this could be due to the fact that its amplitude is comparable to the noise and so it would not be visible. The same procedure was adopted to simulate the Cr^{3+} spectra (Fig. 2b). The results are less clear because the effect of other lines is much larger in the Cr^{3+} samples but the Cr^{3+} spectra can be easily identified both from the effective g values and from the simulation procedure.

These experiments have opened the way for an EPR examination of the behaviour of rutile pigments rather than the single crystals. It has been reported by several authors [7, 8] that the method by which rutile is doped, and whether the impurity is present initially when the crystal is grown or subsequently doped, has an effect on the preferred site for the impurity. Work is continuing to identify the other observed features and also to find spectra of other ions, for example nickel and manganese, both of which can exist in different sites with different charge states in rutile.

Acknowledgement

We wish to thank Tioxide International Ltd, for their support of this work and the award of a Research Scholarship to HSE.

References

1. D. L. CARTER and A. OKAYA, *Phys. Rev.* **118** (1960) 1485.
2. G. J. LICHTENBERGER and J. R. ADDISON, *ibid.* **184** (1969) 381.
3. H. J. GERRITSEN, S. E. HARRISON, H. R. LEWIS and J. P. WITTKE, *Phys. Rev. Lett.* **2** (1959) 153.
4. H. S. EGGLESTON, M.Sc. Thesis, Durham University (1980).
5. J. R. PILBROW, *J. Mag. Reson.* **31** (1978) 479.
6. R. AASA and T. VANNGARD, *ibid.* **19** (1975) 308.
7. J. KERSSEN and J. VOLGER, *Physica* **69** (1973) 535.
8. W. LOW and E. L. OFFENBACHER, *Sol. Stat. Phys.* **17** (1965) 135.

*Received 22 May
and accepted 1 July 1980*

H. S. EGGLESTON
J. S. THORP
*Department of Applied Physics and Electronics,
University of Durham,
Durham, UK*

Reaction sintering of ZnO–Al_2O_3 mixtures

In previous work, attention has been focussed on reaction sintering [1], and more specifically on the system $ZrSiO_4$–Al_2O_3 which has been studied both by pressureless reaction sintering [2] and by reaction hot-pressing [3]. It has been shown that the $ZrSiO_4$–Al_2O_3 system densifies during the reaction process and one of the main results obtained has been that it is possible to correlate the densification kinetics with the reaction kinetics at least for the intermediate stage of the overall process.

The present work reports the results obtained by studying the pressureless reaction sintering of a system which expands during the reaction process, namely, the ZnO–Al_2O_3 system, in which ZnO and Al_2O_3 react in the solid to form a unique stable compound $ZnAl_2O_4$ of a normal spinel structure. An attempt is made to exploit the information provided by the co-existence of the solid-state chemical reaction and the expansion of the material in order to develop a model in which the kinetics of the reaction and the kinetics of the expansion are quantitatively correlated.

The kinetics of the solid-state reaction, as well as the mechanism of formation of $ZnAl_2O_4$, have been studied by various authors [4, 5]. From their work it has been concluded that, firstly, by using alumina grains with sizes larger than the ZnO grains, classical diffusional (Valensi–Carter) models can be applied to the results and, secondly, that the formation of zinc aluminate spinel proceeds through a three-step reaction sequence:

(a) the formation of a solid solution of zinc oxide in alumina oxide;

(b) the formation of a disordered spinel structure;

(c) the formation of the ordered spinel.

So it has been determined that the overall process can be seen as a one-way transfer [4, 6, 7] of ZnO to alumina grains.

The raw materials used (greater than 99.5 wt% purity) were ZnO and Al_2O_3 A15 SG, obtained from UCB, Belgium and from Alcoa, USA, respectively. The grain-size distributions of ZnO and Al_2O_3 were measured using a

