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Solid state reactions in the $ZrO_2 \cdot SiO_2 - \alpha Al_2O_3$ system

E. DI RUPO, M. R. ANSEAU*
Department of Materials Science, University of Mons, 15, avenue Maistriau, 7000 Mons, Belgium

Solid state reactions between $ZrO_2 \cdot SiO_2$ and αAl_2O_3 in mixed powders were studied by quantitative X-ray diffraction, density measurements and qualitative EDAX. Data were obtained at temperatures ranging from 1400 to 1600° C for 5 h; the initial molar ratios of the reactants ($Al_2O_3/ZrO_2 \cdot SiO_2$) varying from 0 to 5. The results indicate that: (1) $ZrO_2 \cdot SiO_2$ and αAl_2O_3 react and form ZrO_2, crystalline $3Al_2O_3 \cdot 2SiO_2$ and a non-crystalline mullite phase; (2) the non-crystalline mullite phase is an important transitional phase towards equilibrium under subsolidus conditions. In the experimental conditions used the amount of the non-crystalline phase varies by as much as about 15%. This phase is of great importance in the mechanisms of reaction sintering between $ZrO_2 \cdot SiO_2$ and αAl_2O_3.

1. Introduction

Many studies about solid state reactions in the $ZrO_2 \cdot SiO_2$ and in the SiO_2–Al_2O_3 binary systems can be found in the literature [1–12]. However, despite the fact that the zircon–alumina based materials are widely used in industry [13–16], solid state reactions in the ternary system $ZrO_2 \cdot SiO_2$–Al_2O_3 have not been given much attention [17, 18]. This is probably due to the complexity of the system in which zircon, alumina, mullite, zirconia and pores are simultaneously present during reactions. It is well known that at high temperatures $ZrSiO_4$ dissociates in the solid state [5] and forms ZrO_2, and that amorphous SiO_2 reacts with Al_2O_3 to yield mullite. Moreover, the presence of a ternary compound in the system ZrO_2–Al_2O_3–SiO_2 has never been reported.

The purpose of the present work is to present results on the solid state reaction: zircon + alumina → zirconia + mullite as a function of the initial alumina/zircon ratios of the unreacted mixtures and of firing temperatures. These studies were undertaken in order to try to correlate densification and reaction processes in the $ZrO_2 \cdot SiO_2/Al_2O_3$ [19].

2. Experimental details

The raw materials used were Australian zircon of 99.3 wt% purity, obtained from S.C.R. Sibelco, Antwerpen, Belgium and tabular α-alumina of 99.7 wt% purity obtained from Alcoa Int., The Netherlands. The zircon was purified by treatment with methyl alcohol and with sulphuric acid. The spectrographic analysis showed the following results: Al_2O_3, 0.3 wt%; TiO_2, 0.15 wt%; FeO, 0.10 wt%; CaO, 0.05 wt%; MgO, 0.04 wt%; Na_2O, 0.03 wt%; K_2O, 0.01 wt%; SiO_2, 32.15 wt% and ZrO_2, 67.17 wt% in the zircon and CaO, 0.06 wt%; MgO, 0.06 wt%; Na_2O, 0.07 wt%; K_2O, 0.08 wt%; and SiO_2, 0.07 wt% in the alumina. The grain-size distribution of the zircon and alumina powders were measured using a Coulter-Counter and a laser granulometer (Compagnie Industrielle de Lasers, type 226). The grain size varied from 2 to 70 μm for the zircon and from 1 to 63 μm for the alumina, the average grain size being 20 and 30 μm, respectively.

The surface areas (BET) were 1.25 $m^2 g^{-1}$ for the zircon and 1.85 $m^2 g^{-1}$ for the alumina. Scanning electron micrographs of the particles confirmed the sizes measured but revealed

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* Present address: Centre de Recherches de l'Industrie Belge de la Céramique, 32, Rue de Malplaquet, 7000 Mons, Belgium.

