JOURNAL OF MATERIALS SCIENCE 16 (1981) 384–388

Grain boundary analysis of MgO-doped Al_2O_3

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Grain boundaries of MgO-doped alumina also containing CaO have been investigated by various authors. The general conclusion of this work is that Ca is enormously enriched at the grain boundaries compared with Mg, which was found either to be slightly or not at all enriched at the grain boundaries. Electron scanning chemical analyses of predominant intergranular fracture surfaces of alumina samples containing different amounts of MgO (100, 250, 1000 and 2000 ppm), as described in this paper, show that Mg is enriched at the grain boundaries below the solubility limit. Above the solubility limit it is probable that $MgAl_2O_4$ precipitates contribute considerably to the Mg content measured at the boundaries. The amount of Mg segregated at the grain boundaries was found to be roughly independent of the amount of MgO added as long as the firing conditions were kept constant. The enrichment found, together with the effect of small amounts of MgO on the development of the microstructure, indicate the possibility that segregated Mg may still be active in the grain growth process.

1. Introduction

It is well known that the addition of small amounts of MgO to Al_2O_3 suppresses discontinuous grain growth, resulting in a nearly 100% dense material, which is necessary for optimal translucency of gas discharge lamp envelopes [1]. A possible explanation for the effect of the MgO addition was that segregation of Mg at the grain boundaries suppresses the grain growth. To determine whether this explanation is correct the grain boundary composition of commercial MgO-doped Al_2O_3 has been analysed by various investigators [2–7]. Although the conclusions reached by the various authors differ depending on the analytical technique used, it now seems to be generally accepted that, in contrast to CaO, the MgO in commercial Al_2O_3 lamp envelope material does not segregate measurably at the grain boundaries [8]. The apparent Mg enrichment found by some authors is ascribed to $MgAl_2O_4$ precipitates found by scanning electron microscopy (SEM) to be present in the multiple grain junctions [8].

Experiments by Peelen [9, 10] show that the addition of only 50 ppm MgO to Al_2O_3 is sufficient to increase the density substantially after sintering, and maximum density is reached under his firing conditions at a 300 ppm MgO doping level. In this paper we describe grain boundary analyses of Al_2O_3 doped with MgO below its solubility level [10] (100, 250 and 1000 ppm) and of Al_2O_3 with $MgAl_2O_4$ precipitates present (2000 ppm MgO).

2. Experimental procedure

2.1. Preparation

Magnesium was added as a solution of Mg-acetate $4H_2O$ (Merck reagent grade) in absolute alcohol to an alcohol suspension of pure Al_2O_3 ($Mg \leqslant 0.8$ ppm and $CaO \leqslant 10$ ppm) of Rubis Synthetique des Alpes, code 20 A 15 RB. The suspension was dried while stirring continuously. After further drying, the powder was sieved, pressed isostatically at 100 MN m^{-2} and preheated in oxygen at 700° C to decompose the acetate to oxide. Next, unless otherwise stated, the samples were sintered at 1800° C for 1 h in a hydrogen atmosphere which

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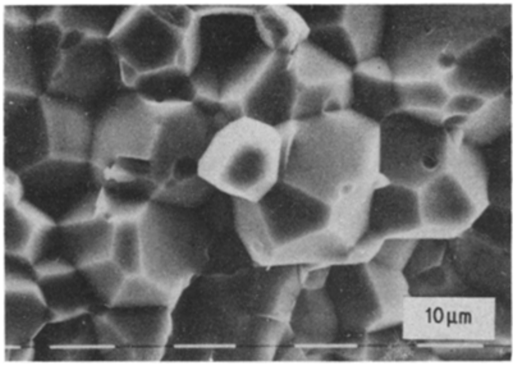


Figure 1 SEM graph of a fracture surface of Al_2O_3 doped with 1000 ppm MgO, analysed with ESCA.

had been passed through H_2O at 25° C. A heating and cooling rate of $200^\circ\,C\,h^{-1}$ was applied. For the grain boundary analysis bars, with a diameter of 8 mm and a length of 30 mm were prepared from these samples. The densities were measured by immersion in H_2O after Archimedes.

