Journal of the European Ceramic Society **12** (1993) 337–341

The Microchemistry and Microstructure of Magnesium-Doped Submicron α-Alumina Powders after Thermal Treatment at 1300°C

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(Received 1 October 1992; revised version received 3 June 1993; accepted 15 June 1993)

Abstract

This paper considers the characterization of submicron α-Al_2O_3 powders, doped with MgO (550 and 1650 ppm by weight), and treated at 1300°C for different times and different cooling rates. X-Ray photoelectron spectroscopy (XPS) shows a strong surface segregation of Mg. The extent of segregation is higher for 1650-ppm-doped material than for 550-ppm-doped material. The outer surface segregation of Mg depends on the thermal treatment conditions. The powders have also been characterized by TEM, electron energy loss spectroscopy (EELS), SEM, surface area measurements and chemical analysis. TEM reveals a considerable agglomeration and some degree of sintering with the higher-doped powders. The size of the particles is between 50 and 500 nm and their thickness is around 100 nm, depending on the amount of magnesium and the thermal treatment.

Im folgenden wird die Charakterisierung von submikrometer α-Al_2O_3-Pulvern betrachtet, die mit MgO (550 and 1650 ppm Gew.%) dotiert, bei 1300°C verschieden lange gehalten und anschließend bei unterschiedlichen Raten abgekühlt wurden. Röntgenphotoelektronenspektroskopie (XPS) zeigte eine starke Oberflächensegregation von Mg. Das Ausmaß der Segregation ist für das 1650 ppm dotierte Material höher als für das 550 ppm dotierte. Die Segregation von Mg auf der äußeren Oberfläche hängt von der Wärmebehandlung ab. Die Charakterisierung der Pulver erfolgte mittels TEM, Elektronenverlustspektroskopie (EELS), SEM. Bestimmung der Oberflächengröße und chemischer Analyse. Die TEM-Aufnahmen ließen eine beträchtliche Agglomeration und in gewissem Umfang Sinterung der höher dotierten Pulver erkennen. Die Größe der Teilchen liegt zwischen 50 and 500 nm und ihre Dicke beträgt etwa 100 nm, abhänig von der Magnesiumzugabe und der Wärmebehandlung.

Cette étude concerne la caractérisation de poudre d'alumine-α submicronique dopée en magnésium (550 and 1650 ppm en poids de MgO), traitée à 1300°C durant des temps différents et refroidie à différentes vitesses. Des analyses XPS nous ont permis de mettre en évidence une forte ségrégation du magnésium. La profondeur de ségrégation est plus importante pour la poudre fortement dopée en MgO. De plus, la teneur en magnésium à la surface des grains dépend des conditions de traitement thermique. Les poudres ont été également caractérisées par analyse chimique, MET, EELS, MEB et leur surface spécifique a été déterminée par BET. L'observation au microscope électronique à transmission des poudres fortement dopées met en évidence une agglomération importante et un début de frittage des grains. La taille des particules dépend des conditions de traitement thermique. Elle est comprise entre 50 et 500 nm et leur épaisseur est voisine de 100 nm.

1 Introduction

Powder densification and the characteristics of sintered ceramics are directly related to the quality of the ceramic powder used in the manufacturing process. Important properties of powders, such as size distribution, agglomeration, purity and surface area can strongly affect their sinterability. The segregation of impurities during powder preparation can be detrimental to subsequent ceramic

Journal of the European Ceramic Society 0955-2219/93/$6.00

performance. It is important, therefore, to characize the microstructure and microchemistry of powders, particularly the nature and extent of impurity segregation. Modern surface techniques such as XPS (X-ray photoelectron spectroscopy), Auger and SIMS (secondary ion mass spectrometry) have the capability to analyse powder surfaces, although there are experimental difficulties with insulating materials like alumina.

