JOURNAL OF MATERIALS SCIENCE 25 (1990) 2227–2232

Pyrolytic preparations of ceramic powders by a spray calcination technique

D. VOLLATH
Kernforschungszentrum Karlsruhe GmbH, Institut für Material-und Festkörperforschung III, Postfach 3640, D-7500 Karlsruhe, FRG

A laboratory-scale facility for pyrolytic preparation of powders used in ceramic materials fabrication is presented. It is shown through examples that application of the technique described allows very homogeneous powders to be prepared which, by conventional techniques, can be prepared either with great difficulty or practically not at all. A typical application in the system ZrO_2–Y_2O_3–Al_2O_3 is shown. From experimental results it is further demonstrated that suspensions can also be profitably processed. Dependent on the system used, the product fabricated is either crystallized or amorphous.

1. Introduction

Homogeneous and well-sinterable powders cannot be conveniently fabricated from ceramic mixed systems. Especially in systems such as $ZrO_2 + Y_2O_3$, $ZrO_2 +$ MgO and $ZrO_2 + Y_2O_3 + Al_2O_3$ the prerequisite of homogeneity is very important and difficult to attain. Generally, two approaches are adopted: either the source powder is mixed mechanically and homogenized in a subsequent grinding step, or the hydroxides are coprecipitated from salt solutions. In the first case, several hours of grinding are required and in the second case the various constituents of a system are frequently precipitated at greatly differing pH values. This necessitates an additional step of homogenization. The problems are similar in fabrication techniques based on the hydrolysis of alcoholates. Fully homogeneous products are obtained if – as is possible with some of the ZrO_2–Al_2O_3 ceramics – organometallic compounds are used as the source material which already contain the metallic constituents at the desired ratio [1].

The problems described can be overcome if, for instance, solutions consisting of nitrates or acetates are sprayed and decomposed thermally to oxides. These processes have been described already for electroceramics fabrication [2]. Under this technique spherical powder particles with diameters in the range from 2 to 50 μm are obtained. In the configuration described ~0.2 M solutions are sprayed in a furnace kept at a temperature between 500 and 600° C. Ultrafine powders with particle sizes from 10 to 20 nm are obtained if nitrate solutions are sprayed and the fine fraction of the sprayed mist is heated in an inductively coupled plasma (ICP) flame. In this way, minimum amounts of MgO, Al_2O_3, ZrO_2 and Fe_2O_3 powders have been fabricated [3–5]. Using the same technique, ceramic powders can also be fabricated from the ZrO_2–Al_2O_3 system; however, some problems of homogeneity have appeared [5].

Starting from the published literature, which has been outlined but briefly here, a facility for the spray calcination of ceramic powders was developed. The following targets were set for development:

(i) A very fast process in order to avoid separation of multiphase systems.

(ii) Highly sinterable powders with small particle sizes.

(iii) Production of about 100 g powder per hour.

(iv) Suitability for promoting the reactions of nitrates, chlorides or other source compounds into the desired oxides.

2. The spray-drying and calcination process (SDC process)

2.1. The overall facility

Fig. 1 shows the principle of the newly developed facility for simultaneous spray drying calcination [6]. The principle of the equipment is comparatively simple:

(i) The aqueous solution or a suspension is finely sprayed through a nozzle.

(ii) A frit surrounds the spray nozzle concentrically

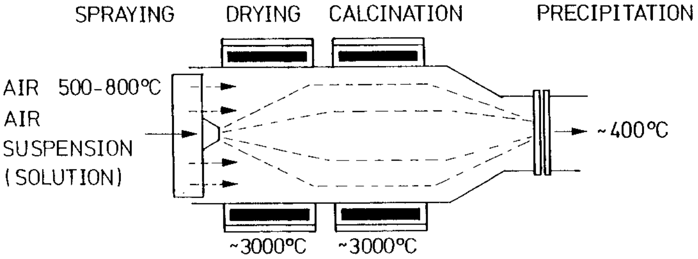

Figure 1 Equipment for the spray drying and calcination process. Particle size 0.1 to 3 μm, capacity 1.0 l h^{-1}.

