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Some factors affecting the reactive hot-pressing behaviour of alumina

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The densification behaviour of metastable cubic aluminas during reactive hot-pressing exhibits a region of enhanced densification followed by a region of reduced rate of densification. It has been established that the transition to the region of reduced rate of densification occurs after the phase transformations to $\alpha-Al_2O_3$ are complete. Results are presented of further studies on the influence of applied pressure and minor additions of impurities on the nature of the region of reduced densification for three different cubic Al_2O_3 powders. It was observed that those parameters that assisted the phase transformations to $\alpha-Al_2O_3$ also reduced the transition temperature between the two regions by a differing amount for each powder. It is believed that the differences in hot-pressing behaviour of the three cubic Al_2O_3 powders arise from their initial powder characteristics, and that these differences may lead to a better understanding of the region of reduced rate of densification.

A further aspect of the present work has been a brief study of the influence of uniaxial pressure upon the high temperature phase transformation of cubic $\theta-Al_2O_3$ to hexagonal $\alpha-Al_2O_3$. Over a limited pressure range up to 1 kbar the influence of pressure on the irreversible phase transformations was observed to be $dT/dp \simeq -0.1$ K bar^{-1}.

1. Introduction

Reactive hot-pressing has received renewed interest as a potential route for the fabrication of high density fine grain alumina. Previous work by the authors [1, 2] and Rice [3] has established that the reactive hot-pressing behaviour of metastable Al_2O_3 (such as, γ, δ, and θ-Al_2O_3) is complex, since the densification curve may have as many as four distinct regions. Hot-pressing experiments on a wide range of alumina powders have shown that a region of reduced rate of densification occurs after the completion of the transformation to α-Al_2O_3. This appears to be a general characteristic of metastable cubic Al_2O_3 powders, for example, hydroxide-derived γ-Al_2O_3 [1], vapour-deposited γ-Al_2O_3 [2], aluminium salt-derived γ-Al_2O_3 [3].

The general conclusion is that high final densities cannot be readily achieved by reactive hot-pressing if the region of enhanced densification that occurs during the phase transformation is followed by a region of reduced rate of densification. The final density obtained by reactive hot-pressing of a metastable cubic Al_2O_3 may be no higher than would be obtained by hot-pressing the *same* powder calcined to α-Al_2O_3. In fact with certain vapour-deposited γ-Al_2O_3 powders the final density achieved by reactive hot-pressing is lower than that obtained from the *same* powder, pre-calcined to α-Al_2O_3, and hot-pressed under the same conditions [2].

The reactive hot-pressing behaviour of Al_2O_3 will be influenced by the various hot-pressing conditions, such as heating rate, maximum applied pressure, addition of impurities, etc. It was considered by the authors that although the reactive hot-pressing behaviour of Al_2O_3 would be influenced by hot-pressing conditions, more important differences in behaviour would be found between various types of cubic Al_2O_3 owing to differences in powder characteristics.

This paper presents the results of a systematic study on the influence of applied pressure and the influence of the addition of minor impurities on the reactive hot-pressing behaviour of three different types of γ-Al_2O_3 namely: boehmite-derived, vapour-deposited, and a commercially obtained cubic Al_2O_3 (probably salt-derived).

2. Experimental details

2.1. Powder characteristics

The three types of cubic Al_2O_3 powders were selected for hot-pressing studies on the basis of their different methods of synthesis. The first type of Al_2O_3 was boehmite-derived and was prepared in the laboratory by the calcination in open trays of Giulini* EP pseudo-boehmite at 900° C in air for 1 h. The EP boehmite is identical to the powder used in previous work by the authors [1]. The second-type of γ-Al_2O_3 was synthesized by a vapour-deposition technique. An ultra-fine γ-Al_2O_3 powder was produced by a DC plasma liquid-wall furnace technique by The National Physical Laboratory [4], and is identical to the powder referred to as NPL liquid wall (A) powder in previous work by the authors [2]. The third type of cubic Al_2O_3, from a commercial source†, was probably produced by careful calcination of an aluminium salt. The reactive hot-pressing of this high purity commercial powder has been studied by Steiner *et al* [5].

