Structural transformation during sintering and annealing of beta alumina

S. N. HEAVENS
Chloride Silent Power Ltd, Davy Road, Astmoor, Runcorn, Cheshire, UK

Changes in the phase content, microstructure and lattice parameter are observed in stabilized β/β'' alumina specimens following extended sintering and annealing treatments. The resulting state is dependent on composition of the starting powder and on temperature and duration of heat treatment; the kinetics of transformation between β and β'' alumina are generally slow and certain β/β'' ceramics remain in a metastable state even after a prolonged high temperature anneal. Following post-sinter heat treatment, splitting of X-ray diffraction peaks reveals a segregation of the β'' phase into two components of differing lattice parameter. With sintering schedules of a long duration the splitting may even be present in the as-fired condition as recently reported by Harbach [1]. The splitting is attributed to a structural change resulting from the expulsion of Na_2O from supersaturated β'' grains.

1. Introduction

The thermodynamic stability of β and β'' phases in polycrystalline beta aluminas is still a matter of controversy. Although the structures of β and β'' alumina are readily distinguishable crystallographically [1], it is uncertain whether β and β'' can be regarded as independent phases [2], whether or not their compositions differ within a sample [2], or whether transformations between β and β'' are so slow [3] that at low annealing temperatures geological time scales might be needed to attain equlibrium.

For reasons of microstructural control, beta alumina ceramics are usually formed by zone sintering [4], residual mechanical stresses being relieved by short duration isothermal annealing. Isothermal "batch" sintering schedules, often involving a two-stage firing process [5, 6], allow longer reaction times but even after further heat treatment, when all transient eutectics have been consumed by exaggerated grain growth, the material is not necessarily in an equilibrium state.

This paper describes structural and phase changes in three beta alumina ceramics, of different composition, following post-sinter annealing at various temperatures and for various durations. As-sintered beta aluminas generally contain mix-tures of β and β'' in varying proportions depending on starting powder composition and firing schedule. With short duration firing schedules it is invariably found that the lattice parameters of the β and β'' phases are equal to within 0.02%. On subsequent heat treatment, either a $\beta'' \rightarrow \beta$ or a $\beta \rightarrow \beta''$ transformation occurs, and in the latter event, splitting of high l index X-ray diffraction peaks, indicating a partial lattice parameter expansion, takes place. This expansion is shown to result not from Na_2O loss from the material, nor from water penetration into the conduction planes, but from one of two possible origins: (i) growth faults such as annealing twins or other stacking fault disorders in the spinel block sequences of β'', or (ii) a structural change due, for instance, to expulsion of Na_2O from supersaturated β'' crystals. The experimental evidence available to decide between these two possibilities is not conclusive but tends to support the latter.

During the preparation of this paper, a similar splitting of X-ray reflections in a range of magnesium-stabilised β''-aluminas was reported by Harbach [1], who argued from a crystallographic standpoint that the line splitting indicated the presence of two component β'' phases, one partly and the other fully magnesium-stabilised. The

present paper confirms his observations, and a similar interpretation is arrived at, except that the argument is based on phase stability considerations. In this context the first β'' component has been regarded as being supersaturated with Na_2O rather than being partly stabilized. Only the second β'' component is thermodynamically stable.

2. Experimental procedure

Beta alumina tubes of diameter 33 mm and thickness 1.6 mm were manufactured by isostatic pressing at 275 MPa of slurry solution spray-dried precursor powders containing reagent grade Na_2CO_3, MgO and/or LiOH, and Alcoa Al6 "superground" alumina in proportions yielding the four compositions listed in Table I. The tubes were fired in air to 98% theoretical density at temperatures of 1900 to 1950 K either by zone sintering [4] or isothermal batch sintering [5]. These sintering methods result in different phase content and microstructure. Phase content and microstructure are also influenced by precursor powder treatment [7], but that aspect was not investigated.

Specimens 20 mm × 20 mm were cut from the as-sintered tubes, polished to provide a flat surface for microstructural examination and X-ray diffraction, and annealed in a C–M Rapid Temp furnace at various temperatures in the range 1600 to 1850 K for a fixed period of 36 ksec (10 h), or at a fixed temperature of 1800 K for durations in the range 3.6 ksec to 1.1 Msec. The furnace heating and cooling rates were approximately 0.3 K sec^{-1}. Specimens were heat treated either open to the furnace atmosphere (air) or enclosed in sintered beta alumina tubes filled with powder of the same composition as the specimen. The latter treatment, referred to as "buffering", serves to prevent loss of volatile components (principally Na_2O) from the specimen during heat treatment.

Both surface and bulk characteristics of the annealed specimens were determined. Phase content and lattice constants were measured by means of a Philips 1720/1050 X-ray diffractometer with $CuK\alpha$ radiation. Microstructures were examined by polishing to 1 μm diamond paste finish and etching for 180 sec in 85% H_3PO_4 at 413 K.

Measurement of the lattice constants of β and β'' alumina is complicated by the sensitivity of the c parameter to rapid atmospheric water pick-up [8–10]. This problem is serious, however, only with powdered specimens. In specimens sintered to near the theoretical density, water penetration is restricted to a surface layer approximately 5 to 10 μm in depth [10] and at room temperature this layer will develop over a period of the order 100 ksec. In the experiments described below specimens were scanned in the diffractometer within 1 ksec of quenching from the annealing temperature. It is possible that even during the quench, water absorption occurred below 1000 K, but this would also have been restricted to a surface layer. For "bulk" measurements, specimens were either polished, removing some 200 μm of surface material, or, in cases of severe preferred orientation, crushed to a powder. The diffraction pattern was scanned in the range 30 to $36°2\theta$ for determination of β/β'' content, 65 to $75°2\theta$ for approximate lattice constant measurement and 143 to $156°2\theta$ for accurate lattice constant determination, at scanning rates of 120, 120 and 480 sec/$°2\theta$, respectively. The phase content measurements were accurate to within approximately ± 3%. Least squares refinement of lattice parameters obtained from measurement of the position of the strong β and β'' lines in the back reflection scan enabled a and c values of precision 1 in 10^4 to be obtained. Use of an annealed aluminium standard confirmed that the accuracy was also of this order.

