

## Letter

### Equivalence of ball milling and thermal treatment for phase transitions in the $\text{Al}_2\text{O}_3$ system

A. Tonejc

Department of Physics, Faculty of Science, PO Box 162, 41001 Zagreb (Croatia)

C. Kosanović

Ruder Bošković, Institute, PO Box 1016, 41001 Zagreb (Croatia)

M. Stubičar and A. M. Tonejc

Department of Physics, Faculty of Science, PO Box 162, 41001 Zagreb (Croatia)

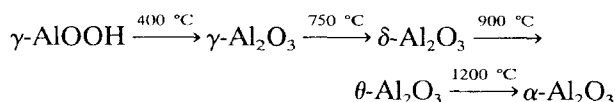
B. Subotić and I. Šmit

Ruder Bošković Institute, PO Box 1016, 41001 Zagreb (Croatia)

(Received February 11, 1993)

High energy ball milling has recently become a very popular research topic, since virtually any composition can be manufactured using a mixture of elemental (mechanical alloying) or readily available master alloy powders (mechanical grinding). Many solid state reactions, which normally occur at elevated temperatures, can be facilitated by high energy milling [1, 2]. However, a very important parameter of mechanical milling, the powder temperature during milling (called an effective local temperature or a peak temperature at the collision site) is still surrounded by controversy (formation of local melts [3], well below the melting point [4], a maximum temperature rise of only 38 °C [5], an excessive heating during milling [6], of up to 407 °C [7], as high as 180 °C [8], about 280 °C [9], exceeding 570 °C [10], over 500 °C [11]). Using the well-known temperature-induced transition sequence of aluminas, we present experimental evidence that the effective local temperature should be even higher than 700 °C.

The transformation of metastable  $\gamma\text{-AlOOH}$  (boehmite) to stable  $\alpha\text{-Al}_2\text{O}_3$  (corundum), obtained through high-temperature treatments, is well known. The transition sequence has been studied for decades [12–17]. When heating the boehmite in air from room temperature to over 1200 °C, the transition sequence occurs through a series of transformations before the final conversion to the stable corundum:



All the transition phases are stable at room temperature but the sequence of transformation was not reversible with decreasing temperature, which showed that the observed phases are transition forms rather than different phases of aluminas.

The temperatures at which transitions have been observed are somewhat variable. Among other factors, they depend upon impurities of the starting materials and thermal treatment. However, the most important fact is that it is not possible to obtain any of the high-temperature structural invariants even on prolonged isothermal heating at temperatures below the transition regions [17].

Because of their very similar structure and very diffuse character of the X-ray diffraction (XRD) patterns of  $\gamma$ - and  $\delta$ -alumina, it is not easy to distinguish between them [13–16, 18, 19]. Diffuse broad lines persist even after prolonged annealing of up to 7 days [20]. However, with transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) it was undoubtedly shown that even if XRD patterns are very similar, the two structures could be distinguished [12, 15, 17, 19]. The stable  $\alpha\text{-Al}_2\text{O}_3$  is the only structure which is easily characterized, and contrary to the broad peaks of  $\gamma$ - and  $\delta\text{-Al}_2\text{O}_3$ ,  $\alpha$ -peaks were shown to be very sharp [16, 21–23].

In this work the milling was performed in air in a planetary micromill Fritsch pulverisette 7, using a set of ten tungsten carbide (WC) balls with a diameter of 10 mm, and a vial of the same material. The starting materials used for milling were well-crystallized commercial boehmite powder (Ventron, Karlsruhe), and  $\gamma$ - and  $\delta\text{-Al}_2\text{O}_3$ , obtained by adequate heating of the boehmite (Fig. 1(a)–1(c)). A total mass of 1 g of powder was ball milled in all experiments. Before and after milling powders were examined using a Philips PW1820 XRD powder diffractometer with Cu  $K\alpha$  graphite-monochromated radiation.

The XRD patterns of powders, before and after the milling, are shown in Figs 2 and 3. XRD analysis of milled  $\gamma$ -alumina powder shows (Fig. 2) that after milling for 30 min, XRD patterns exhibited diffraction peaks typical of  $\alpha$ -alumina, with small broad peaks which could be assigned to  $\gamma$ - or  $\delta$ -alumina. After milling for 1 h only the peaks of  $\alpha$ -alumina could be seen on the XRD patterns. When milling the  $\delta$ -alumina the same

