lines appeared in the V_l–t plots obtained for the investigated powders. These upward deviations suggest the existence of mesopores with limited sizes. This result is also indicated from the mean hydraulic radii calculated for the total pore systems.

TABLE I Surface characteristics of as-prepared zirconia–yttria powders from nitrogen adsorption

Sample	S_{BET} ($m^2 g^{-1}$)	V_p (ml g^{-1})	$\bar{r}_h$ (nm)
Zr- 4Y*	266.2	0.4827	1.8
Zr- 6Y	253	0.4226	1.7
Zr- 8Y	247	0.3962	1.6
Zr-10Y	239.8	0.3557	1.5

*ZrO_2–4 mol % Y_2O_3.

2.3. Effect of heat treatment on the powder characteristics

The 4 mol % Y_2O_3-stabilized ZrO_2 was selected for the calcination experiments. Portions of the powder were calcined in air at various temperatures up to 1400° C. At each temperature, the samples were soaked for 1 h and then quenched in air.

X-ray diffraction analysis showed that up to 1400° C the samples consist only of cubic zirconia with the fluorite structure. The intensity of the cubic phase reflections increased as the calcination temperature increased reflecting the development of larger crystals on heating. The TEM investigations offered similar results where a noticeable increase in particles sizes accompanied the increase in calcination temperature. Fig. 6 shows electromicrographs of samples calcined at 800 and 1200° C where the degree of polycrystalline agglomeration increased compared with the powder as prepared. From the micrographs, the mean particle size was found to be 45 ± 2.5 and 150 ± 3.5 nm for the samples calcined at 800 and 1200° C, respectively.

Adsorption–desorption cycles of nitrogen were obtained for the calcined samples. From the results of nitrogen adsorption, the BET surface areas, S_t, BET-c constants, the total pore volumes and the average hydraulic radii of the total pore systems of these calcined samples could be evaluated and the derived values are given in Table II. S_{BET}, V_p and $\bar{r}_h$ are also plotted as a function of calcination of temperature in Fig. 7. From the obtained data, the specific surface area and total pore volume display an initial increase when the calcination temperature is increased from 200 to 400° C. This is mainly to be attributed to the evolution of the strongly adsorbed water molecules

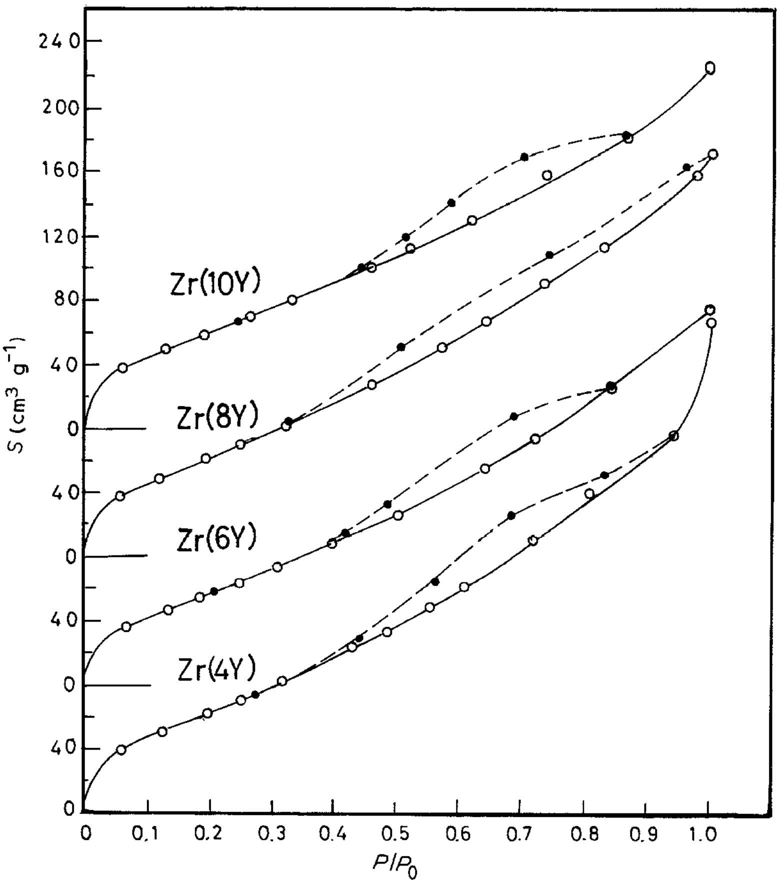


Figure 4 Adsorption (○) and desorption (●) isotherms of nitrogen on as-prepared yttria–zirconia powders.