2.2. Electron scanning chemical analysis

The bars were fractured in the high-vacuum preparation chamber of the electron scanning chemical analysis (ESCA) apparatus (Leybold Heraeus LHS 10) and transferred into the ultra high-vacuum measuring section. Fracture took place primarily along the grain boundaries, as established by microscopical inspection. AlKα radiation (1486.6 eV) was used for excitation and the spectra were measured with a hemispherical analyser ($\Delta E/E$ = constant). Each spectrum was scanned for a preselected number of sweeps which were accumulated in a multichannel analyser (Canberra) in order to obtain a high signal to noise ratio. The fracture surface (≈ grain boundary) composition was derived semi-quantitatively from the peak area of the O_{1s} peak (binding energy (*BE*) = 531 eV), the Mg Auger electron spectroscopy (AES) peak (kinetic energy (*KE*) = 1182 eV) and the Al_{2s} peak (*BE* = 119 eV). The Ca content could not be determined exactly because of the overlap of the Ca_{2p} peaks with Au_{4d} peaks due to the sample holder and a Mg AES peak.

A polished surface of $MgAl_2O_4$ ion-etched for a short period to clean it, as well as (transgranular) fracture surfaces of monocrystalline $MgAl_2O_4$ (Union Carbide), pure Al_2O_3 without CaO or MgO and a Ca silicate glass were used for the determination of the relative sensitivity factors (*sf*) of the various elements for the ESCA or Auger process. The sensitivity factors thus determined were estimated to be correct within 10% of the values given.

3. Results

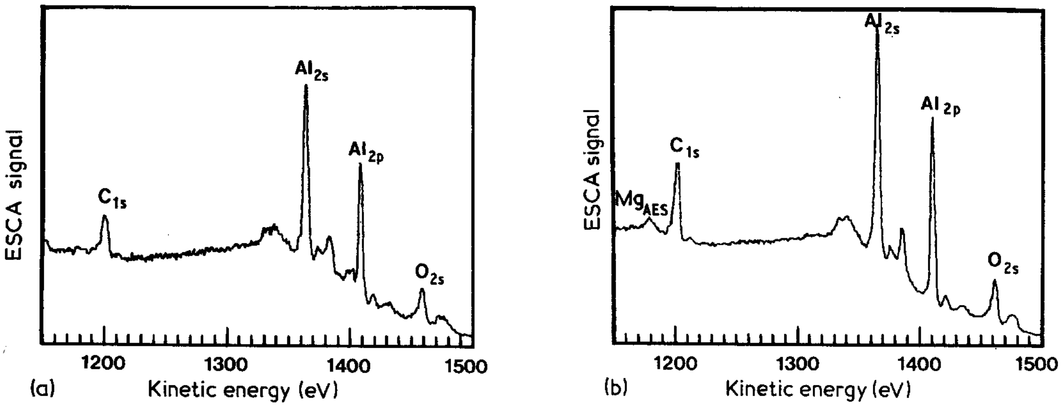
Fig. 1 shows a fracture surface representative of all the samples analysed. Although the addition of CaO resulted in a somewhat broader grain size distribution, the average grain size did not differ much between all the samples (about 15 µm). Table I gives the measured data of the samples used for standardization. Accepting that the sensitivity for the Al_{2s} peak area is 1, the sensitivity for the O_{1s} peak is to be 2.2. The sensitivity factor for Mg varied somewhat for the different samples possibly because of the angular dependence in the case of the monocrystalline $MgAl_2O_4$ or the preferential ion-etching for the polished polycrystalline $MgAl_2O_4$ surface [7]. However, a sensitivity factor of 9.9 for the Mg AES peak seems acceptable. For Ca_{2p} a sensitivity factor of *sf* = 3.1 is used.

