Journal of the European Ceramic Society 15 (1995) 851–858
© 1995 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/95/$9.50

0955-2219(95)00050-X

Surface Segregation and Morphology of Mg-Doped α-Alumina Powders

D. Monceau,[a] C. Petot,[a] G. Petot-Ervas,[a] J. W. Fraser,[b] M. J. Graham[b] & G. I. Sproule[b]

[a]CNRS/LPCM-UPR 211, Univ. Paris XIII, 93430 Villetaneuse, France
[b]Inst. for Microstructural Sci., N.R.C., Ottawa, Canada K1A 0R6

(Received 7 November 1994; revised version received 16 February 1995; accepted 20 February 1995)

Abstract

This work considers the effect of a thermal treatment, at a temperature equal to or higher than 1200°C, on the physical and chemical characteristics of submicron α-alumina powders, doped with 550 and 1650 ppm in weight of MgO. The powders have been characterized by TEM, SEM, BET, XPS and chemical analysis. TEM observations show that the grains have elongated and rounded forms and exhibit considerable agglomeration. The BET surface area of the powder decreases with increasing annealing time and temperature and increases with the amount of MgO. XPS analysis shows a strong segregation of Mg and this effect is more pronounced when the size of the grains increase. In some cases XPS also detected the presence of Na, Ca and Si in the surface region of the grains.

1 Introduction

The fabrication of reliable, high-performance ceramics is an important industrial challenge, and it has long been recognized that further progress will be made by an increased understanding of the role played by the microstructure and microchemistry of the starting powders. Indeed, the processing of a ceramic generally involves the manufacture of a powder, with a suitable composition and microstructure, followed by its compaction and sintering. The characteristics of powders, such as size distribution, agglomeration, purity and surface area, are of course crucial in controlling the densification and therefore the microstructure of the finished material, which may give rise to specific properties. Nevertheless, in the different processing steps leading to the sintered ceramic, surfaces and interfaces play a critical role. At the macroscopic level, a requirement for densification is that the interfacial energy of the sintered material is lower than the surface energy of the powder. However, at the microscopic level it is the rapid movement of atoms that leads to the closeness of the center of the particles and to the densification. The influence of curved surfaces on these atom fluxes has long been recognized. Local variations in surface curvature give rise to local gas partial pressure differences and this in turn leads to local chemical potential gradients which drive the atom transport. For an atom to move, however, it is necessary that point defects be in close proximity. The point-defect concentration is of course related to the surface curvature, but also depends strongly upon the surface composition and the thermodynamic equilibrium conditions (T and P_{O_2}). Various papers have been devoted to the effect of dopants on the microstructure and characteristics of powders and sintered materials.[1–9] To our knowledge, however, there is a lack of data concerning the microchemistry of the powder and therefore the effect of variations in composition at or near the powder surfaces on the early stages of sintering, controlled mainly by surface diffusion, and ultimately on the ceramic densification. This is mainly due to experimental difficulties encountered until recently in characterizing insulating materials, particular in the form of powders.

In the case of alumina, an intensification of research was observed after the discovery by Coble in 1957 concerning the beneficial effect of magnesia on the alumina sintering. Small additions of MgO allow the theoretical density to be achieved without both abnormal grain growth and pores entrapped within grains. In subsequent studies,[5–9] authors have tried to understand the role of MgO and also to determine how to extend those results to other systems. It is now unquestioned that the presence of impurities, such as CaO or SiO_2, also play an important role in the alumina sintering.[5–9] Nevertheless, difficulties arise in understanding the influence of these additives on the mobility of grain boundaries and pores. The results are generally controversial[7] and it is now recognized that an improved characterization of powders and compacts,[10] and a better knowledge of the microstructure evolution during densification, would be beneficial for further progress to be made in predicting the influence of dopants on sintering and grain growth.

This study mainly concerns the influence of the thermal treatment conditions on the nanochemistry and microstructure of α-alumina powders doped with magnesia. In previous papers the authors[11-14] have analysed kinetic demixing effects near surfaces in ceramics under a thermodynamical potential gradient or during cooling. They have also examined the segregation of additives (Y, Zr or Mg) and impurities (Si, Ca,...) to the surface of alumina powders and the effect of dopants on both the microstructure of alumina particles and the sintering kinetics.[15] More recently, XPS analysis of alumina powders doped with magnesium have allowed the determination of the extent of magnesium surface segregation as a function of the thermal treatment conditions and of the amount of dopant.[16] In this paper, we report a systematic study of cation redistributions (dopants and impurities) near the surface of alumina powders, in order to try to understand the parameters that play a critical role in the powder microchemistry.

