JOURNAL OF MATERIALS SCIENCE 25 (1990) 2897–2900

The relative stability of β and β''-phases in Na_2O–Al_2O_3 beta alumina

DONG-DUK LEE, JOON-HONG KIM, YOON-HO KIM
Fine Ceramics Laboratory, Division of Ceramics, Korea Institute of Science and Technology, 131 Cheongryang, Seoul, Korea

To reveal the relative stability of β and β''-phases in beta* alumina, effects of Na_2O content and calcination and annealing history on the relative content of β and β''-phases have been studied for compositions ranging from Na_2O–$5Al_2O_3$ to Na_2O–$9.5Al_2O_3$. The relative stability appears to be dependent on the calcination or annealing history, except holding time such as annealing or re-annealing time, but independent of the Na_2O content and the holding time. From these results it can be demonstrated that the relative stability of β and β''-phases is sensitive to the heat treatment path, except the holding time. The "two stage model" on the β/α polytypic transition in silicon carbide has been quoted to explain the heat treatment path-dependent characteristics.

1. Introduction

In a polycrystalline beta alumina*, which is one of the well-known solid electrolyte materials and has two similar crystalline phases of β and β''. β''-phase is more desirable since the phase has higher electrical conductivity than β-phase [1]. For this reason, much work has been done in attempts to reveal the phase relations mostly in the simple Na_2O–Al_2O_3 system [2–5]. However, the phase diagrams [2–5] formerly proposed do not agree with each other, particularly, in the composition range of beta phase and which of these two phases is a stable phase in the range. These disagreements probably resulted, at least partially, from the fact that previous work did not consider the delicate relationship between β and β'', the phase transition of which differs from those frequently found in metals and ceramics.

The β and β''-phases in beta alumina have basically close packed structures [6] with 2 and 3 spinel blocks, respectively, along the *c*-axis of the hexagonal system. They can be thought as individual polytypes [7–9] with syntactic intergrowth in single beta alumina grain, as shown by transmission electron microscopy [7, 8] and X-ray diffraction [9] studies. (Many researchers involved in phase diagram or phase transition studies on beta alumina, however, did not appear to have noticed this.) Furthermore, β and β''-phases would have similar free energies of formation and negligible β/β'' interface energy because of the crystallographic similarity of the structures and the identical arrangement of the spinel blocks, as suggested by Heuer *et al.* [10].

The purpose of this study is to investigate the effects of Na_2O content on one side and calcination and annealing history on the other side on the relative stability of β and β''-phases in Na_2O–Al_2O_3 beta alumina. The relative stability of β and β''-phases can be revealed by the relative content of β and β''-phases obtained after annealing treatment of sufficiently long time. The investigation showed that the relative stability of β and β''-phases was sensitive to the heat treatment path with the exception of holding time, such as the annealing or re-annealing time, but insensitive to the Na_2O content and the holding time. We will explain the heat treatment path-dependent characteristics of the relative stability based on the fact that the β and β''-phases are polytypes.

2. Experimental procedure

Five powder mixtures were prepared from α-Al_2O_3 and Na_2CO_3 using the usual techniques. These mixtures have compositions ranging from Na_2O–$5Al_2O_3$ to Na_2O–$9.5Al_2O_3$ (10.8 to 6.0 Na_2O by weight per cent) after calcination. The Na_2O–$6.2Al_2O_3$ (8.9 Na_2O by weight percent) composition, however, was used at all experiments except that examining the effect of the Na_2O content. A mixed powder of 50 g was milled for 2 h in a plastic jar of 250 ml with acetone and 140 g of alumina balls. The powder slurry was then dried at 80° C and crushed. Some crushed mixtures were calcined at 1 000° C or 1 250° C for 2 h, and some were followed by annealing without calcination. The calcination conditions for each experiment were selected to observe the relative phase content without ambiguity.

Each mixture was then compacted to pellet types with a diameter of 10 mm under a pressure of about 50 MPa and put into an α-alumina crucible with Na_2O–$6.2Al_2O_3$ packing powder. Annealing was mostly conducted in air at temperatures ranging from 1 300° C to 1 600° C for 10 min or 24 h. Heating and

---

*For the purposes of this paper, "beta" will be used as a generic term signifying both β and β''-aluminas. The Greek symbols will be used to denote the specific phase.

cooling rates were mostly 5° C/min. In the experiment, however, to study the effect of the heating rate, both the pellet heated with a slow rate of 1° C/min and that put directly in a furnace held at 1 400° C were prepared.