Micromeritics IC sedigraph. Mean grain-size diameters were determined to be 2.4 μm for ZnO and 3 μm for alumina, leading to a ratio of the radii of 0.8. The surface areas were measured by a modified BET method [8] and were 4.2 m^2 g^{-1} for ZnO and 6.0 m^2 g^{-1} for Al_2O_3. Equimolar quantities of ZnO and Al_2O_3 (about 183 g) were mixed in distilled water (about 150 ml) and dried according to normal procedures (110° C, 24 h). Samples of weight about 13 g of wet mixed powders (water 3 wt%) were pressed in a cylindrical die under a pressure of 500 kg cm^{-2} for 60 sec, dried at 110° C for 24 h and pre-heated at 500° C (at this temperature if has been checked that no reaction occurs). The pre-heated samples were sandwiched between two alumina plates and placed in a platinum crucible and then introduced into an electrical furnace at one of the firing temperatures (900° C, 950° C and 1000° C) and held for times varying from 10 min to 100 h. The fired samples were then taken out and placed in another electrical furnace at 500° C and then allowed to cool down to room temperature. The density of the fired material, following expansion, was then measured using Archimedes principle, using water as the displacing agent. The progress of the chemical reaction between ZnO and Al_2O_3 was indicated by the amount of $ZnAl_2O_4$ formed as determined by quantitative X-ray diffraction using a PW 1130 Phillips diffractometer. Each fired sample was ground and screened to produce particles of size less than 50 μm. Quantitative estimation of the amount of $ZnAl_2O_3$ was made by comparing the relative intensity of, respectively, cubic (101) ZnO, trigonal (113) alumina and cubic (311) $ZnAl_2O_4$ X-ray lines, after calibration.

Fig. 1 illustrates the variation of the porosity (in vol%), deduced from density measurements with firing times at temperatures of 900° C, 950° C and 1000° C. It can be seen that the porosity increases very rapidly for short firing times and reaches a limit-value for each temperature. (Note that the porosity for zero time of reaction, green porosity, is of the order of 41%.) Under comparable conditions, the progress of the reaction between ZnO and Al_2O_3 can be also traced. In Fig. 2, the degree of reaction is represented as a function of firing time. One can see that the reaction shows a similar evolution to the porosity,

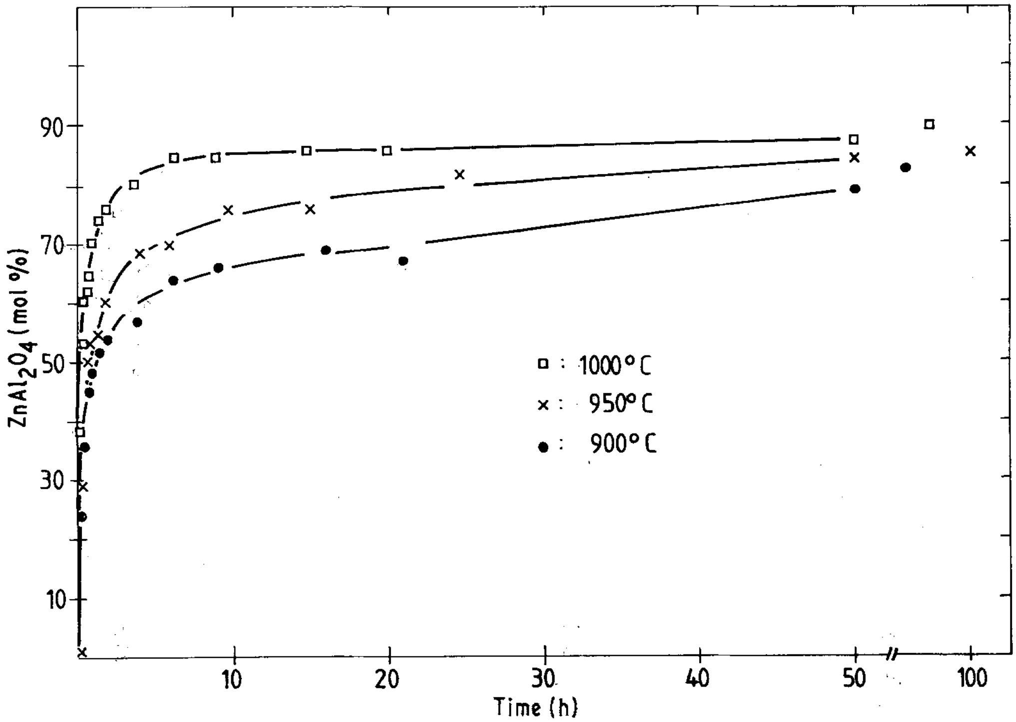

Figure 1 Variation of porosity with firing time at 900° C, 950° C and 1000° C for sintered $ZnO-Al_2O_3$ materials.