In Fig. 2 some partial ESCA spectra obtained from the Al_2O_3 samples are shown. In the case of Al_2O_3 without MgO addition (Fig. 2a) the Mg AES peak is absent while for case of a 100 or 2000 ppm MgO addition (Fig. 2b and c, respectively) the Mg AES signal does not differ very much. The Mg AES peak is also found to be absent in the case of an analysis of a polished surface of Al_2O_3 doped with 250 ppm MgO (Sample 3).

TABLE I

Material	sfO_{1s} *BE* = 533 eV*	$sfAl_{2s}$ *BE* = 119 eV*	$sfMg_{AES}$ *KE* = 1182 eV†	$sfCa_{2p}$ *BE* = 1130–1141 eV*	Remarks
$MgAl_2O_4$	2.3	1	7.7	–	Polished surface polycrystal
$MgAl_2O_4$	2.2	1	9.9	–	Monocrystal
$MgAl_2O_4$	2.3	1	10.5	–	Monocrystal
Al_2O_3	2.2	1	–	–	Transgranular
Ca-silicate	2.2	–	–	3.1	Glass

**BE*–binding energy.
†*KE*–kinetic energy.



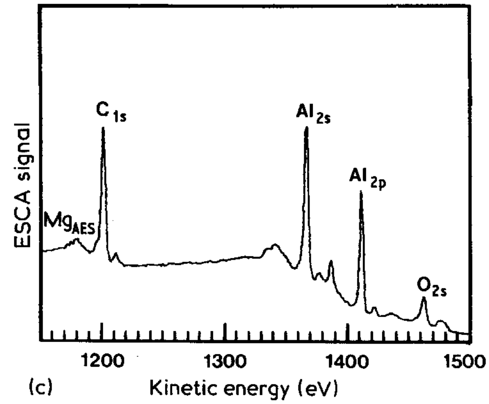


Figure 2(a) Part of the ESCA spectrum of an intergranular fracture surface of Al_2O_3 with 100 ppm CaO (Sample 1, Table II); (b) part of the ESCA spectrum of an intergranular fracture surface of Al_2O_3 with 100 ppm MgO and 50 ppm CaO (Sample 2, Table II); (c) part of the ESCA spectrum of an intergranular fracture surface of Al_2O_3 with 2000 ppm MgO and 50 ppm CaO (Sample 14, Table II).

The measured data of the various samples prepared and their analyses are given in Table II. From this table it is obvious that up to 1000 ppm MgO, the Mg concentration in the fracture surfaces is roughly constant at 0.4 at%, whereas at a 2000 ppm MgO addition level the Mg content doubled to about 0.7 at%. The highest temperature, in particular, but also the time as this temperature (Samples 12 and 13) as well as the cooling rate (Sample 6) influence the amount of Mg found at the fracture surfaces. The Ca concentration in the grain boundaries for the samples to which CaO is added is estimated at about 0.5 at%, as found after a detailed analysis of a sample with only a 50 ppm CaO addition.

TABLE II

Sample number	Addition	O_{1s} (counts)	Al_{2s} (counts)	Mg_{AES} (counts)	Mg (at%)	D_s (g cm^{-3})	Remarks
1	100 ppm CaO	81 102	23 863	–	–	3.79	
2	100 ppm MgO + 50 ppm CaO	427 276	131 342	11 962	0.4	3.973	
3	250 ppm MgO	769 904	226 610	–	–	3.920	Polished surface
4	250 ppm MgO	413 297	129 789	14 529	0.4(5)	3.920	
5	250 ppm MgO	436 568	130 981	10 382	0.3	3.920	
6	250 ppm MgO	295 803	91 535	5 454	0.2(5)	3.924	Within 10 min cooled from 1800 to 1500° C
7	250 ppm MgO + 50 ppm CaO	305 470	91 765	7 232	0.3	3.978	
8	1000 ppm MgO	616 544	192 179	22 096	0.5	3.973	
9	1000 ppm MgO	824 556	249 301	24 460	0.4	3.973	
10	2000 ppm MgO	598 143	192 443	34 639	0.7	3.973	
11	2000 ppm MgO	425 165	127 471	20 813	0.6(5)	3.973	
12	2000 ppm MgO	406 648	124 754	14 930	0.5	3.974	Time at highest temperature, 24 h
13	2000 ppm MgO	33 930	10 818	707	0.03	3.959	Highest temperature, 1900° C for 15 h
14	2000 ppm MgO + 50 ppm CaO	591 701	198 125	30 418	0.6(5)	3.962	