To obtain the X-ray diffraction patterns of the calcined or annealed specimens, they were cut in a direction perpendicular to the height and ground in a SiC paper. For quantitative determination of the amount of β and β''-phases, there have been several suggestions [11–13], all of them choosing their own diffraction peaks characteristic of β and β''-phases, respectively. These suggestions necessarily lead to more or less different values in the relative β and β''-contents. The present study, not regarding this difficulty, used the method of Youngblood *et al.* [11] who chose (1 1 0) and (0 1,1 1) peaks and compared their intensities to appreciate the relative β and β''-contents.

3. Results and discussion

3.1. Effect of Na_2O content

All the annealed specimens contained only β and β''-phases. Figure 1 shows that the fraction of β''-phase is independent of the Na_2O content for the beta alumina compositions ranging from Na_2O–$5Al_2O_3$ to Na_2O–$9.5Al_2O_3$ when they were calcined at 1000° C for 2 h and annealed at 1 480° C for 2 h. This result also means that the relative stability of β and β''-phases is not affected by the Na_2O content. The Na_2O content, which ranged from Na_2O–$5Al_2O_3$ to Na_2O–$9.5Al_2O_3$ (10.8 to 6.0 Na_2O by weight per cent) before the annealing, transferred to the range from Na_2O–$5.1Al_2O_3$ to Na_2O–$11.3Al_2O_3$ (10.6 to 5.1 Na_2O by weight per cent) after the annealing, providing the observed weight loss of about 1% for each composition resulted from the evaporization of Na_2O during the annealing. The result of Fig. 1, however, shows that these slight composition changes will not affect the relative β and β''-contents.

Furthermore, Fig. 1 shows that β and β''-phases are actually not stoichiometric compounds with Na_2O–$11Al_2O_3$ and Na_2O–$5.33Al_2O_3$ [14] compositions as ideal formulas, but are nonstoichiometric compounds with varying compositions ranging, at least, from Na_2O–$5Al_2O_3$ to Na_2O–$9.5Al_2O_3$. This can be deduced from the fact that, provided β and β''-phases would have the above ideal compositions [14], the relative β and β''-contents should vary with the Na_2O content. Therefore, it also seems to be incorrect that the β/β'' phase transition occurs through the growth of existing β and $NaAlO_2$ crystals at the expense of the existing β''-crystals [2, 15].

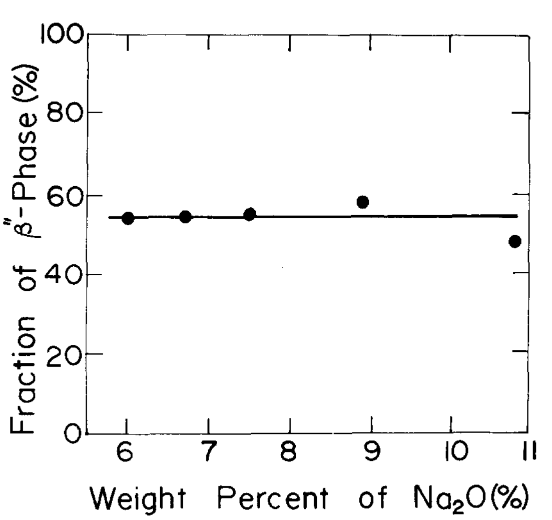

Figure 1 Variation of the fraction of β''-phase with the Na_2O content in Na_2O-Al_2O_3 beta aluminas calcined at 1 000° C for 2 h and annealed at 1 480° C for 2 h.

3.2. Effects of various heat treatments

The relative stability of β and β''-phases was affected by the annealing temperature, as shown in Fig. 2. All annealing treatments were held for 24 h at 1 600° C. The short annealing time (2 h) at 1 600° C was chosen to avoid the severe weight loss of the specimen at that temperature. The fraction of β''-phase was zero at 1 600° C, but increased significantly with decreasing the annealing temperature to below 1 550° C at which Weber and Venero [3] and LeCars *et al.* [5] suggested the stability of β-phase.

The stability problem of beta alumina below 1 550° C, after some controversies [2, 5], now seems to have been concluded as β-phase being thermodynamically stable [15]. But, the Na_2O–$6.2Al_2O_3$ specimen, which contained only a β-phase when annealed at 1 600° C for 2 h (Fig. 2), gave a β''-phase reaching about 22% of the mixture when the specimen was reannealed at 1 400° C for 24 h (Fig. 3B). The result raises a doubt about whether the β-phase is still thermodynamically stable at 1 400° C since the "unstable" β and β''-phases is heat treatment path-dependent. stable.