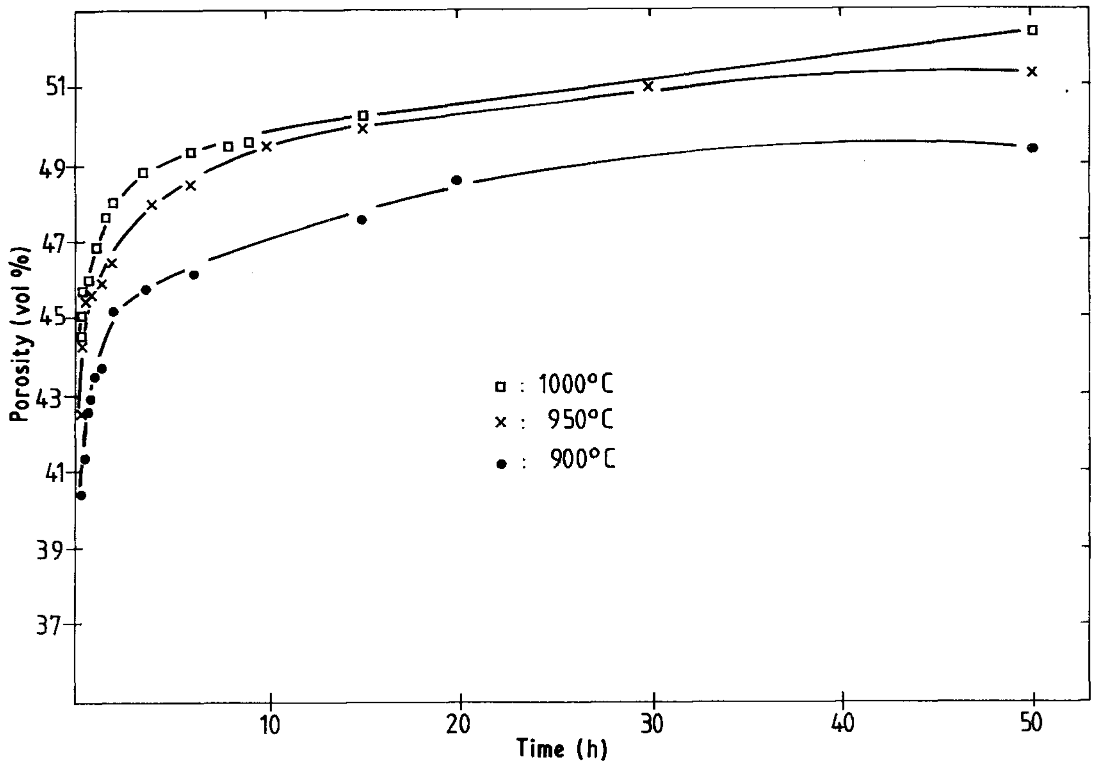

Figure 2 Variation of the amount of Zn–Al_2O_4 product with time at 900° C, 950° C and 1000° C.

indicative of non-conventional diffusional behaviour. In fact, the obtained results show that the porosity of the fired samples increases as a function of the advancement of the reaction. The porosity, P_V, (in vol%) can be described by

$$P_V = 100\frac{V_p}{V_p + V_M}, \quad (1)$$

where V_p is the volume of pores and V_M is the volume of matter, V_M does not change gently as the reaction proceeds; indeed, it can be calculated that, when the reaction is completed, the greatest change in the value of V_M is only 0.3%.

Therefore, in order to fit the observed results, a tentative model, in which chemical reaction generates an increase in the volume of the pores, is presented below. The following hypotheses were taken into consideration:

(a) The equimolar ZnO–Al_2O_3 mixtures are represented by a packing of spheres of ZnO and Al_2O_3 with a ratio of their radiis, R_z and R_A, equal to that of mean grain-size diameters of the used powders.

(b) It has been shown [9] that, for a random packing of two kinds of spheres with a ratio of their radiis close to 1, the most probable coordination number is 6. So it can be considered that each sphere of alumina is in close contact with 6 spheres of ZnO, leading to a cubic array as represented in Fig. 3 and leading to the following condition:

$$\frac{N_A \frac{4}{3}\pi R_A^3}{N_z \frac{4}{3}\pi R_z^3} = \frac{V_A}{V_z}, \quad (2)$$

where N_A and N_z are the number of grains of alumina and zinc oxide and V_A and V_z are the molar volumes of Al_2O_3 and ZnO, respectively.