2 Materials

The alumina powders studied have been prepared from the alum. They are doped with MgO: 550 ppm (0·07 at% Mg with respect to the cationic site number) or 1650 ppm in weight (0·21 at%). In the alum method, the dopants are added before the thermal decomposition of the starting materials (sulfates), close to 400°C. The change by a liquid phase promotes a uniform distribution of the additives in the grains because the nascent crystallites of γ-alumina have a high reactivity due to their high surface area. The next calcination occurs at temperatures higher than 1150°C. This results in the commercial α-alumina. The quality of the powder depends strongly upon this step of the process. Consequently, in the present work we have examined the influence of the conditions of this last thermal treatment on the microchemistry and microstructure of the powder. The calcination was first performed in air at 1300°C, in large silica crucibles which contain approximately 700 g of powder. Pt/Pt–Rh10% thermocouples are placed in the silica crucible, as shown in Fig.1 (positions 1–12), to monitor the thermal history of the powder. As an example, we have reported in Fig. 1 the thermal history of powders from positions 4–9. Chemical analysis, surface area measurements and SEM examinations have been performed on powders taken in the vicinity of the different thermocouples (1–12). Only samples from position 6 and 7, with the largest difference in thermal treatment conditions (Fig. 1), have been analysed by XPS and TEM. Complementary treatments have been carried out between 1200 and 1378°C, in small alumina crucibles containing approximately 7 g of powder, in order to try to separate the role played by different parameters, such as the temperature of calcination, the cooling rate and the size of the grains. Figure 2 shows the thermal history of different samples treated in alumina crucibles and which have been cooled at the furnace cooling rate, i.e. more slowly than the powders treated in the silica crucible.

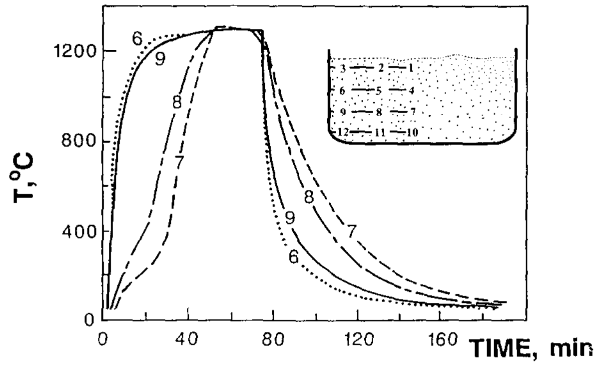

Fig. 1. Position of the thermocouples (1–12) in the silica crucible and thermal history of the powder for positions 6–9.

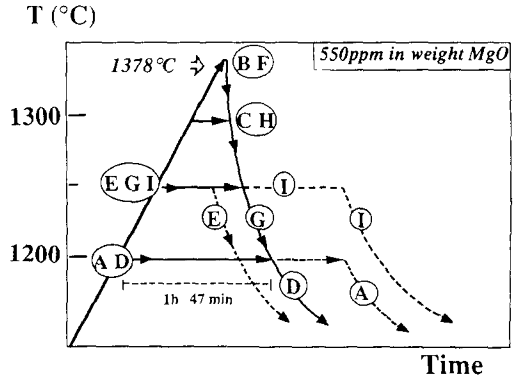

Fig. 2. Thermal history of the powder treated in air in an alumina crucible. Powders B, F, C, D, H, G and D have been maintained for the same time (1 h 47 min) at a temperature equal to or higher than 1200°C and cooled at the furnace cooling rate.

3 Results and Discussion

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

The main impurities found in the powders by inductive coupled plasma spectrometry (ICPS analysis) are: Si, Na, K, Ca and Fe. Their concentration range is reported in Table 1. Whatever the

Table 1. Concentration range of the main impurities (ppm in weight) found in different α-alumina powders (treated in alumina or silica crucibles) doped with 1650 and 550 ppm (by weight) of MgO (0·21 and 0·07 at% Mg), respectively

Amount of MgO	*Fe*	*Na*	*K*	*Si*	*Ca*
1650	3–12	11–27	8–48	13–120	3–11
550	2–9	12–34	12–33	18–143	3–6

type of treatment (alumina or silica crucible), the repartition of impurities is found to be relatively homogeneous, except for Si and Na. When the powder is treated in a silica crucible, the amount of Si increases in the powder taken near the edges of the crucible (Fig. 3), while the opposite is observed for Na. The amount of Na is generally close to 15 ppm for the powders taken near position 6 and between 22 and 34 ppm for powders near position 7. When the powder is treated in a small alumina crucible, the amount of Si is independent of position, but depends upon MgO content: 27 ppm in weight for powders doped with 550 ppm MgO and 13 ppm for those doped with 1650 ppm MgO. A comparison of the results of the amount of silicon from samples in the silica crucible (Fig. 1) with those for powders treated in the alumina crucible, allows determination of the amount of additional Si due to the contamination (Fig. 3).