Figure 3 shows that the relative stability of β and β''-phases are also affected by the previous annealing treatment. The Na_2O–$6.2Al_2O_3$ specimen annealed directly at 1 400° C for 24 h (A) gave a relative β''-content of about 82%, while the same composition previously once annealed at 1 600° C for 2 h before the same annealing at 1 400° C for 24 h (B) gave a relative

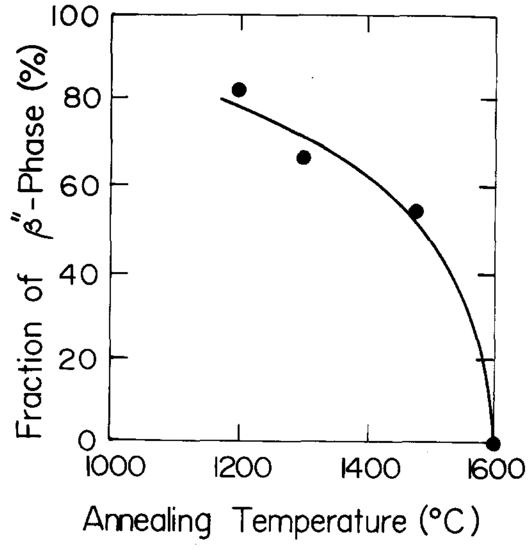

Figure 2 Variation of the fraction of β''-phase with the annealing temperature in Na_2O–$6.2Al_2O_3$ beta aluminas. All were calcined at 1 000° C for 2 h and annealed for 24 h. The point at 1 600° C, however, was obtained after annealing of 2 h due to the severe Na_2O loss of the specimen.

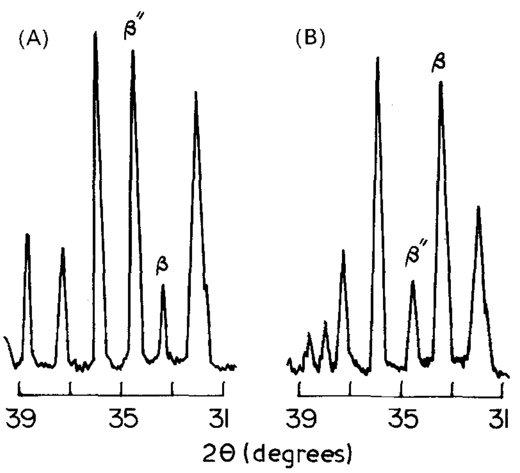

Figure 3 X-ray diffraction patterns showing the effect of the re-annealing in Na_2O–6 Al_2O_3 beta aluminas. Both (A) and (B) were calcined at 1 250° C for 2 h and annealed at 1 400° C for 24 h. For comparison, (B) was previously once annealed for 2 h at 1600° C before the same annealing at 1400° C for 24 h. The only peaks which are not common to both β and β'' phases are labelled.

β''-content of only 22%. The results of Figs 2 and 3 clearly show that the relative stability of β and β''-phases is sensitive to the annealing history (namely, heat treatment path-dependent) and not determined by any rule concerning the equilibrium.

Figs 4 and 5 confirm that the relative stability of β and β''-phases is heat treatment path-dependent. Figure 4 shows the diffraction patterns of the Na_2O–6.2Al_2O_3 specimens calcined at various conditions and finally annealed at 1 400° C for 24 h. (The powder mixture calcined at 1 000° C for 2 h had shown only an α-phase with trace(s) of unknown phase(s), but that calcined at 1 250° C for 2 h had shown a mixture of β (about 20%) and β'' (about 80%) phases. The content of β''-phase, which was about 55% when calcined at 1 000° C (B), increased to about 82% when calcined at 1 250° C (A) before the same annealing. The specimen directly annealed without calcination (C) has a β''-content similar to that calcined at 1 250° C (about 84%). Figure 5 shows that the simple difference of the heating rate gives the difference of about 10% in β''-content. Therefore, as far as the relative stability of β and β''-phases is concerned, the previous phase diagrams and phase analyses cannot be compared without noting the whole heat treatment path containing the calcination and annealing history.