0022-2461/90 $03.00 + .12

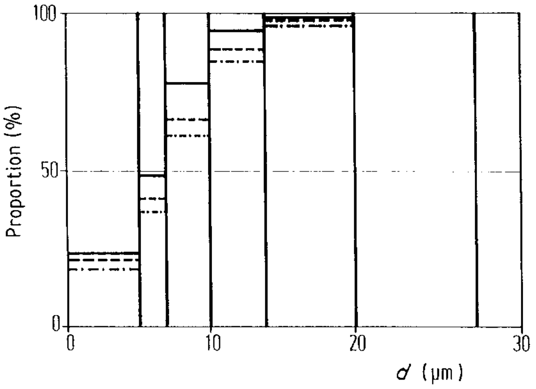

Figure 2 Size distribution for water droplets obtained by the Schlick nozzle [8]: (–·–) 4 bar, (– – –) 5 bar, (——) 6 bar.

and delivers a laminar, highly heated gas stream. The gas stream serves two purposes: firstly it ensures the most uniform possible transport of the droplets generated in the spray nozzle, and secondly it heats and evaporates them. The gas stream can be heated up to 800° C in order to supply sufficient energy for evaporation.

(iii) The nitrate of chloride droplets formed after evaporation of the water are then heated by radiation heating to such a level that the compounds decompose and the desired oxides are formed. On account of the short dwell time of only about 0.5 sec in the drying and calcination zone there is no time for any separation of different phases to take place.

(iv) The product formed is removed into a collector such as a cyclone or a filter.

2.2 The spray nozzle

A commercially available two-fluid nozzle is used to spray the solutions. The selected nozzle gives very small droplets while, at the same time, the consumption of propellant is not excessively high. Fig. 2 shows cumulative spectra of the droplets against propellant gas pressure. These spectra can be achieved with such a nozzle according to information received from the supplier [7]. The mean size of droplets furnished by the nozzle is between 8 and 9 μm with a spraying capacity of 1.5 $1\,h^{-1}$. The maximum spraying capacity of the nozzle is about 6 $1\,h^{-1}$. The nozzle aspirates the liquid by an injector effect, which means that no additional pump is required.

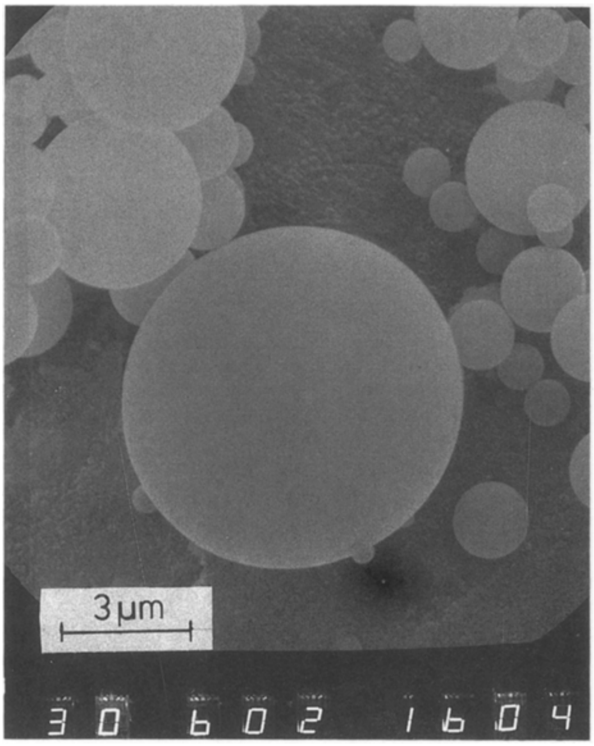

Figure 3 Aluminium–magnesium nitrate particles after evaporation of water.

