ELSEVIER

Ceramics International 25 (1999) 567–575

CERAMICS
INTERNATIONAL

Microstructural and sintering behavior of magnesia doped, seeded, different boehmite derived alumina

L. Radonjic*, L. Nikolic

Department of Material Science, Faculty of Technology, University of Novi Sad, Bul. Cora Lazara 1, 2100 Novi Sad, Yugoslavia

Received 23 March 1998; accepted 8 October 1998

Abstract

The effect of the original boehmite structure, seeding and magnesia doping on the microstructural development and sintering behaviour of alumina was investigated. Magnesia doping has a very important role in the sintering of the sol–gel derived alumina, but it is not the same as in the classical processing of alumina. It decreases the grain size, increases the rate of sintering and changes the temperatures of phase transformation of transitional aluminas. Seeding plays a beneficial role in processing of sol–gel alumina, as was already known. The origin of the boehmite plays an important role in all the phases of sol–gel processing of alumina. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

Keywords: Sol–gel alumina; Magnesia doping; Phase transformations; Seeding

1. Introduction

It is well known [1–3] that the addition of a small amount of magnesia to classically sintered alumina, suppresses abnormal (discontinuous) grain growth, resulting in nearly theoretical density. Even the mechanism by which magnesia suppresses abnormal grain growth (AGG), in alumina is not completely understood (there is still controversy in interpretation), it is widely agreed that a small amount of magnesia doping enhanced the densification rate of alumina, in general accelerated the sintering rate and the grain growth [4–8].

However, in sol–gel processed alumina, due to polymorphic transformations in the course of heating (boehmite $\rightarrow\gamma\rightarrow\sigma\rightarrow\theta\rightarrow\alpha$) the densification process is much more complex and achieving the theoretical density is almost impossible due to development of the specific microstructure. Isostructural seeding of alumina gels, after Messing et al. [9–12] provides the method for controlling the microstructural development and subsequent densification behaviour. Besides, seeding the alumina gel reduces the crystallization temperature for the stable alpha phase, accelerates the transformation kinetics and reduces the sintering temperatures.

Seeding the alumina gel, even if it is beneficial, is not enough for achieving theoretical density during a low temperature sintering [13–15]. The effect of magnesia addition in the sol–gel processing of alumina is rather difficult to clear up since very complex transformations take place in the processing. Very little information on this subject is currently available in the literature. Our previous study [16] showed the beneficial effect of magnesia addition on sintering sol–gel derived alumina, even if some researchers did not find it so [14]. Addition of magnesia to seeded boehmite sol [16] further lowers the transformation temperature to alpha alumina and enhances the densification rate to some extent.

In order to evaluate the potential synergetic effect of seeding and magnesia addition on the microstructural development and densification behaviour both seeded and unseeded boehmite sols were used in this study. Two types of boehmite were also investigated in order to obtain additional information about the boehmite structure effect on the boehmite transformation and sintering during heating. The objective of the present study was to present the results of systematic investigation of the degree of importance of 3 parameters on the sintering and the microstructural evolution of sol–gel derived alumina: seeding, magnesia doping and the type of original boehmite. The results were compared to the previous study [16], in order to elucidate the problem of sol–gel alumina densification.

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* Corresponding author. Tel.: +381-21-54988; fax: +381-21-611-102; e-mail: radonjic@uns.ns.ac.yu

PII: S0272-8842(98)00067-4

2. Experimental procedures

Two kinds of boehmite powders (Disperal-C and Disperal THIX-B, Condea Chem. Co., Hamburg, Germany) were dispersed in deionized water to obtain 20 wt% boehmite sols. In Table 1 are given some properties of the boehmite B, C and A powders (boehmite denoted by A is Advanced Ceramics product, type H-3500, used in the previous study [16]). The pH value of sols was about 2.5 due to nitric acid addition as a peptization agent. The dispersion was periodically sonicated in order to break up agglomerates. The seed dispersion of high purity alpha–alumina (Ceralox TPA 14, Condea Chem. Co.) in water, about the same pH as boehmite dispersion, was added to the boehmite sol while stirring to obtain a 2 and 4 wt% concentration of seeds of alpha alumina on a weight basis. The seeded sols were gelled by slight heating until they were too viscous to stir. Just before the gelling, a water solution of $Mg(NO_3)_2$, was added to seeded sols (Mg:Al atomic ratio was: 0, 300, 3000 and 6000 ppm) and mixed ultrasonically. Samples are noted by letter B or C depending on the boehmite type and index, 0, 2 or 4 meaning: unseeded, seeded with 2 and 4 wt%, respectively. The number ahead of letter B or C, after multiplying by factor 10^2, denotes the concentration of magnesia doped in ppm (for example $3B_2$ and $6OC_4$ means: 300 and 6000 ppm of magnesia doped in boehmite the B and C type, respectively, seeded by 2 and 4wt% of alpha alumina).