In previous work XPS and Raman spectroscopy have been employed to examine yttrium and calcium segregation to the surface of submicron α-alumina powders doped with yttria.[1] Also, preliminary data have been presented regarding XPS and TEM (transmission electron microscopy) studies of magnesium segregation to the surface of submicron α-alumina powders doped with 550 and 1650 ppm wt, or the equivalent, respectively, of 0·07 and 0·21 at.% magnesium.[2] This paper details the effect of thermal treatment at 1300°C on the physical and chemical characteristics of magnesium-doped α-alumina powders, with emphasis placed on the use of XPS to determine the extent of magnesium surface segregation. The powders have also been characterized by TEM, electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), chemical analyses and surface area measurements.

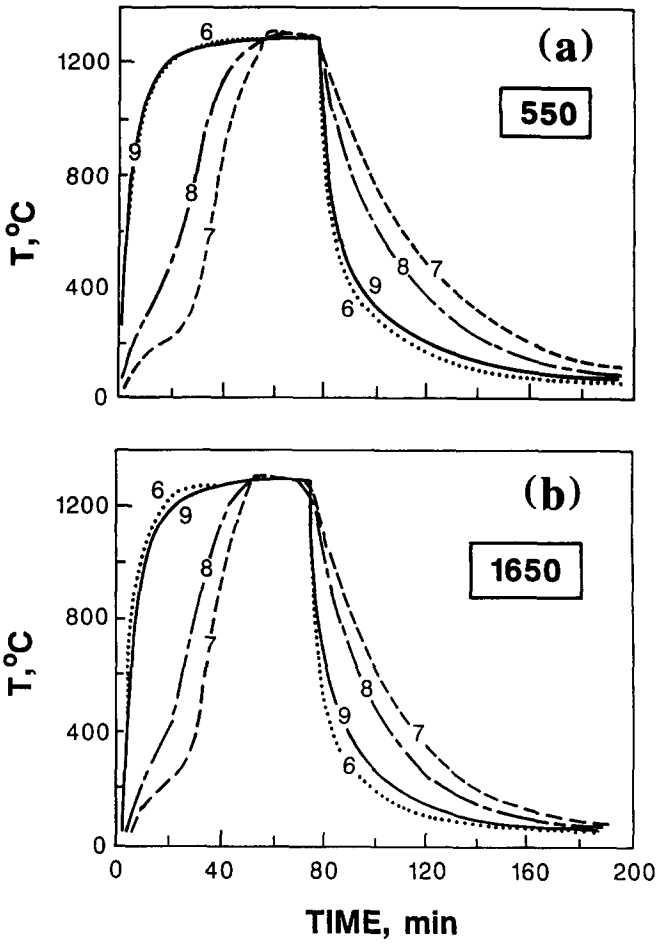

Fig. 2. Thermal treatment of alumina powders at different positions in the crucible: (a) 550 ppm Mg and (b) 1650 ppm Mg.

2 Materials and Methods

The magnesium-doped α-alumina powders were prepared from the alum. By this method, the dopants are added before the decomposition of the hydroxides which occurs during the first calcination at approximately 300°C. This gives a uniform distribution of the dopants, which can react during the calcination with the nascent crystallites of γ-alumina, whose reactivity is very high due to their high surface area. The next calcination was performed at 1300°C in large silica crucibles (20 cm diameter and 15 cm high). Pt/Pt–10% Rh thermocouples placed in the powder, as shown in Fig. 1, were used to monitor the thermal history of the powder at different positions in the crucible (Fig. 2). Samples from positions 6 and 7 with the largest difference in cooling rate were taken for XPS, TEM and SEM analysis.

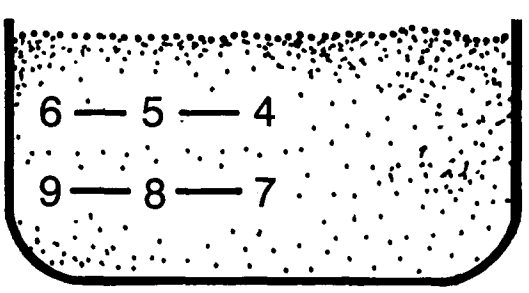

Fig. 1. Position of the thermocouples in the silica crucible.