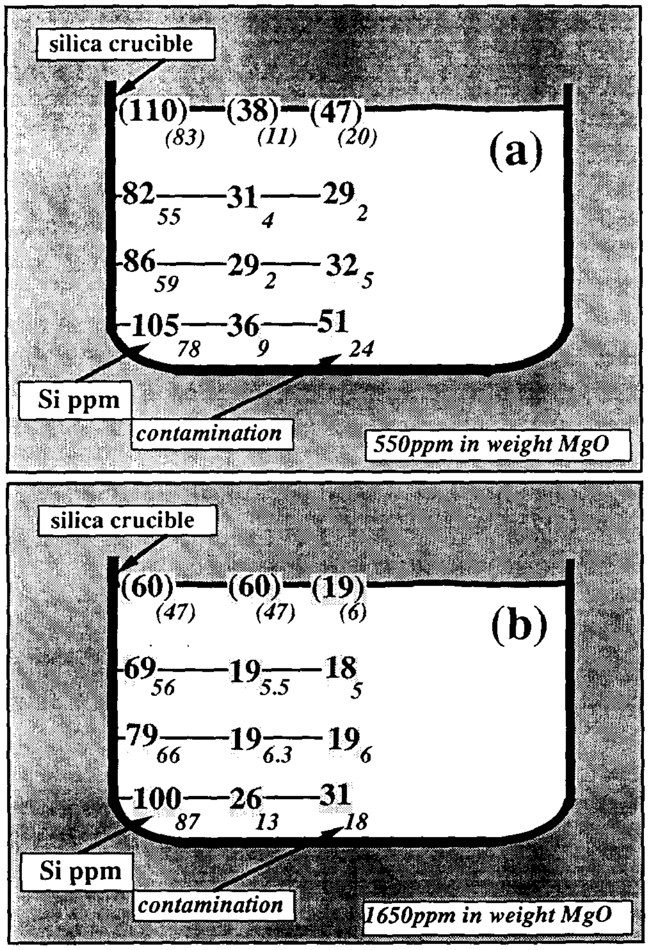

Fig. 3. Amount of silicon in the magnesium-doped alumina powder, as a function of the position in the silica crucible and silicon contamination due to the silica crucible. The surface values are given in parentheses: (a) 550 ppm MgO (average of two experiments); (b) 1650 ppm MgO (average of three experiments).

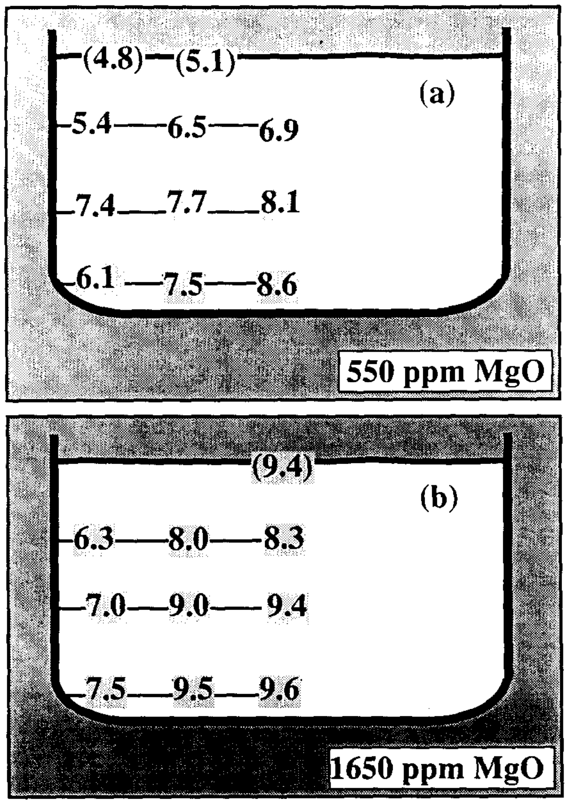

Fig. 4. BET surface area of the alumina powders doped with 550 and 1650 ppm MgO, as a function of the position in the silica crucible. Surface areas of powder near the outer surface are given in parentheses.

BET analyses have been performed only on powders treated in the silica crucible. The surface area depends upon the position of the powder in the crucible, as shown in Fig. 4. The powders from position 7 have the largest surface area, while those taken near position 6 have the lowest values. One can recall that a decrease in surface area seen by BET corresponds to an increase in the grain size. In agreement with the BET analysis, SEM (JEOL 840 microscope) and TEM (80 kV Zeiss Model 902 electron energy loss (EEL) imaging microscope) observations show that the size of the grains increases with annealing time at 1300°C and when the amount of magnesium decreases (Fig. 5). The TEM observations also show that the grains have elongated and rounded forms and that they are highly agglomerated. Their size is between 50 and 400 nm, depending on the thermal treatment. A texture has been observed at the surface of some grains which may be due to spinel precipitates (cf. XPS analysis) but complementary observations must be performed to better define this texture.

