JOURNAL OF MATERIALS SCIENCE 6 (1971) 974–980

The Fabrication of α-Alumina by Reactive Hot-Pressing

D. I. MATKIN, W. MUNRO, T. M. VALENTINE
Materials Development Division, AERE, Harwell, Berks, UK

Polycrystalline α-alumina has been fabricated by reactive hot-pressing, in which low temperature forms of alumina have been transformed to α-alumina at temperature, under pressure. The influence of the phase transformation upon the densification during hot-pressing was studied for a number of commercial aluminium hydrate powders, including gibbsite and boehmite.

The densification of gibbsite-derived powders was slightly enhanced during the γ-Al_2O_3 to α-Al_2O_3 transformations, whereas the densification curves of the boehmite-derived powders had a region of enhanced densification and a region of reduced rate of densification. It is suggested that a critical specimen configuration was developed, as a result of the phase transformations, that prevented densification from approximately 1150 to 1300° C, until plastic flow, diffusion, and/or grain boundary sliding started at the higher temperature.

1. Introduction

The demand for oxide ceramics with controlled microstructure has led to the development of a wide range of hot-pressing techniques, and also to a need to understand the mechanisms of densification during hot-pressing [1]. The influence of phase changes on the densification of ceramic materials during hot-pressing has received considerable attention recently. These hot-pressing techniques have been classified into two types: pressure calcintering and reactive hot-pressing. In pressure calcintering, a decomposable salt is calcined under pressure in a hot-pressing assembly, e.g. magnesium hydroxide to magnesium oxide [2] aluminium hydroxide to aluminium oxide [2-4]. Morgan and Scala [2] showed that whereas there was a greatly enhanced rate of densification during de-hydration of magnesium hydroxide to magnesium oxide, there was virtually no enhancement during de-hydration of aluminium hydroxide; it was suggested that this difference could be explained in terms of the strength of the OH bonding.

Reactive hot-pressing refers to the application of pressure at temperature during a polymorphic phase change, e.g. monoclinic ZrO_2 to tetragonal ZrO_2 [5], and γ-Al_2O_3 to α-Al_2O_3 [3]. Attention has been focused on reactive hot-pressing of alumina, and it has been suggested [1, 3], that reactive hot-pressing of boehmite would permit easy fabrication of high density, fine grain alumina. However initial experiments by the authors on the reactive hot-pressing of pure boehmite at modest pressures, resulted in low final densities. The objective of the present work was to study the influence of both decompositional and polymorphic phase changes, on the rate of densification of boehmite and gibbsite powders, in order to fabricate high density, fine grain α-alumina.

2. Characterisation of Powders

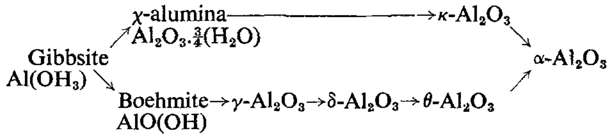
The reactive hot-pressing behaviour of the gibbsite-derived powders and boehmite-derived powders listed in table II, were investigated. All the gibbsite-derived powders were obtained from B.A. Chemicals Ltd. (BACO) gibbsite, while boehmite-derived powders were obtained from three different sources namely Giulini* EP boehmite, B.A. Chemicals "Cera" boehmite, and Dupont "Baymal" boehmite [6].

The sequence of phase transformations during calcination of both gibbsite and boehmite are very complex, and have been studied by a number of workers [7, 8]; the general results are summarised in table I. There is some disagreement in the literature concerning the

---

*Giulini GmbH, Ludwigshafen am Rhein, Germany.