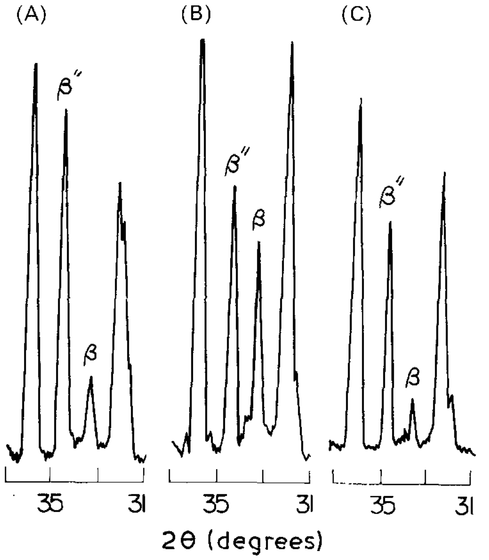

Figure 4 X-ray diffraction patterns showing the effect of the calcination condition in Na_2O–6.2 Al_2O_3 beta aluminas annealed at 1 400° C for 24 h. Calcination conditions were (A) 2 h at 1 250° C, (B) 2 h at 1 000° C, and (C) no calcination, respectively.

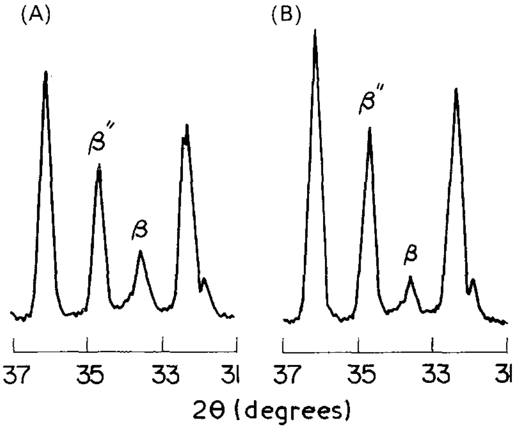

Figure 5 X-ray diffraction patterns showing the effect of the heating rate in Na_2O–6.2 Al_2O_3 beta aluminas annealed at 1 400° C for 24 h without calcination. In (A) the specimen was put directly in the furnace held at 1 400° C, and in (B) the specimen was heated slowly at a rate of 1° C min^{-1}.

The annealing time, however, does not seem to influence the relative stability of β and β''-phases. As shown in Fig. 6, the relative β''-content, which was about 84% when annealed at 1 400° C for 10 min (A), did not change significantly although the annealing time increased to 24 h (B) at the same temperature. A similar change of the re-annealing time at 1 400° C after annealing at 1 600° C for 2 h also gave the constant β''-content of about 22%.

The fact that the relative stability of β and β''-phases appears to be sensitive to the heat treatment path except the holding time such as the annealing or re-annealing time cannot be explained properly by the concept of the phase transitions generally observed in metals and ceramics. Preferably, the relative stability of β and β''-phases has to be described by the viewpoint of the polytypic transition since β and β''-phases are individual polytypes with syntactic intergrowth within a single crystal [7–9].

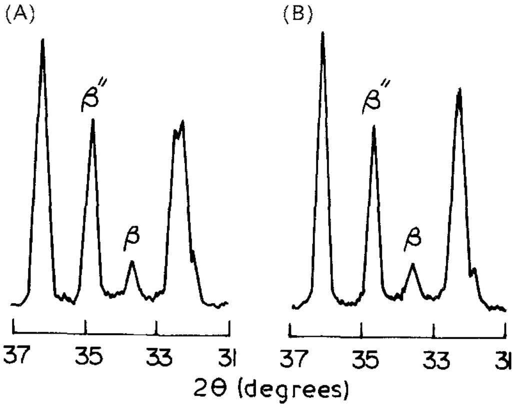

Figure 6 X-ray diffraction patterns showing the effect of the annealing time in Na_2O–6.2 Al_2O_3 beta aluminas. Annealed at 1 400° C for (A) 10 min and (B) 24 h without calcination.

Silicon carbide, with mainly α and β-polytypic forms, can be thought to show the similar phenomenon. In the β/α polytypic transition of silicon carbide, according to Shinozaki and Kinsman [16], α-plates resulting from the transition in sintered β-SiC polycrystals were sandwiched between envelopes of β in a well-defined orientation relation with the α-phase, $\{1\,1\,1\}_{\beta}/(0\,0\,0\,1)_{\alpha}$. In addition to this observation, Heuer *et al.* [10] found that the above composite grains of α and β grew rapidly into the fine grained β-matrix and then these α-plates within the β-envelopes were thickened sluggishly probably due to much lower energies of $\{1\,1\,1\}_{\beta}/(0\,0\,0\,1)_{\alpha}$ interfaces than those of random β/α interfaces. These results led Heuer *et al.* [10] to suggest that the β/α transition occurred in two stages – a rapid one and a sluggish one.