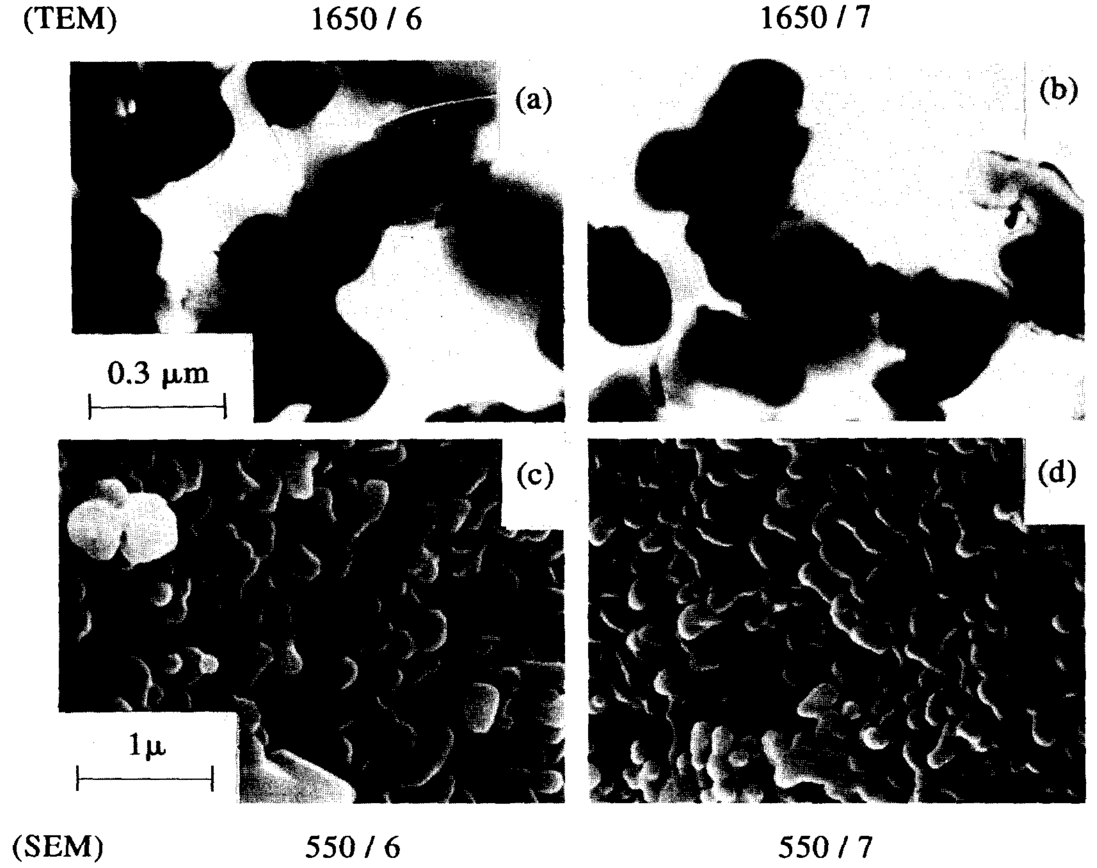

Fig. 5. Influence of the amount of magnesium and thermal treatment conditions on the size and microstructure of the alumina grains. TEM: (a) 1650 ppm MgO/position 6; (b) 1650 ppm MgO/position 7; SEM; (c) 550 ppm MgO/position 6; (d) 550 ppm MgO/position 7.

3.2 Nano-chemical analysis

XPS and EELS analysis has been performed to obtain information concerning the distribution of magnesium near the surface of the grains. Experimental details of these analyses are reported in a previous paper.[16] The trends of the two sets of results are similar. However, the error in quantifying the EELS data is large, and this method allows only an estimate of the magnesium concentration.[16] Consequently, we have concentrated on XPS analysis to examine the surface composition of the powders. Observations have been made on a perfectly flat surface of compacted powder. The results are obtained from a surface area of 0·8 × 0·8 mm. It may be pointed out that it is not possible to distinguish by XPS the Mg segregated in alumina grains from the Mg present in a second phase. Therefore, according to the amount of magnesium we have found, $MgAl_2O_4$ has been used as a standard. By analysing the magnesium lines (Mg_{1s}, Mg_{2s} and Mg_{2p}) it has been possible to obtain information on the total magnesium concentration near the surface of the grains. The escape depth of the Mg_{1s} electrons is about 0·5 nm (kinetic energy = 187 eV), while for the Mg_{2s} and Mg_{2p} electrons (with kinetic energies of 1387 and 1437 eV, respectively) it is about 2·0 nm. The Mg_{1s} signal allows us to determine a mean concentration of magnesium over the first 2 or 3 monolayers at the surface of the grains, while the Mg_{2s} and Mg_{2p} signals give a mean concentration over a depth of about 2·0 nm. The error in quantification is quite large because of the morphology of the samples and can be estimated to be 0·3–0·4 at%. Nevertheless, it should be noted that the reproducibility of the results is generally better than 0·1 at%. Furthermore, the Mg_{2s} peak gives more accurate data than the Mg_{2p} peak, because of peak overlaps.

