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In situ formation of CA_6 platelets in Al_2O_3 and Al_2O_3/ZrO_2 matrices

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ABSTRACT
Al_2O_3 and Al_2O_3/ZrO_2 compacts containing CaO as a dopant have been sintered under different conditions and atmospheres: air, high vacuum ($>10^{-6}$torr). SEM observations have been made on the polished surfaces of sintered and also of annealed samples. Only after the annealing treatment in air at temperatures ranging from 1400° to 1500°C, a massive formation of CA_6 platelets was detected in samples sintered in low oxygen partial pressure atmospheres.In order to clarify the mechanism of formation of this secondary phase at the grain boundaries, CaO has been introduced in the form of either plaster of Paris (to reproduce a possible contamination provided by the molds in slip casting) or $CaCO_3$. The obtained results indicate the important role of the firing atmosphere on the precipitation of secondary phases at grain boundary.

INTRODUCTION

As it has been reported in the literature (1,2), the control of the grain boundary phases in alumina compacts is a critical step in the microstructural development of the sintered body, and consequently, in the behavioural properties of the final material. Most of the research work on this topic has been performed in compacts sintered in air. The aim of the present work is to study the influence of the oxygen partial pressure of the sintering atmosphere on the formation of grain boundary phases in CaO doped alumina.

EXPERIMENTAL

A commercial α-Al_2O_3 powder (Alcoa A16SG) with a mean particle size of 0.5 μm, specific surface area of 9 m^2/g and with the following main impurities: Na_2O, 0.1; SiO_2, <0.08; Fe_2O_3, 0.03, CaO, 0.02 and MgO, 0.1 wt%, has been used. A m-ZrO_2 powder (Dynamit Nobel) with a mean particle size of 0.5 μm, a specific surface area of 50 m^2/g and 0.05 Al_2O_3, 0.05 SiO_2, 0.06 Fe_2O_3, and 0.023 wt% Na_2O of impurity contents has been employed for preparing layered materials by slip casting in plaster of Paris molds. Details of the processing conditions have been reported in a previous work (3).

In Figure 1a the processing flow chart followed to obtain Al_2O_3 and $Al_2O_3/Al_2O_3+4vol\%ZrO_2$ (A/AZ) layered materials is described. In order to study the effect of CaO introduced during the slip casting process in the alumina compacts from the plaster moulds, mixtures of Al_2O_3-$CaCO_3$ and Al_2O_3-Plaster containing 0.2 wt% CaO have been performed in isopropanol. The processing flow chart is given in Figure 1b. Finally, a isopressed alumina sample without additives has been studied for comparative purposes.

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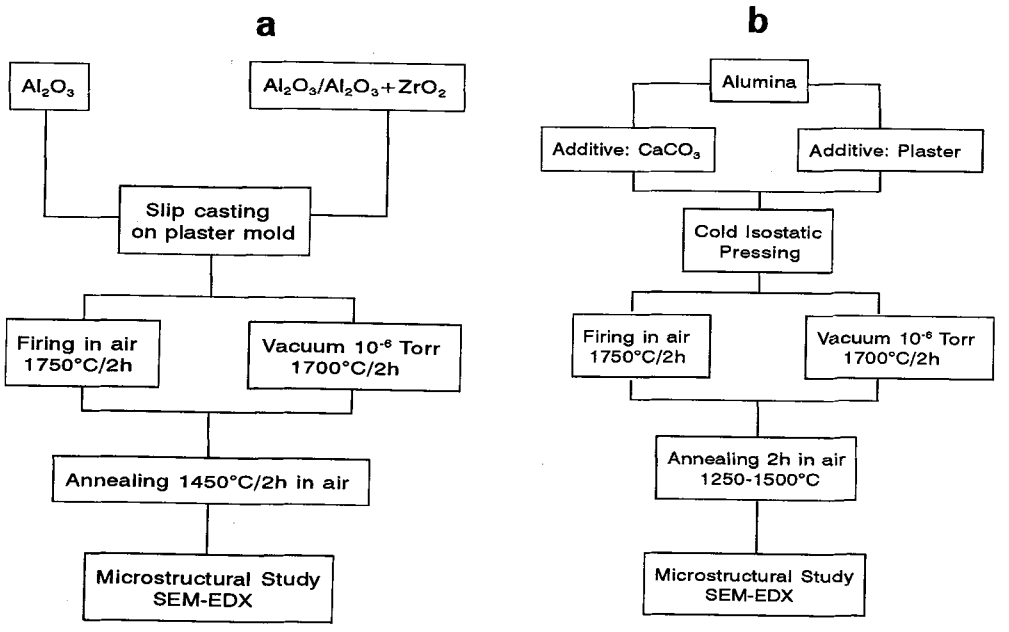

Figure 1. Flow charts corresponding to the processing scheadule of slip cast materials (a) and Ca-doped Al_2O_3 compacts (b).