which lead to some sort of pore vaccation. The IR spectrum of the prepared powder showed the presence of sharp bands at 3450 and 1630 cm^{-1}. These bands are attributed to the adsorbed moisture on the surface of fine zirconia powders [18] and they are eliminated on heating. As the calcination temperature increased to 1200° C, the surface area and total pore volume of the samples decreased continuously. Furthermore, the heat of adsorption of the first adsorbed layer decreased with increasing the calcination temperature, the values of the BET-*c* constants indicate this criterion clearly. Calcination at 1400° C, however, was associated with an increase in the specific surface area measured by nitrogen as an adsorbate while the total pore volume continued to decrease. This increase in the surface area calculated by the BET equation is mainly due to the fact that the adsorption process takes place via a diffusion mechanism.

The average hydraulic radius, $\bar{r}_h$, of the total pore system shows a value of 1.6 to 2.3 nm in the temperature range of 400 to 1200° C. However, the average decreased to a value of 0.9 nm as a result of calcination at 1400° C. This indicated the increased diffusion of nitrogen molecules towards a large fraction of the total pore system.

A typical set of V_l–t plots constructed from nitrogen adsorption data for the calcined samples are shown in Fig. 8. Upward deviations can be seen indicating the existence of mesopores with limited sizes representing the major part of the total pore system.

As mentioned above, calcination at 800° C was accompanied by an increase in the crystallite size and a decrease in the surface area of the power compared with the values obtained for the powder as prepared. However, these values reflect the still-active nature of the powder compared with those calcined at 1200 and 1400° C. Therefore, a series of isothermal heatings at 800° C was carried out to demonstrate the possible effect of the time of heating on the surface characteristics of the yttria–zirconia powders under investigation. Portions of the 4 mol % Y_2O_3-stabilized ZrO_2 dried precipitate were heated at 800° C for various times up to 48 h. The surface properties were measured for the heated samples and the values obtained are given in

TABLE II Surface characteristics of 4 mol % Y_2O_3–ZrO_2 powder calcined at different temperatures

Calcination temperature (° C)	S_{BET} (m^2 g^{-1})	S_t (m^2 g^{-1})	BET-*c* constant	V_p (ml g^{-1})	$\bar{r}_h$ (nm)
as-prepared	266.2	280	18	0.4805	1.8
400	290	320	19	0.5360	2.3
600	231.5	255	16	0.4550	1.9
800	203.9	190	4	0.3479	1.7
1000	160.6	125	3	0.2590	1.6
1200	108.8	93	3	0.2153	2.0
1400	212.9	–	1	0.1841	0.9

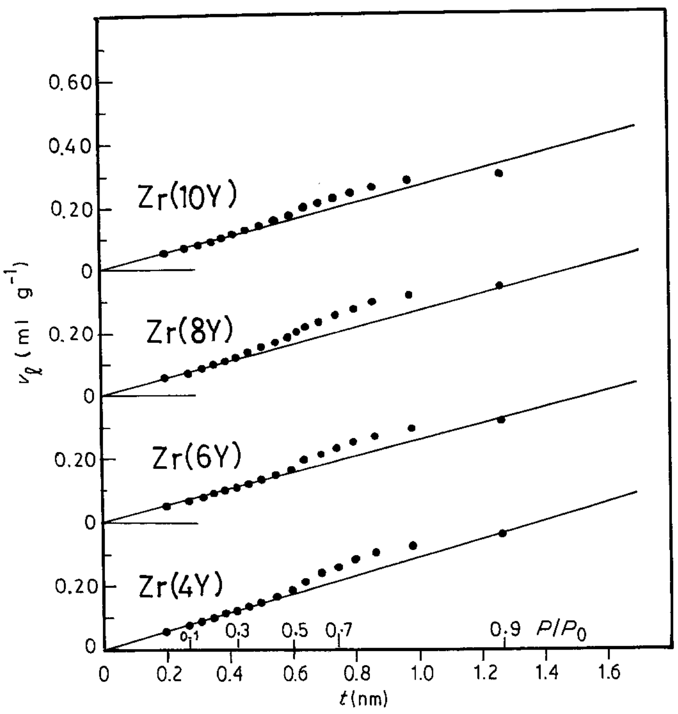


Figure 5 V_l–t plots from nitrogen adsorption data for the prepared yttria–zirconia powders.