3.2.1 Powders treated in silica crucibles

The XPS results obtained with the powders treated in the silica crucible (positions 6 and 7) are given in Table 2. They show a high magnesium concentration over the first two or three monolayers (Mg_{1s}) at the surface of the grains and this

Table 2. Amount of magnesium (at%) determined by XPS at the near surface of the alumina powder treated in a silica crucible. These results represent the mean of 6 different experiments. The reproducibility of the data is better than 0·1 at%

Analysis depth *Sample*	*0·5 nm* *(Mg_{1s})*	*2 nm* *(Mg_{2s})*	*2 nm* *(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

enrichment is related to both the amount of magnesium in the powder and to its position in the crucible. Less surface segregation is observed in the alumina powder doped with 550 ppm MgO (0·07 at% Mg with respect to the cationic site number), and the powder from position 7 appears to have less segregation than the powder from position 6. The magnesium enrichment factor (atomic surface concentration in Mg divided by the average atomic concentration in Mg) over the first 2 or 3 monolayers calculated from these results is about 30 for the powder doped with 0·21 at% Mg (1650 ppm) and 80 for the powder containing 0·07 at% Mg (550 ppm). It is likely that precipitates of $MgAl_2O_4$ are also present at the surface of the grains, according to the limit of solubility of Mg in alumina.[17]

Figure 6 shows the mean concentration of magnesium in a depth of 2·0 nm (Mg_{2s}) as a function of the mean concentration in the first 2 or 3 monolayers (Mg_{1s}). The data exhibit a straight line whose gradient is 1/4. This value corresponds to the ratio of the analysis depth, and therefore suggests that the magnesium segregated mainly on a depth lower than or equal to 0·5 nm, leading to a Mg-enriched near-surface layer including the precipitation of the spinel phase. Figure 7 shows the different information that can be deduced from Mg_{2s}/Mg_{1s} relationships, according to the position of the experimental results in the graph. When the magnesium segregation increases, a saturation effect occurs near the surface (depth equal to 0·5 nm) and this leads to an increase in the segregation depth. The experimental results deviate then from the straight line 1, whose gradient is equal to 1/4 (Fig. 7). In agreement with the results reported in Fig. 6 and Table 2, the saturation effect observed at a depth of 0·5 nm is of course more likely when both the magnesium concentration in the powder and the size of the particles increase.

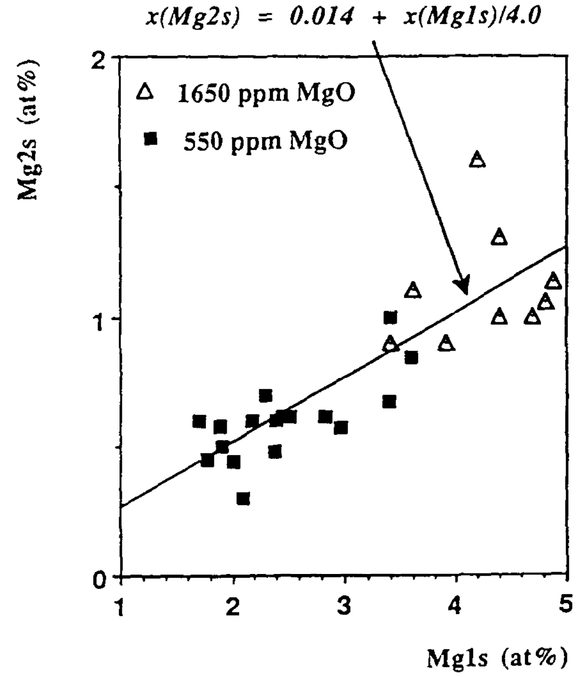

Fig. 6. Concentration of magnesium in a depth of 2·0 nm (Mg_{2s}) as a function of the concentration in a depth of 0·5 nm (Mg_{1s}).

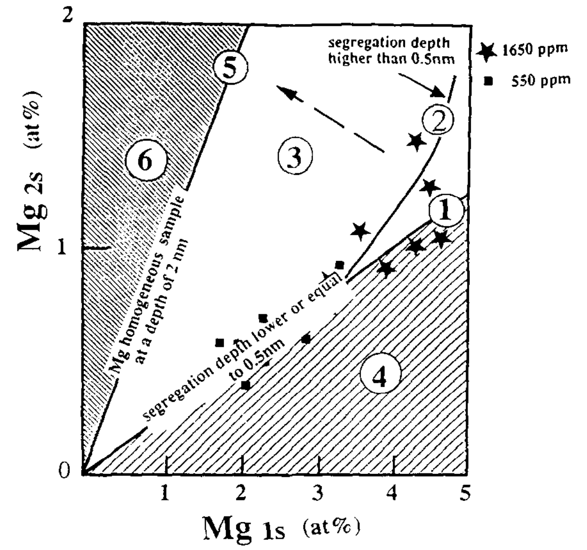

Fig. 7. Information that can be obtained from a representation of the concentration of magnesium in a depth of 2 nm (Mg_{2s}) as a function of the concentration in a depth of 0·5 nm (Mg_{1s}). When the Mg segregation increases, a saturation effect occurs at a depth of 0·5 nm (line 1) and the segregation depth increases (line 2 or in a general way area 3). When the experimental results are in area 6, the concentration of Mg decreases near the surface. The sample is homogeneous on a depth of 2 nm when the experimental results are on line 5.