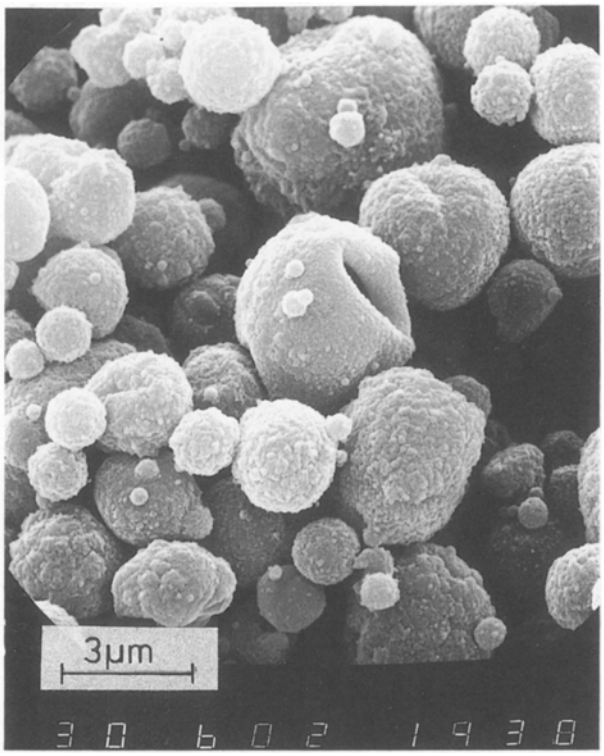

Figure 4 Aluminium–magnesium spinel particle after spray drying and calcination.

2.3. Drying and calcination

After the solvent (water) has evaporated by contact of the droplets with the hot carrier gas stream the molten nitrate or chloride residues are heated by radiation heating until they decompose. Halogen filament lamps are used as sources of radiation heating. In all cases under consideration this has led to the formation of oxides. A high efficiency of radiation heating requires that no powder is deposited in that part of the reaction vessel where the lamp is located. This can be achieved by selection of a suitable flow velocity of the carrier

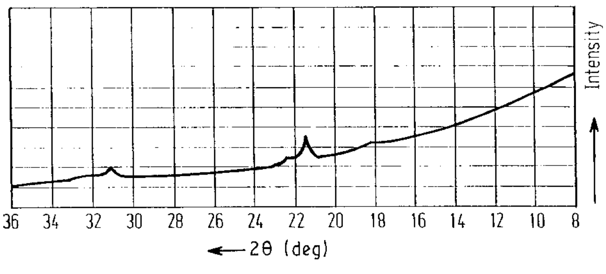

Figure 5 X-ray diffraction diagram of mostly amorphous aluminium–magnesium spinel containing some water. The faint lines belong to MgO.

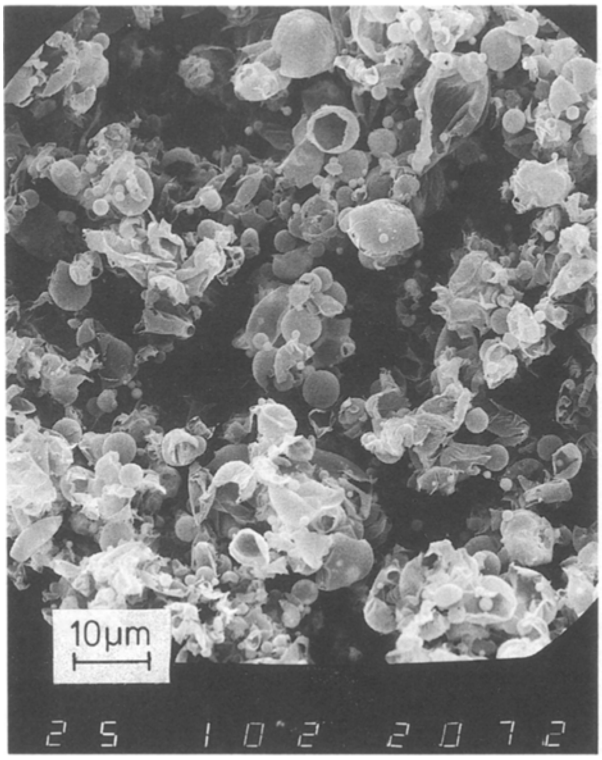

Figure 6 Appearance of 97 mol % ZrO_2 + 3 mol % Y_2O_3 particles after spray drying.

