JOURNAL OF MATERIALS SCIENCE 23 (1988) 185–188

Pore morphology in cryochemically prepared alumina powders and their sulphate precursors

I. K. LLOYD, R. J. KOVEL*
Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, USA

Cryochemically prepared alumina and yttria-doped alumina powders and their sulphate precursors were examined in the SEM and TEM. The TEM examination revealed a typical chained agglomerate structure with subnamometre-sized porosity within the agglomerates and micrometre-sized porosity between the agglomerates. The SEM examination showed that the sulphate solutions had separated into water channels and immiscible hydrates upon freezing. The water channels had ovulated and spheroidized as they were freezing. This morphology was maintained through vacuum drying and calcining.

1. Introduction

Freeze-drying or cryochemical processing was favoured in the 1970s as a simple technique to produce atomically mixed, spherical powders [1–7]. It was used to produce several types of dense ceramics on a laboratory scale [3, 4, 7]. It was not widely applied industrially, probably as a result of four factors. First, it is somewhat difficult to scale up to production volumes. However, Rigterink [6] did propose a technique to produce cryochemical powders continuously. Second, while cryochemically produced powders maintain the spheroidicity of the frozen droplets, the spheres consist of chained agglomerates of spherical crystallites [1, 2, 6, 8]. There is considerable microporosity associated with these agglomerates. Third, the spheres also contain "macroporosity" (usually of the order of a micrometre) as a result of the sublimation of the solvent [7]. (The spheres are occasionally even hollow.) Fourth, the presence of two levels of porosity necessitates grinding or otherwise modifying the powders to achieve high sintered density. This normally negates the advantage of producing spherical powders.

We chose cryochemical processing as a means of distributing yttrium in aluminium oxide for our studies of the effects of yttria on the grains and grain boundaries of alumina. As we examined our materials we found evidence of spheroidization or ovulation of water (solvent) pockets in the "macroporosity". Pores reminiscent of the various stages of ovulation and spheroidization persisted in the powders throughout processing. They were present in the as-dried powders, the calcined powders and even in a few sintered samples which had been made from insufficiently ground powder.

Lord Rayleigh [9] showed that cylindrical shapes under the influence of surface-tension effects are unstable. They break up forming spheres by ovulation or spheroidization. A schematic illustration ovulation and spheroidization is shown in Fig. 1. This phenomenon is important, and is illustrated by both later stage sintering [10] and crack healing [11, 12]. It is also observed in a wide variety of other situations where a cylindrical second phase is present [13]. Ovulation and spheroidization in cryochemical materials can occur during the initial freezing process. This is important as it can help us to understand the freezing process and because the resultant morphology persists throughout processing.

2. Experimental procedure

Solutions containing 1.27 mol Al/l H_2O and 2.7 × 10^{-4} mol Y/l H_2O (700 p.p.m. Y cation by weight) were prepared from reagent grade $Al_2(SO_4)_3 \cdot 8H_2O$, and distilled water. The solutions were atomized in a pneumatic spray nozzle using gaseous nitrogen as a carrier and sprayed into liquid nitrogen. After spraying was complete the excess liquid nitrogen was decanted, the remaining liquid nitrogen and the frozen solution were poured into a Labconco® flask for freeze-drying. The samples were freeze-dried on a Labconco® lyophilization unit for 48 to 72 h depending on the sample size. After drying the samples were stored in a desiccator until they were calcined. All the samples were calcined in flowing air at 1100° C for approximately 24 h. Some of the powders were then dry milled for 1 h using high-purity alumina rods. A few 2.5 cm discs were pressed at 35 MN m^{-2} (5000 lb in.$^{-2}$) and then sintered. Samples were sintered in flowing oxygen between 1500 and 1600° C.

Samples were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Powder samples for the SEM were prepared by sprinkling a small amount of powder on double sticky tape and then applying a gold coating. Powder samples for the TEM were prepared by grinding the powder in hexane and then using an Ernest Fullam Inc., Latham, New York, spray mounter. A conductive coating was not necessary for the TEM samples. Most of the phase identification was done using powder X-ray diffraction (XRD) techniques.