The previous results (Fig. 6) are in agreement with the estimate of the repartition of magnesium in the grains (Fig. 8). Indeed, taking into account the amount of magnesium in the powder and the XPS results, it has been possible to determine the mean concentration of magnesium at a depth of 0·5 and 2 nm, respectively, in the particles assumed to be spherical. Their size has been estimated from

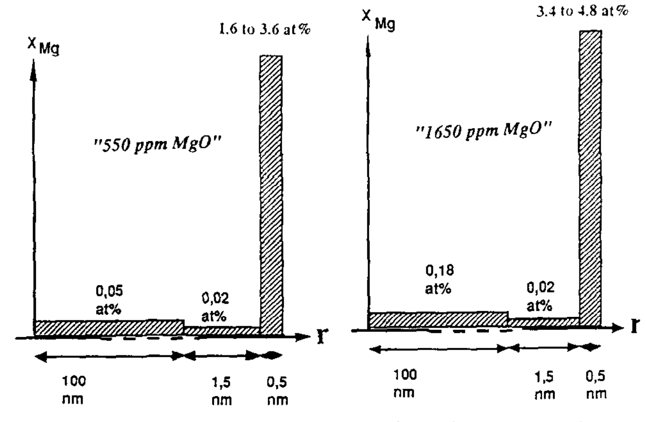

Fig. 8. Distribution profile of magnesium through an alumina grain treated at 1300°C, in a silica crucible for both 550 and 1650 ppm MgO-doped powders. This estimation has been performed assuming the grains to be spherical and taking into account the mean concentration of Mg in the powder (chemical analysis) and the XPS results at 0·5 and 2 nm.

the BET surface-area results. The results reported in Fig. 8 represent schematically the distribution of Mg across the grain. A lowering of the magnesium concentration is observed at a depth higher than 0·5 nm. This observation is consistent with a Mg kinetic demixing during the cooling of the powder. Nevertheless, complementary experiments must be performed to check the influence of this parameter on the Mg redistribution in the alumina grains.

XPS also detected the presence of Na, but the other impurities (Si, Ca, Fe and K) were not found in these powders. It may be noted that the amount of Na in powders from position 6 (0·6 at%) is lower than in powders from position 7 (1·4 at%), in agreement with the chemical analysis reported in the last section.

3.2.2 Powders treated in alumina crucibles

As shown in Fig. 2, samples B, C, D, F, G and H have been maintained for the same time (1 h 47 min) at temperatures equal to or higher than 1200°C, in order that the size of the grains be of the same order of magnitude after the different thermal treatments. They have then been cooled at the furnace cooling rate, i.e. more slowly than the powders treated in the silica crucible. The XPS results reported in Table 3 seem to show a decrease in the magnesium segregation when the maximum temperature of annealing decreases. However, a small increase in the size of the grains seems to occur when the annealing temperature increases (Table 3) and complementary experiments must be performed to substantiate this conclusion, as we shall see in the next section. Concerning the effect of the annealing time, the results at 1250°C are consistent with those obtained in the silica crucible at 1300°C (positions 6 and 7). The segregation of Mg increases when the annealing time increases and the TEM observations show that this effect is accompanied by an increase in the size of the grains.

3.3 Effect of grain size and cooling rate

According to the results reported in Figs 4 and 5 and in Table 3, the size of the grains is strongly related to the thermal history of the powder. Consequently, it was important to check the influence of this parameter on the segregation phenomena. Figure 9 reports the mean concentration of magnesium in the first 2 or 3 monolayers (Mg_{1s}), as a function of the size of the grains, assumed to be spherical. The size has been estimated from the BET surface area measurements. In a few cases this has also been measured on the SEM images. Whatever the amount of magnesium in the powder, the segregation increases with the size of the grains. This effect is so important that it overshadows the influence of the other parameters. It is thus difficult to draw definite conclusions with regard to the influence of annealing temperature and cooling rate on magnesium surface segregation. However, it seems that a decrease in cooling rate favors the segregation of silicon. Indeed, this impurity has been detected by XPS only in powders treated in alumina crucibles, which have a lower amount of silicon (around 13 and 26 ppm in the powders doped with 1650 and 550 ppm of MgO, respectively), than those treated in a silica