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agglomerates of equi-axed grains in both cases, with agglomeration coefficients [20] of 16 for the zircon and 16.3 for the alumina. Zircon and alumina powders were mixed with methyl alcohol for 12 h. About 100 g mixed wet powders (water 2 wt %) were pressed in a cylindrical stainless steel die under a pressure of 1 MN m^{-2} for 2 min, dried at 110° C and pre-heated at 1000° C (at this temperature, it has been checked that no sintering and no reaction occur). The pre-heated samples were then introduced into an electric furnace at the firing temperature (1400, 1450, 1500, 1500 and 1600° C). At the end of the isotherms, the fired samples were taken out and placed in another electric furnace at 1000° C in order to prevent any thermal shock. The samples were then cooled down to room temperature for 5 h.

In all cases the progress of the chemical reaction between alumina and zircon was measured with the amount of zircon, alumina, mullite and zirconia using X-ray analyses obtained with a Philips PW 1130 diffractometer. The sintered samples were ground and scanned down to particle sizes below 30 μm. The various phases present after sintering were measured by comparing the relative intensity of, respectively, tetragonal zircon (1 1 3), monoclinic zirconia (1 1 1), orthorhombic mullite (2 1 0) and trigonal alumina (1 1 3) and NaF (2 0 0) lines. The calibration curves were obtained from X-ray diffraction patterns of mixtures of zircon, alumina, zirconia, mullite and NaF of known compositions. A tentative estimation of the accuracy of the quantitative analysis indicated that compositions could be determined to ± 3 wt %.

The density of every sintered sample was measured by both water and mercury displacement. True densities were calculated taking into account the phase composition as given by X-ray quantitative analysis together with the true density value of zircon, alumina, zirconia and mullite, namely 4630, 3850, 5680 and 3160 kg m^{-3}, respectively. In order to check the values of these calculated true densities, a complete set of direct density measurements was performed on ground samples using a pycnometer. The observed experimental densities were found to be in good agreement with the calculated values.

EDAX was used for qualitative analysis, in order to estimate the chemical composition of the different phases in the materials.

3. Results and discussion

The amount (wt %) of every crystalline phase as a function of the initial reactant molar ratios is presented in Fig. 1 for mixtures in which the initial moles ratio ($Al_2O_3/ZrSiO_4$) varies as follows: 1/10, 2/5, 1/2, 1/1, 3/2, 2/1, 5/2 and 5/1. At 1400 and 1425° C, after 5 h, it has been noted that crystalline mullite did not appear whereas zircon and alumina reacted yielding monoclinic zirconia (after quenching to room temperature). However, at 1450° C orthorhombic mullite began to appear in the mixtures with initial ratios between 2:1. The total weight percent of crystalline phases, computed from X-ray data, was respectively 87% and 86% at 1400 and 1425° C, and 90% at 1450° C. These data show that at 1400 and 1425° C the solid state reaction between $ZrSiO_4$ and Al_2O_3 occurs, producing crystalline quadratic zirconia (monoclinic at room temperature) and a non-crystalline phase, whereas at 1450° C quadratic zirconia, crystalline orthorhombic mullite and a non-crystalline phase form. From the results obtained at 1450° C, the chemical composition of the non-crystalline phase was calculated from the measured amounts of the crystalline components present, with crystalline mullite assumed to be $3Al_2O_3 \cdot 2SiO_2$ and was found to have compositions in the range of $2Al_2O_3 \cdot 3SiO_2$ to $2Al_2O_3 \cdot SiO_2$. Qualitative EDAX analysis of fractured surfaces of reacted materials carried out by comparing with crystalline mullite shows

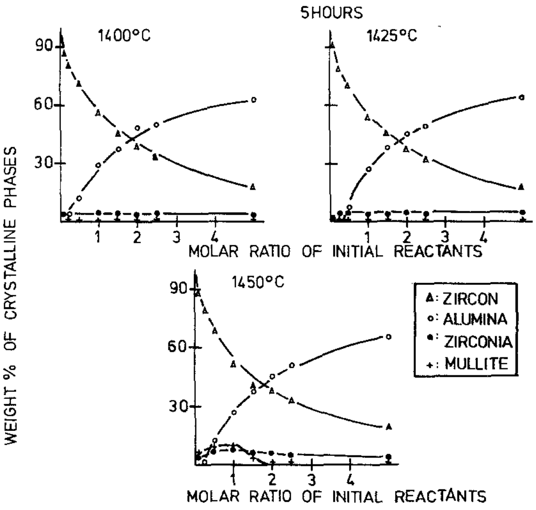

Figure 1 Variations in the amount of crystalline phases versus initial molar ratios of reactants (alumina/zircon) for the solid state reaction at 1400, 1425 and 1450° C for 5 h.