X-Ray photoelectron spectroscopy (XPS) analysis was performed in a Perkin Elmer Model 5500 system. Monochromatic aluminium K_α radiation was used (1487 eV). The electrons emitted from the sample were filtered in a hemispherical analyser with a pass energy of 58 eV. The vacuum in the analyser chamber was lower than 10^{-6} Pa. Calibration of the XPS spectra was performed using 'pure' alumina and $MgAl_2O_4$ samples prepared by the sol–gel method. The observations have been made on compacted powder. Figure 3(a) and (b) shows the spectra obtained from the standard specimens. The results are obtained from a surface area of 0·8 mm × 0·8 mm. By analysing magnesium lines: Mg_{1s}, Mg_{2s} and Mg_{2p}, it has been possible to get an indication of the magnesium concentration with depth.[3] Indeed, for Mg_{1s}, with a kinetic energy of the electrons ($KE = h\bar{\omega} - E_b$ with E_b the binding energy) equal to 187 eV, the electron escape depth is about 0·5 nm, while for Mg_{2s} and Mg_{2p}, with kinetic energies equal to 1387 and 1437 eV, respectively, the electron escape depth is about 2 nm. Thus the Mg_{1s} data is more surface sensitive, giving the magnesium concentration over a depth of 2 or 3 monolayers, while the amount of magnesium calculated from the Mg_{2s} and

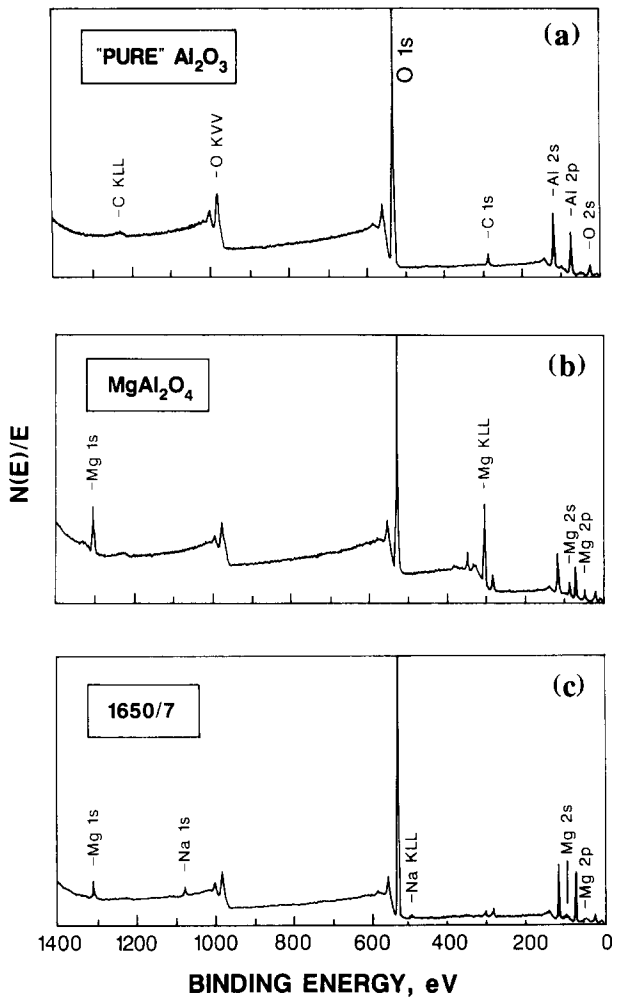

Fig. 3. XPS spectra of the standard specimens (a) 'pure' Al_2O_3 and (b) $MgAl_2O_4$ powders, and (c) specimen 1650/7 showing surface segregation of Mg and Na.