Harbach [1] used a Guinier camera with monochromator, which is claimed to have a higher resolution than a powder diffractometer; nevertheless, the line splitting in the β''-Al_2O_3 diffraction pattern reported by him is readily observable with a standard diffractometer. The diffractometer has the advantage of being a more rapid technique, and atmospheric water adsorption by the β''-Al_2O_3 crystals is more easily avoided. There is good agreement between Harbach's and the present lattice constant measurements on magnesium-stabilized β/β''-Al_2O_3, indicating that both techniques are equally suitable.

TABLE I

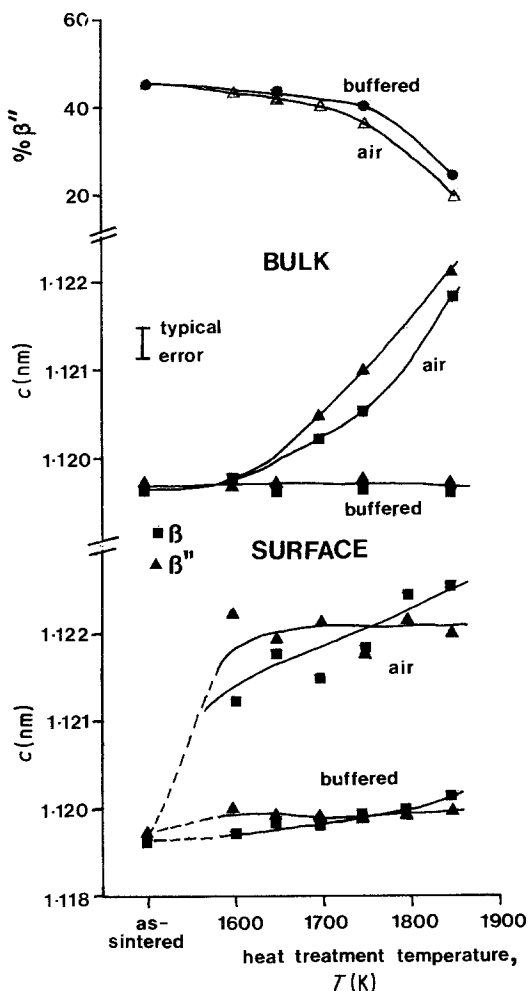| Name	Composition (mol %)			
	Na_2O	MgO	Li_2O	Al_2O_3
A	12.1	4.7	0.0	83.2
B	13.1	2.3	1.6	83.0
C	13.6	0.0	2.2	84.2
D	13.2	9.1	0.0	77.7

Figure 1 Heat treatment of zone-sintered A; phase content and c parameter (bulk and surface).

3. Results

Except where otherwise stated, the results described refer to bulk measurements on specimens annealed for 36 ksec in buffered conditions.

3.1. Composition A

The bulk phase content ($\%\beta''$ in the β/β'' mixture) of heat treated A, following annealing under the two conditions (air and buffered), is shown in Fig. 1. Similar behaviour was observed at the surface of the specimen. In all cases the β'' phase tended to transform to β. The tendency was slightly greater in samples annealed in air but generally the fall in β'' content could not be attributed to loss of Na_2O.

In comparing lattice parameters of β and β'' phases it is more convenient to refer to the dist-

ance between adjacent conduction planes rather than to the unit cell length, since β and β'' are respectively 2- and 3-block structures [1]. Measurements of the interplanar spacing ($c/2$ for β alumina, $c/3$ for β'') — hereafter referred to as the "c parameter" — are also shown in Fig. 1. The error bars indicate that the c parameters of the β and β'' phases, which are identical to within experimental error in the as-sintered ceramic, start to diverge during subsequent heat treatment. Only the c parameter is shown; an increase in c was invariably accompanied by a small decrease in a.

Fig. 1 shows that with buffering no c parameter change occurs in heat treated A. On heat treatment in air, c expands by 0.2% due to loss of Na_2O particularly at the surface of the specimen; the variation of a and c in batches of A containing slightly differing Na_2O contents as determined by X-ray fluorescence analysis (Fig. 2) shows that a increases and c decreases as the Na_2O content increases, as observed by Harbach [1]. With heat treatment at 1850 K the lattice expansion persists throughout the bulk of the specimen, whereas at 1600 K Na_2O loss occurs only within 0.2 mm of the surface. This lattice expansion remains approximately constant at 0.2%, independent of heat treatment temperature, and corresponds to a fall in the Na_2O content to ~ 11.5 mol %, below which A can lose Na_2O only by decomposition to α-Al_2O_3 and $MgAl_2O_4$; α-Al_2O_3 is generally found at the surface of β/β'' alumina specimens heated in air to 1700 K or more.

3.2. Compositions B and C

B and C specimens showed similar behaviour during heat treatment, β''-Al_2O_3 being the stable phase in both materials. Under all conditions the β'' content increased, except close to the surface of a specimen heated in air (Fig. 3), the decrease here being attributable to Na_2O loss.