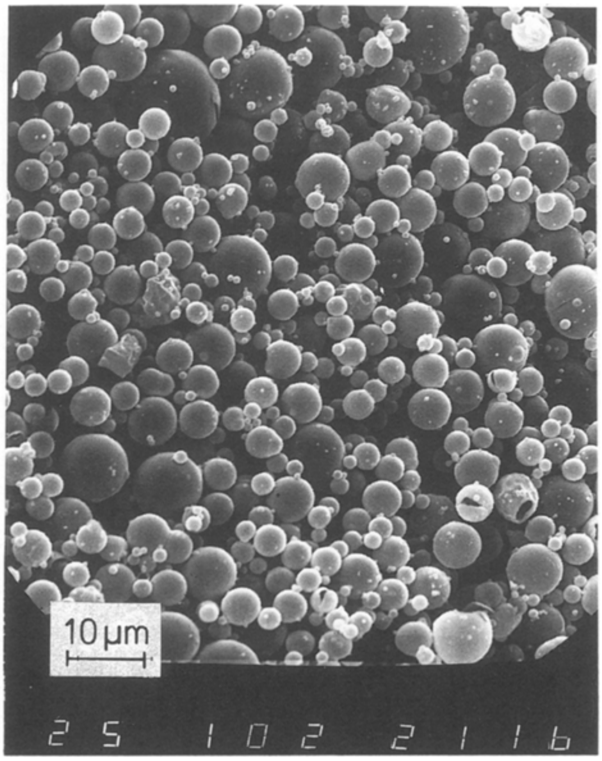

Figure 8 Typical appearance of 85 mol % ZrO_2 + 15 mol % MgO powder.

gas and by thermostating. The powders formed in the process described are so fine that as a result of thermolysis they would preferably deposit at the colder part of the walls of the reaction chambers. This is avoided by thermostating.

In order to be able to demonstrate the postulated sequence of the process, investigations were made on the magnesium spinel model system. In the experiments aluminium and magnesium were used as the nitrates $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$, respectively.

Fig. 3 shows a powder particle after evaporation of the water. A clean smooth surface can be seen which has been formed by solidification of the remaining nitrate melt. By energy-dispersive X-ray analysis it can be recognized that up to that time separation has not yet occurred. Rather large particles can already be hollow in this state. If the process of heating is continued, the nitrates begin to decompose. The onset of surface structuring can be observed which develops further while decomposition goes on (Fig. 4). Although it could be assumed that this is a process of segregation, no evidence can be provided in support of this assumption because the particles are small ($< 0.1\ \mu m$). However, X-ray diffraction micrographs of the powder are indicative of separation beginning. The first signs of MgO crystallization (Fig. 5) are visible. The diffraction lines attributable to the spinel do not yet occur at this stage, which means that a substantial part of the powder remains amorphous.

3. Practical examples

3.1. ZrO_2 ceramics

Among the oxide ceramic materials those based on zirconium oxide offer a particularly high potential of application, especially in the partially stabilized tetragonal modification. The following source powders for zirconium-based ceramics were studied in the framework of our activities:

$$97\,\text{mol}\,\%\ ZrO_2 + 3\,\text{mol}\,\%\ Y_2O_3$$

$$85\,\text{mol}\,\%\ ZrO_2 + 15\,\text{mol}\,\%\ MgO$$

$$78\,\text{mol}\,\%\ ZrO_2 + 2\,\text{mol}\,\%\ Y_2O_3 + 20\,\text{mol}\,\%\ Al_2O_3$$

