JOURNAL OF MATERIALS SCIENCE 31 (1996) 267–271

Sol gel preparation, structure and thermal stability of crystalline zirconium titanate microspheres

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Very pure and crystalline $ZrTiO_4$ microspheres (15–50 μm) were prepared by two sol gel methods using a zirconia sol and two types of titania sols and characterized by scanning electron microscopy, X-ray diffraction and simultaneous differential thermal and thermogravimetric analysis. On gelation of the mixed sols, microspheres of an amorphous material with Zr/Ti ratio of ~ 1.0 were obtained by each route. The amorphous materials obtained by the two routes transformed to fully crystalline $ZrTiO_4$ at 500 and 600 °C, respectively. The high temperature thermal stabilities of these materials were also studied.

1. Introduction

Zirconium titanate, $ZrTiO_4$ is an important ceramic material and finds application in transducers, microwave and communication devices [1–5] and in the manufacture of high temperature pigments [6]. It is also useful as a bi-functional catalyst [7–9].

$ZrTiO_4$ is normally synthesized by a solid-state reaction of its constituent oxides at temperatures of 1200–1700 °C over a prolonged period to achieve homogeneity [5, 10]. Recently, however, crystalline $ZrTiO_4$ powder has been prepared by the calcination of a co-precipitated hydroxyperoxo compound of Zr and Ti at a lower temperature [11].

Irregular shaped powdered ceramic particles are both difficult to handle and use on an industrial scale. Production of spherical particles are therefore preferred as they have some distinct advantages. These are

(i) ease of handling,
(ii) ease of feeding of an automatic press,
(iii) improved quality of coating by plasma spray,
(iv) better control of microstructure during sintering,
(v) low temperature densification through better compaction.

The present paper deals with the preparation and characterization of crystalline $ZrTiO_4$ microspheres by two sol gel methods.

2. Experimental procedure

2.1. Preparation

Samples were prepared by two distinct preparative techniques as described below:

2.1.1. Method 1

A titanium (IV) hydroxide hydrate was precipitated from an aqueous solution of titanium chloride using dilute ammonia solution. The resulting gel was washed thoroughly and peptised by standard techniques [12] using mineral acid. The resultant TiO_2 sol was translucent with a density of 1.08 $g\,l^{-1}$, a concentration of 45 $g\,l^{-1}$ and a counter ion/Ti (IV) ratio of 0.2.

A salt of zirconium (basic carbonate or hydroxide) was converted to the oxide hydrate with sufficient counter ion present to prevent aggregation. The resultant transparent sol had a density of 1.3, a concentration of 240 $g\,l^{-1}$ ZrO_2 and a counter ion/Zr (IV) ratio of ~1.0. The two sols were then mixed in an equimolar ratio. 20 ml of the mixed sol was added to 800 ml of ethyl-hexanol/surfactant mixture to produce concentrated sol spheres. The spheres were then gelled using an organic anion extracting agent and oven-dried at 105 °C. The gel spheres were subsequently heat treated and characterized.

2.1.2. Method 2

A zirconia sol was prepared as described for method 1. A TiO_2 sol was prepared by solvent extracting Cl^- ions from an aqueous titanium chloride. This sol had a density of 1.35, a concentration of 295 $g\,l^{-1}$ TiO_2 and a Cl^-/TiO_2 ratio of ~0.4. Sols were then mixed in an equimolar ratio. 10/20 ml of the mixed sol was dispersed in 1.1.1 trichloroethane and stirred. Appropriate amount of a solvent containing anion extraction agent was added slowly to form gel spheres. The gel spheres were thoroughly washed in acetone to remove solvents and carefully dried in an oven maintained at 105 °C. The gel spheres were subsequently heat treated and characterized.

