Discussion

Comments on "Effect of the starting Al_2O_3 and of the method of preparation on the characteristics of Li-stabilized β''-Al_2O_3 ceramics"

In the article by Kvachkov *et al.* [1], the authors demonstrate that they are well aware of the great complexity of the formation of β or β'' from precursor aluminas, especially below any eutectic temperature. Above a eutectic point, crystal growth of, for example, β'' can simply proceed by solution-reprecipitation and near-equilibrium be easily reached. At low temperatures, however, there is great complexity indeed. In work conducted by the present author, the formation of β-type ceramics from aluminium alkoxides and aluminium hydroxides has been reported in [2, 3], respectively, and has been referred to in [4] and it was found that the formation of, for example, β'' at lower temperatures, 1000 to 1200° C is a topotactically controlled diffusional problem. The development of β-type ceramics from γ-alumina must be entirely different from that of similar ceramics when α-alumina is the source and, seemingly different again from the case where additives, for example, Na and Li, are added to pre-existing γ or added to a spray dry-roasted precursor (made from nitrates), which subsequently is converted to a γ-type ceramic at about 1000° C. (See [5] for some related magnetoplumbite studies.)

It is concluded that it matters very much whether γ- or α-alumina is used as the source, because γ-alumina can convert to β-alumina and *retain* pre-existing spinel blocks. When α-alumina converts to β-alumina, complete reconstruction is necessary. Furthermore, the distribution of added elements especially in the γ-alumina case is important, because these seemingly may diffuse into (or already be dissolved in) the γ-alumina and so topotactically form the new spinel block β-alumina. The development of β- or β''-alumina from γ-alumina depends closely on whether the γ pre-exists as γ and is then mixed with the additives, or whether the mixing is done with amorphous spray dry-roasted powder, alkoxide powder, or pre-existing aluminium hydroxide, which subsequently goes through a γ-type transition [2, 5] on heating. Large differences have been observed when starting with different hydroxides, e.g., Alcoa C331, Hydral 705, $Al(OH)_3$, or Remet Corporation Dispural, AlO(OH), boehmite derived from an alkoxide. Also, syntactic intergrowths of β and β'' are always seen at the lower temperatures and it is certainly not sufficient to adjudge the phase content of a powder simply by the intensities of β (2 0 6) and (2 0 7) and the β'' (2 0,1 0) X-ray diffraction lines. The intensity of these X-ray lines, and indeed most of the lines, is greatly affected by syntactic intergrowth effects and these are implicit in the diffusional process required to convert γ-alumina to β-type aluminas.

The likely variation to be seen in the phase content (as appraised by X-ray diffraction patterns) will certainly include the possibility that it may *seem* that lithium can stabilize β (as opposed to β'') at a lower temperature with a particular starting powder, as the authors indicate [1]. However, *none* of these materials at the lower temperatures are in thermodynamic equilibrium and thus, the present author has observed that lithium additions, starting with Alcoa C331, $Al(OH)_3$, can dramatically *appear* to stabilize β'' especially when water vapour is also present [3].

In recent studies [6], very complex effects are being seen in the related magnetoplumbite family of structures (e.g., $CaAl_{12}O_{19}$) where the crystallization at lower temperatures of such phases as $Na_{0.5}La_{0.5}Al_{12}O_{19}$, $K_{0.5}La_{0.5}Al_{12}O_{19}$, $Cs_{0.5}La_{0.5}Al_{12}O_{19}$ and $La_{0.75}Li_{0.5}Al_{11.75}O_{19}$ are similarly extremely complex.

This is a realm of study where only the most exotic and exhausting work is going to reveal the mechanisms of these processes: it is required that the mixing state and diffusional processes leading to the development of, for example, β'' should be examined almost atom-by-atom.

The present author has restricted this discussion to the crystal phase development. It is apparent that the difficulties of explanation are magnified when considering low-temperature sintering/densification in these systems, where the effect of aggregates, topotactical relic structures, distributions, etc., are almost beyond comprehension when countenanced in any detail.

It is, however, intended, with these comments,

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to endorse strongly the type of wide ranging studies that the paper [1] and the other references attempt rather than the narrow studies, often made during ceramics processing (with usually, quite unwarranted generalization of such results).

References

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Authors' reply to 'Comments on "Effect of the starting Al_2O_3 and of the method of preparation on the characteristics of Li-stabilized β''-Al_2O_3 ceramics"'

In connection with our paper Dr Morgan [1] raises several issues. We should like to take this opportunity to clarify some of the views expressed in our article.

We feel that our approach towards the problem under consideration is correct despite the inevitable pitfalls which may be encountered.

Let us now turn to some specific points stressed by Dr Morgan.

It is by now certain that the structural state of the precursor Al_2O_3 as well as the effect of specific additives such as Mg, Li and F are of decisive importance for the phase composition of the β-alumina phases formed during synthesis and sintering. In a previous paper [2] the reaction of β-alumina phase formation has been described as topotactic in the sense used by Dent Glasser *et al.* [3].

The phase formation process proceeds via a syntactic intergrowth between the hexagonal β-Al_2O_3 and the rhombohedral β''-Al_2O_3 phases which can cause disorder at a level of about 5.0 nm i.e., at a certain number of spinel blocks. However, in principle, the spinel blocks themselves are regularly arranged [4]. This does not preclude the existence of vacancies and point defects. This may be connected with the observation that as structural elements the spinel blocks are first formed at the lowest temperatures (appearance of the $hk\bar{i}\,0$ reflections in the X-ray diffraction patterns) when synthesis is started from sulphates and the powdered material passes through an amorphous state [5].

Of course, the case in which the precursor is γ-Al_2O_3 or α- γ-Al_2O_3 is a more specific one since already existing spinel blocks are involved in the topochemical reaction. As already shown [2, 4] a drastic rearrangement of the structure is unnecessary for generating the β-alumina phases. However, under these conditions the stacking faults of the precursor γ-Al_2O_3 are inherited by the β-alumina formed [2].

We think that the intensity ratios of characteristic diffraction peaks is the only way to assess the quantitative relationship between β- and β''-Al_2O_3. This has already been done by other authors [6, 7] using various peaks. We selected the $2\,0\,\bar{2}\,6$ and $2\,0\,\bar{2}\,7$ reflections of β-Al_2O_3 and the $0\,2\,\bar{2}.10$ reflection of β''-Al_2O_3 because they are well separated and their intensities can be accurately measured. Furthermore, in classical X-ray powder diffractometry it is improbable that syntactic intergrowths would significantly affect the intensity ratios, since the mode of preparation of the samples and the geometry of the instrument lead to an averaging of the intensities.

The conclusions drawn by different authors concerning the phase changes and interactions in the high-temperature range of existence of the β-alumina phases are sometimes conflicting but are based on the analysis of the system under equilibrium or quasi-equilibrium conditions. Naturally, at this high energy level, the process proceeds at a high rate and equilibrium can be achieved rapidly.

According to us and to the views expressed

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