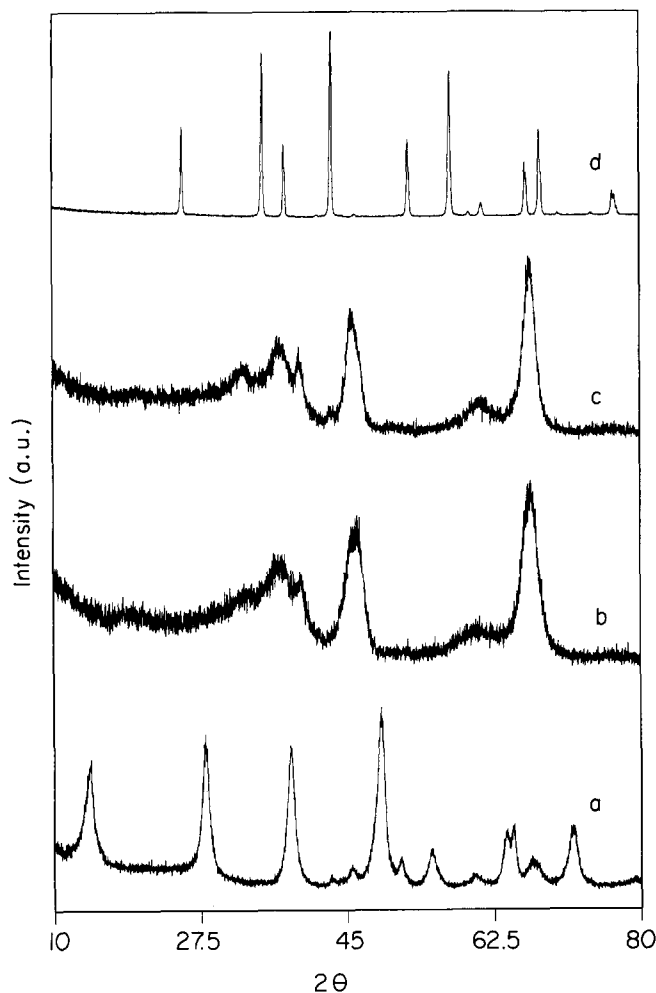


Fig. 1. X-ray diffraction patterns: curve a, boehmite as supplied; curve b,  $\gamma$ - $\text{Al}_2\text{O}_3$  obtained on heating the boehmite at 400 °C for 1 h; curve c,  $\delta$ - $\text{Al}_2\text{O}_3$  obtained on heating the boehmite at 930 °C for 3 h; curve d,  $\alpha$ - $\text{Al}_2\text{O}_3$  obtained on heating the boehmite at 1230 °C for 3 h.

sequence was observed and the milling time necessary for the  $\delta$  to  $\alpha$  transformation was also 1 h. However, when starting with boehmite, a longer milling period was necessary to perform the conversion to  $\alpha$ -alumina (Fig. 3). After 30 min of milling boehmite peaks could still be detected, and  $\gamma$ - (or  $\delta$ -) peaks and the strongest  $\alpha$ -peak were also visible. On further milling for 0.5 h, there no more boehmite peaks were visible, only  $\gamma$ - (or  $\delta$ -) and  $\alpha$ -peaks. After milling for 2.5 h the peaks of  $\alpha$ -alumina could be detected on the XRD pattern (Fig. 3(d)). (The lines of WC were very expressive in all powders after milling, which means that the wear of the balls and vial during milling was very intensive.)

Although it was not possible to distinguish between the  $\gamma$ - and  $\delta$ -alumina on XRD patterns, it was obvious that the milling-induced transformation from boehmite to  $\alpha$ -alumina was not direct but via  $\gamma$ - (or  $\delta$ -) alumina

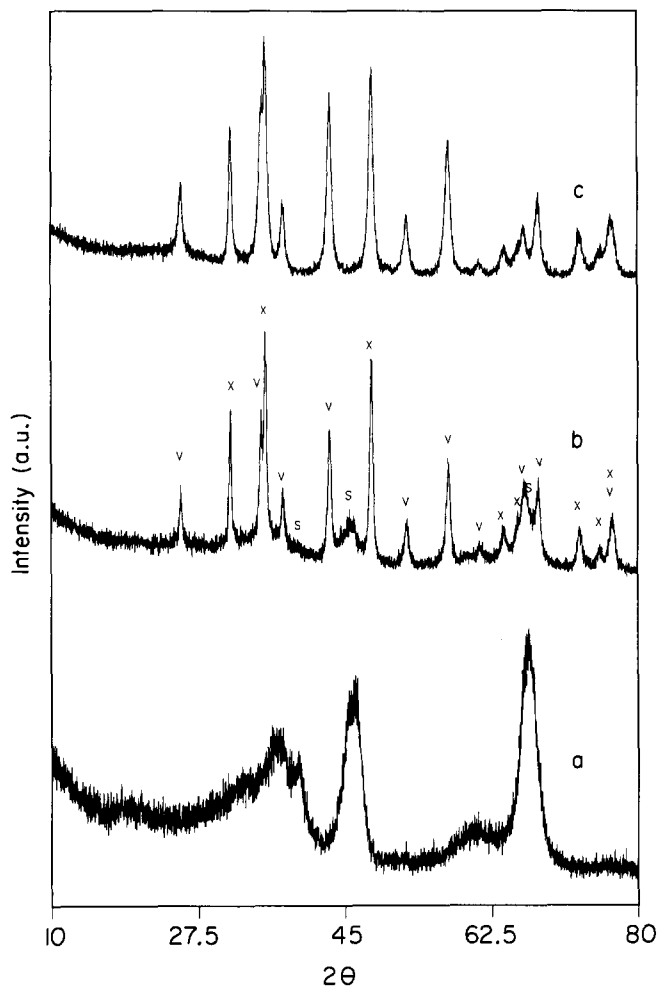
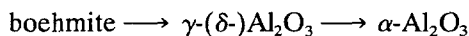