TABLE I Summary of phase transformations of aluminium hydrates



identification of these phases from their X-ray powder diffraction lines, the authors have adopted the classification summarised by Lippens and de Boer [9]. Scott and Horsman [8] studied the calcination route followed by BACO gibbsite, and investigated the influence of the atmosphere and the initial particle size on the sequence of phase transformations. In the present work, the general pattern of phase transformations for the BACO gibbsite, and the three boehmite powders (after calcination in open trays in air), was investigated by X-ray crystallography, differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and BET surface area analysis. The BACO gibbsite was characterised in both the micronised condition (mean agglomerate size of 4 μm) and the unmicronised size (agglomerate size in range 30 to 200 μm). Scott and Horsman [8] observed the influence of agglomerate size on the sequence of phase transformations during calcination of gibbsite. In the present work the unmicronised gibbsite was observed to follow the lower transformation route through γ-Al_2O_3 (see table I), while the micronised gibbsite partially followed the lower route through γ-Al_2O_3 and partially the upper route through κ-Al_2O_3, see table II. It was confirmed by X-ray analysis that micronised gibbsite calcined at 500°C was predominantly γ-Al_2O_3, while gibbsite calcined at 900°C was entirely γ-Al_2O_3, and gibbsite calcined at 1150°C was mainly α-Al_2O_3 with a trace of κ-Al_2O_3 and θ-Al_2O_3. The complex nature of the dehydration of gibbsite is also illustrated by T.G.A. results shown in fig. 1. It can be seen that the micronised gibbsite powder follows a two-stage dehydration process.

The general pattern of phase transformations for boehmite as outlined in table I, was followed by Giulini, Cera and Baymal boehmite, the T.G.A. results on two boehmites are shown in fig. 1. The difference in weight loss during dehydration of the two powders is probably due to the absorbed water present on the higher surface area of the Giulini powder.

The question arises as to whether the sequence of phase transformations observed during

TABLE II Characteristics of as-received and calcined (1 h in air) alumina powders

Powder	B.E.T. Surface Area	Crystallographic Phases Present	Major Impurities (p.p.m.)
Micronised B.A. Gibbsite			
As-received	6.8 m^2/g	α-$Al(OH_3)$	Na, 3000
Calcined at 500°C	196 m^2/g	γ-Al_2O_3	
Calcined at 900°C		γ-Al_2O_3	
Calcined at 1150°C	19 m^2/g	α-Al_2O_3 (Trace of κ-Al_2O_3 and θ-Al_2O_3)	
Giulini Boehmite			
As-received	170 m^2/g	α-AlO(OH)	Fe, 50
Calcined at 500°C	170 m^2/g	γ-Al_2O_3	
Calcined at 900°C		γ-Al_2O_3	
Calcined at 1150°C	17 m^2/g	α-Al_2O_3	
Cera Boehmite			
As-received	2.8 m^2/g	α-AlO(OH)	Na, 300; Ca, 50; Fe, 100; Ga, 100
Calcined at 500°C		γ-Al_2O_3	
Calcined at 1150°C		α-Al_2O_3 (Trace of θ-Al_2O_3)	
Baymal Boehmite			
As-received	310 m^2/g	α-AlO(OH)	
Calcined at 500°C		γ-Al_2O_3	

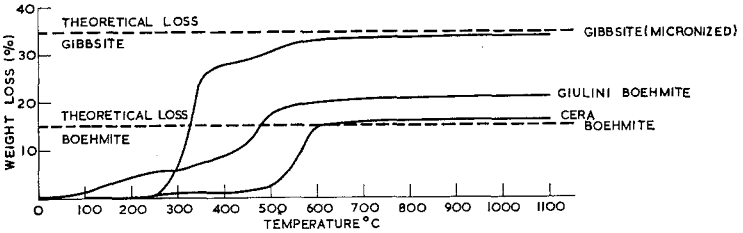


Figure 1 Thermal gravimetric analysis of aluminium hydroxide powders; heating rate 400°C/h.

calcination of powders was the same as occurred under load during hot-pressing. Although the heating rate during calcination was different from that in the hot-pressing experiments, it was confirmed that loose powders heated in the hot-pressing assembly transformed at similar temperatures to the powders calcined in open trays. Regarding the phase transformations occurring under load, the results presented in section 4 indicate that the applied load did not influence the pattern of phase transformations of the powders. This is important because Wheat and Carruthers [4] observed that certain high surface area boehmite gels transformed directly to α-Al_2O_3 at low temperatures, as a result of the hydrothermal conditions inside the hot-pressed specimen due to trapped water vapour. However they reported that this did not occur in the coarser powders such as Cera boehmite.