When zone-sintered B was annealed in a buffered atmosphere, the $\beta \to \beta''$ transformation occurred without any c parameter change at temperatures up to 1700 K. From 1700 to 1850 K the β''-phase appeared to split into two components (Fig. 4a), one with a c parameter unchanged from the original, the other with c increased by 0.5%. To avoid unnecessary confusion, Harbach's [1] nomenclature "k" and "g" has been adopted, although the origin of these labels is obscure. In addition, the residual β-phase appears to undergo a lattice contraction, although the c parameter
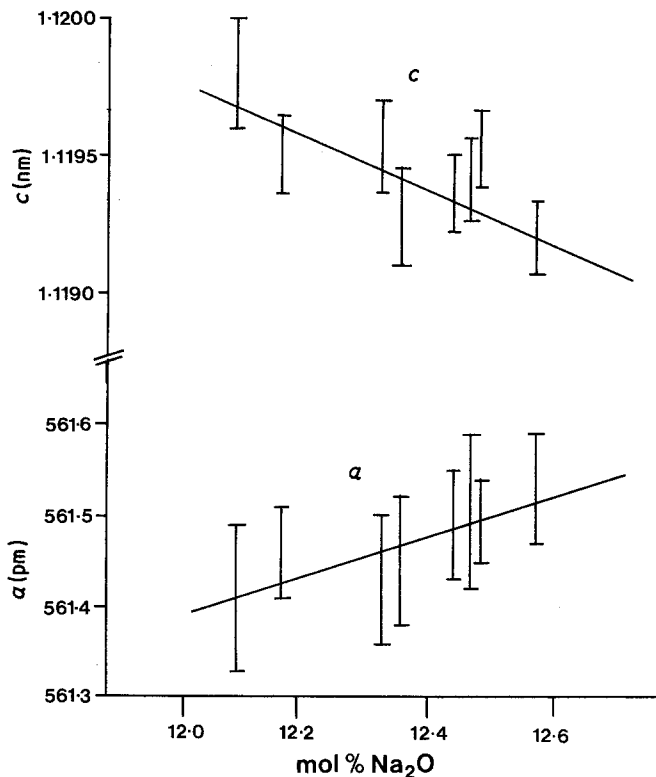
2225

Figure 2 Effect of varying Na_2O content on the lattice parameters a and c in zone-sintered A.

measurements are much less accurate, the small proportion of β precluding the possibility of lattice parameter refinement. Fig. 4a shows bulk measurements; similar values were found at the surface. Fig. 4b shows c parameter measurements in samples of zone-sintered B heat treated in air, in which the loss of Na_2O at the higher temperatures results in a broad spectrum of c values.
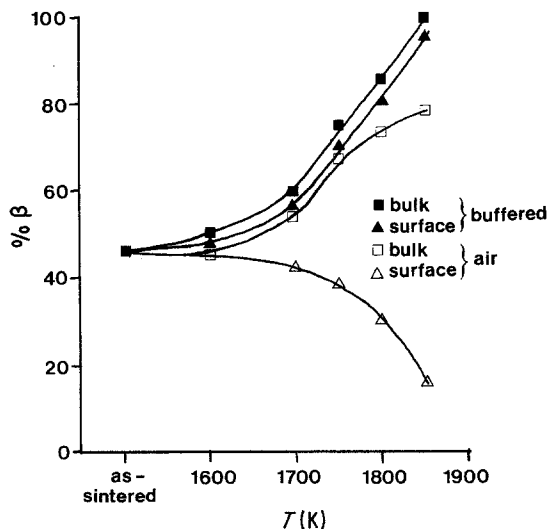

Figure 3 Phase content of B, zone-sintered and annealed. Similar behaviour was shown by zone-sintered C.

The segregation of the β'' phase in Fig. 4 is manifested in the X-ray diffraction pattern by a splitting of the strong β'' lines of high l index $(10\,10)$, $(10\,11)$, $(20\,20)$, $(20\,22)$, $(42\,20)$ and $(20\,40)$, which are particularly sensitive to c parameter changes. A section of the X-ray diffraction pattern illustrating the splitting in composition C is shown in Fig. 5. Fig. 5a was characteristic of zone-sintered B and C; Fig. 5c was characteristic of B and C annealed at 1850 K. The lines which split following post-sinter annealing are the $(20\,20)$ and $(20\,22)$; this should not be confused with the $K\alpha_1$-α_2 doublets present in all lines.

Composition C, zone-sintered, behaved similarly to zone-sintered B. Batch sintered C contained 90% β''; this increased to 99.5% β'' on annealing (Fig. 6). Even in the as-sintered condition the β'' lines showed some tendency to split (Fig. 5b), although the splitting becomes more marked following postsinter annealing (Fig. 5c). Harbach [1] did not describe the Brown Boveri sintering method, but since his samples were annealed only at 1073 K for 7.2 ksec, and yet showed strong line splitting, it can be inferred that a sintering schedule of long duration had been used.