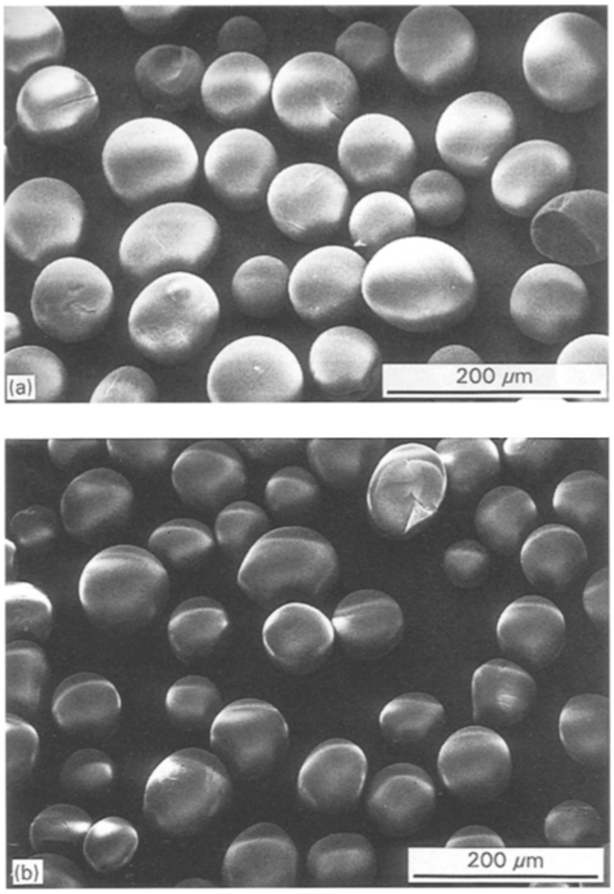

Figure 1 Scanning electron micrographs of dried gels: (a) ZRTM1 and (b) ZRTM2.

2.2. Characterization

2.2.1. Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX)

Morphology and elemental analysis of the samples were carried out on a Cambridge Stereoscan (model S90B) equipped with an energy dispersive X-ray analyser. Conducting samples were prepared by either coating carbon or sputtering gold on finely ground powder specimens. Broad beam and point EDX analysis of the samples were performed using pure ZrO_2 and TiO_2 as well as cobalt as standard.

2.2.2. Thermal analysis

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the samples was carried out using a Polymer Laboratories thermal analyser (model STÅ1500) in static air and the temperature was ramped at a rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$.

TABLE I EDX analysis of Zr/Ti elemental ratios

Oven dried gel spheres	Broad beam	Point
ZRTM1	1.04	1.07 1.01 1.04
ZRTM2	1.03	1.04 1.06 1.00