The source products used for zirconium were zirconium nitrate and zirconyl chloride, respectively, and for all the other oxides the nitrates or chlorides. At least from the point of view of powder fabrication there are no

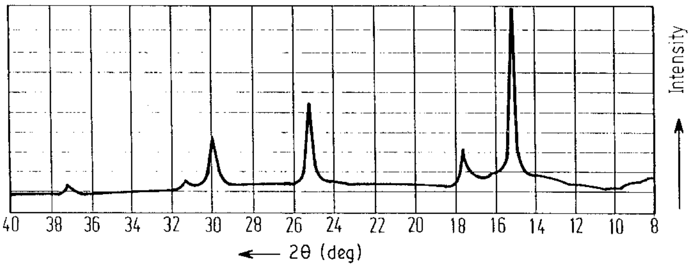

Figure 7 X-ray diffraction diagram of 97 mol % ZrO_2 + 3 mol % Y_2O_3 after spray drying.

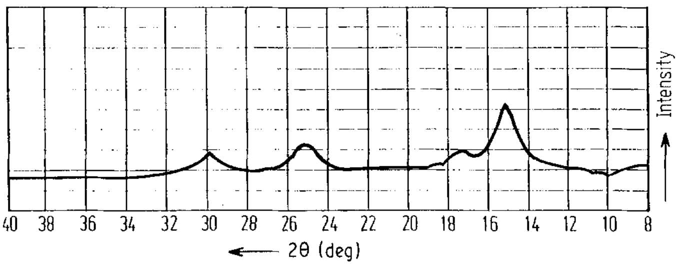

Figure 9 X-ray diffraction diagram of 85 mol % ZrO_2 + 15 mol % MgO after production by the SDC process.

differences whether chlorides or nitrates are used. The behaviour is clearly different only if nitrates are mixed with chlorides. In that case, powders with elevated percentages of volatile materials (almost exclusively water) are obtained which, however, can be expelled only at relatively high temperatures.

Fig. 6 shows the typical appearance of the individual powder particles after spray calcination if zirconium oxide with 3 mol % Y_2O_3 is prepared from nitrates according to the process described. As shown by the X-ray diffraction diagram in Fig. 7, the powder has crystallized poorly. As the diffraction lines are very broad, the structure cannot be determined in an unambiguous manner. However, cubic modification is probably involved. This would also be in line with the Ostwald rule.

A zirconium oxide powder containing 15 mol % MgO resembles in appearance that prepared from the chlorides (Fig. 8). Whereas the individual powder particles are very much like the Y_2O_3-doped material, X-ray diffraction exhibits a material whose crystallized state is even poorer. The X-ray diffraction diagram has been represented in Fig. 9. As in the case under consideration, the powder might be present in the cubic modification.

If aluminium oxide is added to the zirconium oxide containing Y_2O_3, the result is completely different. Although the appearance of the powder particles does not change (Fig. 10), X-ray diffraction shows that such a mixture is amorphous. The X-ray diffraction diagram in Fig. 11 suggests only a weak tendency towards short-range order. As Al_2O_3 is practically insoluble in ZrO_2, there are probably conditions developing an amorphous state similar to those in metals. First analyses have shown that in the case considered aluminium is present as hydroxide or hydrate immediately after powder preparation. Differences between the powders made from chlorides or nitrates are not detectable at this stage.