After gelling, the gels were dried at room temperature, in air, for 2 weeks and then at 110°C to achieve the constant weight. Dried samples were heated, at the rate of 2°C/min, up to 450°C and held for 2 h in order for boehmite to be transformed to γalumina. After that, the samples were heated up to 1050°C and held for 1 h. This temperature was used as a temperature of α-alumina formation (it was the lowest temperature of α-alumina formation in our experiments, determined by differential thermal analysis). After the phase transformation to α-alumina was completed, the samples were heated (very quickly) to 1200°C for sintering experiments. Only a part of the samples was isothermally sintered at 1200°C for 30, 60, 120, 180 and 300 min.

Table 1
Some properties of the boehmite powders

Type of Boehmite	A	B	C
Properties	Adv.Cer. H3500	Condea Disperal (THIX)	Condea Disperal
Content of Al_2O_3 (%)	85	73.6	76.6
Specific surface (m^2/g)	250÷300	180	160
Agglomerate size (μm)	20÷40	30	50
Crystallite size (nm)	10÷40	10÷20	20÷40
Purity (%)	99.99	99.90	99.95

The bulk density was measured by Archimedes' method, with water as the immersion media. The samples with a high porosity were coated with wax before the density was measured. Differential thermal analysis (DTA) (30 to 1100°C range) was performed with a Dupont de Nemours Instrument. DTA heating curves of some samples were used to observe the thermal behaviour of samples during heating up to 1100°C. Identification of phases formed during heating, and the influence of magnesia addition on the new phase formation was examined by XRD. The X-ray crystallite size was determined using the Scherrer equation:

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where D is the crystallite size, λ is the wave length of the X-rays, B is the half height peak width in radian and θ is the angle of diffraction. Infrared spectra (IR) were recorded on a 783 Perkin–Elmer spectrometer using KBr pellets. The microstructural development was observed by SEM on a gold coated fractured surface, using a Jeol-35 instrument.

3. Results and discussion

3.1. *Effect of magnesia and seeds addition on gellation and α-alumina formation*

The original boehmite powders B and C used in all experiments have different local structures, shown in Figs. 1 and 2. Fig. 1 showed XRD results for A, B and C original boehmite powders. Diffraction diagrams differ in both: the position of the strongest boehmite peak (002) and its broadening. Shifting of the strongest peak (002) from $d = 0.605$ nm for C-boehmite to $d = 0.63$ nm for B-boehmite can be explained by the presence of excess water in the interlayer of B-boehmite structure. Distortion of the lattice occurs due to excess water. Besides, the grain size of B-boehmite (~10 nm) is smaller than the crystal grain size of the C-boehmite (35 nm) as indicated by the broadening of the strongest peak (002). Difference in the local structure of B- and C-powders is confirmed by the difference observed in their IR spectra (Fig. 2). Both stretching and bending vibrations of the OH-group shift towards higher frequencies for C-boehmite. Symmetric band at 1060 cm^{-1} belongs to the bending vibration of the OH group of B-boehmite, shifts to an asymmetric resolved band at 1070 cm^{-1} for C-boehmite and the stretching vibrations of the OH-groups at 3070 and 3270 for B-boehmite shift to 3080 and 3288 cm^{-1} for C-boehmite. Significant differences are observed in the spectrum of AlO_6 octahedral vibrations (both stretching and bending) of B- and C-powders. These differences indicate that the strength of the