**Present address*: GTE Valenite Ceramics, Troy, Michigan 48007, USA.

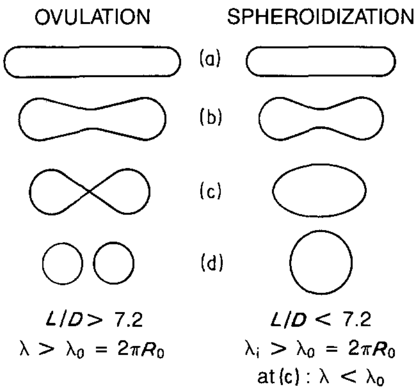

Figure 1 Schematic illustration of ovulation and spheroidization of a finite cylinder, λ = wavelength of perturbation and $\lambda_0 = 2\pi R_0$.

3. Results and discussion

Cyrochemical processing's original popularity was based on two main advantages. First, the powders which were produced were spherical. Second, the process was a solution technique which allowed mixing on an atomic level. Ideally, the atomically mixed state is maintained throughout the atomization, freeze-drying and calcining steps producing a homogeneous multicomponent or doped powder.

As already noted in Section 1 and as shown in Fig. 2, the calcined alumina powders consist of chained agglomerates with two levels of porosity. There is considerable microporosity associated with the chained agglomerates and larger pores between the agglomerates. The bimodal distribution makes sintering difficult, and may necessitate the grinding of the powders. This negates the advantage of producing spherical powders. The chained agglomerates appear to result from the transformation of the sulphate to γ-alumina because they are present in samples which have not yet transformed from γ-alumina to α-alumina. However, as shown by the vermicular region in Fig. 3b, the microstructure of the powders becomes even more complicated (and less sinterable) when the γ-alumina transforms to α-alumina.

SEM characterization of the as-freeze-dried sulphate precursor powders and the calcined alumina powders indicated that the calcined aluminas largely maintained both the spherical shape of the atomized sulphate solution droplets and the pore morphology of the freeze-dried sulphates. Fig. 3 shows surfaces from both the sulphate and alumina powders. The powders are very porous with a large number of the pores 0.5 to 1 μm diameter. The porosity is uniformly distributed. Its most striking characteristic is its shape. Many of the pores are cylindrical or egg-shaped and appear to have begun to ovulate or spherodize. Ovulation and spherodization of cracks, voids and second phases have been observed in crack healing, sintering, strengthening of metals and ceramics and the behaviour of composites [10–13]. However, until this study, they have not been associated with the freeze-drying powder preparation process.

The porosity visible in Fig. 3 is the result of the sublimation of the solvent (water) during vacuum drying. While the porosity is uniformly distributed, its morphology suggests that the water which sublimated was originally in the form of cylindrical channels or pockets (otherwise it could not spheroidize or ovulate). Therefore, some phase separation must have occurred. This is not surprising as salt solutions tend to form immiscible hydrates upon freezing [1]. Thus, the separation into "salt pockets" (aluminium–yttrium sulphate hydrate) and water channels probably occurred during freezing. The water and sulphate then froze separately. This fits experimental observations as the spheroidization–ovulation (SO) morphology was not observed in the very smallest spheres ($< 100\ \mu$m) produced. The freezing rate of the droplets is proportional to their diameter. The larger droplets would take longer to freeze so that the water could separate more completely from the sulphate hydrates