Table III. From the data it can be seen that the surface properties as measured by nitrogen adsorption do not exhibit any significant change in their values due to change in duration of heating at 800° C.

3. Discussion and conclusions

Crystallization of Y_2O_3–ZrO_2 cubic solid solutions from the hydrolysis of zirconium and yttrium mixed hydroxides by hydrolysis in an autoclave occurs at extremely low temperature (200° C for 2 h) contrary to the alkoxide-derived coprecipitate. The latter required a firing at 800° C to get the cubic solid solution. Below this temperature monoclinic zirconia was present [5]. Haberko *et al.* [6] calcined their coprecipitate, obtained from the chloride solution treated with ammonium hydroxide, at 400° C to obtain the yttria-stabilized zirconia powder. These facts suggest the coprecipitates obtained by the high temperature hydrolysis technique are homogeneous on an atomic scale.

Noticeably high specific surface areas have been reached with the prepared powders. A value of 266.2 ± 10 m^2 g^{-1} has been achieved for the 4 mol % Y_2O_3–ZrO_2. Such value is higher than the BET surface areas recorded by other investigators [6, 7, 15] for the same system. Fig. 1 shows that the increase in the amount of lattice stabilizer, Y_2O_3, is accompanied by an increase in the degree of crystallinity of the cubic phase of zirconia. Such increase in crystallinity explains the decrease in the BET surface area and total pore volume [6, 21] as Y_2O_3 content increases in the same direction (Table I). The 10 mol % Y_2O_3–ZrO_2 exhibited the lowest surface area value; 239.2 ± 10 m^2 g^{-1}. Such a value is still high enough for this system and reflects the active nature of the powder. The prepared powders are mesoporous and very slightly narrowing of the hydraulic radius, $\bar{r}_h$, takes place as Y_2O_3 content increases.

Most workers consider that the reduction of surface energy is the driving force for sintering; therefore, high surface energy powders are desirable as a starting material for this process. The high surface area materials prepared in the present investigation are recommended as rather sinterable to dense ceramic bodies at relatively moderate temperatures when their compacts are fired.

X-ray diffraction analysis of the calcined samples showed a continuous increase in the intensity of the cubic phase reflections as the calcination temperature increased over 400° C. Such increase in intensity reflects the crystallite growth that took place on heating and explains the continuous decrease in the surface areas and total pore volumes of the powders as calcination temperature increased. This is substantiated by the results of the TEM investigations where a noticeable and gradual increase in the particle size of the samples was recorded on heating to higher calcination temperatures. This behaviour is continued up to 1200° C. The observed discrepancies in the values of surface properties for the sample calcined at 1400° C can be explained by the fact that at this temperature the powder had already been sintered and the nitrogen

TABLE III Surface characteristics of 4 mol % Y_2O_3–ZrO_2 powder calcined at 800° C for various periods of time

Soaking time (h)	S_{BET} (m^2 g^{-1})	S_t (m^2 g^{-1})	BET-*c* constant	V_p (ml g^{-1})	$\bar{r}_h$ (nm)
1	203.9	190	4	0.3479	1.7
10	196	197	5	0.3650	1.9
24	199.7	196	5	–	–
48	202.9	205	5	0.3719	1.8