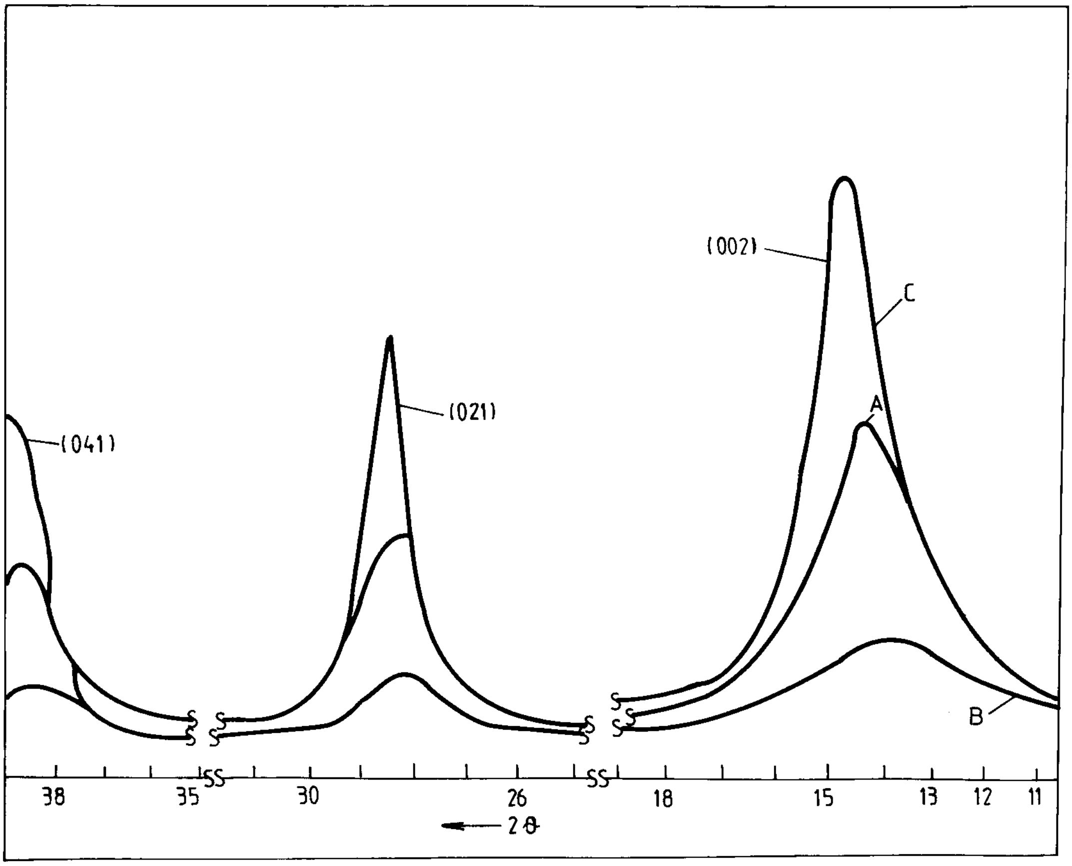

Fig. 1. X-ray diffraction patterns of boehmite powders: A, B, C.