3. Experimental Details of Hot-Pressing Equipment

Reactive hot-pressing experiments were carried out in a graphite die and plunger assembly, heated by a molybdenum wound furnace within a vacuum chamber. Pressure was applied to the graphite plungers through a Wilson Seal. During a hot-pressing run the procedure was as follows. The 1.27 cm I.D. graphite die was filled with approximately 2 grams of the starting powder on a vibrating table. After inserting the graphite die and plunger assembly into the vacuum furnace, the vacuum chamber was pumped overnight to reach a typical pressure of 10^{-3} torr. The temperature was slowly raised at approximately 6°C per min and at a pre-determined temperature a pressure of 4000 psi (28 Mn/m^2) was applied to the plungers; the temperature was then raised at 6°C per min to a maximum of around 1450°C, held for 1 min, and allowed to cool. The shrinkage of the sample during hot-pressing was continuously monitored using a linear displacement transducer*.

At the completion of each run the density of the hot-pressed sample was measured by a water immersion technique, and after correction for the thermal expansion of the whole assembly, the shrinkage was transformed to a density/temperature curve (based on the theoretical density of α-Al_2O_3). Hot-pressed samples were analysed by the X-ray powder method, and were also ground and polished and the microstructure examined by optical microscopy and scanning electron microscopy (SEM).

4. Reactive Hot-Pressing of Gibbsite-Derived Powders (Micronised)

As-received BACO gibbsite and gibbsite-derived powders were reactively hot-pressed under the standard conditions; the results are summarised in fig. 2.

It can be seen that the densification curves for all the gibbsite-derived powders are very similar although the α-Al_2O_3 obtained from gibbsite calcined at 1300°C had a slightly lower rate of densification than those powders that transformed to α-Al_2O_3 under load during the hot-pressing cycle.

The as-received gibbsite powders showed a region of slightly enhanced densification associated with dehydration at 200 to 300°C, and also a small change in the rate of densification around 1300°C. The actual sequence of phase transformations occurring under load during the reactive hot-pressing cycle was determined by X-ray analysis of samples stopped at pre-determined temperatures. The X-ray analysis of specimens stopped at 600, 1180 and 1200°C are summarised in table III. It can be seen that micronised gibbsite transformed partially through the γ-Al_2O_3 route and partially through the κ-Al_2O_3 route within a single specimen.

---

*Sogenique, type D.

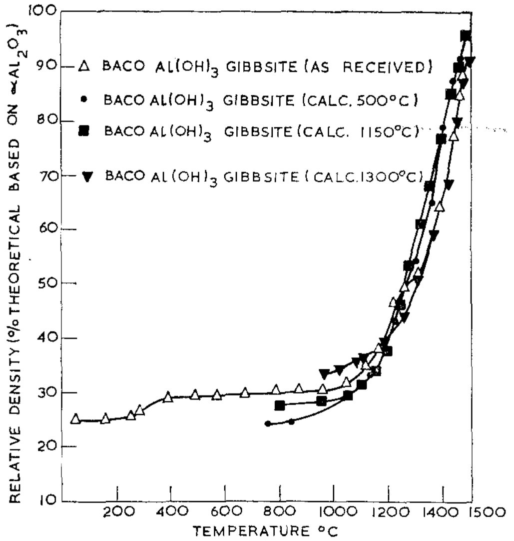


Figure 2 Densification of gibbsite and gibbsite-derived powders.

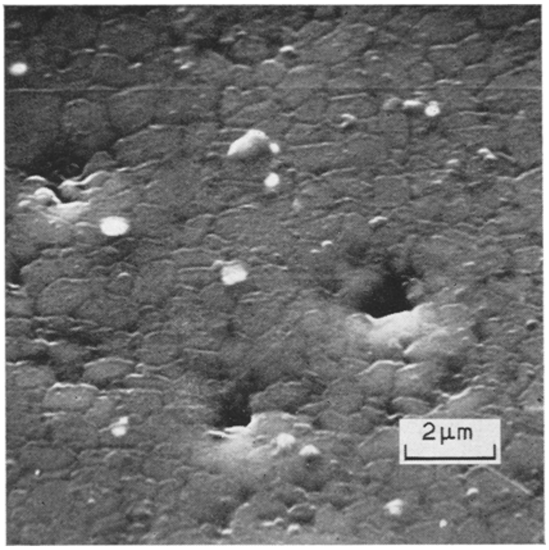


Figure 3 Stereoscan micrographs of hot-pressed alumina, from gibbsite (calcined 1150°C).