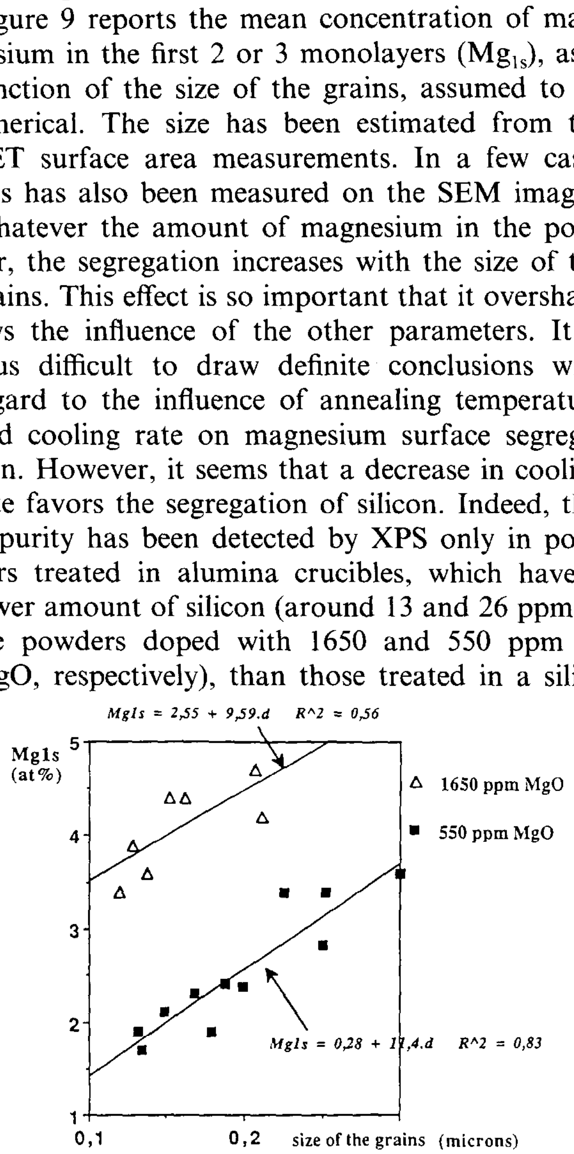

Fig. 9. Influence of the amount of magnesium and of the size of the grains on the magnesium concentration in the first 2 or 3 monolayers (depth 0·5 nm) at the surface of the grains.

Table 3. Amount of magnesium, silicon and sodium (at%) determined by XPS at the near surface of the alumina powder treated in an alumina crucible and cooled at the furnace cooling rate. (Concentration of Si over a depth of 2·4 nm; concentration of Na over a depth of 1·0 nm)

Experiment	*Temperature (°C)*	*Time*	*Grain size (SEM)*	*XPS Mg_{1s} (at%)*	*XPS $Mg_{2s,2p}$ (at%)*	*XPS Na_{1s} (at%)*	*XPS Si_{2s} (at%)*
A1	1200		0·3 μm	3·57	0·85–1·13	2·30	–
A2				3·60	0·82–0·67	2·19	0·56
D	1200	1 h 47 min	0·18 μm	1·89	0·58–0·58	1·06	0·25
E	1250	1 h		2·00	0·44–0·56	0·65	–
G	1250	1 h 22 min		2·18	0·60–0·69		
I	1250	2 h 30 min		3·39	0·67–0·53	1·53	0·20
C	1300	56 min	0·2 μm	2·38	0·48–0·60	0·52	–
H	1300	56 min		2·52	0·61–0·57	1·39	–
B	1378	1 s	0·25 μm	2·83	0·61–0·52	1·01	0·23
F	1378	1 s		2·97	0·57–0·64	0·88	–

crucible (Fig. 1) but which have been cooled more slowly (furnace rate).

It may be pointed out that the results reported in Fig. 9 are consistent with the estimation of the repartition of Mg through the grain, assumed to be spherical (Fig. 8). Indeed, if we take into account that practically all the dopant has segregated at the near surface of the grain, i.e. over a thickness equal to 'e' (0·5 nm, for example), with $e << R_{\text{grain}}$, it is possible to write, for a given amount of dopant: $V_{\text{total}}/V_{\text{grain}})4\ \pi\ R^2 e\ C_{\text{surf}}$ = constant (where V_{total} is the total volume of the powder, C_{surf} the near-surface concentration of the dopant in a thickness 'e' and R is the grain radius). One obtains from this expression:

$$C_{1\text{surf}}/R_1 = C_{2\text{surf}}/R_2 = \text{constant}$$

Then one can verify that the surface concentration is proportional to the grain radius (R_{grain}).

4 Conclusions

This study has allowed us to illustrate the influence of the thermal treatment conditions on the microchemistry and microstructure of alumina powders doped with 550 and 1650 ppm by weight of MgO. SEM and TEM observations, as well as surface-area measurements, have allowed us to show that the size of the grains is strongly related to the amount of magnesium and to the thermal treatment conditions (temperature and annealing time). Quantitative XPS analysis shows that Mg, Na and Si are segregated at the near surface of the grains. In the case of Mg, this is likely to lead to the formation of $MgAl_2O_4$ precipitates. Furthermore, the results obtained show clearly that the magnesium surface enrichment increases with the size of the grains. However, it is difficult to draw conclusions regarding the influence of the cooling rate, as well as the effect of the temperature and annealing time. These effects are overshadowed by the effect of grain size. Complementary experiments must be performed on powders of the same grain size, in order to eliminate the important influence of this parameter. For Si and Na, their surface concentration seems to increase when the cooling rate decreases.