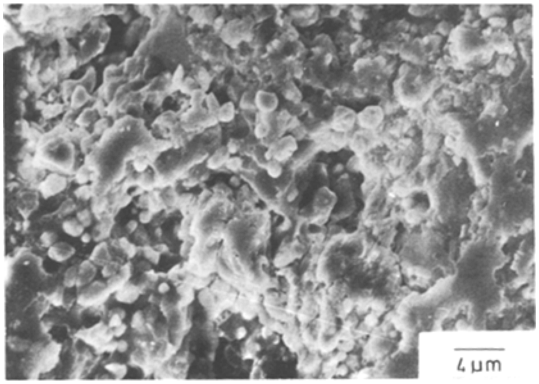

Figure 2 Micrograph of a fractured surface of reacted zircon–alumina materials (1425° C, 5 h) showing the non-crystalline phase.

that the amorphous phase has a composition of about $3Al_2O_3 \cdot 2SiO_2$; such phase has then been called "non-crystalline mullite". The formation of non-crystalline mullite probably results from more than one process. It is thought that at least two important mechanisms are involved: (1) the formation of a liquid phase; (2) the subsolidus reaction between zircon and alumina.

The firing temperatures (from 1400 to 1450° C) are far below 1540° C, which is generally considered as the eutectic temperature of the $Al_2O_3-SiO_2-ZrO_2$ system [21], but are far above 1104, 1325, 1355 and 1166° C which are the eutectic temperatures of the "$Al_2O_3-SiO_2$ impurities" ternary systems and "SiO_2-ZrO_2- impurities" ternary systems, the impurities present in the initial powders being Na_2O, K_2O, CaO, MgO and FeO [22]. The different liquid fractions created by the $Al_2O_3-SiO_2-Na_2O$, $Al_2O_3-SiO_2-K_2O$, $Al_2O_3-SiO_2-CaO$, $Al_2O_3-SiO_2-MgO$ and SiO_2-ZrO_2-FeO ternary systems have been taken into account in order to give an approximative value of the amount of liquid phase present in the materials at 1400 and 1425° C. Using this procedure it has been estimate [23] that only 2 wt % liquid phase may be created by impurities, and this quantity of liquid phase is far too small to explain the formation of about 14 wt % non-crystalline phases. Therefore, one must admit that the non-crystalline phase mainly results from a subsolidus reaction between the reactants. A similar situation has been found by other authors [7–11] for the $SiO_2-Al_2O_3$ solid state reaction at temperatures below 1547° C which is the eutectic temperature of the $SiO_2-Al_2O_3$ binary system. Fig. 2 shows an electron microscope pattern of a fractured surface of a zircon–alumina material which has been reacted at 1425° C for 5 h.

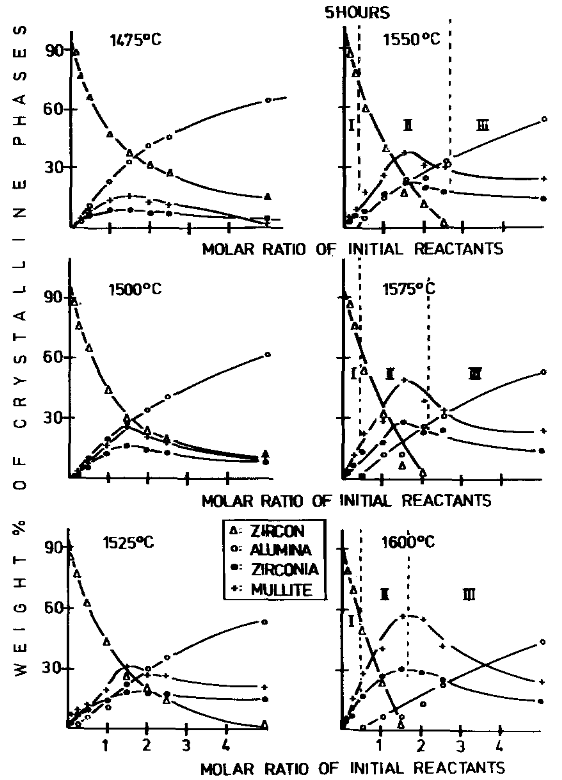

Figure 3 Variation in the amount of crystalline phases versus initial molar ratios of reactants (alumina/zircon) for the solid state reaction at 1475, 1500, 1525, 1550, 1575 and 1600° C for 5 h.