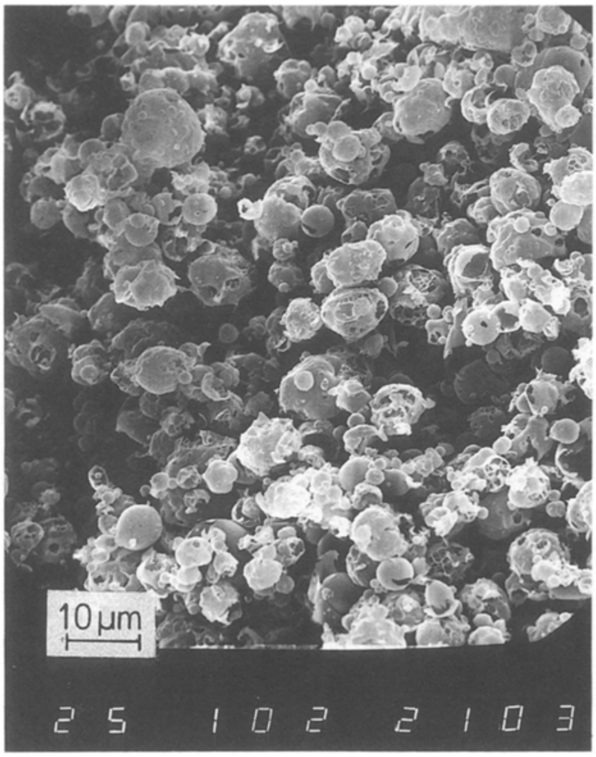

Figure 10 78 mol % ZrO_2 + 2 mol % Y_2O_3 + 20 mol % Al_2O_3 powder as produced by the SDC process.

All powders prepared according to the described process of spray calcination have in common a rather large specific surface. The values range from 10 to 70 $m^2 g^{-1}$ for the ZrO_2-base powders, dependent on the parameters selected for spraying.

3.2. Lithium-containing ceramics

To demonstrate that not only solutions but also suspensions can be favourably processed by the technique described, two further examples of lithium-containing ceramics will be described here.

If $LiAlO_2$ is prepared by precipitation of $Li(Al_2(OH)_7) \cdot nH_2O$ in water, foliated aggregates of lithium dialuminate and perfectly developed LiOH crystals are obtained after normal spray drying [8, 9]. If the spray calcination process described is applied, most of the reaction between $Li(Al_2(OH)_7) \cdot nH_2O$ and LiOH, in which lithium aluminate is produced, takes place as early as during the process of powder preparation. This can be seen very clearly from a comparison of the appearances of powders prepared according to both techniques (Fig. 12). In the powder obtained by spray calcination the LiOH particles can no longer be recognized because the reaction to $LiAlO_2$ is already complete.

The difference in the preparation of lithium orthosilicate, Li_2SiO_4, is not so clearly visible. The suspension used to prepare this powder is obtained by reaction of LiOH with amorphous SiO_2 in methanol. Before spraying, water is substituted for methanol [9, 10]. Fig. 13 shows the powder particles obtained both after normal spray drying and with the technique described here. Above all, the difference in particle size can be clearly seen. The powders of lithium ceramics prepared according to this technique have specific surfaces around 50 $m^2 g^{-1}$.

4. Summary

A laboratory-scale facility for preparing source powders for use in ceramic materials fabrication has been presented. It has been illustrated by examples

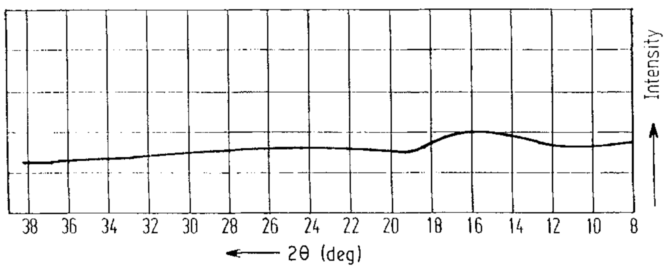

Figure 11 X-ray diffraction diagram of 78 mol % ZrO_2 + 2 mol % Y_2O_3 + 20 mol % Al_2O_3 directly after production.