Finally, this study shows that it is possible to control the concentration of dopants or impurities at the near surface of the grains by changing only the thermal treatment conditions of the powder. Of course, such segregation phenomena, which can lead to the precipitation of a second phase at the near surface of the grains, confer specific properties to the powder. Nevertheless, complementary experiments must be performed in order to obtain a better understanding of the role played by parameters such as the cooling rate and the surrounding atmosphere.

Acknowledgements

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

References

1. Brook, R. J., The Materials science of ceramic interfaces. In *Surfaces and Interfaces in Ceramic Materials*, eds. L. C. Dufour, C. Monty & G. Petot-Ervas. Kluwer Acad. Press, 1989, E 173, pp. 23–37.
2. Clarke, D., Intergranular phases in polycrystalline ceramics. In *Surfaces and Interfaces in Ceramic Materials*, eds. L. C. Dufour, C. Monty & G. Petot-Ervas. Kluwer Acad. Press, 1989, E 173, pp. 57–79.
3. Carter, C. B., Structure of interfaces in ceramic materials. In *Surfaces and Interfaces in Ceramic Materials*, eds. L. C. Dufour, C. Monty & G. Petot-Ervas. Kluwer Acad. Press, 1989, E 173, pp. 29–53.
4. Kingery, W. D., Segregation phenomena at surfaces and at grain boundaries in oxides and carbides. *Solid State Ionics*, **12** (1984) 299–308.
5. Handwerker, C. A., Cannon, R. M. & French, R. H., A retrospective. *J. Am. Ceram. Soc.*, **77**(2) (1994) 293–7.
6. Badley, R. D. & Johnson, D. L., Effect of magnesia on grain growth in alumina, structure and properties of MgO and Al_2O_3 ceramics. *Adv. in Ceram.*, **10** (1984) 666–78.
7. Bennison, S. J. & Harmer, M. P., A history of the role of MgO in the sintering of α-alumina, sintering of advanced ceramics. *Ceram. Trans.*, **7** (1990) 13–49.
8. Handwerker, C. A., Morris, P. A. & Coble, R. L., Effects of chemical inhomogeneities on grain growth and microstructure in Al_2O_3. *J. Am. Ceram. Soc.*, **72**(1) (1989) 130–6.
9. Bae, S. I. & Baik, S., Critical concentration of MgO for the prevention of abnormal grain growth in alumina. *J. Am. Ceram. Soc.*, **77**(10) (1994) 2499–504.
10. Coble, R. L., Song, H., Brook, R. J., Handwerker, C. A. & Dynys, J. M., Sintering and grain growth in alumina and magnesia, structure and properties of MgO and Al_2O_3 ceramics. In *Advances in Ceramics*, Vol. 10, ed. W. D. Kingery. The American Ceramic Society, 1984, pp. 839–52.
11. Petot-Ervas, G. & Petot, C., Surface segregation in ceramic materials during cooling or under a temperature gradient. *J. Eur. Ceram.*, **6** (1990) 323–30.
12. Monceau, D., Petot, C. & Petot-Ervas, G., Kinetic demixing profile calculations in oxide solid solutions under a chemical potential gradient. *Solid State Ionics*, **45** (1991) 231–7.
13. Monceau, D., Petot, C. & Petot-Ervas, G., Kinetic demixing profile calculation under a temperature gradient in multi-component oxides. *J. Eur. Ceram.*, **9** (1992) 193–204.
14. Monceau, D., Modélisation des phénomènes de 'ségrégation dynamique' dans les céramiques — Conséquences sur l' élaboration des poudres et des monocristaux d'alumine-α dopée. Thesis, University Paris XIII (1992).

15. Petot-Ervas, G., Lartigue, S., Severac, C., Barj, M. & Petot, C., Surface impurity segregation in submicronic alumina. In *Structural Ceramics, Proceeding, Microstructural and Properties*, eds J. J. Bentzen & J. B. Sorensen. Risø National Laboratory, Roskilde, Denmark, 1990, pp. 459–63.
16. Monceau, D., Petot-Ervas, G., Petot, C., Fraser, J. W., Graham, M. J. & Sproule, G. I., Influence of the thermal treatment on the microstructure and microchemistry of α-alumina powders doped with magnesium, *J. Eur. Ceram. Soc.*, **12** (1993) 337–41.
17. Roy, S. K. & Coble, R. L., Solubilities of magnesia, titania and magnesium titanate in aluminum oxide. *J. Am. Ceram. Soc.*, **51** (1968) 1–6.