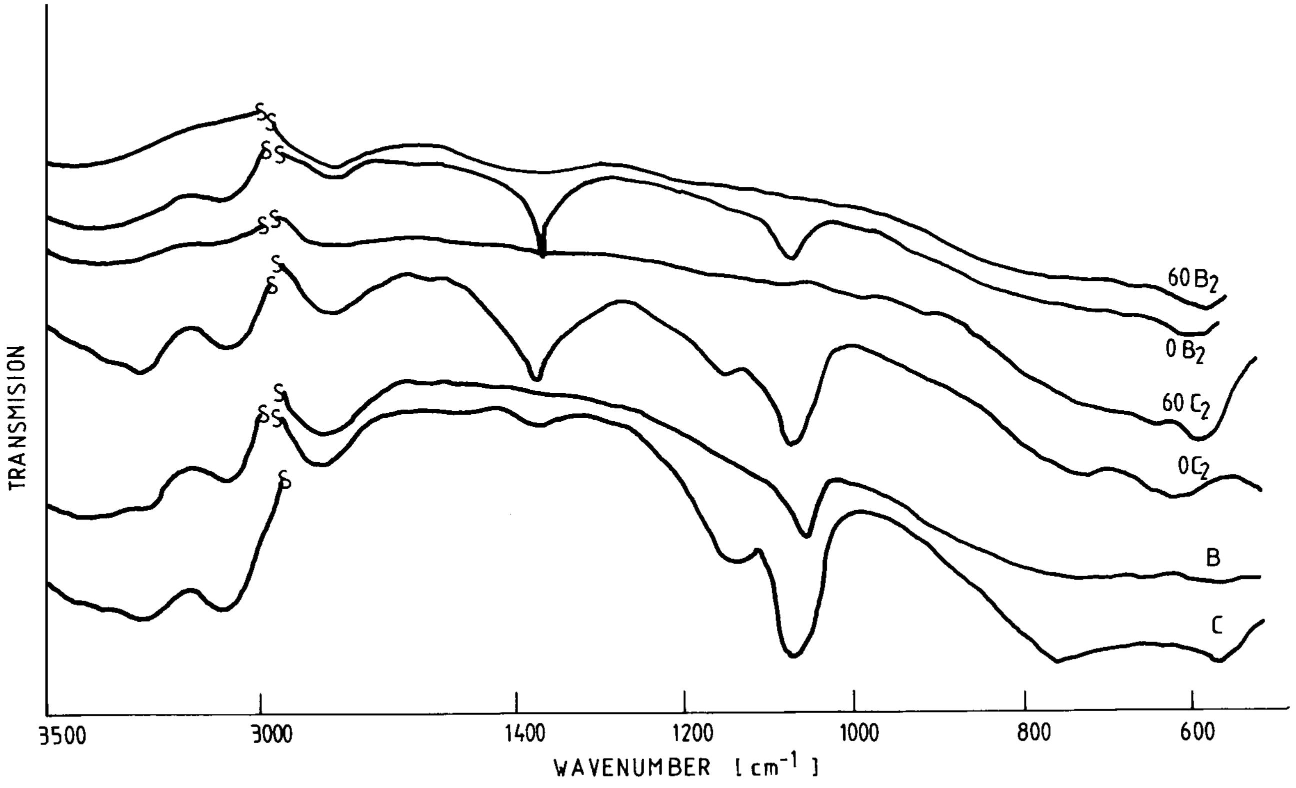

Fig. 2. IR spectra of original boehmite powders and seeded and magnesia doped gels.

Al–O–Al and Al–OH bonds are different. Unfortunately, we cannot exactly assign all types of vibrations the AlO_6 octahedral (range 550–800 cm^{-1}). However, the observed differences in the IR spectra suggest that C-boehmite has essentially different bonding to B-boehmite.

After gellation of B and C-boehmites the main changes in their XRD diagrams (Fig. 3) is only a slight broadening of the strongest peak (002) (grain size decreases to 20 nm or increased local structure disorder in the process of gellation) for C-gels (pH of the sols was about 2.5 due to acidic peptization). However, acidic peptization does not change the B-gels grain size. This result is confirmed by their IR spectra (Fig. 2).

Seeding of B and C-boehmite gels does not considerably change the mechanism of gelling and the gels properties, but addition of magnesia does change the local boehmite structure (Figs. 2 and 3) and gelling volume–gel density (Table 2 gives only a part of the results of the density measurement). Magnesia cations in sols readily peptize boehmite [17]. The mechanism of the boehmite peptization by the salts apparently differs from that by acid [17]. Diffraction diagrams (Fig. 3) for B and C seeded and doped gels, exhibit broadening of the strongest peak (002) with increasing magnesia addition and shifts the diffraction line (002) from 0.632 to 0.606 nm for B-gels. Intensive broadening of the diffraction peaks (002) with magnesia addition could be