The three cubic Al_2O_3 powders were not calcined or treated prior to reactive hot-pressing. The as-received powder characteristics were assessed by X-ray powder diffraction techniques, chemical analysis, BET surface area, and differential thermal analysis (DTA) techniques.

The identification of the crystallographic phases present in all three powders was based on the classification adopted by Lippens and De Boer [6], and is consistent with the classification used by the authors in previous work [1, 2]. A summary of the powder characteristics is presented in Table I. A major difference between the powders is the crystallographic phases; the EP boehmite-derived and NPL vapour-deposited being primarily γ-Al_2O_3 and the "Cerac" powder‡ primarily θ-Al_2O_3. The total cation impurity content of each powder is 0.005%, 0.5 and 0.05 wt % respectively.

The α-Al_2O_3 transformation temperature for each powder was determined by differential thermal analysis (DTA), on a Linseis L81 combined DTA/TGA/DTG apparatus. The sample of each powder weighing 0.05 g was loosely packed into a platinum sample holder; the rate of heating was 10° C min^{-1}, which was similar to the rate of heating during reactive hot-pressing. DTA traces were obtained for each powder, and also (see Section 3.2) for two powders containing 1 and 5 wt % addition of Fe_2O_3 powder. The Fe_2O_3 powder (Analar Grade) and metastable Al_2O_3 powder were dispersed in methyl alcohol, thoroughly mixed, and then allowed to dry. A feature common to all powders was the exothermic peak associated with the conversion to α-Al_2O_3. From the DTA traces the peak temperature (T_p) was measured, see Table II.

2.2. Hot-pressing equipment

The experimental details of the hot-pressing equipment have been previously described [1]. Briefly the apparatus was a vacuum hot-pressing rig capable of a maximum temperature of 1450° C and an applied pressure from 50 to 12000 psi, with a facility to continuously monitor the shrinkage of the specimen during the hot-pressing cycle. Specimens (approx. 3 g weight)

TABLE I Powder characteristics of the three metastable Al_2O_3 powders.

Powder	Chemical analysis		BET surface area (m^2 g^{-1})	Alumina phase
	Fe	Other major impurities		
EP boehmite-derived	50 ppm	None detected	120	γ
NPL vapour-deposited	0.1%	Si, 0.2%; Na, 0.2%	160	γ (with trace of α)
'Cerac'	50 ppm	Si, 0.05%	60*	θ(with traces of δ and α)

*Reference [5].

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*Giulini GmbH, Ludwigshafen am Rhein, Germany.

†Cerac Inc, Butler, Wisconsin, USA.

‡An early sample batch of this powder was analysed as a mixture of γ and θ-Al_2O_3 with no detectable α-Al_2O_3 present.

TABLE II DTA analysis of pure and doped (Fe_2O_3) EP boehmite-derived, vapour-deposited, and "Cerac" Al_2O_3, compared with the transition temperature (${}_{50}T_t$) from hot-pressing results.

Powder	Additive	DTA T_p(°C)	Reactive hot-pressing ${}_{50}T_t$ (°C)
EP boehmite derived	None	1210	1200
	1% Fe_2O_3	1160	1160
	5% Fe_2O_3	1150	1140
NPL vapour-deposited	None	1265	1250
	1% Fe_2O_3	1220	1200
	5% Fe_2O_3	1165	1140
'Cerac'	None	1260	1250

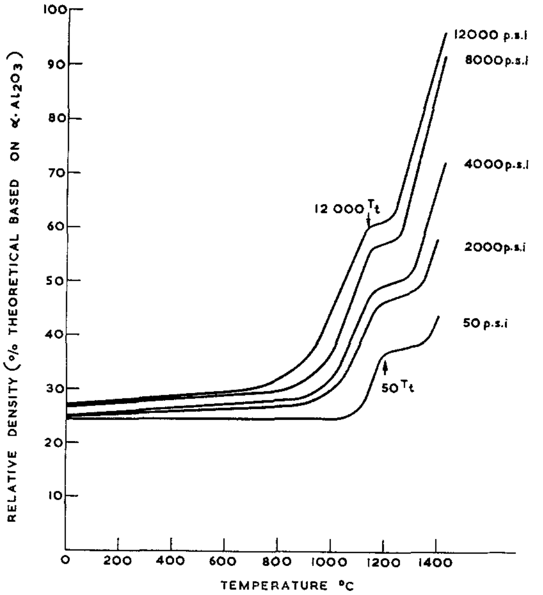

Figure 1 Densification of EP boehmite-derived Al_2O_3, hot-pressed at various applied pressures.