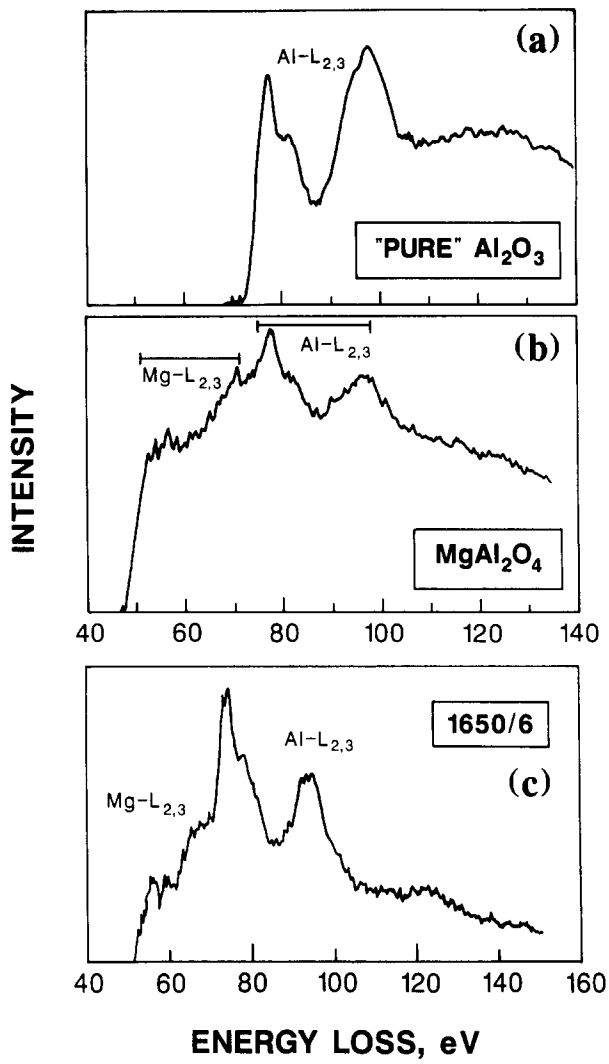

Fig. 4. EEL spectra of (a) 'pure' Al_2O_3 and (b) $MgAl_2O_4$ and (c) specimen 1650/6 showing Mg-$L_{2,3}$ and Al-$L_{2,3}$ edges (background stripped). The bars in (b) indicate the threshold and extent of the Mg-$L_{2,3}$ and Al-$L_{2,3}$, respectively. (The 20 eV windows for integration are taken from 52 eV for Mg-$L_{2,3}$ and 75 eV for Al-$L_{2,3}$.)

Mg_{2p} lines concerns a depth close to 2 nm. The XPS error in quantification is quite large because of the morphology of these samples and can be estimated to be around 0·3–0·4 at.%. Furthermore, because of peak overlaps the Mg_{2s} data is more accurate than the Mg_{2p} values.

Transmission electron microscopy (TEM) and electron energy loss (EEL) experiments were carried out using a 80 kV Zeiss Model 902 electron energy loss imaging microscope. The powder was finely dispersed on carbon grids. Bright field images provided an indication of oxide grain size, and EEL quantification was attempted to determine the surface magnesium concentration. EEL spectra of 'pure' alumina and $MgAl_2O_4$ are shown in Fig. 4. Powder quantification was made possible by comparison of the unknown with the spectrum obtained from the $MgAl_2O_4$ standard shown in Fig. 4(b). In Fig. 4(b), the brackets indicate the threshold and extent of the Mg-$L_{2,3}$ and Al-$L_{2,3}$ edges. To quantify an unknown sample, both edges are integrated over an energy window of 20 eV. The spectrum is background stripped and its Al-$L_{2,3}$ edge normalized to the standard $MgAl_2O_4$ spectrum. The Mg-$L_{2,3}$ edge is then integrated and the Mg concentration calculated relative to the standard. However, the error in quantifying the edges of the spectrum is significant (around 50%), due both to the small energy window (20 eV) necessitated by the proximity of the edges, and to the difficulty in background stripping these low energy edges due to interference from plasmon transitions. The thickness of analysed particles is around 100 nm and surface areas ranged from 8×10^{-3} to 0·5 μm^2. Consequently, in order to get segregation information, analysis has been performed on the edges of the grains.