The importance of the non-crystalline phase can be easily seen in this micrograph.

Fig. 3 shows the variations in weight per cent of each crystalline component with the initial reactant molar ratios at 1475, 1500, 1525, 1550, 1575 and 1600° C for 5 h. In all materials, orthorhombic mullite has been identified and the total of crystalline phases is about 95 wt %. The amount of possible non-crystalline phase is then not far from the experimental errors (± 3 wt %). It appears that the formation of crystalline mullite is much influenced by the temperature. Moreover, the non-crystalline phase appears to be an intermediate step leading to the crystallization of the mullite.

At each temperature (from 1400 to 1600° C) 2 mol zircon reacted with 3 mol alumina. For the temperatures above 1450° C, the maximum amounts of zirconia and crystalline mullite are obtained when 2 mol zircon and 3 mol alumina have been initially mixed.

As the grain-size distributions of zircon and

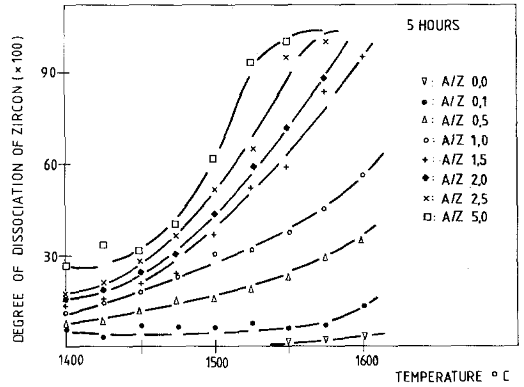

Figure 4 Variation in the degree of dissociation of zircon versus temperatures for the zircon–alumina solid state reaction over 5 h, the initial molar ratio of reactants (alumina/zircon) varying as follows: 1/10, 2/5, 1/2, 1/1, 3/2, 2/1, 5/2 and 5/1.

alumina are quite close, the number of contacts between zircon and alumina grains is maximum for an initial zircon–alumina molar ratio of 2/3.

In Fig. 4, variations of the degree of dissociation of zircon versus temperature are reported for different initial alumina–zircon molar ratios. It appears clearly first that the temperature dissociation of pure zircon is between 1525 and 1550° C (which confirms the work of Curtis and Sowman [2] and of Anseau *et al.* [5]), secondly that the degree of dissociation of zircon is strongly dependent on the alumina fraction present in the initial mixture. This is due to the fact that the solid state reaction:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 2ZrO_2 + 3Al_2O_3 \cdot 2SiO_2$$

is thermodynamically more favourable than the solid state dissociation:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2.$$

This is illustrated in Fig. 5.

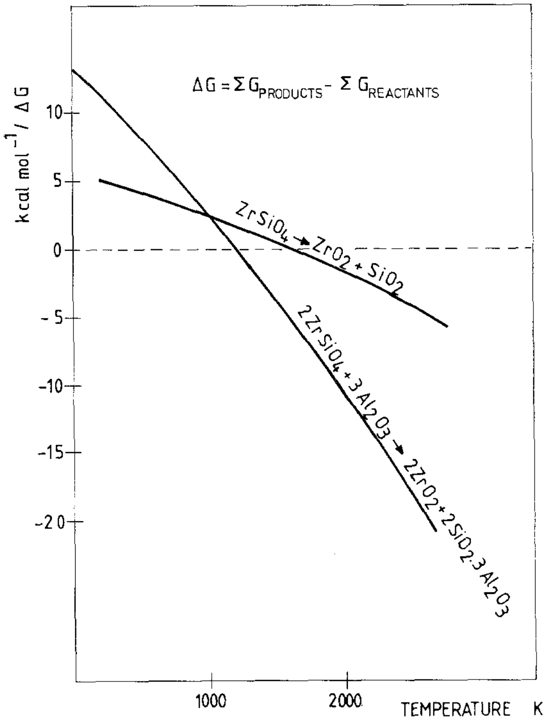

Figure 5 Free energy versus temperature for the solid state dissociation of zircon and for the solid state reaction of alumina and zircon.