The sintered samples were polished and annealed for 2 hours at temperatures ranging from 1400° to 1500°C in air and subsequently analyzed by scanning electron microscopy (SEM/EDX).

RESULTS

Slip Cast Materials

In the Al_2O_3 compacts obtained by slip casting treated at 1750°C under vacuum, the presence of large platelets of CA_6 (5-20 μm) has been detected after annealing at 1450°C in air. Figure 2 shows the SEM micrograph in which these platelets can be observed. The Al:Ca ratio corresponds to that of calcium hexaaluminate, as shown in Table 1. A similar effect was observed in Al_2O_3/Al_2O_3-ZrO_2 multilayers also obtained by slip casting. The presence of these platelets has not been observed in any of both samples when they were sintered in air.

Table I. EDX microanalysis correponding to the platelets observed in slip cast materials. Average of 5 determinations (wt%).

Al_2O_3	CaO	MgO
87 ± 3	10.0 ± 0.5	1.5 ± 0.5

CaO doped materials

The samples prepared with $CaCO_3$ addition do not develop CA_6 after annealing. However, those samples in which plaster has been added after annealing at temperatures higher than 1450°C develop a secondary phase (Figure 3) quite similar to that obtained in slip casting layered composites. The Al:Ca ratio is that shown in Table II. The presence of Al_2O_3.MgO spinel precipitates can be also seen in the sample containing plaster as additive.

For the samples heat treated and annealed in air the following observations can be stated: i) When $CaCO_3$ is added to the starting Al_2O_3 powder, grains containing CaO located at the grain boundaries and inside of the Al_2O_3 grains can be occasionally observed after thermal treatment.

Table II.- EDX microanalysis correponding to the platelets observed in plaster doped alumina compacts. Average of 5 determinations (wt%).

Al_2O_3	CaO	MgO
87 ± 1.5	8.7 ± 1.5	3 ± 0.5

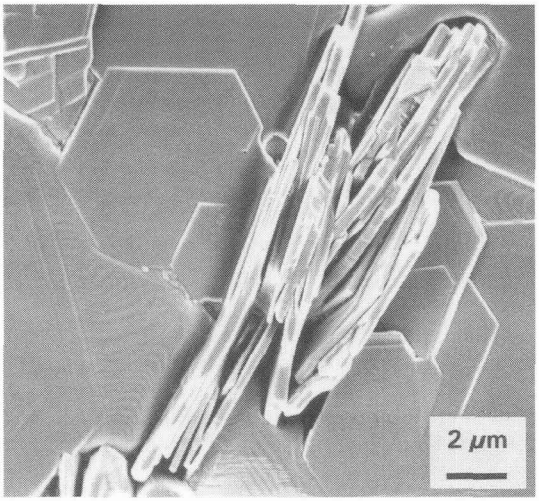

Figure 2.- SEM micrograph showing the CA_6 platelets formation in slip cast Al_2O_3 compacts.

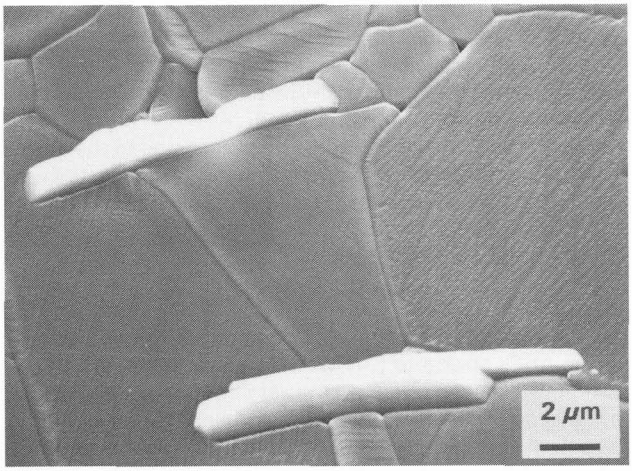

Figure 3.- SEM micrograph of Al_2O_3 doped with plaster, *after annealing* in air.

The Al:Ca ratio seems to correspond to that of calcium dialuminate (CA_2). Some Al_2O_3.MgO spinel grains have been also observed in these samples.

ii) When plaster is added to the starting powder, a significant amount of Al_2O_3.MgO spinel

precipitates at grain boundaries were observed (Figure 4a). Similar effect was detected in Al_2O_3 sample obtained by slip casting (Figure 4b).