Fig. 2. X-ray diffraction patterns: curve a,  $\gamma$ - $\text{Al}_2\text{O}_3$  before milling; curve b, after milling  $\gamma$ - $\text{Al}_2\text{O}_3$  for 0.5 h ( $v = \alpha$ - $\text{Al}_2\text{O}_3$ ,  $s = \gamma$ - (or  $\delta$ -) $\text{Al}_2\text{O}_3$ ,  $x = \text{WC}$ ); curve c, after milling  $\gamma$ - $\text{Al}_2\text{O}_3$  for 1 h ( $\alpha$ - $\text{Al}_2\text{O}_3$  and WC).

intermediates. Therefore we could conclude that the transformation obtained by milling



shows a similar sequence to that obtained by heating: we did not observe  $\theta$ - $\text{Al}_2\text{O}_3$ . However, this is not unusual because from previous heating experiments we know that direct transformations  $\gamma$  to  $\alpha$  [21, 23, 24] and  $\delta$  to  $\alpha$  [13, 23] have been observed.

Pach *et al.* [22] were able to detect  $\alpha$ -alumina by XRD after 15 h of heating of boehmite at 1040 °C. By extrapolation of the time-temperature-transformation diagram at temperatures below about 750 °C, Wilson and McConnell [13] concluded that  $\alpha$ - $\text{Al}_2\text{O}_3$  would nucleate directly from  $\gamma$ -alumina for very long heating times. These facts, and our experimental evidence for the production of the  $\alpha$ -alumina from boehmite, and from  $\gamma$ - and  $\delta$ -alumina by ball milling, indicate that the local peak temperature at the collision