(c) The zinc aluminate spinel forms as layers on the alumina spheres at each point of contact within an angle of aperature of 2θ as shown in Fig. 4.

Taking into account the above hypotheses, if it is considered that the number of moles, $dn_{s,t}$, of zinc aluminate spinel formed between times t and $t + dt$ is distributed on the N_A spheres of alumina, at the six points of contact, with a thickness dK_t and a surface area, A_t, the following expression

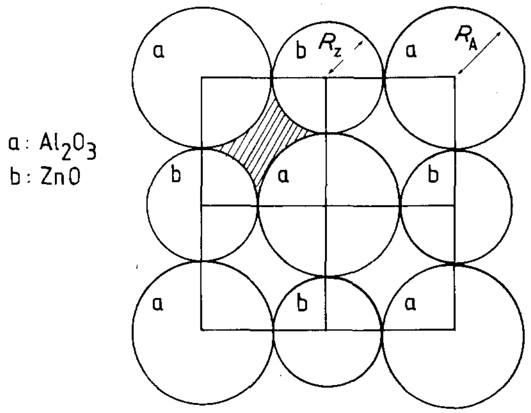

Figure 3 Cubic array of grains of Al_2O_3 and ZnO.

can be written:

$$6N_A A_t \, dK_t = dn_{s,t} \frac{M_S}{\gamma_S}, \tag{3}$$

where M_S and γ_S are the molar mass and the bulk density of the zinc aluminate spinel, respectively and the subscripts A and S designate alumina and zinc aluminate spinel, respectively. A_t, which is the spherical surface of angle of aperature 2θ can be expressed as

$$A_t = 2\pi R^2_{A,t} (1 - \cos^3 \theta), \tag{4}$$

where,

$$R_{A,t} = R_A (1 - x)^{1/3}, \tag{5}$$

where $R_{A,t}$ is the radius of the alumina sphere after a time of reaction t, and x is the degree of advancement of the reaction.

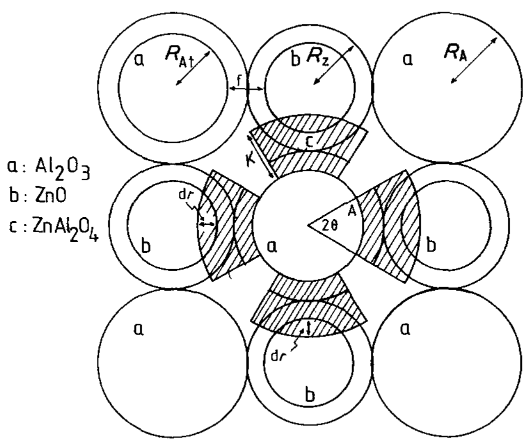

Figure 4 Geometrical arrangement showing the formation of layers of zinc aluminate spinel on the alumina grains within an angle of aperture of 2θ.

Moreover, from Equation 2,

$$N_A = \frac{M_A}{\gamma_A} \frac{3}{4\pi R_A^3}. \tag{6}$$

By substituting for Equations 4–6 into Equation 3,

$$dK_t = \frac{2}{27} \frac{R_A}{(1 - \cos^3 \theta)} \frac{M_S}{\gamma_S} \frac{\gamma_A}{M_A} \frac{dx}{(1 - x)}. \tag{7}$$

At each point of contact, the thickness of the consumed reactant products, d_{ft}, removed between t and $t + dt$ reaction time can be expressed as

$$d_{ft} = \frac{2}{3} (R_A + R_z) (1 - x)^{-2/3} dx. \tag{8}$$

The total variation of distance dr_t between the centres of one grain of Al_2O_3 and one grain of ZnO between time t and $t + dt$ is equal to

$$dr_t = dK_t - d_{ft}$$

$$= \left(\frac{2}{27} \frac{R_A}{1 - \cos^3 \theta} \frac{M_S}{\gamma_S} \frac{\gamma_A}{M_A} - \frac{4}{19} (R_A + R_z) \right) \frac{dx}{(1 - x)}. \tag{9}$$

Integration of Equation 9 gives

$$r_t = 3A \int_0^x \frac{dx}{(1 - x)^{1/3}} = 3A \left(1 - (1 - x)^{1/3} \right) \tag{10}$$

where

$$A = \frac{1}{9} \frac{R_A}{1 - \cos^3 \theta} \frac{M_S}{\gamma_S} \frac{\gamma_A}{M_A} - \frac{2}{3} (R_A + R_z). \tag{11}$$

A is an expression depending only on θ for a given system in which the radii of the two reacting powders are fixed. It is assumed that θ is not a function of x, A being then considered as a constant.