TABLE III Crystallographic phases of hot-pressed specimens rate of rise of temperature 6°C/min, and held at temperature 1 min.

Powder	Maximum Hot-Pressing Temperature	Crystallographic Phases Present
Micronised	600°C	γ-Al_2O_3
	1180°C	κ-Al_2O_3 (Trace α-Al_2O_3 and θ-Al_2O_3)
B.A. Gibbsite	1200°C	α-Al_2O_3 (Trace of κ-Al_2O_3 and θ-Al_2O_3)
Giulini boehmite (Calcined 500°C)	1080°C	θ-Al_2O_3 + α-Al_2O_3 (Trace of δ-Al_2O_3)
	1180°C	α-Al_2O_3

The highest final density obtained was 96% theoretical density, from a starting powder of micronised gibbsite calcined at 1150°C. Microstructural examination of this sample revealed a fine microstructure, see fig. 3. The average grain size was 1.3 μm, and it can be seen that there is no evidence of discontinuous grain growth, although no grain growth inhibitor had been incorporated.

5. Reactive Hot-Pressing of Boehmite-Derived Powders

The results of reactive hot-pressing of Giulini boehmite-derived powders are shown in fig. 4.

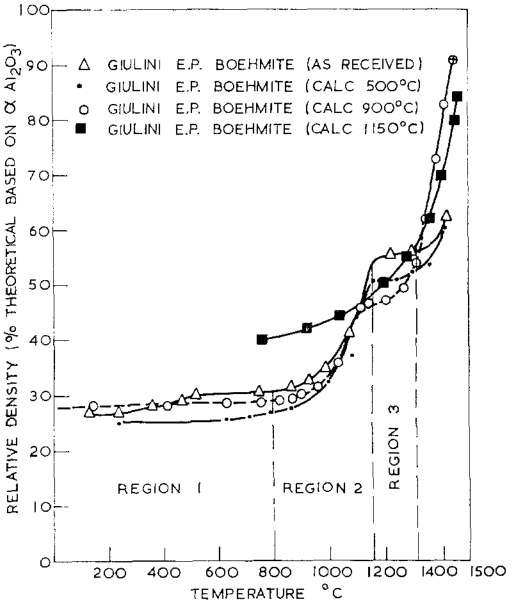


Figure 4 Densification of Giulini boehmite-derived powders.

The densification behaviour of the boehmite-derived powders is clearly quite different to that of the gibbsite-derived powders described in the previous section. The densification curve of as-received boehmite powder showed a number of different regions viz: Region 1 up to 800°C had a region of slightly enhanced densification associated with dehydration in the temperature range 300 to 500°C. Region 2 from 800 to 1150°C was a region of enhanced densification, and Region 3 from 1150 to 1300°C was a region of virtually zero rate of densification. A comparison of the densification curves of as-received boehmite (calcined 500°C), and boehmite (calcined 900°C), with the densification curve for boehmite (calcined 1150°C), see fig. 4, shows clearly that Regions 2 and 3 are associated with the γ-Al_2O_3 to α-Al_2O_3 phase transformation. The existence of Region 3 is a major obstacle to obtaining high density, fine grain size alumina from a boehmite-derived powder by reactive hot-pressing; if the enhanced rate of densification had continued, then fully dense, fine grain size alumina would have been obtained at 1400°C.

Therefore it was important to establish that Region 3 was characteristic of the hot-pressing behaviour of all boehmite and boehmite-derived powders. The reactive hot-pressing behaviour of Baymal boehmite and Cera boehmite was also investigated. It can be seen from the results shown in fig. 5 that the hot-pressing behaviour of all three boehmite powders are similar; there are in fact small differences in detail, for example the temperature (T_t) for the transition from Region 2 to Region 3 occurs in Giulini boehmite at 1150°C and "Cera" and Baymal boehmite at 1200°C.

