

## Letters

### *A comment on "Some factors affecting the reactive hot-pressing behaviour of alumina"*

In their paper concerning the densification behaviour of metastable aluminas during reactive hot-pressing, Matkin *et al.* [1] have made repeated reference to a "cubic  $\theta$ - $\text{Al}_2\text{O}_3$ ". The existence of  $\theta$ - $\text{Al}_2\text{O}_3$  as one of the discrete metastable polymorphs of alumina encountered in the thermal decomposition of gibbsite, an aluminium hydrate  $\text{Al}(\text{OH})_3$ , was first demonstrated by Stumpf *et al.* [2]. In actuality, the manner in which the initial aluminium hydrate is formed and subsequently heat-treated determines the sequence by which the material ultimately transforms to the stable high temperature corundum,  $\alpha$ - $\text{Al}_2\text{O}_3$ . Due to the generally fine grained product formed during thermal decomposition of aluminium hydrate as well as the often found presence of more than one of the metastable phases, characterization of the crystal structure of  $\theta$ - $\text{Al}_2\text{O}_3$  was not immediately determined. Shortly afterwards, Foster and Stumpf [3] showed conclusively that  $\theta$ - $\text{Al}_2\text{O}_3$  was isostructural with the high temperature stable form of gallia known as  $\beta$ - $\text{Ga}_2\text{O}_3$  [4]. They pointed out that the two structures were not merely similar but identical in crystal structure with allowance for the slightly different cation size. Kohn *et al.* [5] were first to show that the structure of  $\beta$ - $\text{Ga}_2\text{O}_3$  was monoclinic, belonging to space group  $\text{C}_{2h}^2$ . They determined the unit cell dimensions and number of molecules per unit cell. At the same time they indexed the powder pattern of  $\theta$ - $\text{Al}_2\text{O}_3$  and estimated the unit cell dimensions. The indexed powder pattern of  $\theta$ - $\text{Al}_2\text{O}_3$  appears on Card No. 15-517 of the JCPDS file.\* Several years afterwards, Geller [6] determined the crystal structure of  $\beta$ - $\text{Ga}_2\text{O}_3$  and Saalfeld [7] determined the crystal structure of  $\theta$ - $\text{Al}_2\text{O}_3$  in agreement with the earlier characterization by Kohn *et al.* [5].

For these reasons it was surprising to read about a "cubic  $\theta$ - $\text{Al}_2\text{O}_3$ " in the paper by Matkin *et al.* [1]. Although  $\beta$ - $\text{Ga}_2\text{O}_3$  and  $\theta$ - $\text{Al}_2\text{O}_3$  belong to the monoclinic crystal system, the oxygen ions are arranged in a distorted cubic

close-packed array [6, 7]. However, they are not classified as cubic materials. Structurally they conform to the monoclinic crystal system, are anisotropic and exhibit monoclinic bi-refringence under the polarizing microscope. There is no contention in the fact that  $\theta$ - $\text{Al}_2\text{O}_3$  undergoes an irreversible three-dimensional phase transformation when it converts to  $\alpha$ - $\text{Al}_2\text{O}_3$ . There is a change in crystal system from monoclinic to hexagonal with a simultaneous change in the oxygen ion arrangement from a distorted cubic close-packed to a hexagonal close-packed array. A mechanism for the transformation of the cubic close-packed form of cobalt to the hexagonal close-packed form was postulated by Christian [8]. It is accomplished by a simple shear in the  $[11\bar{2}]$  direction of the cubic structure. It is this transformation which is of importance to the reactive hot-pressing process. Since the mechanism of the transformation from the theta to alpha form of alumina was not involved in this study, the incorrect designation of  $\theta$ - $\text{Al}_2\text{O}_3$  does not affect the validity of the findings. However, the choice of the term "cubic  $\theta$ - $\text{Al}_2\text{O}_3$ " was an unfortunate one.

### References

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The identification of the crystallographic phases in our paper was based on the classification adopted by Lippens and De Boer [1], and we fully accept that  $\theta$ - $\text{Al}_2\text{O}_3$  has a monoclinic crystal structure, and should not be referred to as a cubic metastable form of alumina.

However, the important conclusion of our paper was that the reactive hot-pressing behaviour of the three metastable aluminas was primarily determined by the general powder

agglomerate properties, and was not dependent upon the detailed crystallographic structure of the starting powder, even though the same basic set of phase transformations occurred during reactive hot-pressing.

### Reference

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*On crystallography of topotaxy and transformation in the system  $\text{MnO}-\text{Mn}_3\text{O}_4$  and the ferrite  $(\text{Mn}, \text{Co})_3\text{O}_4$*

Topotaxial chemical reactions are common in production of inorganic materials. Topotaxy means that there is a three-dimensional correspondence between the positions of at least one set of ions (e.g. X) in parent and product. Reactions in which a close-packed array of oxygen ions persists provide the clearest examples. These include ferrite synthesis and the oxidations, and spinel precipitation which occur in scales in ferrous alloys. The correspondence implies that X ions do not interchange: the array is merely deformed. The way in which the correspondence can be maintained over many unit cells when there is an immiscibility gap and a significant change of interatomic spacing exceeding the small amount which can be taken up by elastic strain does not appear to have been examined in detail. The problem of maintaining coherency, in order that the product array will continue to be produced as a deformation of the parent could, however, be regarded as the same problem that underlies martensite crystallography, in which the lattices are kept in register. Whilst embryos are probably formed from ordered defects [1], and initial precipitates will be oriented and may be platelets to reduce elastic strain energy irrespective of martensite geometry, in fully developed regions the orientation and substructure such as twinning should conform to martensite theory. Another problem of topotaxy is the angular spread of X-ray reflections which occurs even

when the specimen is not grossly distorted by loss of material [2]. If martensite geometry applies, one of the factors which might contribute to the spread is the presence of variants in irrational orientations clustered around a rational one. The individual reflections could overlap because of smearing due to substructure and to plastic deformation caused by the mutually incompatible shape-changes of impinged variants.

It is more difficult to test for martensite geometry in topotaxy because of the lack of clearly defined habit planes, the orientations of which are data for the theory. The presence of appropriate twinning, which can be a mode of accommodating misregistry could, however, suggest a martensitic mechanism.

An electron-optical study by Delavignette and Amelinckx [3] of cubic MnO which had been annealed at 900°C showed coherent single-phase regions of tetragonal  $\text{Mn}_3\text{O}_4$  II (Hausmannite), which was finely and regularly twinned on  $\{110\}_{\text{MnO}}$ . Individual fine striations due to product were also  $\parallel \{110\}$  but it was not certain whether they contained substructure. The orientation relation accorded with the expected correspondence, in which  $[010]_{\text{MnO}} \rightarrow [1\bar{1}0]_{\text{H}}$ ,  $[001]_{\text{MnO}} \rightarrow [001]_{\text{H}}$ , the *c*-axis being doubled.  $\text{Mn}_3\text{O}_4$  also has a cubic spinel form I stable above 1160°C. Crystals cooled through the transformation cracked and were twinned; the twinning was attributed to mechanical effects [4]. It adversely affects properties.

Four types of path can be imagined for the oxidation reaction. (1) Both MnO and  $\text{Mn}_3\text{O}_4$  retain nearly their normal stoichiometry and