Figs. 7 and 8 show microstructures of zone-sintered and batch sintered ceramic, and the
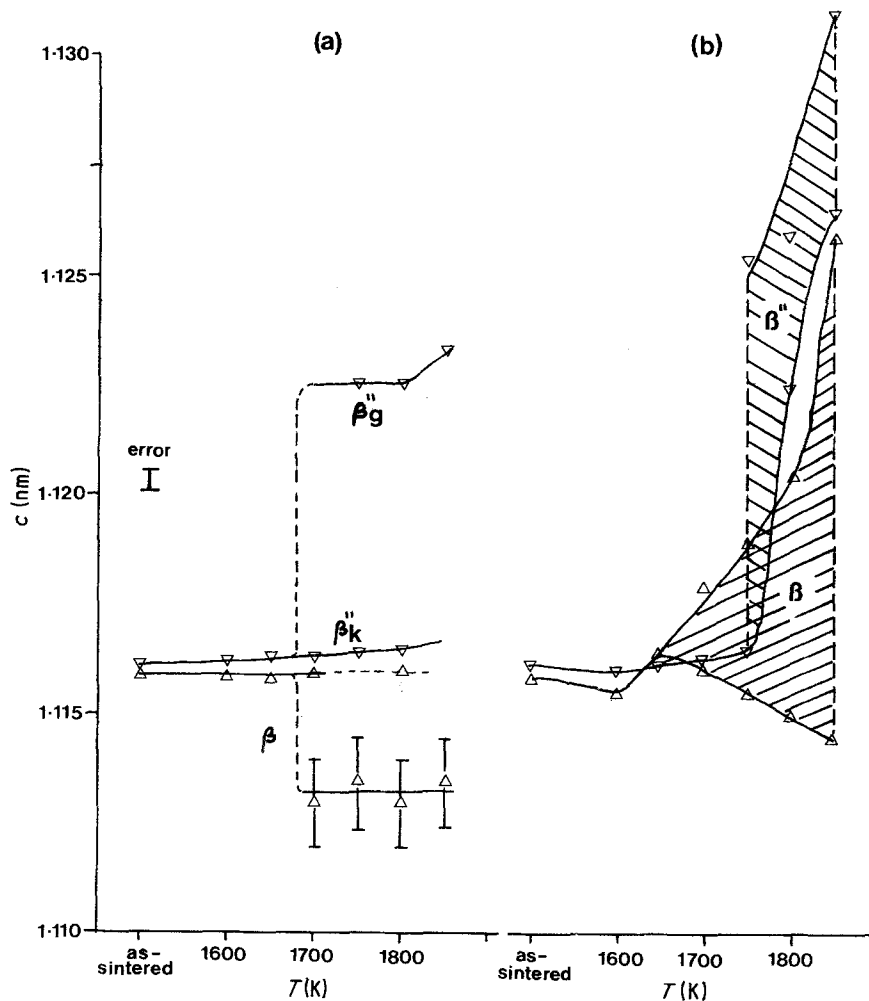
Figure 4 Lattice parameter change on heat treatment of zone-sintered B. Similar behaviour was shown by zone-sintered C. (a) Buffered, (b) annealed in air.

differing mode of grain growth on heat treatment of the two types of material. In the latter type, grain growth is restricted by grain-boundary impingement. Since both types show a similar tendency for the β'' phase to segregate, it is unlikely that the splitting is connected with microstructural changes.

3.3. Composition A, seeded with β'' crystals

One means of obtaining microstructural control and a high proportion of β'' in zone-sintered β/β'' alumina is by the use of seeding [7]. β''-alumina powder, prepared by high temperature calcination of composition D, was ground to $1\,\mu m$ and introduced, at a concentration of $5\,mol\%$, into the precursor powder, maintaining the overall composition as that of A. Attempts to fabricate

durable tubes directly from composition D usually failed owing to their moist sensitivity. The phase content and lattice parameters of seeded A are shown in Fig. 9. Only bulk measurements are shown; very similar measurements were obtained at the surface when buffering was used. In the as-sintered ceramic 75% β'' was obtained, and heat treatment produced essentially no change in the overall β'' content, except in air at 1850K, at which a substantial loss of Na_2O presumably occurred.

Seeded A also demonstrated splitting of the β'' lines (Fig. 9). An attempt was made to determine whether one of the c parameters corresponded to that of the seed powder measured independently, but it was difficult to obtain an accurate value for the latter owing to extremely rapid
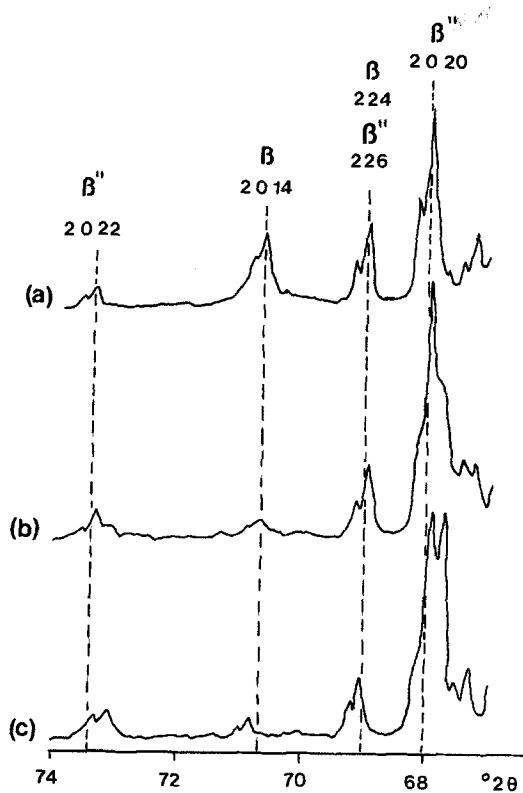
2227

Figure 5 Section of X-ray diffraction pattern of C (a) zone-sintered, (b) batch sintered, (c) zone-sintered and annealed at 1850 K.

Figure 6 Heat treatment of batch-sintered C; phase content and c parameter.

uptake of water in this material. By measuring the position of the $(2\,0\,2\,0)$ β'' peak immediately after quenching from a 1400 K calcination the unit cell length was estimated at 3.354 nm, very close to the literature values for single crystal magnesium-stabilized β'' [1], and similar to the value for β''_k in seeded A. Owing to preferred orientation effects it was difficult to ascertain a systematic trend in the relative intensities of β''_k and β''_g on heat treatment of B, C and seeded A, although there was a general tendency for the β''_g peaks to grow on heat treatment. In any case the formation of β''_g cannot be associated with the growth of seed crystals on heat treatment, since the c parameter of the latter corresponds to that of β''_k, not β''_g. Fig. 10 shows the microstructural change taking place as a result of heat treatment of seeded A. As in Fig. 8, grain growth is competitive and is limited by grain-boundary impingement.

