Reply to comments on "Some factors affecting the reactive hot-pressing behaviour of alumina"

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 $\theta.Al_2O_3$ 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 $MnO–Mn_3O_4$ and the ferrite $(Mn, Co,)_3O_4$

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 Mn_3O_4 II (Hausmannite), which was finely and regularly twinned on $\{110\}_{MnO}$. 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 $[010]_{MnO} \rightarrow [1\bar{1}0]_H$, $[001]_{MnO} \rightarrow [001]_H$, the *c*-axis being doubled. Mn_3O_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 Mn_3O_4 retain nearly their normal stoichiometry and lattice parameters and the product grows at an interface. (2) The composition and lattice parameters of "MnO" change continuously until it approximates closely to metastable cubic Mn_3O_4 I, which then inverts to II by polymorphic transformation. (3) The structure becomes tetragonal at an earlier stage than in (2). (4) The initial changes of stoichiometry are already accompanied by an incipient change to tetragonal symmetry which occurs by periodic alternation of two symmetry – options which ultimately appear as the twins.

To test whether martensite geometry favours or disfavours any of these, calculations have been made as previously described [5] according to the Wechsler-Lieberman-Read formulation on a CDC 6400 computer. To examine the occurrence of twinning in the transformation I to II, the geometry was also calculated for (1) pure Mn_3O_4, and the spinel containing (2) 24% Co at 800° C and (3) 55% Co at 25° C. The values of the lattice parameters were for MnO $a = 4.45$ Å, for Mn_3O_4 II $a = 5.57$ Å, $c = 9.42$ Å [6], (expected to correspond to a somewhat non-stoichiometric product), and for transformation at 1150°C $a = 5.81$ Å, $c = 9.46$ Å, with $a_{Mn_3O_4} = 8.52$ Å [7]. The lattice parameters of both phases, and the transformation temperature, are sensitive to the Cobalt content [8]. All indices below refer to parent cubic phase.

The results eliminated path 1 for the reaction since the observed twinning did not even approximately satisfy the geometry. Assessment of the probability of path 2 depends on the existence of a detectable habit plane, or on precise measurements of the orientation relation. Path 4 is more appropriate when there is nearly complete miscibility of the end compositions. The concept of an interface is probably not relevant. In path 3, accommodation by twinning becomes possible when the ratio of final to initial parameters has become $\eta_1 = \eta_2 = 0.936$, $\eta_3 = 1.083$. With the quoted parameters for Mn_3O_4, a of MnO has then decreased to 4.35 Å. If $\{110\}$ is a martensitic interface, then a must further decrease to $\sim$ 4.30 Å. About half of the volume change then occurs homogeneously within the reacting phases. In the resuting orientation relation, the product lattice is rotated relative to the parent through 4.1° about [0.62, − 0.78, 0.07].

It was found that in ferrite specimens cooled through the transformation I $\rightarrow$ II, twinning would satisfy the geometry and, therefore, would not be avoided at any composition within which a tetragonal phase is stable. The predicted orientation relations and the habit planes vary detectably with composition. The habit planes and lattice rotations are, respectively, (i) (0.045, − 0.565, − 0.824), 3.51° about [034]; (ii) 0.06, − 0.63, − 0.77), 3.61° about [0.76, − 0.65, 0.04]; (iii) (0.02, − 0.67, − 0.74), 1.42° about [$01\bar{1}$].

The twinning at the transformation may reasonably be attributed to the mechanism by which coherence is maintained at a I-II interface, and the cracking to the incompatible shape changes of different variants. For the reaction, the geometrical arguments at least limit the number of possible reaction paths. In both reaction and transformation, since the orientations are irrational there will be twenty-four variants. These are clustered around rational orientations – in these examples within 4° – and when the corresponding reflections are broadened they could contribute to spread of reflections as suggested above. Some indication of irrational orientations in topotaxy might nevertheless be expected when the product is not very distorted. Reactions present special problems in that atomic spacings, elastic strain and composition are interrelated, as has been shown by Cahn [9] for spinodal decomposition. However, the geometry relating to accommodation of structures no longer leads to merely phenomenological theories but is closely correlated with electron microscopy which reveals at least the participation of twinning in the lattice-invariant shear [10]. This approach together with measurements of shape change, when apparent, should lead to more penetrating views of structure-changes in chemical compounds.

References

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Fracture parameters in Refel silicon carbide

The critical stress intensity factor in plane strain (K_{Ic}) for ceramics is generally determined from three- or four-point bend tests. Summers *et al.* [1] have determined the correct equation to use for three-point bend tests but no similar evaluation has been made for four-point bending. The purpose of this note is to report and compare values of K_{Ic} for Refel silicon carbide calculated by applying various analytical expressions to data obtained from four-point bend tests. In addition we have investigated the effects of precracking on K_{Ic}.

The specimens were cut from blocks, lapped with 13 μm silicon carbide on a cast iron wheel, and cleaned in hydrochloric acid then alcohol. A notch 250 μm wide with a tip radius ~ 120 μm was machined in each specimen. In some cases, notched specimens were precracked by bending in a jig, heating to 600°C and quenching in water. The specimen dimensions are given in Fig. 1. The range of a/W ratios used in the present tests was 0.2 to 0.7. Four- rather than three-point bend tests were performed to avoid interaction between the contact stress and that at the root of the crack [2] and the difficulties of aligning the upper loading rod directly over the notch. In all tests a constant cross-head velocity of 0.05 cm min^{-1} was applied. Uncontrolled fracture always occurred, i.e. the load displacement curves had no tails.

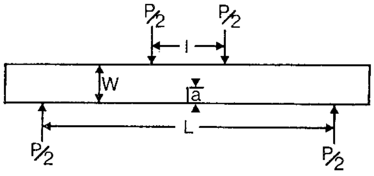

Figure 1 Specimen dimensions used in the present four-point bend tests. W = specimen height (5 mm), B = specimen width (2.5 mm), a = crack length (1 to 3.5 mm), A = area of fracture face = $B(W - a)$, L = major span (40 mm), l = minor span (10 mm), d = bending arm = $(L - l/2)$ (15 mm), P = applied load.

Expressions for K_{Ic} can be derived in various ways. According to the Griffith criterion, fracture occurs when the strain energy release rate $\partial U/\partial A$ reaches a critical value G_c, i.e.

$$\frac{\partial U}{\partial A} = G_c \cdot \tag{1}$$

G_c is related to the critical stress intensity factor K_c by the expression

$$G_c = \frac{\alpha K^2{}_c}{E} \cdot \tag{2}$$

In plane strain $K_c = K_{Ic}$ and $\alpha = (1 - \nu^2)$ where ν is Poisson's ratio. G_c is obtained from conventional work of fracture tests for the case of controlled fracture, i.e. crack arrest, which is indicated by a tail on the load displacement curve. In this case U is estimated from the total area under the load displacement curve taking the projected surface area as A [3]. This method has the disadvantage that the values depend on a/W and the compliance of the test machine. An alternative treatment is as follows. Integration of Equation 1 gives:

$$U = G_c A + U_0 \,. \tag{3}$$

The energy constant U_0 relates to the energy losses not involved in the creation of new surfaces. Thus, G_c and hence K_{Ic} can be determined graphically from a series of values of U and A for the case of uncontrolled fracture. The appropriate relationship is Equation A in Table I. A fracture mechanics approach has been used to derive a modified version of Equation A [4, 5]. This analysis has not previously been applied to four-point bending, but the appropriate expression (Equation B Table I) can be obtained similarly. The more usual fracture mechanics formulae (Equations C to E, Table I) have been derived by boundary collocation of a stress