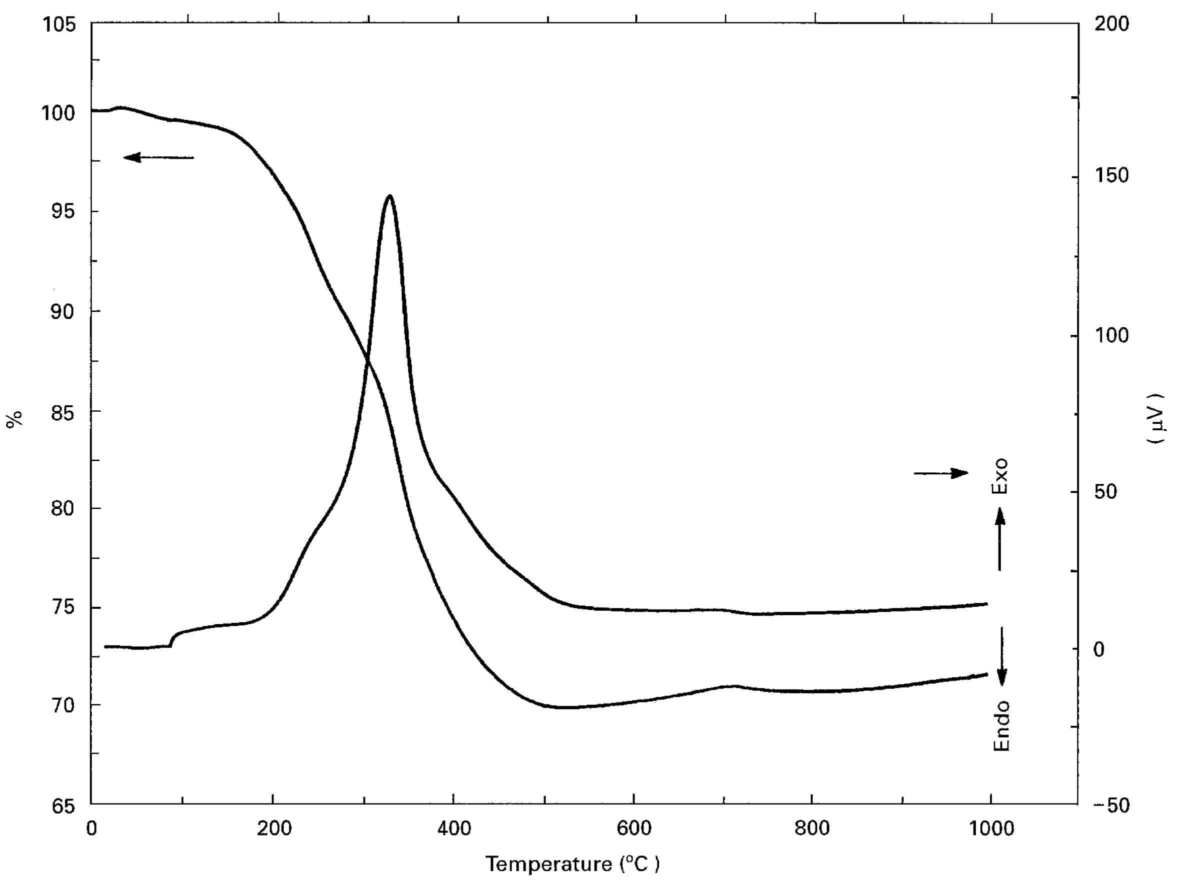

Figure 2 Simultaneous differential thermal analysis and thermogravimetric analysis plots of dried ZRTM1 gel.

2.2.3. X-ray powder diffraction (XRD) measurement

X-ray powder diffraction patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 10$–80° with a scanning speed of $\frac{1}{4}^\circ\ \mathrm{min}^{-1}$ on a Philips diffractometer (Model PW1710) using CuK_α radiation with a nickel filter. Cell parameters were calculated and further refined using linear regression procedures applied to the measured peak positions of all major reflections up to $2\theta = 60^\circ$ with the Philips APD 1700 software. This software was also used to calculate the average size of the crystallites in a sample using the well known Scherrer equation

$$D = k\,\lambda/h_{1/2}\cos\theta$$

where D = average size of the crystallites, k = Scherrer constant, λ = wavelength of radiation, $h_{1/2}$ = peak width at half-height and θ corresponds to the peak position.

2.2.4. Surface area and porosity measurements

Surface area and pore size distribution of the gel and calcined powder were performed on a Micromeritics apparatus (model ASAP 2000) using N_2 as the adsorption gas. Samples were degassed at 105 °C for 6 h prior to analysis.

3. Results and discussion

On gelation, both the preparative techniques produced spherical particles (Fig. 1) with particle sizes