3 Results and Discussion

3.1 Chemical analysis, surface area measurements (BET) and SEM observations

The main impurities found in the powder are silicon, sodium, potassium (13 ppm by weight), calcium

(< 10 ppm) and iron (< 10 ppm). The silicon and sodium level depended on the position in the silica crucible (Fig. 1), the amount of Si varying from 19 ppm (position 7) to 63 ppm (position 6), and sodium from 15 ppm (position 6) to 22 ppm (position 7). The BET analysis showed that the powder in position 7 had the largest specific surface area and the powder corresponding to position 6 the lowest. For 1650-ppm-doped material the values in position 7 and 6 were 9·4 m^2/g and 6·3 m^2/g, respectively, whereas for 550-ppm-doped material the areas measured were 8·1 m^2/g and 5·4 m^2/g.

3.2 Microchemical analysis

XPS and EELS have been carried out on 550 ppm and 1650 ppm Mg-doped powders taken from positions 6 and 7 after treatment at 1300°C (Figs 1 and 2) as well as the standard Al_2O_3 and $MgAl_2O_4$ powders. The different Mg-doped samples have been denoted as 550/6, 550/7, 1650/6 and 1650/7, respectively.

Regarding the XPS results, a strong segregation of Mg was observed for all powders. Ca, Fe, K and Si were not detected in these samples by XPS. The extent of magnesium segregation is given in Table 1, calculated from the Mg_{1s}, Mg_{2s} and Mg_{2p} peaks. For 1650-ppm-doped material, about 4·5 at.% Mg is present in the outer 0·5-nm thick layer. This may correspond to an average of one monolayer of Mg. Precipitates of $MgAl_2O_4$ are also likely to be present. The mean concentration of Mg is about 1 at.% when the thickness of the outer layer analysed is 2 nm. Less surface segregation is observed for 550/6 and 550/7 samples, and the powder from position 7 appears to have less segregation (about 2·3% Mg in the outer 0·5-nm thick layer and 0·5 at.% in the top 2 nm) than the powder from position 6 (about 3·4% Mg in the outer 0·5-nm thick layer and about 1 at.% when the thickness of the outer layer analysed is 2 nm). XPS also detected the presence of Na near the surface of powder from positions 6 (0·6 at.%) and 7 (1·4 at.%). A typical XPS spectrum from sample 1650/7 is shown in Fig. 3(c).

Table 1. Near surface concentration (at.%) of magnesium from XPS analysis of the Mg_{1s}, Mg_{2s} and Mg_{2p} peaks (error ±0·3–0·4%) in powders doped with 1650 and 550 ppm by weight of MgO (0·21 and 0·07 at.% Mg); analysis depths for $Mg_{1s} \simeq 0{\cdot}5$ nm and for Mg_{2s} and $Mg_{2p} \simeq 2{\cdot}0$ nm

Sample and position in the crucible	Mg_{1s}	Mg_{2s}	Mg_{2p}
Al_2O_3 1650/6	4·7	1·0	0·9
Al_2O_3 1650/7	4·4	1·0	1·0
Al_2O_3 550/6	3·4	1·0	0·7
Al_2O_3 550/7	2·4	0·6	0·5

Regarding EEL analysis, estimation of Mg concentrations is also possible by comparison of the spectrum of Mg for the doped α-alumina powder with that obtained with the $MgAl_2O_4$ standard specimen. A typical EELS spectrum for sample 1650/6 is shown in Fig. 4(c). However, as mentioned previously, the error is large and it is not reasonable to quote concentrations to compare with the XPS values. Nevertheless, the trends of the results are similar as for XPS, with magnesium concentrations being higher for specimens 1650/6 and 1650/7.