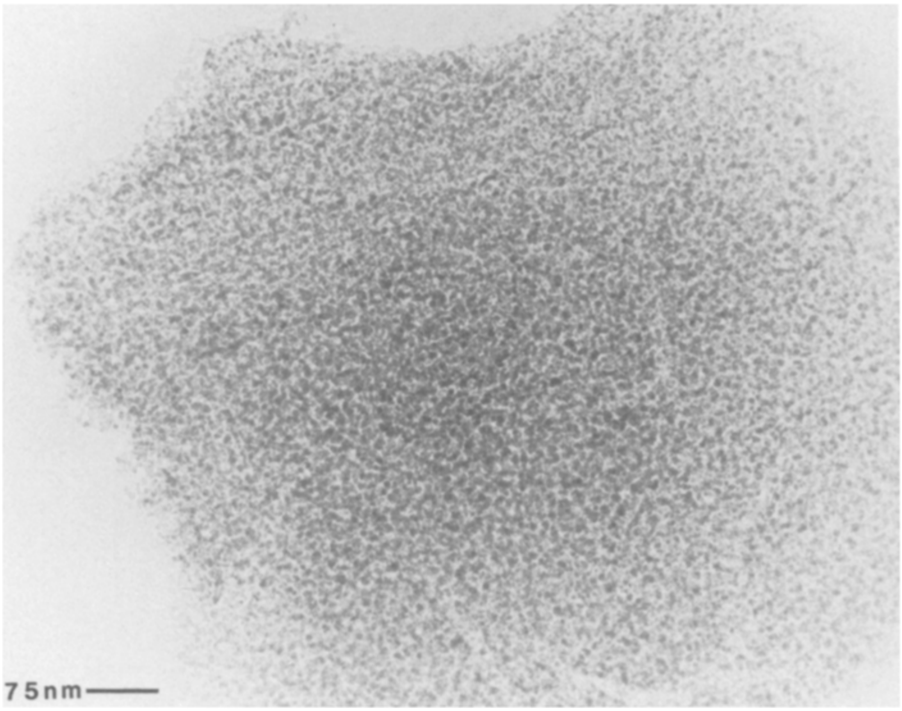

Figure 2 Calcined freeze-dried yttrium-doped Al_2O_3.

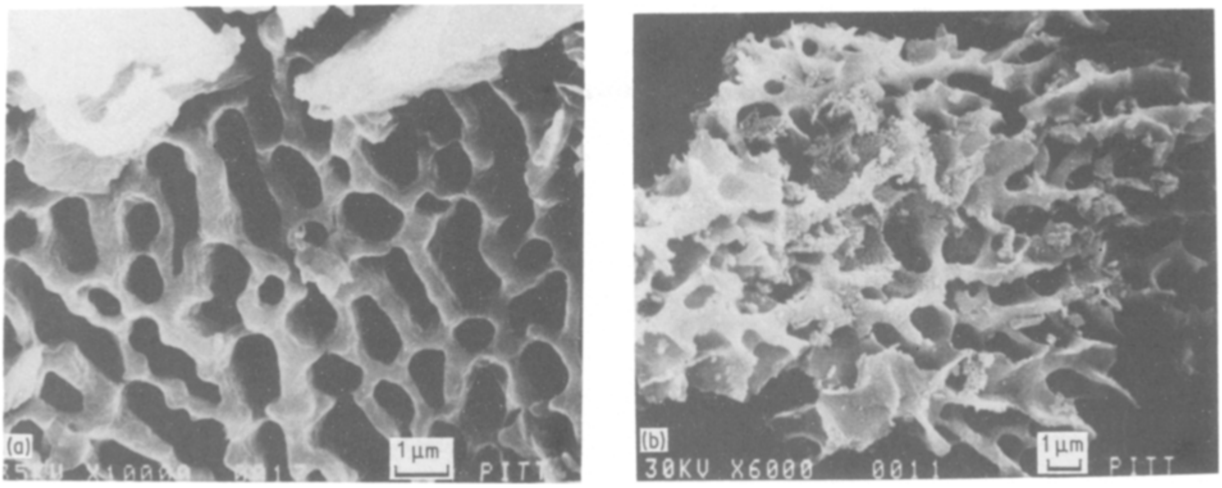

Figure 3 Surface morphology of (a) as-freeze-dried and (b) as-calcined powders showing evidence of spheroidization and ovulation.

and form "channels" or at least channel-like pockets. Within the broad limits of our chemical analyses, no segregation of yttrium or yttrium sulphate resulting from the hydrate-water phase separation was observed.

Cylinders are only stable within certain dimensional limits [13, 14]. Theoretically, cylinders are only stable when their length is less than or equal to their circumference. Once the limit of stability is exceeded, the cylinder will transform via spheroidization ($L/D < 7.2$, L = cylinder length and D = cylinder diameter) or ovulation ($L/D > 7.2$) when it is perturbed. In our system, the perturbation is most likely to be the collision of freezing droplets with one another, the container walls or with the stirrer in the liquid nitrogen bath. As the droplets were in the process of freezing, the SO process would stop when the water in the channels froze. Fig. 4 shows that at least in some areas the ovulation process was nearly complete. While both ovulation and spheriodization occurred in our samples, ovulation was much more common, indicating that the water was separating into longer, narrow channels. As in crack healing and sintering, minimization of interfacial energy should be the driving force for the SO process.