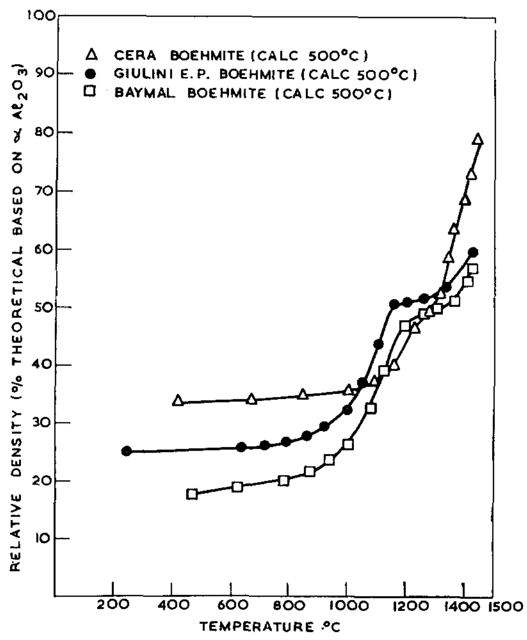


Figure 5 Densification of Giulini boehmite, "Cera" boehmite and "baymal" boehmite.

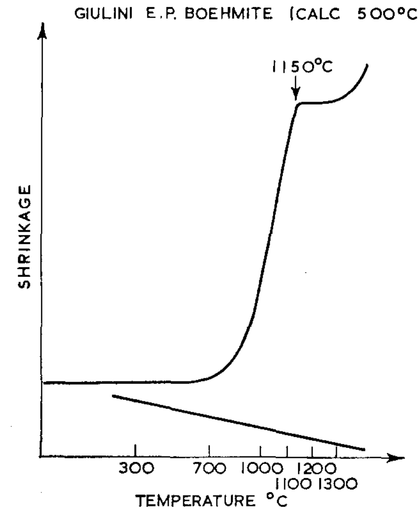


Figure 6 Shrinkage curve recorded during reactive hot-pressing of boehmite (calcined 500°C), showing abrupt transition from Region 2 to Region 3.

The transition for Giulini boehmite was investigated in more detail by stopping the hot-pressing cycle at 1080 and 1180°C. Fig. 6 is an example of the recorded shrinkage curve during reactive hot-pressing of boehmite (calcined 500°C). The crystallographic structure and the microstructure of specimens hot-pressed to 1080°C and 1180°C were analysed. The results in table III show that prior to the abrupt transition at 1150°C specimens were a mixture of θ and of α-Al_2O_3 with a slight trace of γ-Al_2O_3 present, while after the transition the specimens were entirely α-Al_2O_3. The conclusion is that the region of enhanced densification (Region 2) occurs during the γ-Al_2O_3 to α-Al_2O_3 transformation and this transformation is complete by 1150°C. Therefore, there are no further phase transformations after the transition temperature (T_t). In further experiments, Giulini boehmite (calcined 500°C) powder was reactively hot-pressed up to 1100°C and kept at that temperature for 20 h, after which the temperature was raised at the normal 6°C per min. It can be seen in fig. 7 that the densification curve of this specimen also has a Region 3. In other experiments, the same starting powder was heated at 6°C per min. inside the die in the hot-pressing vacuum assembly, and the load was then applied at different pre-determined temperatures; the results of applying the load at 1080 and 1180°C respectively is shown in fig. 7. It can be seen from the results in fig. 7 that in all