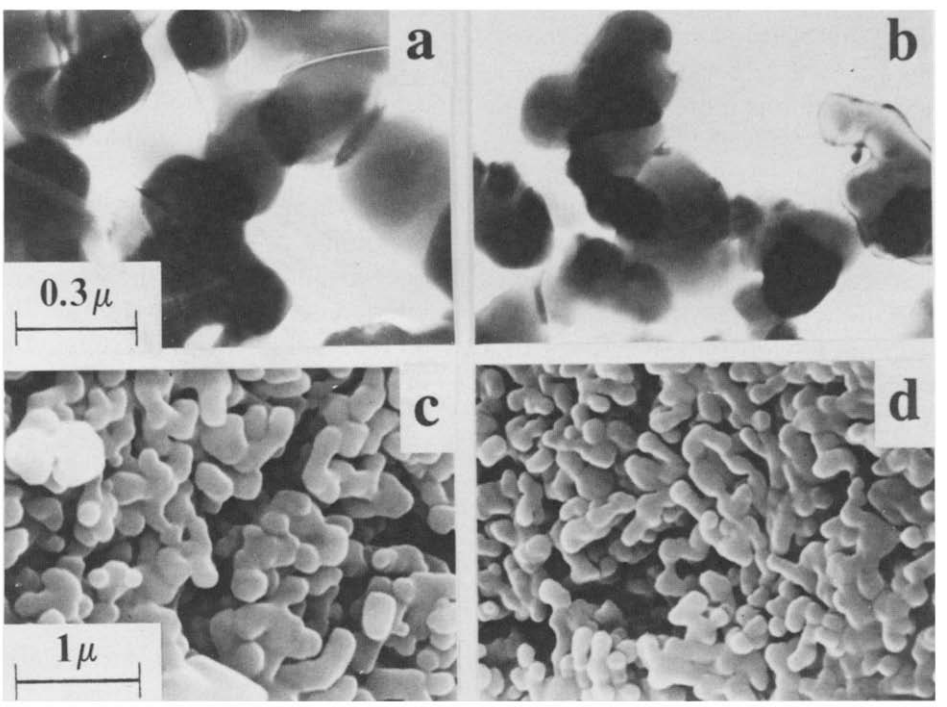

Fig. 5. Bright field TEM and SEM images of Mg-doped alumina powders. TEM of (a) 1650/6 and (b) 1650/7, and SEM of (c) 550/6 and (d) 550/7.

3.3 Microstructural analysis

TEM observations of the differently treated samples revealed that they possess similar microstructures. The grains often have elongated shapes (Fig. 5(a) and (b)) and their size varies from 50 to 500 nm depending on the amount of Mg and the thermal history. Grain thickness (determined by EELS) is around 100 nm. Consistent with the surface area measurements, as seen in Fig. 5, the size of grains in position 6 is larger than those in position 7 after the thermal treatment in Fig. 2. Experiments are in progress to examine the effect of these thermal treatments on the sintering kinetics and physical properties of alloy and ceramic coatings.

4 Conclusion

After thermal treatment at 1300°C, magnesium-doped α-alumina powders are comprised of elongated grains. The surface area of the powder decreases with increasing annealing time and increases for higher magnesium doping. A high segregation of Mg appears at the periphery of the grains leading to some precipitation of $MgAl_2O_4$. XPS also detected the presence of Na in the surface region of the samples but no Si. The extent of magnesium segregation and precipitation is higher for 1650-ppm-doped material than for 550-ppm-doped powder. For the 550-ppm-doped powder the amount of Mg increases for faster cooling rates. However, this effect is coupled with an increase of the size of the grains. Experiments are in progress to examine the influence of the cooling rate using powders of the same grain size.

Acknowledgements

The authors are indebted to J. C. Droguet and L. Du Repaire (Baikowski-Chimie, Annecy) for their collaboration and fruitful discussions and J. W. Fraser for the electron micrographs. This work has been sponsored by the Ministère de la Recherche et de la Technologie-département Matière et Matériaux, Contract No. 90 A 0220.

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