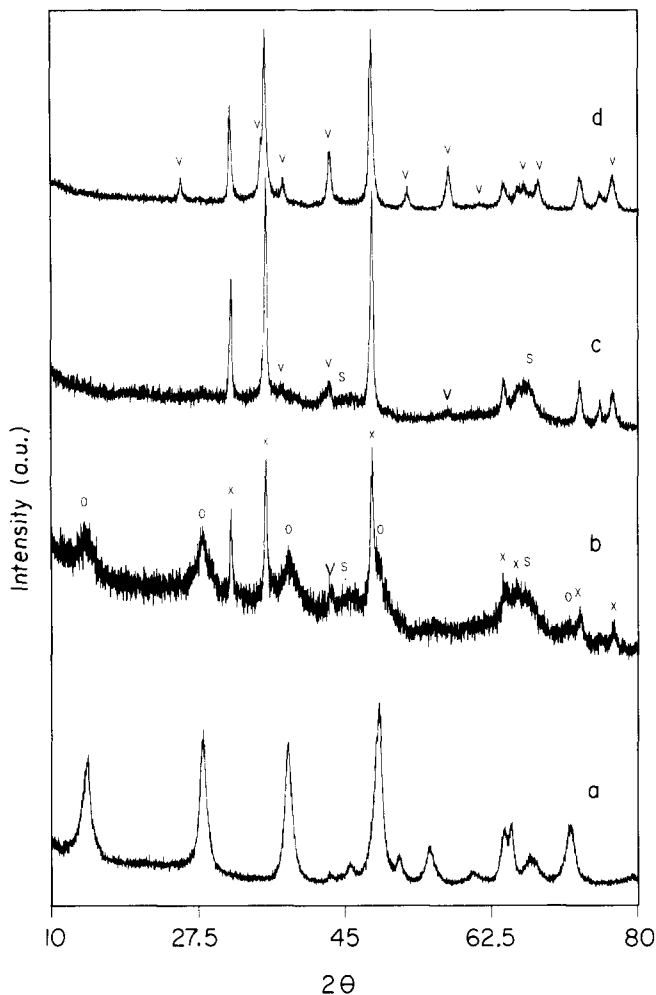


Fig. 3. X-ray diffraction patterns: curve a, boehmite before milling; curve b, after milling the boehmite for 0.5 h (o = boehmite, v =  $\alpha$ - $\text{Al}_2\text{O}_3$ , s =  $\gamma$ -( $\delta$ -) $\text{Al}_2\text{O}_3$ , x = WC); curve c, after milling the boehmite for 1 h (s =  $\gamma$ -( $\delta$ -) $\text{Al}_2\text{O}_3$ , v =  $\alpha$ - $\text{Al}_2\text{O}_3$ , and WC); curve d, after milling the boehmite for 2.5 h ( $\alpha$ - $\text{Al}_2\text{O}_3$  and WC).

site could reach at least 700 °C. This agrees with other results [7, 10, 11] that the local peak temperature should be rather high. Our experiments on the transformation of boehmite to  $\alpha$ -alumina, induced by ball milling, also showed the equivalence of ball milling and thermal treatment of the aluminas.

The broad peaks of  $\gamma$ - and  $\delta$ -alumina, of milled and heated powders, and well-defined sharp  $\alpha$ -alumina peaks

which appeared on XRD patterns after milling and heating (Figs. 1–3), give further evidence of the equivalence of the milling and thermal treatment on the aluminas.

## References

- 1 A. W. Weeber and H. Bakker, *Physica B*, 153 (1988) 93.
- 2 P. H. Shingu (ed.), *Proc. Int. Symp. Mech. Alloying (ISMA)*, Kyoto, Japan, May 7–10, 1991, *Mater. Sci. Forum*, 88/90 (1992).
- 3 A. E. Yermakov, E. E. Yurchikov and Y. A. Barinov, *Fiz. Met. Metallov.*, 52 (1981) 1184.
- 4 R. B. Schwarz, R. R. Petrich and C. K. Saw, *J. Non-Cryst. Solids*, 76 (1985) 281.
- 5 R. B. Schwarz and C. Koch, *Appl. Phys. Lett.*, 49 (1986) 146.
- 6 L. Schultz, *Mater. Sci. Eng.*, 97 (1988) 15.
- 7 J. Eckert, L. Schultz, E. Hellstern and K. Urban, *J. Appl. Phys.*, 64 (1988) 3224.
- 8 R. Schulz, M. Trudeau, J. Y. Huot and A. Van Neste, *Phys. Rev. Lett.*, 62 (1989) 2849.
- 9 M. L. Trudeau, R. Schulz, D. Dussault and A. Van Neste, *Phys. Rev. Lett.*, 64 (1990) 99.
- 10 A. Tonejc, A. M. Tonejc, and D. Dužević, *Scr. Metall.*, 25 (1991) 1111.
- 11 J. S. Benjamin, in P. H. Shingu (ed.), *Proc. Int. Symp. Mech. Alloying (ISMA)*, Kyoto, Japan, May 7–10, 1991, *Mater. Sci. Forum*, 88/90 (1992) 1.
- 12 B. C. Lippens and J. H. de Boer, *Acta Crystallogr.*, 17 (1964) 1312.
- 13 S. J. Wilson and J. D. C. McConnell, *J. Solid State Chem.*, 34 (1980) 315.
- 14 R. S. Zhou and R. L. Snyder, *Acta Crystallogr. B*, 47 (1991) 617.
- 15 J. E. Bonevich and L. D. Marks, *J. Mater. Res.*, 7 (1992) 1490.
- 16 H. S. Santos and P. S. Santos, *Mater. Lett.*, 13 (1992) 175.
- 17 V. Saraswati, G. V. N. Rao and G. V. Ram Rao, *J. Mater. Sci.*, 22 (1987) 2529.
- 18 D. X. Li and W. J. Thompson, *J. Mater. Res.*, 5 (1990) 1963.
- 19 K. J. Morrissey, K. K. Czanderna, R. P. Merrill and C. B. Carter, *Ultramicroscopy*, 18 (1985) 379.
- 20 V. Saraswati and G. V. Rama Rao, *J. Mater. Sci. Lett.*, 5 (1986) 1095.
- 21 L. A. Xue and I. W. Chen, *J. Mater. Sci. Lett.*, 11 (1992) 443.
- 22 L. Pach, R. Roy and S. Komarneni, *J. Mater. Res.*, 5 (1990) 278.
- 23 P. G. Lucuta, J. D. Halliday and B. Christian, *J. Mater. Sci.*, 27 (1992) 6053.
- 24 R. A. Shelleman, G. L. Messing and M. Kumagai, *J. Non-Cryst. Solids*, 82 (1986) 277.