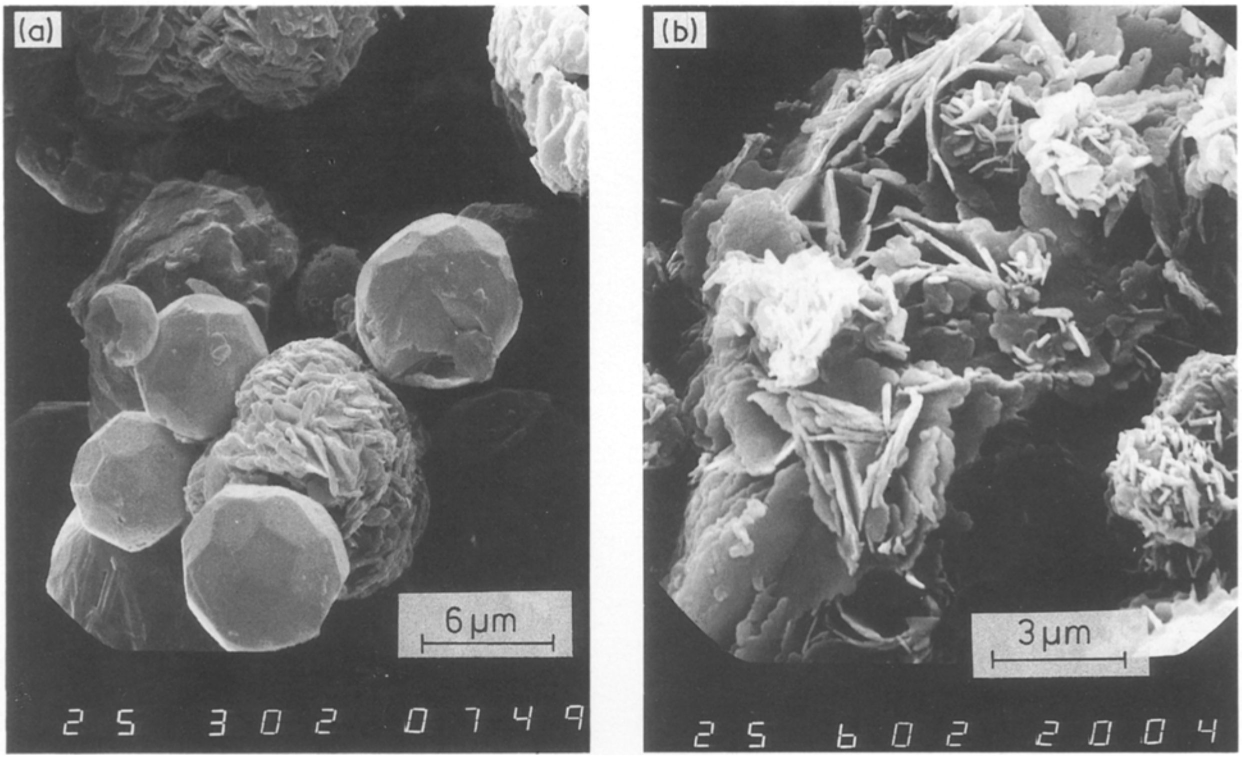

Figure 12 Lithium aluminate particles (a) after normal spray drying and (b) obtained by the SDC process.