Fig. 9 indicates that with buffering the β'' content remains stable at around 75%, indicating either that this is an equilibrium value, or that the kinetics of transformation between β and β'' are
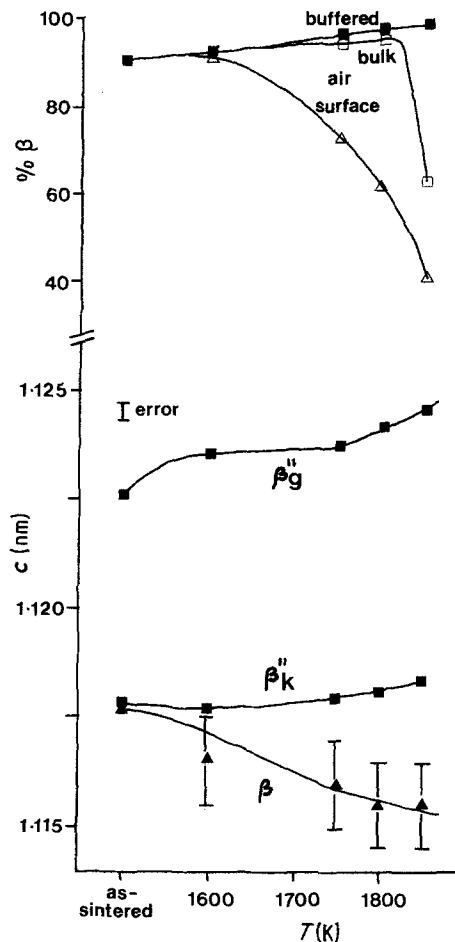
extremely slow in seeded A. In a further experiment, seeded A was heat treated under buffered conditions at 1800 K for 1.1 Msec; the β'' content remained unchanged at 75%. In contrast, unseeded A yielded 25% β'' on similar treatment. Since both seeded and unseeded A were at the same point of the $Na_2O–MgO–Al_2O_3$ phase diagram, they cannot both represent stable states, in spite of the observation that in neither material did any significant change take place between 3.6 ksec and 1.1 Msec at 1800 K. It is probable, nonetheless, that seeded A represents a metastable configuration, for reasons discussed in Section 4.2.

Seeding experiments were also conducted with composition B, using heat treated B powder (99.5% β'') as the seed material. With zone sintering the β'' content as-fired was increased from 45% (unseeded) to 95% (seeded), and as expected the β'' lines split strongly.
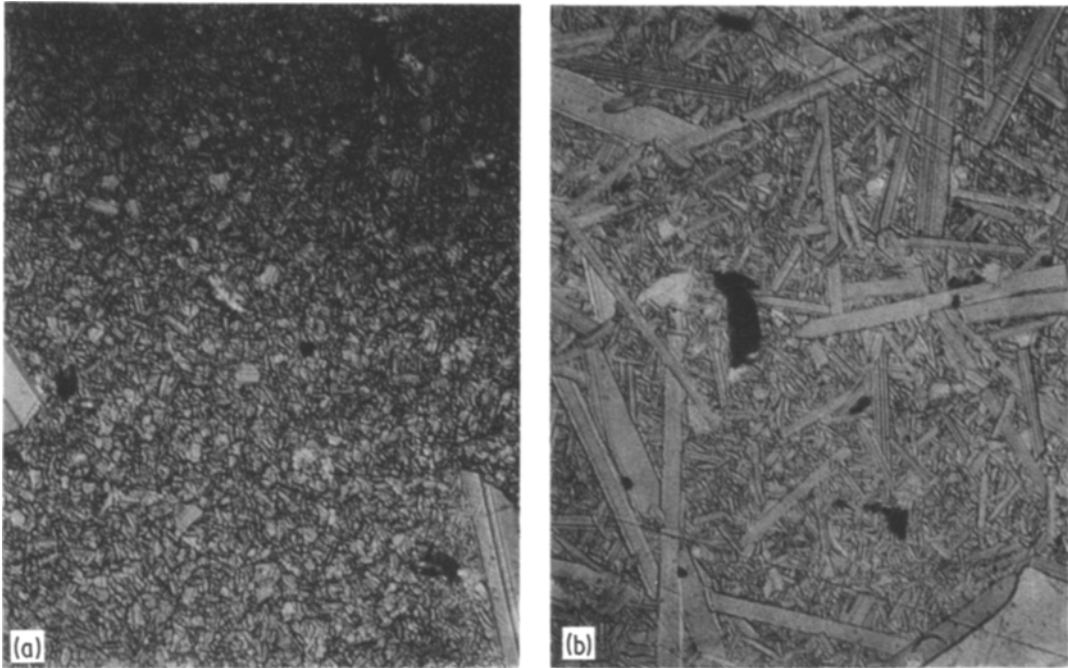
2228

Figure 7 Microstructure of zone-sintered B (a) as-sintered, (b) annealed at 1850 K. × 1000. Similar behaviour was shown by zone-sintered A.