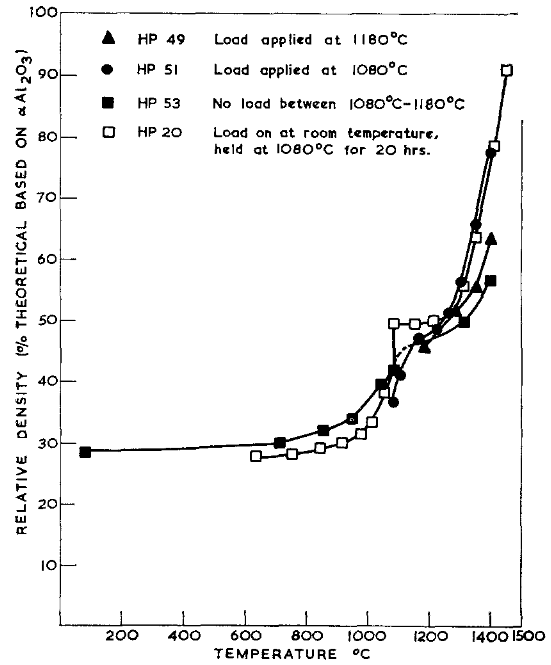


Figure 7 Densification of Giulini boehmite (calcined 500°C) hot-pressed under various conditions.

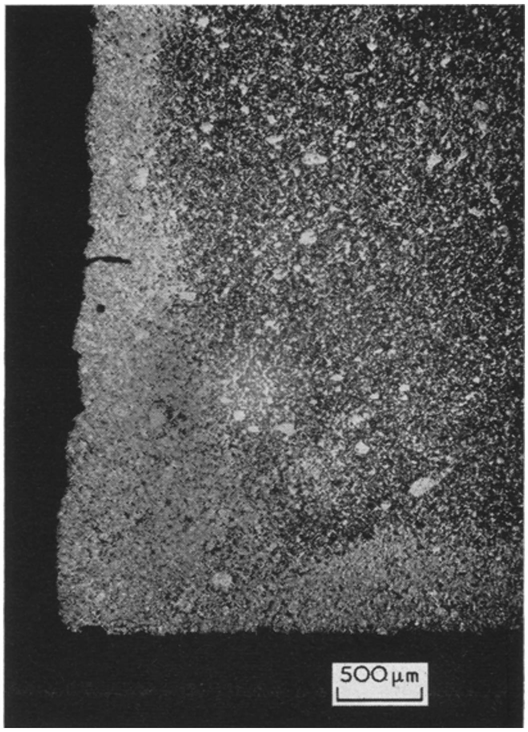


Figure 8 Optical micrograph of section of reactive hot-pressed Giulini boehmite specimen stopped at 1180°C, showing the denser outer skin.

cases where the phase transformation γ-Al_2O_3 to α-Al_2O_3 occurred under an applied load there was a region with a reduced rate of densification (Region 3).

It is concluded from this series of experiments that during the region of enhanced densification (Region 2) hot-pressed samples developed a "configuration" that prevented further shrinkage. Optical microstructural examination of a specimen hot-pressed to 1180°C, showed a dense skin surrounding a porous central region (see fig. 8), and it is suggested that this skin prevented further densification until plastic flow, rapid diffusion and/or grain boundary sliding began above 1300°C, at the end of Region 3.

The highest density attained for reactive hot-pressed Giulini boehmite was 91% theoretical density, from a starting material of boehmite (calcined 900°C); the microstructure of this material was very fine with an average grain size of 1.6 μm. It was observed that there were areas of fully dense material separated by regions with large pores with diameters greater than the average grain size. In the fully dense areas, there is no evidence of discontinuous grain growth, although it should be noted that no grain growth inhibitor had been incorporated in this particular sample.

6. Summary of Reactive Hot-Pressing Behaviour of Gibbsite and Boehmite-Derived Powders

The sequence of phase changes during hot-pressing of all three boehmite powders followed the γ-Al_2O_3 to α-Al_2O_3 transformation route. However the sequence of phase changes for the BACO micronised gibbsite was more complex, and transformations through both the κ-Al_2O_3 and through the boehmite route occurred in the same specimen.