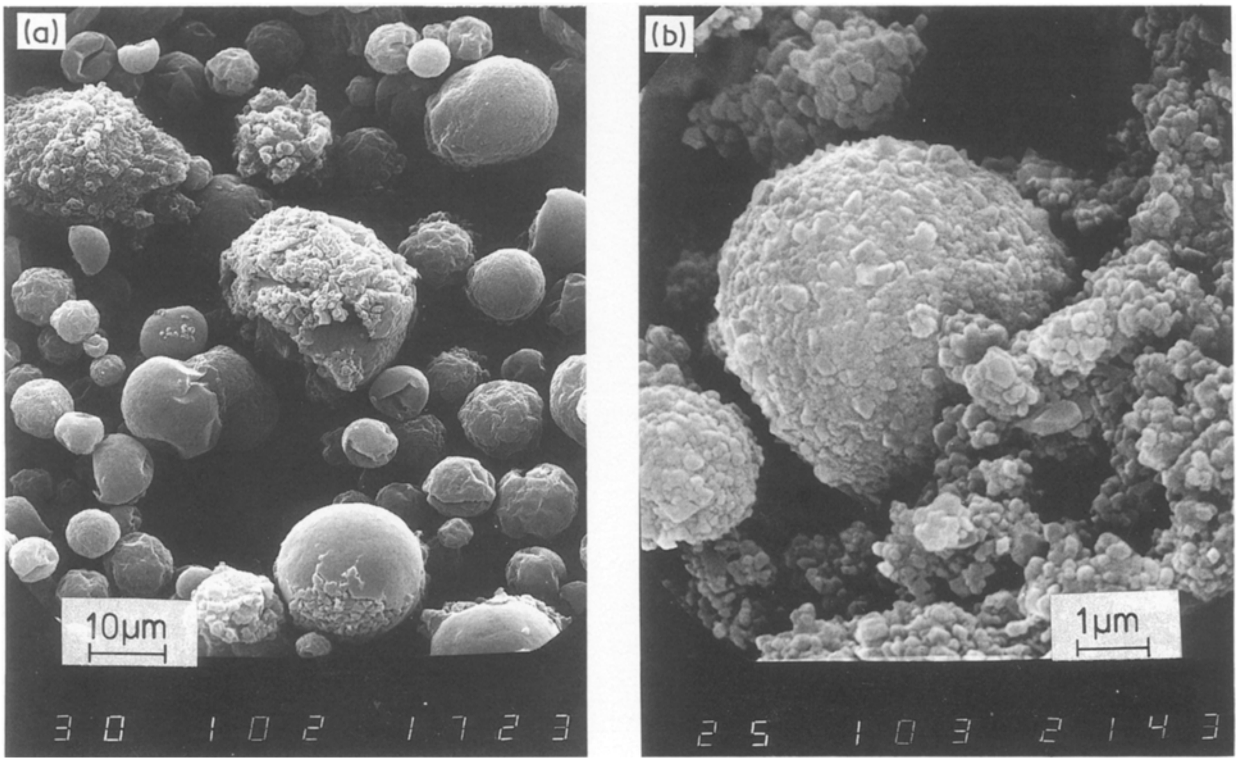

Figure 13 Lithium orthosilicate powder obtained (a) by normal spray drying and (b) by the SDC process.

showing that by application of the technique described, these systems also allow very homogeneous powders to be prepared which, by conventional techniques, can be prepared either with great difficulty or practically not at all. The experimental results further demonstrate that suspensions can also be profitably processed.

Dependent on the system used, the product fabricated is either poorly crystallized or amorphous. With the large surfaces achievable this leads to a product with interesting sintering properties. To prepare solutions, either nitrates or chlorides can be used as source products. Mixing of nitrates with chlorides has proved to be disadvantageous.

References

1. H. YOSHIMATSU, H. KAWASEKA and A. ORAKA, *J. Mater. Sci.* **23** (1988) 332.
2. E. R. IVERS-TIFFÉE and V. MAGORI, German Patent DE 053409815 (1985).
3. M. KAJAWA, M. KIKUCHI and R. OHNO, *J. Amer. Ceram. Soc.* **64** (1981) C7.
4. M. KAJAWA, F. HONDOR, H. ONODERA and T. NAJAE, *Mater. Res. Bull.* **18** (1983) 1081.
5. N. KAJAWA, Y. IMAMURA, S. USUI and Y. SYONO, *J. Mater. Sci. Lett.* **3** (1984) 699.
6. D. VOLLATH and B. DÖRZAPF, German Patent P3719825.4 (1987).
7. G. SCHLICK GmbH, Coburg, Leaflet No. D19/1.
8. D. VOLLATH, H. WEDEMEYER and E. GÜNTHER, in Proceedings of 13th Symposium on Fusion Technology, 1984, Vol. 2, pp. 967–972.
9. D. VOLLATH and H. WEDEMEYER, *Adv. Ceram.* **25** (1988) 93.
10. *Idem, J. Nucl. Mater.* **141–143** (1986) 334.

*Received 13 December 1988
and accepted 17 August 1989*