After a time of reaction, t, a geometrical situation is obtained as illustrated in Fig. 5, in which the cell parameter of the cubic array is given by $R_{A,t} + R_{z,t} + r_t$. The increase of the volume of the pores resulting from the reaction may then be expressed as

$$\Delta V_{p,t} = N [3(R_A + R_z)^2 r_t + 3 (R_A + R_z) r_t^2 + r_t^3], \tag{12}$$

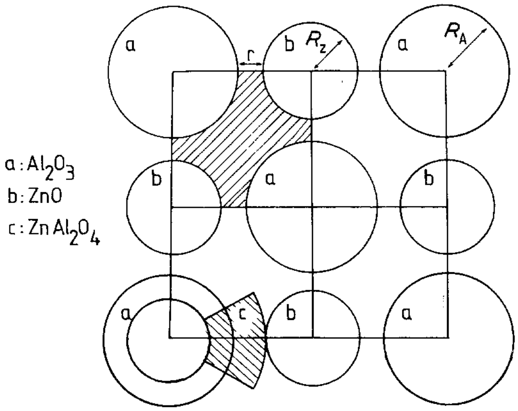

Figure 5 Geometrical arrangement after a time, t, of reaction leading to a new cubic array with a cell parameter equal to $R_{A,t} + R_{Z,t} + r_t$.

and the total variation of the volume then is $\Delta V_t = \Delta V_{p,t} + \Delta V_M$, where ΔV_M is the variation of the volume of matter due to the reaction, where

$$\Delta V_M = x\left(\frac{M_S}{\gamma_S} - \frac{M_A}{\gamma_A} - \frac{M_z}{\gamma_z}\right) \qquad (13)$$

and where x is the degree of advancement of the reaction, see the Appendix. The density, d_t, of a sample after a time of reaction, t, is equal to

$$d_t = \frac{1}{\Delta V_t + d_0}, \qquad (14)$$

where d_0 is the green density of the material and the porosity, P_V, is

$$P_V = 100\left(1 - \frac{d_t}{d_b}\right), \qquad (15)$$

where d_b is the bulk density of the material after a time t of reaction.

From the Equations 12 to 15, variation of volume porosity with the degree of advancement of the reaction can be calculated for all values of 2θ. The best theoretical values fitting the experimental results are represented by Figs 6 to 8. Values of fitting the proposed model with experimental data are very close (from 24.38 to 24.45°). It can be observed that these values could correspond to the value of the angle (24°) from which a sphere of ZnO can be seen from the centre of the sphere of alumina (see Fig. 4). One can think that θ represents a physical meaning in relation to the radii of the reactant particles R_A and R_z for this particular system. In order to confirm this point, it appears necessary to generalize the proposed model by taking into account not only the radii but also the actual number of particles in the system.

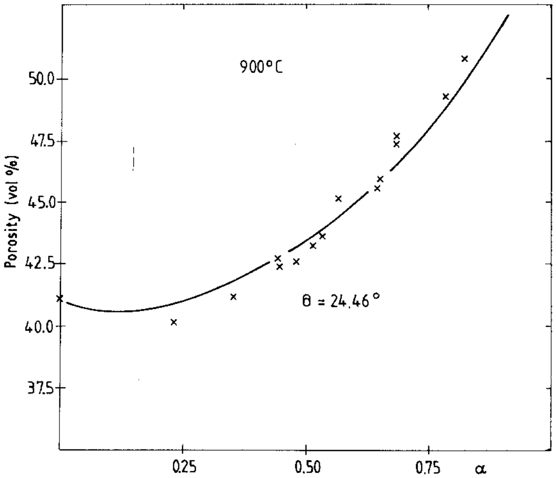

Figure 6 Variation of porosity with the molar fraction of the formed spinel phase at 900° C, as calculated from the proposed model (the best fit being obtained with $\theta = 24.46°$).

Acknowledgements

The authors wish to thank Professor R. J. Brook for helpful comments and for a critical review of the manuscript. This paper is partly based on a B.Sc. thesis (University of Mons, 1979) by M. Charlot.