were pre-pressed in a ½ in. diameter die at room temperature at a pressure of 4000 psi, irrespective of the final hot-pressing pressure. The standard hot-pressing cycle was to apply the required pressure at room temperature, raise the temperature at approx. 8°C min^{-1} up to a maximum of 1400°C, hold under pressure for 1 min, and allow to cool. The densities of hot-pressed specimens were measured by the water immersion method, and after correction for the linear 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 (N.B. crystallographic densities are as follows: $\alpha = 3.987$ g cm^{-3}; $\gamma = 3.67$ g cm^{-3}). Hot-pressed specimens stopped at different temperatures during the hot-pressing cycle were analysed by the X-ray powder diffraction method, and after ceramographic polishing were examined by optical microscopy and scanning electron microscopy (SEM).

3. Experimental results

3.1. The influence of pressure on reactive hot-pressing of alumina

The EP boehmite derived γ-Al_2O_3 was reactively hot-pressed under the standard conditions at applied pressures in the range 50 to 12000 psi; the results are summarized in Fig. 1. It can be seen that each densification curve has an initial region with a low rate of densification, followed by a region (during the phase transformations) when the densification rate is high (region 2), which is then abruptly terminated at a specific transition temperature (T_t), and followed by a plateau region of reduced rate of densification (region 3); finally the densification rate increases in region 4. The most interesting effects of increased applied pressure on the densification behaviour are the change in transition temperature (T_t) between region 2 and region 3 and also the change in length of the plateau of reduced rate of densification. It can be seen that with an applied load of 50 psi the transition temperature, (${}_{50}T_t$) is 1200°C, while at an applied pressure of 12000 psi the transition temperature ${}_{12\,000}T_t$ has been reduced to 1130°C. In addition the length of the plateau has reduced by 150°C at 50 psi to 90°C at 12000 psi. The phase composition of hot-pressed specimens stopped at various stages of the hot-pressing cycle was determined by X-ray powder diffraction techniques. Analysis indicated that for powder pressed at 50 psi, specimens stopped at 1170°C (before ${}_{50}T_t$) were a mixture of α-Al_2O_3 and θ-Al_2O_3, while specimens stopped at 1230°C (after ${}_{50}T_t$) were entirely α-Al_2O_3. Similarly for powder pressed at 12000 psi, specimens stopped at 1090°C (before ${}_{12\,000}T_t$) were a mixture of α-Al_2O_3 and θ-Al_2O_3, while specimens stopped at 1160°C (after ${}_{12\,000}T_t$) were entirely α-Al_2O_3.

The initial reason for studying the influence of applied pressure on the region of reduced rate of densification was the belief that the plateau was due to a critical specimen "configuration" that developed during the phase transformation and therefore increased applied pressure would reduce

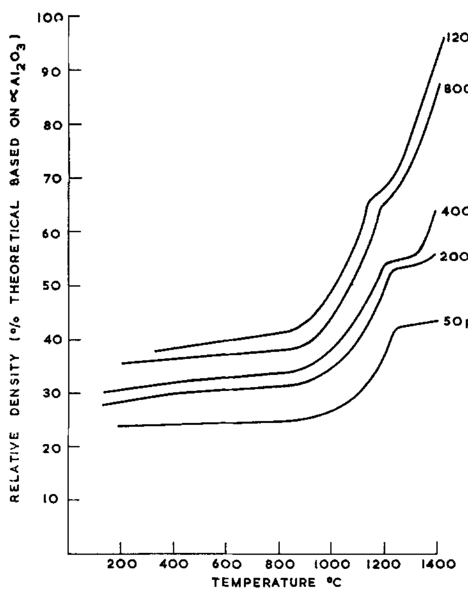

Figure 2 Densification of NPL vapour-deposited Al_2O_3, hot-pressed at various applied pressures.