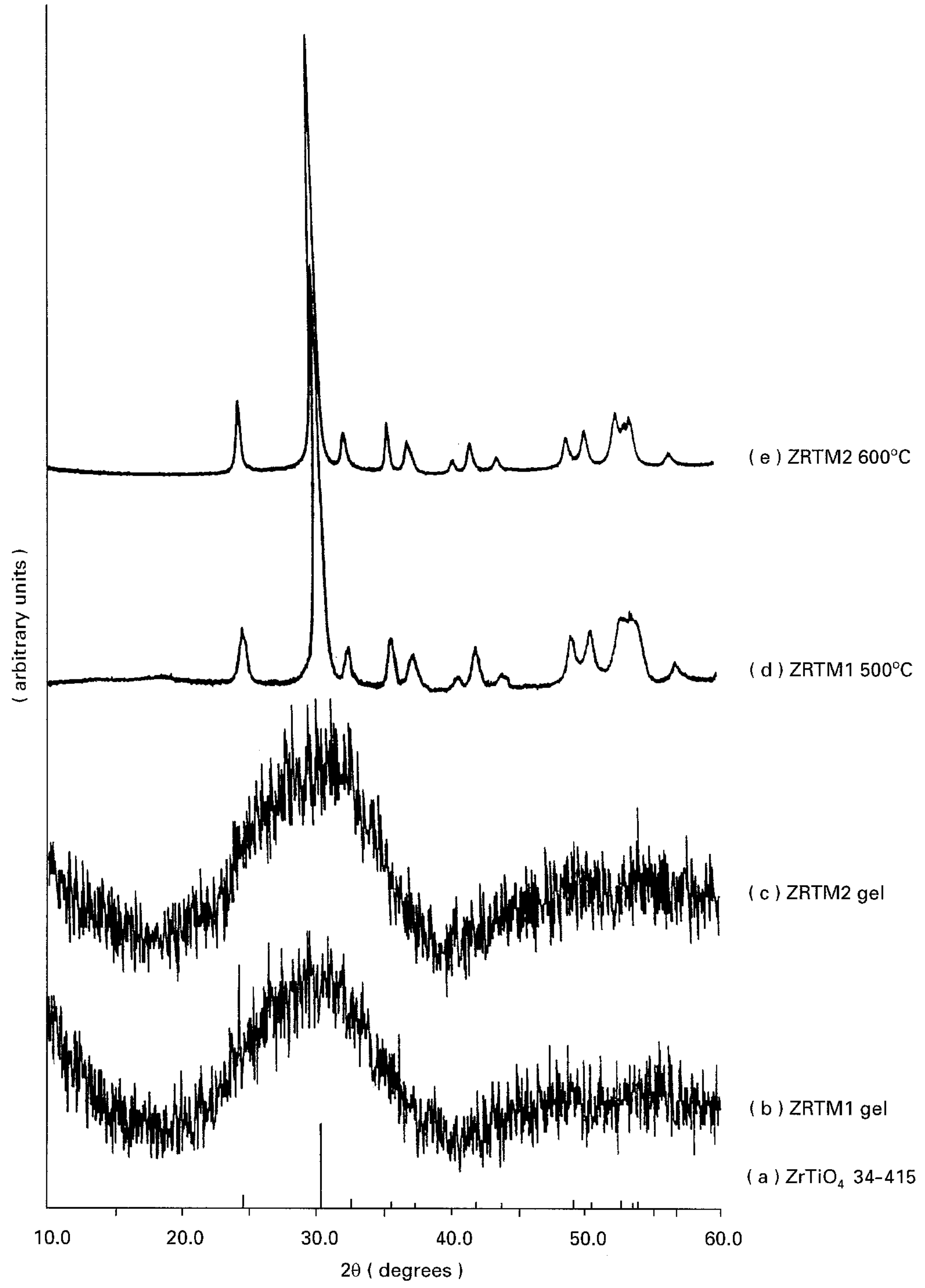

Figure 3 Powder X-ray diffraction patterns of: (a) crystalline $ZrTiO_4$ (JCPDS standard: 34–415); (b) dried ZRTM1 gel; (c) dried ZRTM2 gel; (d) (b) heated to 500 °C and (e) (c) heated to 600 °C.

varying between 15–50 μm. The results of a broad beam EDX analysis of the two gel samples, ZRTM1 and ZRTM2, are shown in Table I. The EDX analysis of randomly selected particles of each sample using a spot size of 100 nm are also shown. These results clearly show that the spherical particles produced by both methods are homogeneous on a nanoscale with a Zr/Ti ratio of ~1.0.

TABLE II Size (nm) of crystallites at different temperatures

Sample	500 °C	600 °C	700 °C
ZRTM1	20	35	60
ZRTM2	30	45	68

The DTA-TGA plots of a sample of a ZRTM1 gel (Fig. 2) show a series of endothermic transitions which are associated with decrease in weight of the sample. This characteristic behaviour is also shown by other gel materials of this type. These are attributed to the removal of structural hydroxy and anionic species. The plots show a sharp exothermic transition at 320 °C with a significant (20%) loss in weight. There is another weak exothermic transition at around 450 °C at which temperature the weight of the sample stabilizes. No other DTA peak nor any change in weight of the sample is observed on further heating to 1200 °C and subsequent cooling to room temperature.

The thermal behaviour of ZRTM2 and ZRTM1 gel microspheres is broadly similar. The notable difference