The retention of the SO morphology after vacuum drying and calcining indicates that the spheres did not melt during either drying or calcining. Thus, the initial homogeneity of the frozen droplets was maintained. However, there is still the possibility of dopant segregation during the freezing process. (In our current studies we are using more sensitive techniques to determine if segregation does occur upon freezing.) The same powder morphology was observed for both the yttria-doped alumina and the undoped alumina samples. This indicates the yttrium sulphate did not have a major effect on the SO process.

4. Conclusions

Cyrochemically processed alumina and yttria-doped alumina powders and their sulphate precursors were examined in the SEM and TEM. The calcined powders maintained the overall shape and the pore morphology of their sulphate precursors. Very small pores (~ 20 nm) were observed within the chained

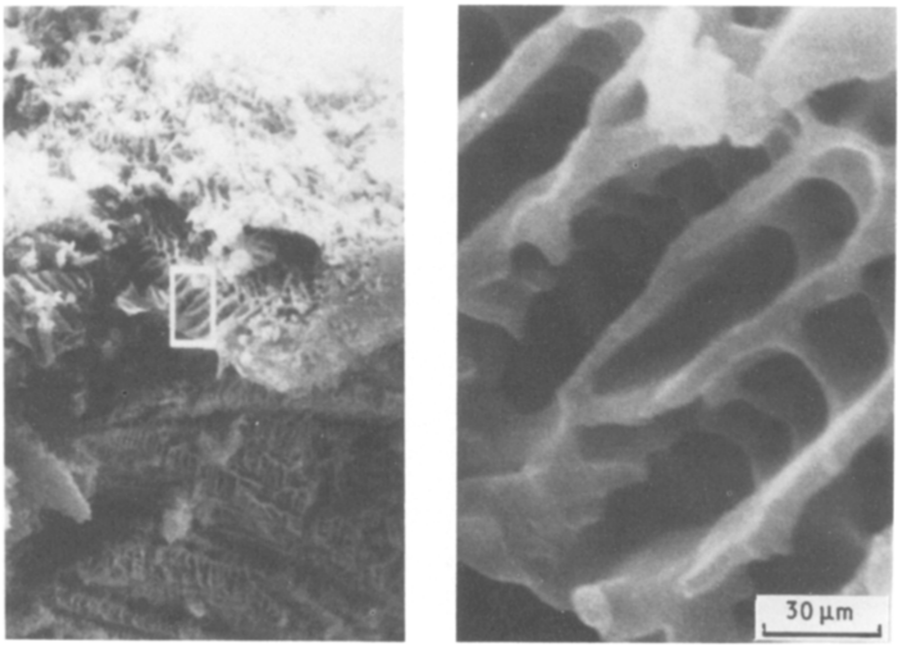

Figure 4 The interior of the freeze-dried powders also showed evidence of spheroidization and ovulation in various stages.

agglomerates in the TEM. Larger pore channels ($\sim 1\,\mu$m diameter) resulting from the sublimation of water were observed in the SEM. Many of the pore channels appeared to be in the process of ovulation or spheroidization, a phenomenon which has not been previously observed in freeze-dried powder. These channels resulted from separation of the water and the sulphate hydrates during freezing and were only observed in the larger droplets which would have frozen relatively slowly. The formation of the water channels in the larger droplets indicates that care should be taken to produce small droplets during the atomization process. This will minimize the opportunity for dopant segregation during freezing by increasing the cooling rate and limiting the extent of the phase separation reaction. As the SO morphology is maintained throughout vacuum drying and calcining, it appears that no melting occurs after the droplets are frozen and that the homogeneity of the frozen droplets is maintained.

Acknowledgements

We thank Dr T. K. Gupta, Alcoa Laboratories, for many helpful discussions, and C. E. Kalnas for her help in characterizing our materials using transmission electron microscopy. This paper is based in part on the thesis submitted by R. J. Kovel for the MS degree in Materials, University of Pittsburgh, 1987, and was partially supported by a grant from the Aluminum Company of America.

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Received 16 February
and accepted 28 April 1987