4. Discussion

In agreement with previous results [2–10], these experiments show that Ca is enriched at the grain boundaries of Al_2O_3. The ESCA analyses also show that the Mg concentration in the grain boundaries for samples with a MgO addition up to 1000 ppm, fired under the conditions as described, is nearly independent of the amount of MgO added and is about constant at 0.4 at%. However, in the case of a 2000 ppm MgO addition, which is the approximate amount found in commercial Al_2O_3, the Mg concentration in the fracture surface is found to double to about 0.7 at%. This result explains in part the uncertainty which exists as far as the Mg enrichment in the grain boundaries of Al_2O_3 is concerned. The bulk solubility for the present firing temperature (1800° C) according to Roy and Coble [11] is about 0.05 at% as measured for vacuum and even somewhat higher for the atmosphere used in the present investigation. The 0.05 at% Mg corresponds to about the 1000 ppm MgO added and it is therefore acceptable to assume that in the case of 1000 ppm MgO addition and below, none or only a very small amount of $MgAl_2O_4$ precipitate is present. In the case of a 2000 ppm MgO addition, however, the surplus MgO is present in the form of $MgAl_2O_4$ particles. These precipitates contribute substantially to the Mg signal of a fracture surface [7] and cause the increase in Mg content observed. Therefore Johnson and Stein [7] are correct in stating that $MgAl_2O_4$ precipitates contribute substantially to the Mg content in the fracture surface of e.g. Lucalox. However, the present investigation shows that, far below the solubility limit, an enrichment of Mg in the fracture surfaces (≈ grain boundaries) is still found. The analysis of the polished surface of Al_2O_3 with 250 ppm Mg (Sample 3) compared with that of its fracture surfaces (Samples 4 and 5) once more confirms that Mg enrichment is found in the grain boundaries.

An increase of especially the firing temperature but also of the time at the highest temperature (Samples 12 and 13) results in a lowering of the Mg content measured at the grain boundaries. This observation can be explained by the evaporation of MgO, which is known to occur. Furthermore quenching influences the Mg content in the grain boundaries (Sample 6) indicating that part of the Mg enrichment measured is introduced during cooling because of the lowering of the solubility of MgO in Al_2O_3. The degree of MgO enrichment measured therefore depends on the firing conditions.

From the present investigation it might be concluded that the model in which the segregated Mg is thought to be active in the inhibition of the discontinuous grain growth [1, 10] still cannot be rejected. The grain boundaries obviously first obtain their (energetically) most favourable composition upon MgO addition (even when 100 ppm MgO at about 0.4 at% Mg solubility bulk is found in the fracture surface). The enrichment of Mg is most probably connected with a lowering of the interfacial energy of the grains. A lowering of the interfacial energy implies an increased mobility of the pores [10, 12] and will therefore result in an increased density, as observed.

5. Conclusions

From the experiments described in this paper it may be concluded that:

(a) Ca, in agreement with previous observations, is found to enrich the grain boundaries;

(b) Below the solubility limit, ESCA shows that the Mg is enriched at the grain boundaries;

(c) Below its solubility limit the Mg content in the grain boundaries is found to be independent of the amount of MgO added;

(d) Above its solubility limit, as measured before, Mg precipitates contribute significantly to the Mg signal measured;

(e) The model of inhibition of discontinuous grain growth may still be valid because of segregated Mg.

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Received 29 May and accepted 1 July 1980.