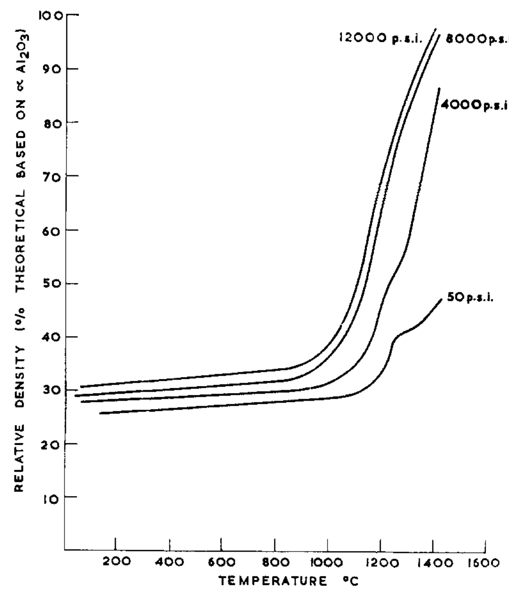

Figure 3 Densification of "Cerac" Al_2O_3, hot-pressed at various applied pressures.

the temperature of the beginning of region 4. This reduction was observed, and furthermore the transition temperature (T_t) at the beginning of region 3 was also reduced. This latter observation will be discussed later in Section 4.

The reactive hot-pressing behaviour of the NPL vapour-deposited γ-Al_2O_3 powder is summarized in Fig. 2. The general pattern of densification is similar to the EP boehmite-derived γ-Al_2O_3; however, there are several important differences. First, the plateau of reduced rate of densification was progressively reduced in length by increased pressure until 8000 psi, when the plateau was reduced to a point of inflexion in the densification curve. Secondly, there was a greater reduction in the transition temperature (T_t) over the pressure range 50 to 12000 psi. It can be seen that at an applied pressure of 50 psi that ${}_{50}T_t$ is 1245° C while at an applied pressure of 12000 psi the transition temperature ${}_{12\,000}T_t$ is 1130° C, i.e. a reduction of 115° C.

The reactive hot-pressing behaviour of the as-received "Cerac" θ-Al_2O_3 powder is summarized in Fig. 3. It can be seen that the plateau region is even less pronounced at the higher pressure than the vapour-deposited powder. In fact at applied pressures of 8000 and 12000 psi there is no sign of any discontinuity in the densification curve. A plateau was present at the very low applied pressure of 50 psi thus underlining the fact that the densification behaviour of "Cerac" powder followed the same general pattern of other metastable cubic Al_2O_3 powders. The plateau present at pressures of 50 psi could be removed (as predicted from earlier work [1, 2]) by calcining the "Cerac" θ-Al_2O_3 for 1 h at 1200° C to convert to α-Al_2O_3, see Fig. 4. The same calcined powder hot-pressed at 4000 psi also had no discontinuity in the densification curve.

3.2. The influence of additions of impurities on reactive hot-pressing of alumina

Recent studies have demonstrated that small amounts of certain impurity additions can influence the temperature of transformation from γ-Al_2O_3 to α-Al_2O_3. Wakao and Hibino [7] studied the influence of a wide range of metallic oxides upon the transformation of γ-Al_2O_3 to α-Al_2O_3 by X-ray analysis and DTA. They concluded that additions of Fe_2O_3 had the greatest influence upon transformation temperature. Simpkin and Bye [8] have studied in detail the influence of small additions of chromium and iron on the transformation of amorphous aluminium hydroxide gels through intermediate forms to corundum. They concluded that small additions of iron reduced the temperature for complete transformation to α-Al_2O_3, although the BET surface area of the resultant impure α-Al_2O_3 was approximately the same as pure α-Al_2O_3