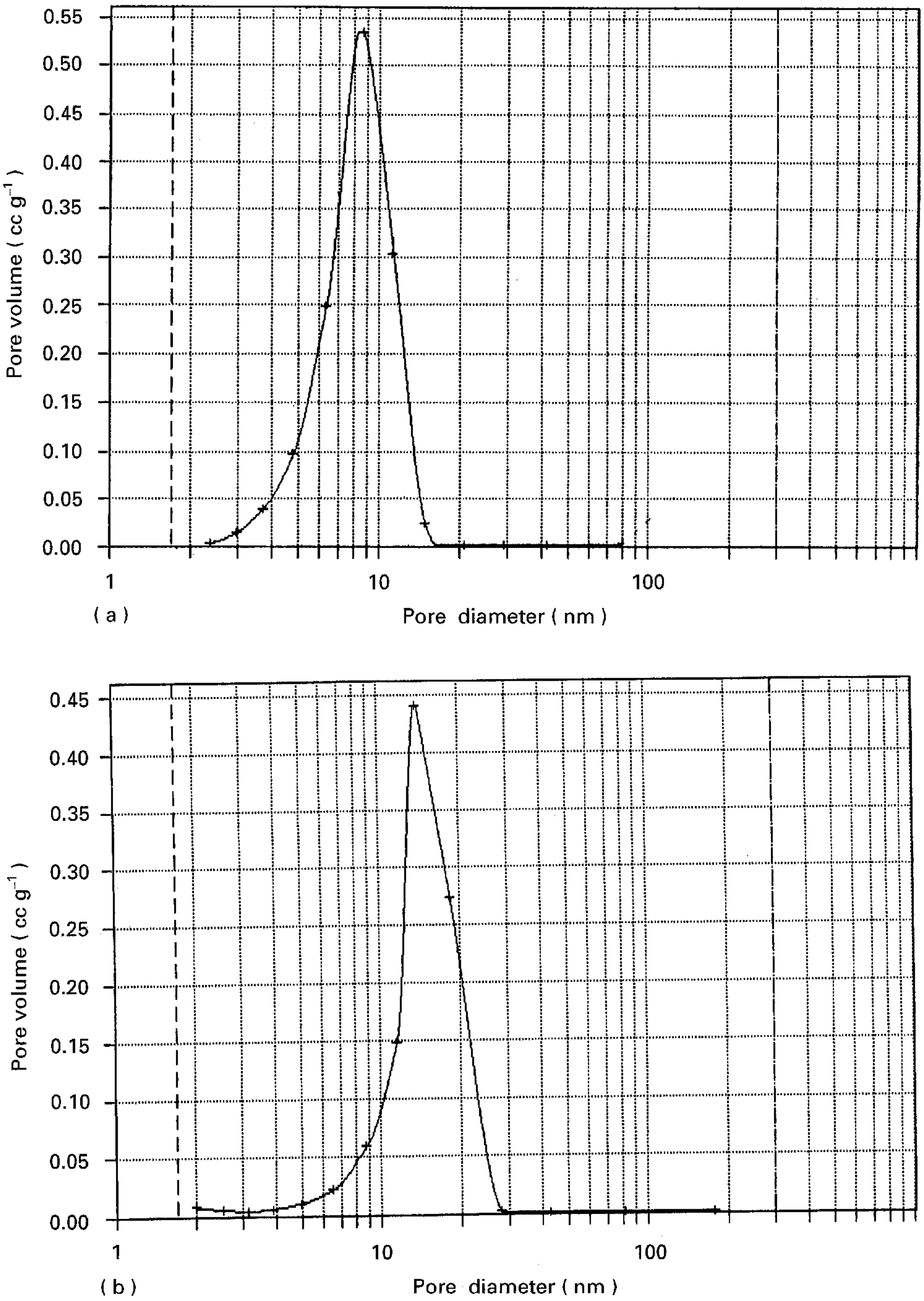

Figure 4 Pore size distribution of: (a) ZRTM1 gel heated to 500 °C and (b) ZRTM2 gel heated at 600 °C.

being the exothermic transitions observed in the case of ZRTM1 now appears at a slightly higher temperature. The thermal behaviour on further heating or cooling is similar to that of ZRTM1.

The XRD patterns of the two dried gel samples, ZRTM1 and ZRTM2 (Fig. 3b and c), show that both these gels are amorphous. Each of the samples was subsequently heated to selected temperatures based on its thermal behaviour and its XRD patterns was recorded. The patterns (Fig. 3d and e) show that ZRTM1 and ZRTM2 fully crystallize at 500 and 600 °C, respectively. The XRD patterns of both crystalline samples match the JCPDS standard (Fig. 3a) for $ZrTiO_4$ (34-415). The delay in crystallization of a sample of ZRTM2 gel is probably due to difference in the rates of extraction of the two counter anions present in the mixed sol leading to a certain degree of inhomogeneity. Since the counter anions are the same for the two sols used in method 1 this phenomenon is not encountered thus leading to a lower crystallization temperature of ZRTM1 gel. It may therefore be inferred that the exothermic peak at 450 °C observed in the DTA-TGA plot of ZRTM1 and the corresponding peak for ZRTM2 are due to transition from amorphous to crystalline state.

The crystallization temperatures observed in the present investigation are considerably lower than any reported earlier [11]. This earlier study produced a material which was mostly amorphous at 650 °C and its XRD pattern showed small crystalline peaks over a largely amorphous background. The material became fully crystalline at 800 °C.

An analysis of the XRD pattern of crystalline $ZrTiO_4$ presented here shows that its structure is orthorhombic with a space group *Pnab*. The cell dimensions were found to be $a = 0.503200$ nm, $b = 0.551753$ nm and $c = 0.480676$ nm. These values agree with the published data for $ZrTiO_4$ prepared at 1700 °C [13].