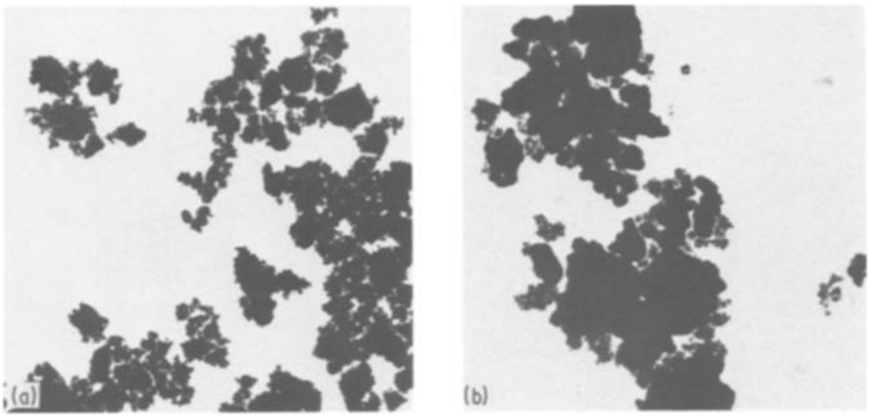


Figure 6 TEM photomicrographs of 4 mol % Y_2O_3-stabilized ZrO_2 calcined for 1 h at (1) 800° C and (b) 1200° C. × 12 500

adsorption process takes place in the material via a diffusion mechanism. Up to 1200° C the calcination temperature has limited effect upon the pore system. The powder remained mesoporous and the mesoporosity represented the major pore system.

The BET-*c* constant is a measure of the heat (energy) of interaction between the adsorbed nitrogen molecules and the yttria–zirconia powder surface. Therefore, the decrease in the BET-*c* constant as a result of increase in calcination temperature indicates a low heat of adsorption in the first adsorbed layer, due to irreactivity of the calcined surfaces.

Although at calcination temperatures up to 800° C crystallite growth is perhaps the dominant influence on the pore structure and surface area, the degree of sintering of the crystallites becomes increasingly important at higher temperatures. The results of the isothermal heating at 800° C (Table III) proves that it is the athermal rather than the isothermal heatings that can influence the surface characteristics of the prepared fine yttria–zirconia powders.

References

1. P. DUWEZ and F. ODELL, *J. Amer. Ceram. Soc.* **33** (1950) 274.
2. P. DUWEZ, F. ODELL and F. H. BROWN, *ibid.* **35** (1952) 107.
3. A. DIETZEL and H. TOBER, *Ber. Deut. Keram. Ges.* **30** (1953) 47.
4. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *J. Amer. Ceram. Soc.* **48** (1965) 372.
5. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *ibid.* **50** (1967) 532.
6. K. HABERKO, A. CIESLA and A. PRON, *Ceramurgia Int.* **1** (1975) 111.

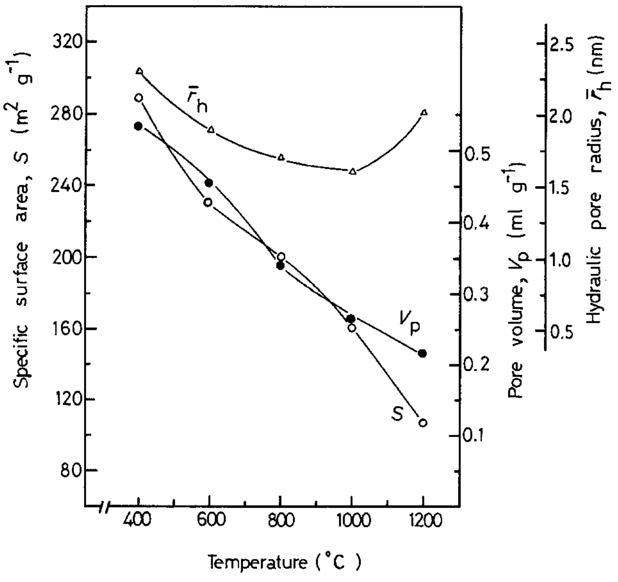


Figure 7 Effect of calcination temperature on the surface characteristics of the 4 mol % Y_2O_3-stabilized ZrO_2 powder.