The densification rate of the gibbsite-derived powders was slightly enhanced by the phase transformations compared with the gibbsite calcined at 1300°C (α-Al_2O_3); however in general the densification curves for all gibbsite-derived powders were fairly similar. This behaviour is in marked contrast to the hot-pressing characteristics of boehmite-derived powders, which were found to have a region of enhanced densification during the γ-Al_2O_3 to α-Al_2O_3 transformation (compared with α-Al_2O_3 starting powder); this enhanced densification was followed by a region of virtually zero rate of densification. These results modify a conclusion of Chaklader and Cook [3], who only reported the region of enhanced densification, and thus implied that reactive hot-pressing of boehmite would allow the fabrication of high density alumina at low temperatures. In fact the occurrence of Region 3 is a major obstacle to achieving high density, fine grain polycrystalline alumina by reactive hot-pressing. Furthermore Region 3 is characteristic of the three boehmite powders investigated. It is suggested that a critical specimen configuration was developed as a result of the phase transformations that prevented further densification until plastic flow, rapid diffusion, and/or grain boundary sliding occurred at a higher temperature.

This suggestion is supported by results on the reactive hot-pressing of ultra-fine vapour deposited γ-Al_2O_3 powder [10]. It was observed that the densification curve for a pure vapour deposited γ-Al_2O_3 exhibited a Region 3, whereas an impure powder with identical characteristics exhibited no Region 3. It was concluded that a liquid glassy phase (CaO, FeO, SiO_2) present in the impure powder allowed grain boundary sliding to occur between 1150 and 1300° C, and hence allowed densification to take place.

Rice [11] observed a region (1120 to 1250° C) of reduced rate of compaction during vacuum hot-pressing of Linde B powders (γ-Al_2O_3) and showed that during this region the rate of outgassing of anionic impurities was a maximum. No increased out-gassing was observed during Region 3 of the hot-pressing cycle of boehmite-derived powders, also no increase in the rate of loss of weight was observed during T.G.A. of these powders at 1200 to 1300° C. While the reduced rate of densification for certain Linde B powders may be associated with out-gassing, any reduced rate of densification observed in the present work is attributed to the specimen configuration developed during the phase transformations γ-Al_2O_3 to α-Al_2O_3.

A number of mechanisms can be postulated to account for the occurrence of Region 3, based on geometrical packing to a critical density. However it must be emphasised that the transition from Region 2 to Region 3 was very abrupt at the transition temperature T_t, and furthermore the transition was directly related to the phase transformation γ-Al_2O_3 to α-Al_2O_3. The detailed mechanism of how the critical configuration prevents further densification during Region 3 is not well understood, and future work is planned to investigate the influence of higher applied loads, and also the influence of minor impurity additions that are known to effect the transformations of γ-Al_2O_3 to α-Al_2O_3.

References

1. R. M. SPRIGGS and L. ATTERAAS, "Ceramic Microstructure" (John Wiley, 1968) p. 701.
2. P. E. D. MORGAN, and E. SCALA, "Sintering and Related Phenomena" (Gordon and Breach, 1967) p. 861.
3. A. C. D. CHAKLADER and R. C. COOK, *Amer. Ceram. Soc. Bull.* **47** (1968) 712.
4. T. A. WHEAT and G. T. CARRUTHERS, *Trans. Brit. Ceram. Soc.* **69** (1970) 85.
5. A. C. D. CHAKLADER and V. T. BAKER, *Amer. Ceram. Soc. Bull.* **44** (1965) 258.
6. J. BUGOSH, R. L. BROWN, J. R. MCWHORTER, G. W. SEARS, and R. J. SIPPEL, "Ultra Fine Particles" (John Wiley and Sons, 1963) p. 206.
7. G. W. BRINDLEY, "Progress in Ceramic Science", Vol. **1** (Pergamon Press, 1963) p. 1.
8. B. A. SCOTT and W. H. HORSMAN, *Trans. Brit. Ceram. Soc.* **69** (1970) 37.
9. B. C. LIPPENS and J. H. DE BOER, *Acta Cryst.* **17** (1964) 1312.
10. D. I. MATKIN, T. M. VALENTINE, W. MUNRO, and J. A. DESPORT, *Proc. Brit. Ceram. Soc.* **21** in press.
11. R. W. RICE, *Proc. Brit. Ceram. Soc.* **12** (1969) 99.

Received 17 March and accepted 5 April 1971