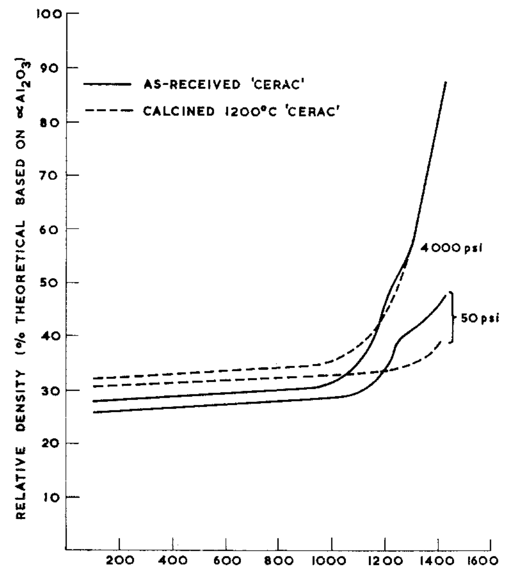

Figure 4 Densification of "Cerac" Al_2O_3 powder, as-received and as-calcined (1200°C for 1 h), hot-pressed at two applied pressures.

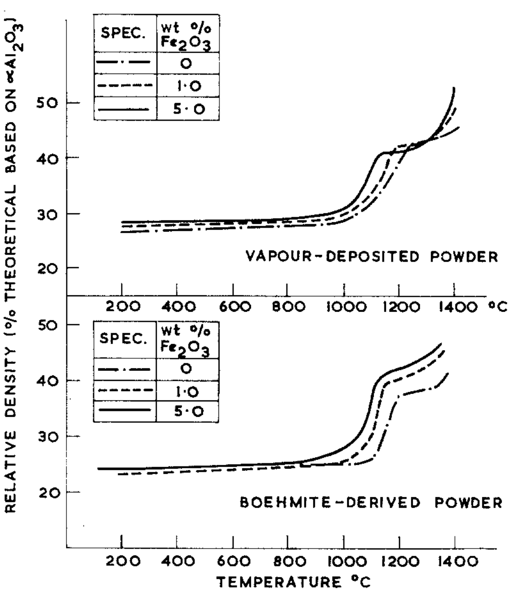

Figure 5 The influence of Fe_2O_3 impurity additions on the densification of two Al_2O_3 powders hot-pressed at 50 psi.

produced by calcination at the higher temperature.

The actual temperature for completion of the transformation of a metastable Al_2O_3 to α-Al_2O_3, and the influence of added impurities on this temperature will be strongly influenced by the initial powder characteristics. Therefore, the influence of additions of 1 and 5 wt % of Fe_2O_3 upon the transformation temperature of the EP boehmite-derived γ-Al_2O_3, and the NPL vapour-deposited γ-Al_2O_3 was determined by DTA, for loose powder and the results are summarized in Table II.

The influence of additions of 1 and 5 wt % Fe_2O_3 upon the reactive hot-pressing behaviour of the two γ-Al_2O_3 powders was also studied at a range of pressures. The addition of 1 wt % Fe_2O_3 on the EP boehmite-derived γ-Al_2O_3 showed little influence at applied pressures of 4000 psi since T_t was only reduced from 1150 to 1130°C, whereas the DTA results suggested a reduction of 60°C. However, at the lower applied pressures of 50 psi the influence of additions of Fe_2O_3 was more marked, and the results for the EP boehmite-derived γ-Al_2O_3, and the NPL vapour-deposited γ-Al_2O_3 hot-pressed at 50 psi are summarized in Fig. 5. It can be seen that for the EP boehmite-derived γ-Al_2O_3, the transition temperature ${}_{50}T_t$ was reduced from 1200°C (pure) to 1160°C by the addition of 1 % (ΔT_t = 40°C) and reduced to 1140°C by the addition of 5 wt % Fe_2O_3 (ΔT_t = 60°C). The influence of additions of Fe_2O_3 on the transition temperature ${}_{50}T_t$ for the NPL vapour-deposited γ-Al_2O_3 powder was even greater, from 1250°C (pure) to 1200°C by the addition of 1 wt % Fe_2O_3 (ΔT_t = 50°C, and to 1140°C by the addition of 5 wt % Fe_2O_3 (ΔT_t = 130°C).