4. Discussion
4.1. Phase stability and reaction kinetics

It has been noted [2] that in the $Na_2O-Li_2O-Al_2O_3$ system the time to attain equilibrium varies with composition. Within a very limited compositional range the reaction is rapid and β'' alumina is the stable phase. In the binary $Na_2O-Al_2O_3$ system β'' is unstable [3] but the kinetics are slow; this also appears to be the case for compositions with intermediate stabilizer levels
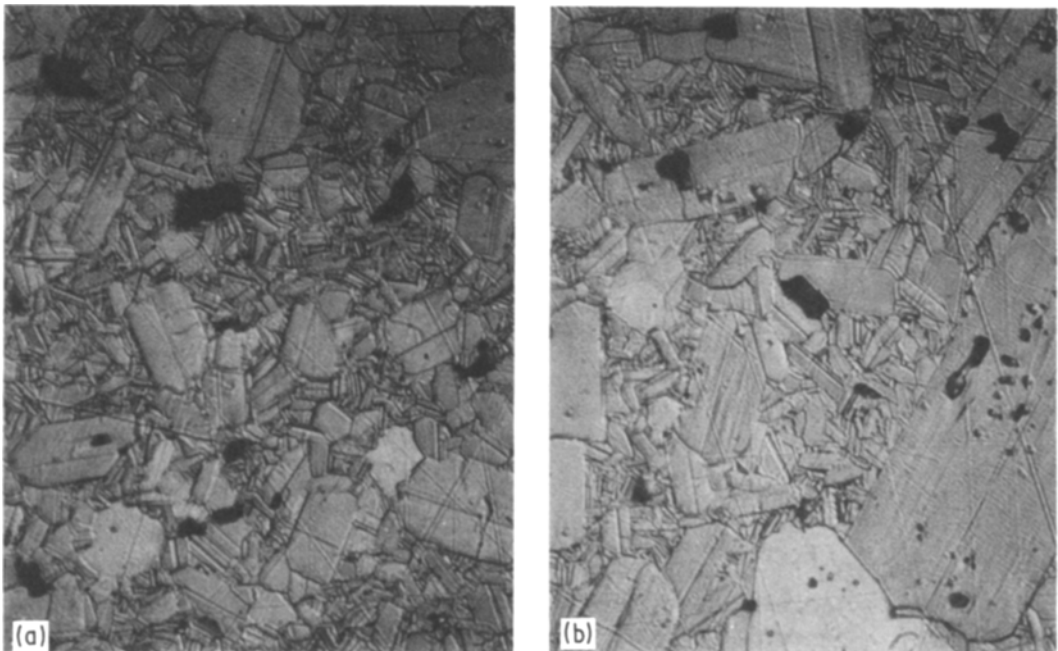

Figure 8 Microstructure of batch-sintered C (a) as-sintered, (b) annealed at 1750 K. × 1000.
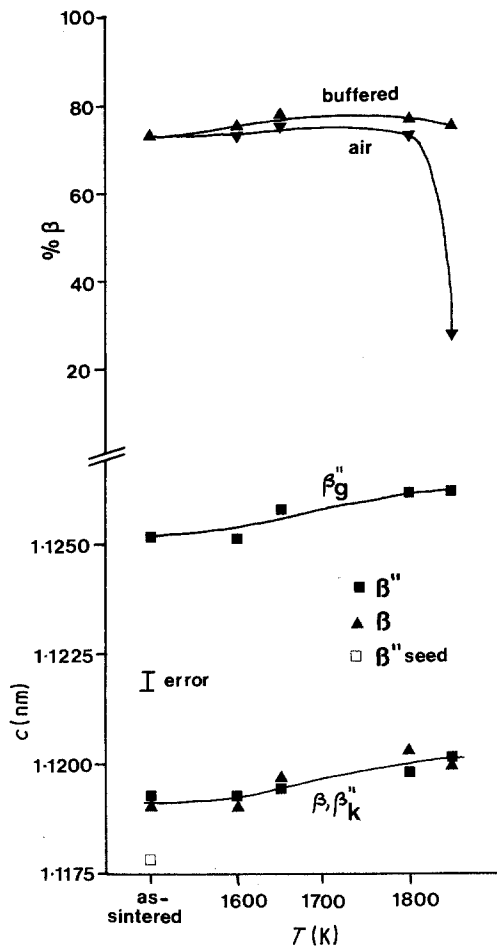
2229

Figure 9 Heat treatment of seeded A: phase content and c parameter.

such as A. On the other hand B and C, being almost fully stabilized, react quickly to form essentially phase pure $\beta''\text{-Al}_2\text{O}_3$.

The quenching rate used $(0.3\,\text{K}\,\text{sec}^{-1})$ was sufficiently rapid for the final β''/β content to be representative of the heat treatment temperature, with little change occurring during cool-down. In any case Hodge [3] found that in the Na_2O–Al_2O_3 system the β/β'' content was somewhat insensitive to cooling rate. Furthermore, in the Na_2O–Li_2O–Al_2O_3 system there is little change in the phase diagram between 1773 and 1573 K

TABLE II

Composition	Transformation	Activation energy (eV)
A zone sintered	$\beta'' \to \beta$	3.55
B zone sintered	$\beta \to \beta''$	3.45
C batch sintered	$\beta \to \beta''$	2.07
35 Na_2O 65 Al_2O_3 [3]	$\beta'' \to \beta$	2.56

[2], except that no phase-pure β'' region forms at 1573 K. Any variation in β''/β content with temperature may be attributable to incomplete transformation, the higher temperature results being closer to equilibrium.

The data in Figs. 1, 3 and 6 can be used to calculate an activation energy for the phase change. On the assumption of first-order kinetics [3] the values in Table II are obtained.