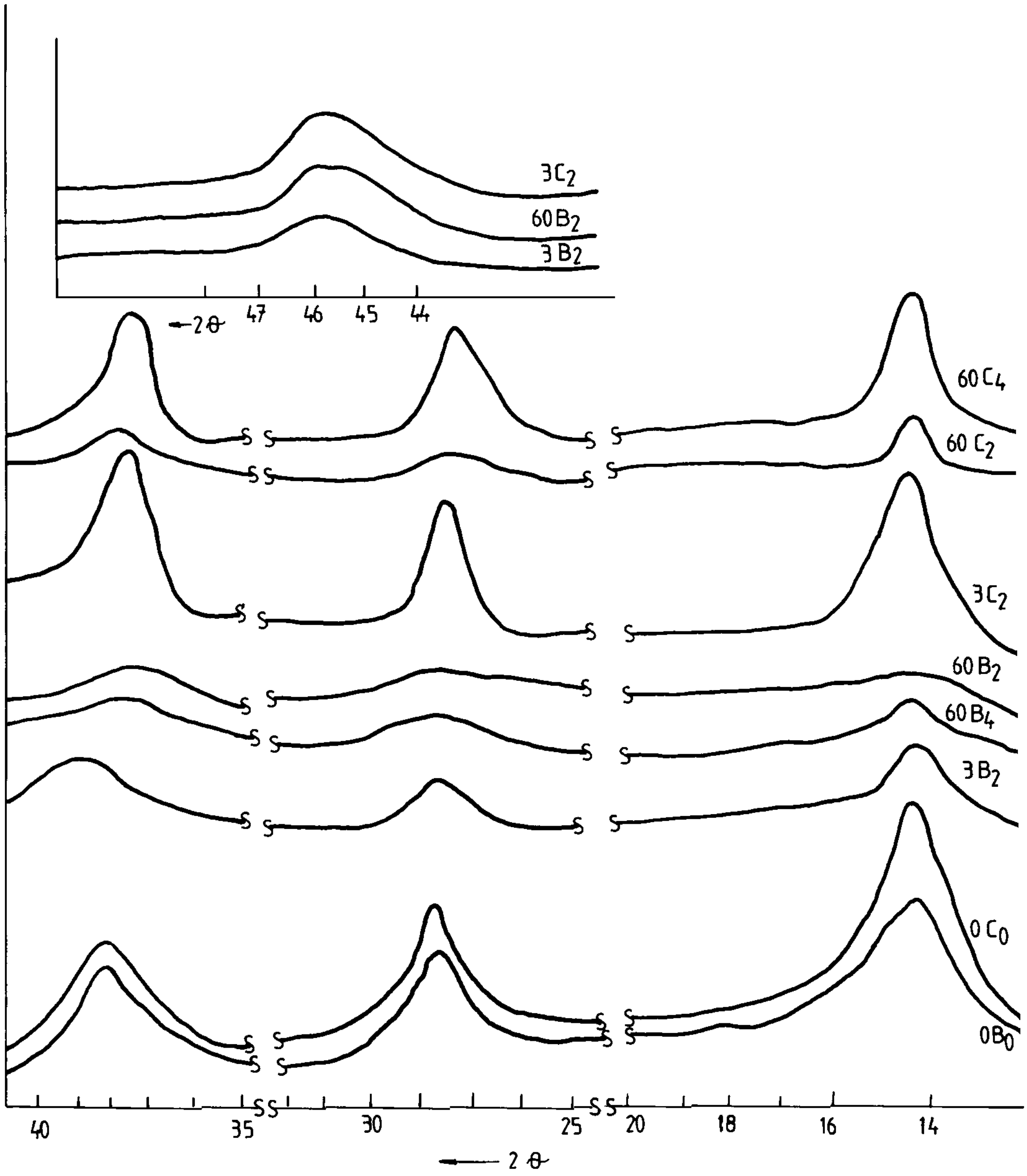

Fig. 3. X-ray diffraction patterns of the unseeded, seeded and magnesia doped gels B and C (in the left corner are given a few patterns of γ-alumina formed at 450°C).

attributed to the grain size decrease or increase of local disorder of the boehmite structure. The shifting of the strongest peak (002) from 0.632 to 0.606 nm for B-gel is due to the decrease of the interlayer distance between double layers of the AlO_6 octahedral. The observed shifting in the position of the strongest peak in the B-gels indicates that the gels B formation is accompanied by the removal of water molecules from the interlayer space of the B-gels. From these facts one can conclude that the appearance of the electronic charge (from magnesia cations) on the boehmite colloidal particles is accompanied by the redistribution of the electronic density of the boehmite bond. This causes excess positive charge at the hydrogen atoms of the boehmite hydrogen bonds. The hydrogen bonds are strengthened (their length becomes shorter and the distance between the double layers of the AlO_6 octahedral decreases). This effect was confirmed by the changes in their IR spectra (Fig. 2). Both stretching and bending vibrations of the OH group shift towards higher frequencies such that the position of the IR bands for B-gels is very close to the bands for C-gels. These changes in the local structure of the B-boehmite gel after magnesia addition but not in the C-gels could be understood by the original differences in the structural features of the B- and C-boehmite powders (the interlayer distance in the C-powder was already short, 0.605 nm and bond rather strong and C-gels were much stronger than B ones). These structural changes in the B-gels by addition of magnesia is not reflected in the density change (Table 2). Addition of magnesia to B- and C-gels has stronger influence on the B-gels than on the C one, probably because of the original differences in the local structure of the boehmite powders.

Table 2
Densities of alumina gels, γ- and α-aluminas

Samples/Densities (g/cm^3)	$0B_2$	$3B_2$	$60B_2$	$0B_4$	$3B_4$	$60B_4$	$0C_2$	$3C_2$	$60C_2$	$0C_4$	$3C_4$	$60C_4$
Gels	1.62	1.58	1.50	1.68	1.66	1.60	1.95	1.90	1.86	1.96	1.92	1.89
γ-Al_2O_3	1.72	1.60	1.55	–	1.68	1.66	–	–	1.99	1.98	1.96	–
α-Al_2O_3	2.80	2.78	2.70	2.88	2.80	2.78	2.99	2.96	2.90	3.05	3.0	2.95

Densities of unseeded, undoped, gels: $0A_0$—1.98; $0B_0$—1.92 and $0C_0$ 2.08 g/cm^3 and A—seeded is 1.92 and A doped, seeded is 1.88 g/cm^3.