These changes in ${}_{50}T_t$ with impurity additions during reactive hot-pressing correlate well with the shift in DTA peaks of the α-Al_2O_3 transformations owing to the influence of Fe_2O_3 additions, see Table II. It has, therefore, been established that as the temperature for complete transformation to α-Al_2O_3 was reduced by the additions of Fe_2O_3 so the transition temperature (${}_{50}T_t$) between region 2 and region 3 was also reduced.

The phase composition of specimens reactively hot-pressed at 50 psi from NPL vapour-deposited γ-Al_2O_3, with 1 wt % Fe_2O_3, was determined by X-ray analysis. Analysis showed that specimens stopped at 1160°C (before ${}_{50}T_t$) were a mixture of α-Al_2O_3 and θ-Al_2O_3, while specimens stopped at 1220°C (after ${}_{50}T_t$) were entirely α-Al_2O_3.

3.3. Microstructural studies

The microstructure and compressive strength was assessed for a number of hot-pressed samples that had been stopped at different stages of the hot-pressing cycle, particularly during region 3.

Specimens from EP boehmite-derived powder were stopped during the hot-pressing cycle (applied pressure 4000 psi) in the range 1050 to 1350° C. Certain specimens were diamond-ground on the circumference, and the top and bottom faces to produce suitable compression specimens. The density of such cylinders was measured by water immersion techniques, and the variation of compressive strength with total porosity was measured using an Instron testing machine. There was considerable scatter in the results; however, specimens stopped at various parts of the region of reduced rate of densification (region 3), tended to have increased compressive strength across the plateau, (from 40000 to 55000 psi), even though there is little increase in density across this region.

The microstructure of fracture faces of the compression samples that had been stopped at various stages across the plateau were studied by scanning electron microscopy (SEM). However, no significant differences in the microstructure were observed.

4. Discussion

The experimental results have confirmed the existence of a region of reduced rate of densification during reactive hot-pressing of a range of different metastable cubic Al_2O_3 powders. Furthermore it has been confirmed that the transition temperature (T_t) at the beginning of this region is uniquely related to the temperature at which the phase transformations to α-Al_2O_3 are complete. It was observed for both the EP boehmite-derived and the NPL vapour-deposited Al_2O_3 powders, that the application of increased pressure and additions of Fe_2O_3 impurities reduced the temperature for the completion of the phase transformations to α-Al_2O_3, and also reduced the transition temperature (T_t) during reactive hot-pressing.

Reactive hot-pressing at pressures as low as 50 psi is almost equivalent to normal atmospheric pressure sintering, and a similar region of reduced sintering rate was observed by Badkar *et al* [9], during studies on the sintering behaviour of boehmite gels. It is worthwhile noting that one of the boehmites used by those authors, Balgel, is identical to as-received EP boehmite; the transition temperature ${}_{50}T_t$ for EP boehmite-derived γ-Al_2O_3 obtained in the present work agrees with the value obtained from dilatometric shrinkage curves for Balgel, by Badkar *et al.*

The shape and extent of the plateau region of reduced rate of densification is as important as the actual transition temperature (T_t); it was observed that the length of the plateau for EP boehmite derived γ-Al_2O_3 was considerably shortened (from 150 to 90° C) by increasing the applied pressure from 50 to 12000 psi. The plateau region on the densification curve of NPL vapour-deposited powders was reduced to a point of discontinuity at pressures above 4000 psi. These results appear to confirm the suggestion that the plateau is partially the result of mechanical locking within the specimen that developed during the phase transformations. Furthermore, the compressive strength of various specimens stopped during region 3 increased across the plateau, although the density was virtually constant. This would suggest that the densification during the phase transformations (region 2) occurs within the aggregates by reactive hot-pressing, and that the bonding between these α-Al_2O_3 aggregates increases across the plateau (region 3) as the hot-pressing temperature increased.