Occurrence of such two stages may also be applied to explain phenomenally the β/β″ polytypic transition in beta alumina, although a satisfying mechanism of the polytypic transition is not yet given [17]. Figure 6 shows apparently that the first rapid stage was already achieved before the annealing time of 10 min and that the second sluggish stage was already in progress at that time. Here, the second stage is sluggish probably due to much lower energy of the $(0\,0\,0\,1)_{\beta}/(0\,0\,0\,1)_{\beta''}$ interface. Recently, Hodge [18] showed that the β/β″ intergrowth structure in MgO-stabilized beta alumina which had been formed by 1200° C annealing was extremely persistent until the specimen was re-annealed at 1 500°C for 110 h. This also appears to be due to the second sluggish stage of the β/β″ polytypic transition. Finally, the heat treatment path-dependent characteristics of the relative stability of β and β″-phases appears to be mainly due to the second sluggish stage of the β/β″ polytypic transition.

4. Conclusions

The most important result of this study is that the relative stability of β and β″-phases in beta alumina is sensitive to the heat treatment path with the exception of the holding time, such as the annealing or re-annealing time. This was revealed in the dependence of the relative content of β and β″-phases on the heat treatment path except the holding time. Therefore, as far as the relative stability of β and β″-phases is concerned, the previous phase diagrams and phase analyses cannot be compared without considering the whole heat treatment path containing the calcination and annealing history. Secondly, the "two stage model" suggested by Heuer *et al.* [10] in silicon carbide was, at least partially, able to explain the heat treatment path-dependent characteristics of the relative stability of β and β″-phases in this system. For further explanation, however, the satisfying mechanism of the polytypic transition should be given. Finally, it is also noted that the relative stability of β and β″-phases did not depend on the Na_2O content.

Acknowledgement

The authors are grateful for Dr P. Hagenmuller at the University of Bordeaux I, France for helpful discussions. This work was supported by the Ministry of Science and Technology, Korea.

References

1. J. B. BATES, J. C. WANG, and J. C. DUBNEY, *Phys. Today* **35** (1982) 46.
2. R. C. DeVRIES and W. L. ROTH, *J. Amer. Ceram. Soc.* **52** (1969) 364.
3. See J. T. KUMMER, *Progr. Solid State Chem.* **7** (1972) 145.
4. V. J. LIEBERTZ, *Ber. Dt. Keram. Ges.* **49** (1972) 288.
5. Y. LeCARS, J. THERY and R. COLLONGUES, *Rev. Int. Hautes Temper. et Refract.* **9** (1972) 153.
6. P. T. MOSELEY, in the "Sodium-Sulfer Battery", edited by J. L. Sudworth and A. R. Tilley (University Press, Cambridge, 1985) p. 19.
7. D. J. M BEVAN, B. HUDSON and P. T. MOSELEY, *Mat. Res. Bull.* **9** (1974) 1073.
8. H. SATO and Y. HIROTSU, *Mater. Res. Bull.* **11** (1976) 1307.
9. P. E. D. MORGAN, *Mater. Res. Bull.* **11** (1976) 233.
10. A. H. HEUER *et al.*, *J. Amer. Ceram. Soc.* **61** (1978) 406.
11. G. E. YOUNGBLOOD *et al.*, *Amer. Ceram. Soc. Bull.* **56** (1977) 206.
12. D. W. JOHNSON, S. M. GRANSTAFF and W. W. RHODES, *Amer. Ceram. Soc. Bull.* **58** (1979) 849.
13. G. K. DUNCAN, *Solid State Ionics* **9/10** (1983) 259.
14. R. COLLONGUES, J. THERY and J. P. BOILOT, in "Solid Electrolytes: General Principles, Characterization, Materials, Applications", edited by P. Hagenmuller and W. Van Gool (Academic Press, New York, 1978) p. 253.
15. J. D. HODGE, *J. Amer. Ceram. Soc.* **66** (1983) 166.
16. S. SHINOZAKI and K. R. KINSMAN, for abstract see *Amer. Ceram. Soc. Bull.* **54** (1975) 739.
17. A. R. VERMA and P. KRISHNA, in "Polymorphism and Polytypism in Crystals" (John Wiley and Sons, Inc., New York, 1966) p. 233.
18. J. D. HODGE, *Amer. Ceram. Soc. Bull.* **62** (1983) 244.

Received 2 February
and accepted 24 August 1989