Harbach [1] has described fully stabilized $\beta''\text{-Al}_2\text{O}_3$ by the formula $\text{Na}_{1+z}\text{Mg}_z\text{Al}_{11-z}\text{O}_{17}$. In stoichiometric $\beta''\text{-Al}_2\text{O}_3$ [11] $z = 2/3$ (not $z = 1$ as is commonly stated); the superlattice extends over three (and possibly many more) of the conventional hexagonal unit cells, the overall composition corresponding to the ternary compound $5\text{Na}_2\text{O}\cdot4\text{MgO}\cdot31\text{Al}_2\text{O}_3$. This is conjectured to be the only thermodynamically stable form of $\beta''\text{-Al}_2\text{O}_3$ in the Na_2O–MgO–Al_2O_3 system. Harbach's data show that no structural change occurs in the β'' phase between $z = 0.73$ and $z = 1.0$; all excess Na_2O and MgO is presumably precipitated as separate phases, e.g. NaAlO_2 and MgAl_2O_4. The amount of supersaturation with Na_2O possible in $\beta''\text{-Al}_2\text{O}_3$ is very limited in comparison with $\beta\text{-Al}_2\text{O}_3$.

4.2. Segregation of the β'' structure

Splitting of the β'' peaks on heat treatment into β''_k and β''_g, the latter with a c parameter expanded by 0.5 to 0.6%, may indicate the appearance of two distinct forms of crystallite or may be a diffraction artefact. There are a number of possible causes for the expansion of the c-axis in β'' alumina:

1. *Water.* Penetration of H_2O into the conduction planes, or ion exchange of H_3O^+ for Na^+, is known to cause a c expansion [8–10], but in the present context this possibility can be safely eliminated except in the case of the $1\,\mu\text{m}$ β'' powder used as a seed (Section 3.3). Specimens were inserted into the X-ray diffractometer immediately following quenching from the annealing temperature. In sintered ceramics, H_2O penetration from exposure to air is limited to a surface layer [10] of depth 5 to $10\,\mu\text{m}$ which requires a period of the order 100 ksec to develop. The c expansion detected in specimens heat treated under buffered conditions was a bulk not a surface effect, as demonstrated by the use of polishing, grinding and back-reflection X-ray diffraction techniques.
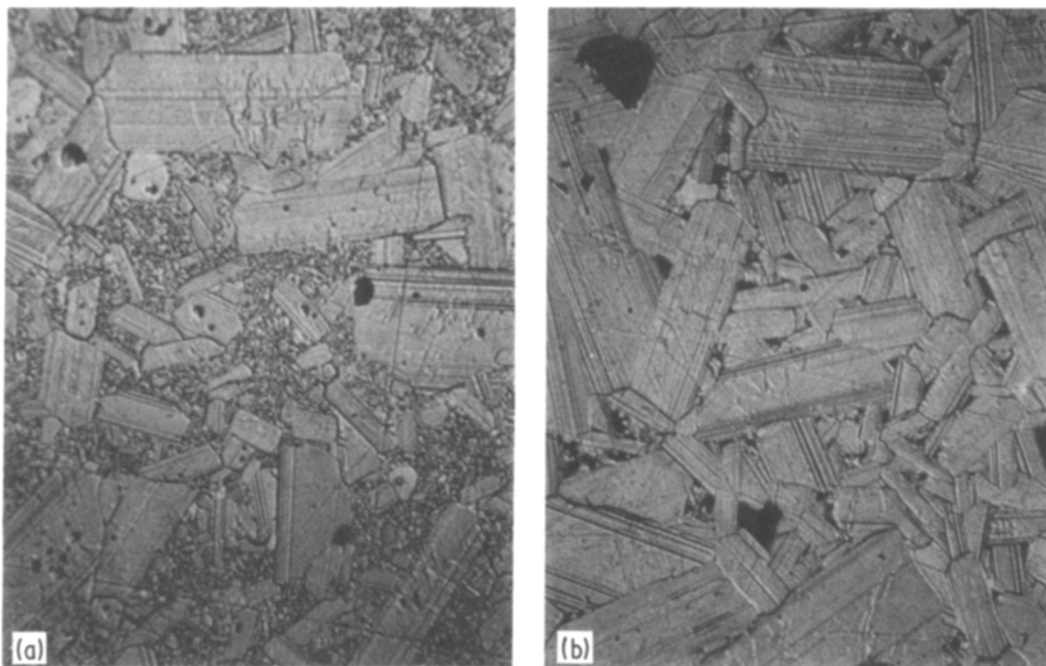
Figure 10 Microstructure of seeded A (a) as-sintered (b) annealed at 1850 K. × 1000.

2. Growth defects. The apparent change in c may be due not to a chemical change in the β'' phase but to a diffraction effect associated with annealing twins or other stacking fault disorders generated during grain growth. If α is the probability of a fault occurring in the spinel block sequence of β'', and δ the change in lattice spacing as a result of the fault, an apparent change in the measured c parameter from c_0 to $c_0(1 + \alpha\delta)$ may occur [12].

Evidence of twinning is prevalent in most heat treated specimens, notably seeded A (Fig. 10b). However, the local structure in the region of the twin fault is not known, and there is no evidence currently available to suggest that the conduction plane spacing does change in that region. When there is no change in interplanar spacing, twin faulting will produce line broadening and/or peak asymmetry in f c c, b c c and h c p structures, but not peak displacement. Only in the specific instance of deformation faulting in f c c structures is the fault expected to result in peak displacement [13]. It is unlikely, therefore, that growth faults will cause a c parameter change in β'' alumina. Furthermore, the microstructural observations do not suggest a connection between grain growth and the formation of β''_g.