The results of previous work [1, 2] and the present results show that there are important differences in the reactive hot-pressing behaviour of different metastable cubic Al_2O_3 powders hot-pressed under identical conditions. For example, the value of the transition temperature (${}_{4000}T_t$) hot-pressed at 4000 psi and a heating rate of 8° C min^{-1}, ranges from 1120° to 1200° C for all the various metastable cubic Al_2O_3 powders studied by the authors. The differences must be due to the influence of powder characteristics, and hence the powder preparation route on the temperature of transformation to α-Al_2O_3. A more striking example of the influence of powder characteristics is a comparison of the shape and extent of the plateau region of the EP boehmite-derived and the NPL vapour-deposited powders compared with the "Cerac" Al_2O_3 powder (see Figs. 1, 2 and 3). The authors believe that an understanding of the cause of the reduced rate of densification should be possible from a detailed understanding of the influence of the differences in initial powder characteristics. There is very little systematic difference between the powder characteristics of the "Cerac" powder and the two γ-Al_2O_3 powders as far as crystallographic phases, transformation behaviour as studied by DTA, surface area, or impurity levels (see Tables I and II). However, we believe that the detailed structure of the individual aggregates, particularly strength, will be very important.

We have no detailed understanding yet of the influence of the initial powder characteristics on hot-pressing behaviour, or of the mechanism operating during the phase transformations. However, the difference between the final hot-pressed density achieved for metastable powders from different sources will be important technologically.

Steiner *et al* [5] have suggested that heating rate is the most important parameter in obtaining high final densities by reactive hot-pressing, and they compared their results on "Cerac" powder hot-pressed at heating rates of 150° C min^{-1} with previous studies [1, 10] on different powders hot-pressed at much lower heating rates of around 10° C min^{-1}. We believe that this approach is an over-simplification of a complex matter, and that one cannot compare the influence of one set of hot-pressing parameters on powder A with a different set of hot-pressing parameters on powder B. We conclude that "Cerac" θ-Al_2O_3 is an unusual metastable cubic Al_2O_3 powder that can be hot-pressed to high final densities even at low heating rates. Future work is planned to assess the influence of heating rates on EP boehmite-derived and NPL vapour-deposited γ-Al_2O_3 powders.

A number of different factors may contribute to the cause of the region of reduced rate of densification following the completion of the phase transformations to α-Al_2O_3. It may be that the cation or anion diffusion in the α-Al_2O_3 is slower than diffusion in the cubic metastable γ-Al_2O_3, resulting in a lower densification rate. An additional factor was suggested by Badkar *et al* [9] who studied the changes in the microstructure of specimens of boehmite gel sintered in the region of the transition temperature (1200° C). They observed that the α-Al_2O_3 formed at 1200° C had a crystallite size of 1 µm compared with a crystallite size of 150 Å for the θ-Al_2O_3 matrix and, they suggested that the change in sintering rate in boehmite gels may be due to the associated loss in surface energy following the phase transformation. However, any explanation of the reduced rate of densification must account for the differences in reactive hot-pressing behaviour observed for different metastable Al_2O_3 powders, e.g. EP boehmite-derived powder compared with "Cerac" powder.

In summary, we believe that during region 2 rapid densification is occurring within the aggregates until the transformations to α-Al_2O_3 are completed. The question of whether this region of reactive hot-pressing (region 2) is followed by a reduction of reduced rate of densification is largely determined by the structure of the α-Al_2O_3 pseudo-morphs resulting from the initial aggregates. In some cases, e.g. "Cerac", modest pressure (4000 psi) is able to overcome the internal mechanical locking at temperatures near to T_t while in the case of EP boehmite-derived powder the temperature has to be increased until plastic deformation or diffusional processes allow grain-boundary sliding to occur.