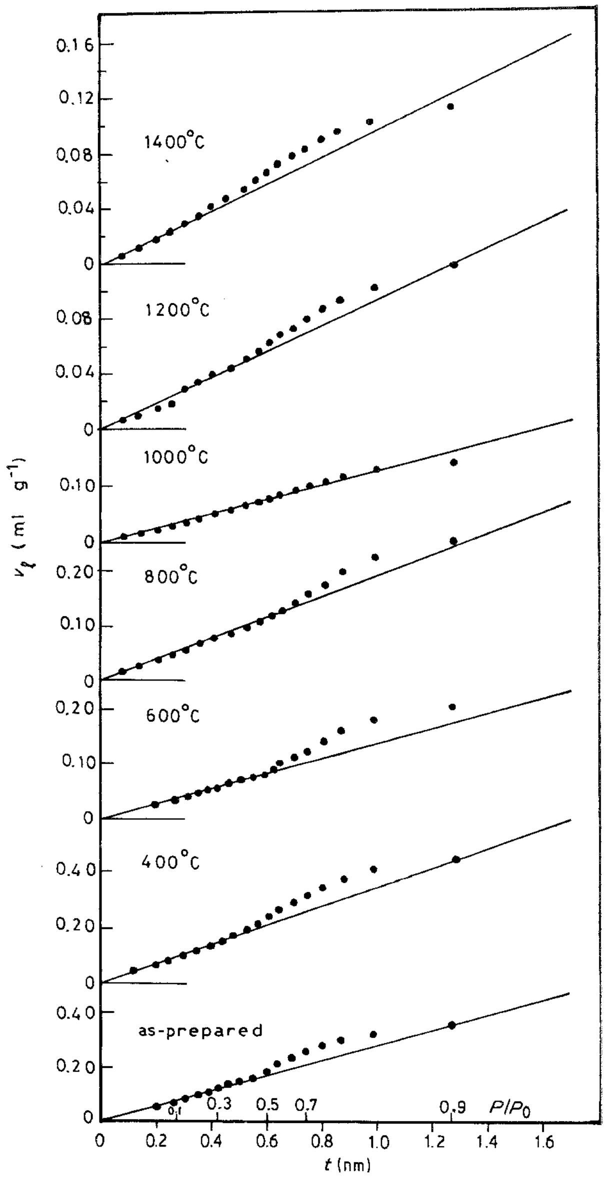


Figure 8 V_t–t plots from nitrogen adsorption data for the 4 mol % Y_2O_3-stabilized zirconia calcined at different temperatures for 1 h.

7. M. A. G. G. VAN DE CRAAF, K. KEIZER and A. J. BURGRAAF, *Sci. Ceram.* **10** (1980) 83.
8. L. DEL OLMO, P. DURAN and C. MOURE, in "Sintering Theory and Practice", edited by D. Kolar, S. Pejovnik and M. M. Ristic (Elsevier, Amsterdam, 1982) p. 401.
9. G. Y. ONODA and L. L. HENCH, "Ceramic Processing Before Firing", (Wiley, New York, 1978).
10. M. A. THOMPSON, D. R. YOUNG and E. R. McCARTNEY, *J. Amer. Ceram. Soc.* **58** (1973) 648.
11. C. E. SCOTT and J. S. REED, *Bull. Amer. Ceram. Soc.* **58** (1979) 587.
12. H. TH. RIJNTEN, in "Physical and Chemical Aspects of Adsorbents and Catalysts", edited by G. Linsen, (Academic Press, New York, 1970) p. 315.
13. J. H. DeBOER, *Proc. Brit. Ceram. Soc.* **5** (1965) 5.
14. S. A. SELIM and T. M. EL-AKKAD, *J. Appl. Chem. Biotechnol.* **27** (1977) 58.
15. A. R. BURKIN, H. SARICIMEN and B. C. H. STEELE, *Trans. J. Brit. Ceram. Soc.* **79** (1980) 105.
16. T. H. ETSELL and S. N. FLANGAS, *Chem. Rev.* **70** (1970) 339.
17. S. YAMAGUCHI and T. KATSURAI, *Z. Anorg. Allgem. Chem.* **350** (1969) 327.
18. C. M. PHILLIPPI and K. S. MAZDIYASNI, *J. Amer. Ceram. Soc.* **54** (1971) 254.
19. R. D. CADLE, "Particle Size Determination", (Interscience Publishers Ltd., London, 1965).
20. R. SH. MIKHAIL, N. M. GUINDY and S. HANAFI, *Egypt. J. Chem.* **16** (1973) 53.
21. E. CRUCEAN and B. RAND, *Trans. J. Brit. Ceram. Soc.* **78** (1979) 58.

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