4. Conclusions

The work presented in this paper was carried out in order to investigate the reaction sintering processes using pressureless sintering [19] and hot pressing [24, 25]. The main feature of the study of solid state reactions between $ZrO_2 \cdot SiO_2$ and Al_2O_3 is the occurrence of a transitional non-crystalline mullite phase, the amount of which being important (up to 15%) at 1400 and 1425° C. This phase appears to be the boundary phase between $ZrO_2 \cdot SiO_2$ and αAl_2O_3 grains. Reaction sintering in the $ZrO_2 \cdot SiO_2/\alpha Al_2O_3$ system proceeds by atomic solution – diffusion – reprecipitation [19, 24–26] both in pressureless sintering and in hot pressing. During hot pressing the boundary phase is only of liquid nature [24, 25]; in the case of pressureless sintering [19] the boundary phase is the non-crystalline mullite phase formed by subsolidus reactions.

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References

1. W. J. BALDWIN, in "High Temperature Oxides", edited by A. M. Alper (Academic Press, New York, 1970).
2. C. E. CURTIS and H. G. SOWMAN, *J. Amer. Ceram. Soc.* 36 (1953) 190.
3. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Mineral.* 52 (1967) 880.
4. S. V. RAMANI, E. C. SUBBARAO and K. V. G. K. GOKAALE, *J. Amer. Ceram. Soc.* 52 (1969) 619.
5. M. R. ANSEAU, J. P. BILOQUE and P. FIERENS, *J. Mater. Sci.* 11 (1976) 578.

6. F. M. WAHL, R. E. GRIM and R. B. GRAF, *Amer. Mineral.* 46 (1961) 1064.
7. W. G. STALEY and G. W. BRINDLY, *J. Amer. Ceram. Soc.* 52 (1969) 616.
8. R. F. DAVIS and J. A. PASK, *ibid* 55 (1972) 525.
9. S. ARAMAKI and R. ROY, *ibid* 45 (1962) 229.
10. R. F. DAVIS and J. A. PASK, in "Mullite" (Academic Press. New York, 1971) p. 38.
11. S. H. RISBUD and J. A. PASK, *J. Mater. Sci.* 13 (1978) 2449.
12. S. H. RISBUD, V. F. DRAPER and J. A. PASK, *J. Amer. Ceram. Soc.* 61 (1978) 470.
13. E. A. THOMAS, U.S. Patent 90229 (1961).
14. E. DI RUPO, M. R. ANSEAU, J. P. BILOQUE and P. FIERENS, Belgian Patent 181 362 (1977).
15. J. P. HOLT, T. P. CASH and D. B. DAY, U.S. Patent 3 972 722 (1976).
16. K. SHAW, "Refractories and their Uses" (Applied Science. London, 1972) p. 238.
17. K. MIYATAKE, K. SEMBA and M. SEKIME, *Taikabutsu* 21 (1969) 105.
18. A. KOBAYASHI and T. OYAMA, *ibid* 29 (1971) 54.
19. E. DI RUPO, M. R. ANSEAU and R. J. BROOK, *J. Mater. Sci.* 14 (1979) 2924.
20. V. BALEK, *J. Mater. Sci.* 5 (1970) 714.
21. P. P. BUDNIKOV and A. A. LITVAKOVSKII, *Dokl. Akad. Nauk. S.S.S.R.* 106 (1956) 267.
22. E. M. LEVIN, C. E. ROBBINS and H. F. MAC MURDIE, "Phase Diagrams for Ceramics" (The American Ceramic Society, Columbus, 1964) pp. 156, 181, 219, 241, 246; p. 64 (1969).
23. E. DI RUPO, Ph.D. Thesis, University of Mons (1978).
24. E. DI RUPO, T. G. CARRUTHERS and R. J. BROOK, *J. Amer. Ceram. Soc.* 61 (1978) 468.
25. E. DI RUPO, E. GILBART, T. G. CARRUTHERS and R. J. BROOK, *J. Mater. Sci.* 14 (1979) 705.
26. W. D. KINGERY, *J. Appl. Phys.* 30 (1959) 301.

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