The position and width of the (0 1 1) diffraction peak was used to calculate the average crystallite size after sequentially heating both ZRTM1 and ZRTM2 to increasingly elevated temperatures. The results are summarized in Table II.

As expected from their DTA-TGA plots, the XRD patterns of crystalline ZRTM1 and ZRTM2 remain unchanged even at 1200 °C. The only phase present at this temperature is $ZrTiO_4$. Contrary to this observation, a previous study [14] reported separation of TiO_2 phase in samples of $ZrTiO_4$ when heated to similar temperatures.

The surface areas of ZRTM1 and ZRTM2 are 55.6 and 33.1 $m^2 g^{-1}$ at their respective crystallization temperatures. At these temperatures, both samples have similar pore volumes. However their average pore sizes differ, being 8 and 15 nm, respectively (Fig. 4a and b). The lower pore size can be attributed to the more densifiable nature of the low anion titania sol.

Both the samples were subjected to repeated thermal cycling up to 1200 °C. SEM micrograph of a typical sample of ZRTM1 following thermal cycling is shown in Fig. 5. It is seen that both the shape and size of the microspheres are unaffected by the process.

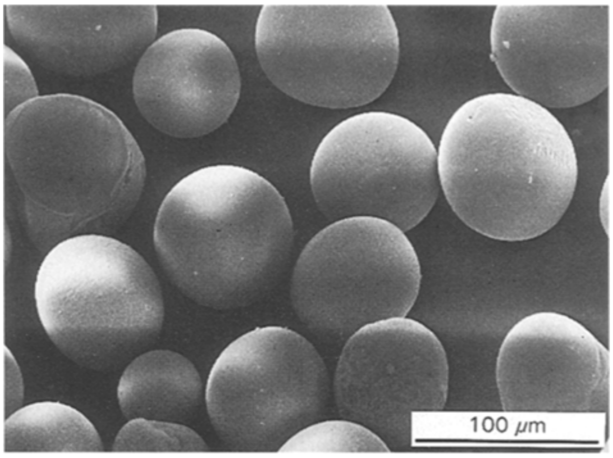

Figure 5 Scanning electron micrograph of crystalline ZRTM1 after repeated thermal cycling.

4. Conclusions

The preparative techniques, developed in the present investigation, each produced homogeneous microspherical particles of very pure crystalline $ZrTiO_4$, at a temperature lower than any previously reported for this material. These microspheres are very stable, their composition and structural integrity remain unaffected by repeated thermal cycling up to a temperature of, at least, 1200 °C.

References

1. R. C. BUCHANAN, "Ceramic Materials for Electronics" (Dekker, New York, 1986) p. 154.
2. B. JAFFE, W. R. COOK and H. JOFFE, "Piezoelectric Ceramics" (Academic Press, London, 1971) p. 237.
3. A. J. MOULSON and J. M. HERBERT, "Electroceramics" (Chapman and Hall, London, 1990) p. 239.
4. T. NEGAS, G. YEAGER, S. BELL and R. AMREN, in Proceedings of International Conference on "Chemistry of Electronic Ceramic Materials" NIST Special Publication 804 (1990) 21.
5. R. W. LYNCH and B. MORRISON, *J. Amer. Ceram. Soc.* **55** (1972) 409.
6. F. HUND, *Z. Anorg. Allg. Chem.* **525** (1985) 221.
7. K. TANABE, "Solid Acids and Bases, Their Catalytic Applications" (Academic Press, New York, 1970).
8. K. TANABE, T. SUMIYOSHI, K. SHIBATA, T. KIYOURA and J. KITAGAWA, *Bulletin Chem. Soc. Japan* **47** (1974) 1064.
9. K. ARAKA and K. TANABE, *ibid.* **53** (1980) 299.
10. A. E. McHALE and R. S. ROTH, *J. Amer. Ceram. Soc.* **69** (1986) 829.
11. J. A. NAVIO, F. J. MARCHENA, M. MACIAS and P. J. SANCHEZ-SOTO, *J. Mater. Sci.* **27** (1992) 2463.
12. S. GLASSTONE "Textbook of Physical Chemistry" 2nd edn (MacMillan & Co.) p. 1274.
13. National Bureau of Standards (US) Monograph **25**; 20 (1983).
14. JUNG-CHUNG WU, CHUNG-SUN CHUNG, CHING-LAN AY and IKAI WANG, *J. Catalysis* **87** (1984) 98.

Received
and accepted 11 May 1995