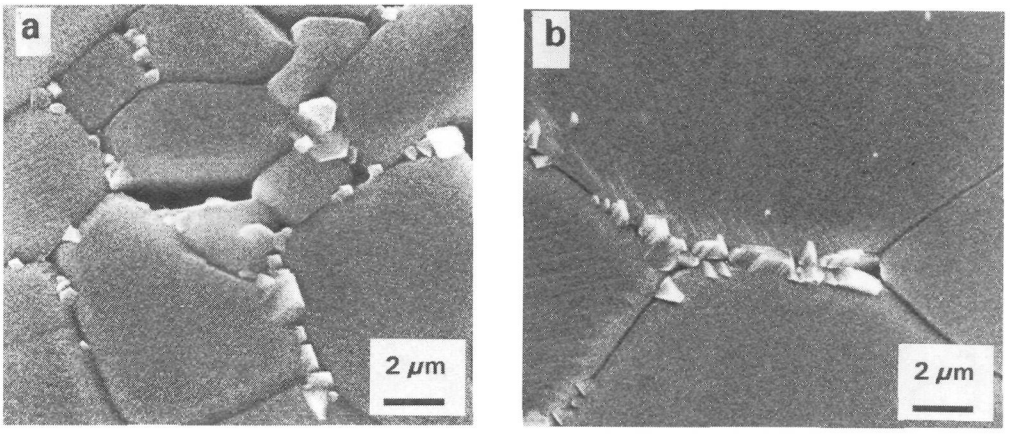

Figure 4.- Al_2O_3.MgO spinel located at the grain boundaries in Al_2O_3 doped with plaster (a) and slip cast Al_2O_3 compact (b) fired and annealed in air.

No secondary phases have been detected in the isostatic pressed Al_2O_3 compact for both sintering atmospheres after annealing treatments in air up to 1450°C.

DISCUSSION

The samples sintered in air do not show the presence of CA_6 platelets after annealing. However, plaster containing samples sintered in vacuum developed CA_6 as secondary phase at the grain boundaries. This fact can be explained taking into account the Ellingham's diagram. At very low oxygen partial pressures ($< 10^{-9}$ atm), the more stable phases at temperature of 1700°C would be CaO, MgO and Al_2O_3, being eliminated the rest of the impurities (alkalines and Fe_2O_3) present in the glassy phase. Therefore, a metastable Ca-rich glassy phase developed because of the presence of sulfate will remain at triple points. After annealing in air at temperatures high enough to ensure the cations diffusion (i.e. >1400°C) the formation of the most stable phase (CA_6) is thermodinamically promoted.

The presence of MgO in the CA_6 structure has been reported in the literature: the CA_6 has a magnetoplumbite type structure (Figure 5) where Mg^{2+} cations can partially substitute the Al^{3+} cations (4). When the calcium is added as $CaCO_3$, the amount of liquid phase present will be lower than in the case of plaster containing samples. Consequently, the formation of calcium aluminates will take place through solid state reaction. This fact is supported by the presence of an aluminate richer in calcium (CA_2).

The presence of Al_2O_3.MgO spinel precipitates in Al_2O_3 compacts containing plaster (Figure 4) and occasionally in those containing $CaCO_3$ can be also explained considering that the solid solution limit of MgO in Al_2O_3 structure (0.1 wt% at 1500°C) (5) will decrease when a third cation (Ca^{2+}) is present, then MgO exsolution at the grain boundaries and subsequent formation of spinel takes place. In the case of plaster containing samples this equilibrium is reached faster because of the higher amount of liquid phase. Consequently, higher amount of spinel can be expected at the grain boundary.

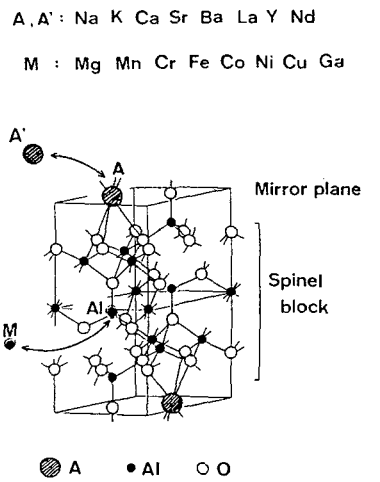

Figure 5.- CA_6 with magnetoplumbite type structure, showing the possible modification by partial substitution.

CONCLUSIONS

The following conclusions can be drawn:

1.- The firing atmosphere strongly affects kinetic of formation of minoritary phases in Al_2O_3 compacts.

2.- It is possible to form in situ large CA_6 precipitates (10-20 μm) in plaster doped Al_2O_3 compacts when they are fired in vacuum and subsequently annealed in air.

3.- Al_2O_3 compacts with Al_2O_3.MgO spinel precipitates at grain boundaries can be obtained when MgO and CaO are present as dopants. This effect is more important in air becuase in vacuum the MgO tends to enter in the CA_6 structure.

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