Finally, one very interesting additional result that arose from the present work was a study of the influence of pressure upon the high temperature phase transformation from cubic metastable θ-Al_2O_3 to hexagonal α-Al_2O_3. Several workers have previously studied the influence of pressure at elevated temperatures upon phase transformations in ZrO_2 [11, 12] and TiO_2 [13]; no reference has been found to Al_2O_3. It has been confirmed by X-ray studies that the transition temperature (T_t) occurs at the completion of the phase transformations to α-Al_2O_3, and, therefore, the influence of pressure upon T_t (taken from Figs. 1 and 2) has been replotted in Fig. 6, for both EP boehmite-derived and NPL vapour-deposited Al_2O_3. It can be seen that over the pressure range 0 to 1 kbar the relationship is linear:

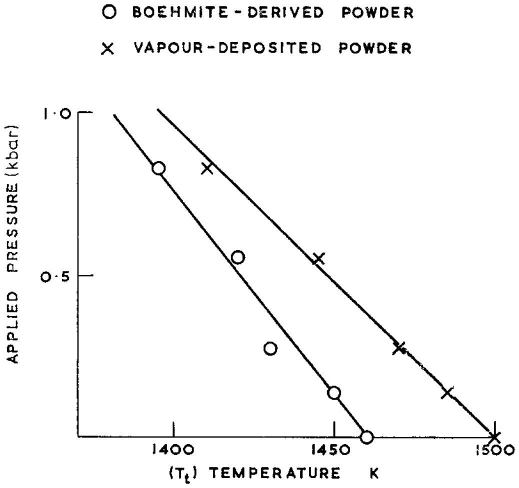

Figure 6 The influence of applied pressure on the high temperature phase transformation to α-Al_2O_3.

EP boehmite-derived Al_2O_3
$dT/dP = -0.08$ K bar^{-1}
NPL vapour-deposited Al_2O_3.
$dT/dP = -0.11$ K bar^{-1}

Previous workers have carried out detailed studies on phase transformations over a wider pressure range up to 60 kbars, and therefore the present results over a very limited pressure range up to 1 kbar, can only be considered as indicative. These values should be compared with those obtained experimentally by Vahldiek and Lynch [11] for mono-clinic to tetragonal ZrO_2 transformation ($-$ 0.01 K bar^{-1}), as obtained theoretically by Whitney [12] from thermodynamic data for the ZrO_2 transformation ($-$ 0.03 K bar^{-1}), and as obtained experimentally by Vahldiek [13] for anatase to rutile TiO_2 transformation ($-$ 0.02 K bar^{-1}). A value of dT/dP for a reversible phase transformation can yield thermodynamic data of the two phases [12]. However, this approach is not justified for an irreversible phase transformation from a metastable phase (θ-Al_2O_3) to a stable phase (α-Al_2O_3).

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References

1. D. I. MATKIN, W. MUNRO, and T. M. VALENTINE, *J. Mater. Sci.* **6** (1971) 974.
2. D. I. MATKIN, T. M. VALENTINE, W. MUNRO, and J. A. DESPORT, *Proc. Brit. Ceram. Soc.* **20** (1972) 133.
3. R. W. RICE, *ibid* **12** (1969) 99.
4. D. A. EVEREST, I. G. SAYCE, and B. SELTON, *J. Mater. Sci.* **6** (1971) 218.
5. C. J. P. STEINER, R. M. SPRIGGS, and D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **55** (1972) 115.
6. B. C. LIPPENS and J. H. DE BOER, *Acta Cryst.* **17** (1964) 1312.
7. Y. WAKAO and T. HIBINO, *Reports of the Japanese Government Industrial Research Institute, Nagoya* **11** (9) (1962) 588.
8. G. T. SIMPKIN and G. C. BYE (private communication).
9. P. A. BADKAR, J. E. BAILEY, and H. A. BARKER, Third International Conference on "Sintering and Related Phenomena", Notre Dame, USA, June 1972 (to be published).
10. G. E. GAZZA, J. R. BARFIELD, and D. L. PREAS, *Amer. Ceram. Soc. Bull.* **48** (1969) 606.
11. F. W. VAHLDIEK and C. T. LYNCH "Sintering and Related Phenomena" (Gordon and Breach, New York, 1967) p. 637.
12. E. D. WHITNEY, *J. Amer. Ceram. Soc.* **45** (1962) 612.
13. F. W. VAHLDIEK, *J. Less-Common Metals* **11** (1966) 99.

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