3. Na_2O loss. Soda loss in samples annealed in air was also identifiable from the lattice expansion at the surface. This expansion corresponded to a broad distribution of β and β'' crystals which had undergone different degrees of Na_2O loss. In samples annealed under buffered conditions the lattice expansion in β''_g was at a constant level of 0.5 to 0.6% relative to β''_k. This could correspond to Na_2O ejection from the β'' grains, but not from the specimen as a whole; consequently, precipitation of a soda-rich grain-boundary phase would be expected. Attempts to estimate $NaAlO_2$ precipitation by microstructural and X-ray diffraction analysis were inconclusive, although qualitatively, traces of $NaAlO_2$ were in evidence. The difficulty is that if the reaction proceeds according to

$$\beta + \beta''_k \rightarrow \beta''_g + NaAlO_2 \qquad (1)$$
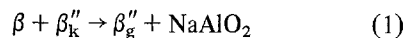
the degree of supersaturation in β''_k will be rather small, assuming that β''_g is fully stabilized [1] and that β and β''_k have equal Na_2O contents, since their lattice parameters are identical. Consequently, the proportion of $NaAlO_2$ formed would be less than 1 wt %, which is difficult to measure accurately by X-ray diffraction owing to peak overlap with strong β and β'' lines, and it was not possible to establish quantitatively whether or not this proportion had increased following the annealing treatment.

Soda loss from β''_k would, however, account for the observed behaviour of seeded A on heat treatment. In Section 3.3, it was shown that unseeded

A and seeded A yielded 25% β'' and 75% β'', respectively, following heat treatment at 1800 K for 1.1 Msec, and that these cannot both represent stable states. It is probable that the seed crystals, obtained from composition D, whose c parameter corresponds closely to β''_k (Fig. 9) are supersaturated with Na_2O. On sintering and annealing these seed crystals grow at the expense of the remainder of the matrix, even though they are metastable; the driving force for grain growth is presumably greater than that for decomposition. But the growth of the supersaturated β''_k seed crystals is an effective driving force for the removal of excess Na_2O from the residual (non-seed) β'' crystals, which decompose to form stable β''_g in seeded A even during rapid zone-sintering (Fig. 9). Consequently the seeded A specimens were in a metastable state, and the grain growth occurring on annealing may have driven them curiously, into an even less stable (more supersaturated) state. Unlike B and C, in which traces of $NaAlO_2$ were detected following heat treatment in buffered conditions, seeded A showed no traces of $NaAlO_2$ after such treatment.

The splitting of the β'' peaks is unlikely to originate from spinodal decomposition of the β'' phase. Periodic compositional fluctuations result in X-ray diffraction side-bands or satellite peaks as observed in metastable alloys following annealing [14, 15], but these bands are symmetrical about the main peak and tend to move towards the main peak as the transformation proceeds; the split β'' peaks, on the other hand, diverge as in Fig. 5.

The structural transformation $\beta''_k \to \beta''_g$ in stabilized β'' alumina described here is analogous to Hodge's model [3] for the $\beta'' \to \beta$ transformation that occurs when no stabilizer is present. In both cases it is necessary for a grain-boundary $NaAlO_2$ phase to be formed. Hodge has suggested that the kinetics are controlled primarily by diffusion of the least mobile ions (Al^{3+}) to the boundary. It is possible that below the onset of creep at around 1750 K the internal stress associated with the volume expansion may also be a factor inhibiting the transformation.

5. Conclusions

Conventional sintering and annealing schedules for beta alumina ceramic do not usually allow the material to attain equilibrium. Since transformation between β and β'' phases is slow, mixtures of the two phases are normally present, the phases having identical conduction plane spacing (and hence identical composition) in as-fired specimens. During post-sinter annealing, either the $\beta \to \beta''$ or the $\beta'' \to \beta$ transformation may occur depending on starting composition. When β'' is the more stable phase, it undergoes a lattice expansion due to the expulsion of Na_2O to form a grain-boundary $NaAlO_2$ phase, indicating that the original β'' grains were supersaturated with Na_2O; this may be a characteristic of as-grown β''-Al_2O_3 crystals.

References
1. F. HARBACH, *J. Mater. Sci.* **18** (1983) 2437.
2. G. K. DUNCAN and A. R. WEST, 4th International Congress on Solid State Ionics, Grenoble (1983).
3. J. D. HODGE, *J. Amer. Ceram. Soc.* **66** (1983) 166.
4. S. R. TAN and G. J. MAY, *Sci. Ceram.* **9** (1977) 103.
5. J. H. DUNCAN and W. G. BUGDEN, *Special Ceramics* **7** (1980) 221.
6. R. KVACHKOV, A. YANAKIEV, C. N. POULIEFF, P. D. YANKULOV, S. RASHKOV and E. BUDEVSKI, *Solid State Ionics* **7** (1982) 151.
7. A. D. JATKAR, I. V. CUTLER, A. V. VIRKAR and R. S. GORDON, *Mat. Sci. Res.* **11** (1978) 421.
8. W. L. ROTH and S. P. MITOFF, G. E. Report 71-C-277 (1971).
9. P. E. D. MORGAN, US ERDA Report COO-2942-1 (1977).
10. S. N. HEAVENS, *J. Mater. Sci.* **17** (1982) 965.
11. W. L. ROTH, private communication (1982).
12. S. LELE, *Acta Crystallogr.* **A26** (1970) 344.
13. B. E. WARREN, "X-ray Diffraction" (Addison-Wesley, Reading, Mass., 1969) p. 275.
14. V. DANIEL and H. LIPSON, *Proc. R. Soc.* **A182** (1944) 378.
15. M. HILLERT, M. COHEN and P. L. AVERBACH, *Acta Metall.* **9** (1961) 536.