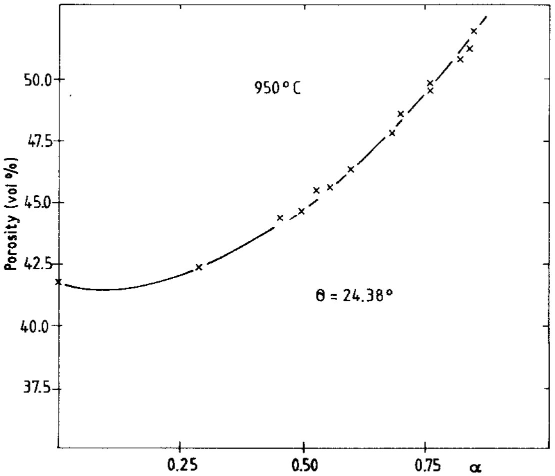

Figure 7 Variation of porosity with the molar fraction of the formed spinel phase at 950° C, as calculated from the proposed model (the best fit being obtained with $\theta = 24.38°$).

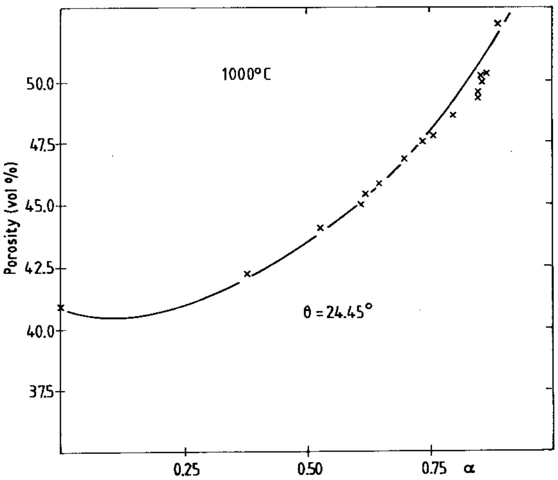

Figure 8 Variation of porosity with the molar fraction of the formed spinel phase at 1000° C, as calculated from the proposed model (the best fit being obtained with $\theta = 24.45°$).

Appendix

Equations 12 to 15 are established using the degree of advancement of the reaction x, which can be defined as:

$$x = \frac{n_S}{n_{S\,\mathrm{Max.}}} = \frac{n_S}{n_A + n_S}, \qquad \text{(A1)}$$

where n_A and n_S are the molar number of Al_2O_3 and spinel, respectively, in the sample, and $n_{S\max}$ is the molar number of spinel when the reaction is complete. In Figs 6 to 8 the porosity volume is plotted against α which can be defined as the molar fraction of the formed spinel phase, defined by

$$\alpha = \frac{n_S}{n_A + n_z + n_S} = \frac{n_S}{2n_A + n_S}, \qquad \text{(A2)}$$

where n_z is the molar number of ZnO in the sample. The relation between α and x is

$$\alpha = \frac{x}{2 - x}. \qquad \text{(A3)}$$

References

1. M. B. WALDRON and B. L. DANIEL, "Sintering" (Heydon, London, 1978) p. 27.
2. E. DI RUPO, M. R. ANSEAU and R. J. BROOK, *J. Mater. Sci.* 14 (1979) 2924.
3. E. DI RUPO, E. GILBART, T. G. CARRUTHERS and R. J. BROOK, *J. Mater. Sci.* 14 (1979) 705.
4. D. L. BRANSON' *J. Amer. Ceram. Soc.* 48 (1965) 591.
5. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics" (John Wiley and Sons, New York) p. 424.
6. B. BENGTSON and R. JAGITSCH, *Ark. Kem. Mineral Geol.* 24A (1947) 1.
7. R. LINDNER and A. AKERSTROM, *Z. Phys. Chem.* 6 (1956) 162.
8. F. CAMBIER, P. FIERENS and G. LAMBIN, *Silic. Ind.* 39 (9174) 21.
9. R. BEN AÏM and P. LE GOFF, *Powder Technology* 2 (1968) 1.

Received 22 May
and accepted 1 July 1980

C. LEBLUD
M. R. ANSEAU*
E. DI RUPO
F. CAMBIER*
P. FIERENS
Université de l'Etat à Mons,
Department of Materials Science,
Avenue Maistriau,
7000 Mons, Belgium

***Present address: Centre de Recherche de l'Industrie Belge de la Céramique, 4 Avenue Gouverneur Cornez, 7000 Mons, Belgium.**