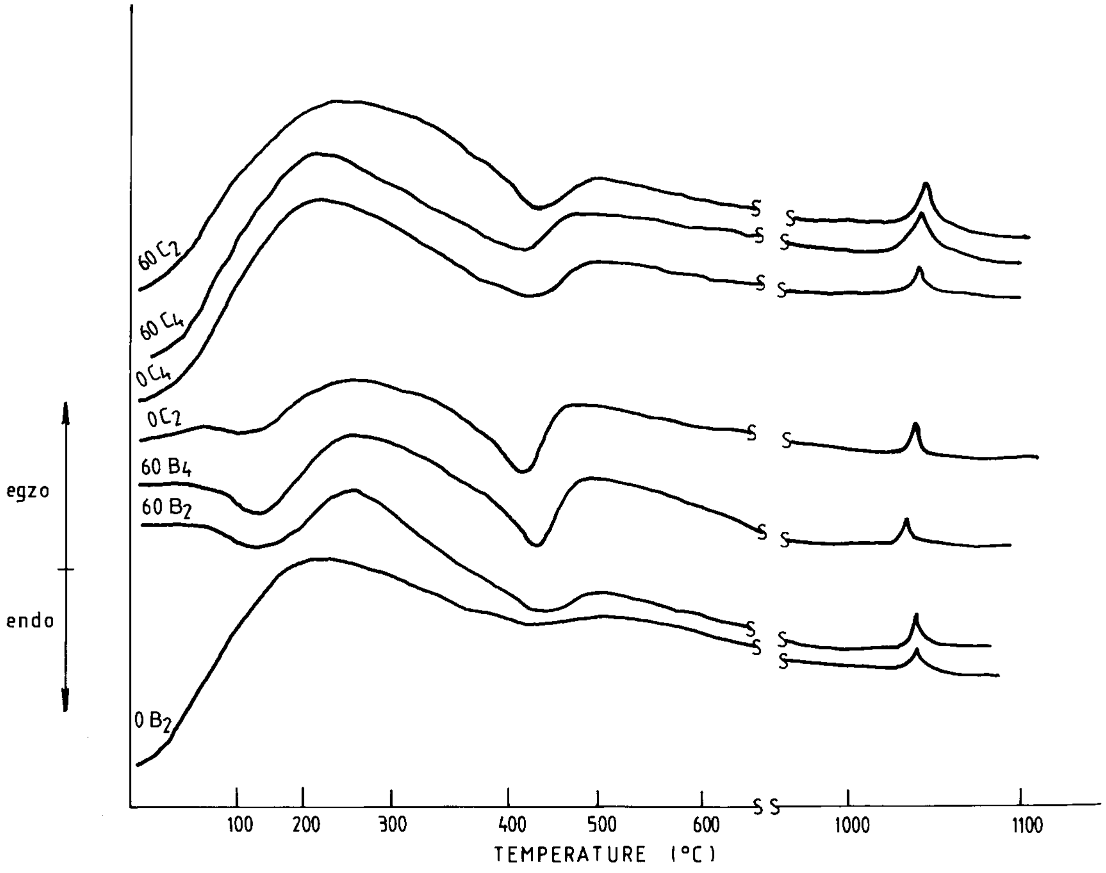

Fig. 4. DTA heating curves of seeded, undoped and magnesia doped boehmite gels.

After heating of the B- and C-gels, seeded and magnesia doped, up to 450°C (in order to form γ-alumina, with defect spinel structure, after boehmite transformations). XRD results (Fig. 3) did not show remarkable differences between different samples (only a small part of the XRD results are shown in the left-hand corner of Fig. 3). It was expected that magnesia addition would change the temperature of the phase transformation of boehmite to γ-alumina [18]. DTA results presented in Fig. 4 did not show any shifting of the transformation temperature. DTA diagrams differ only in the depth of the peak at which γ-alumina is formed from undoped C and B-gels. After magnesia addition the peak of γ-alumina formation, at 440°C, broadens for both B- and C-gels. The density change after addition of magnesia (Table 2) is negligible after heating up to 500°C.

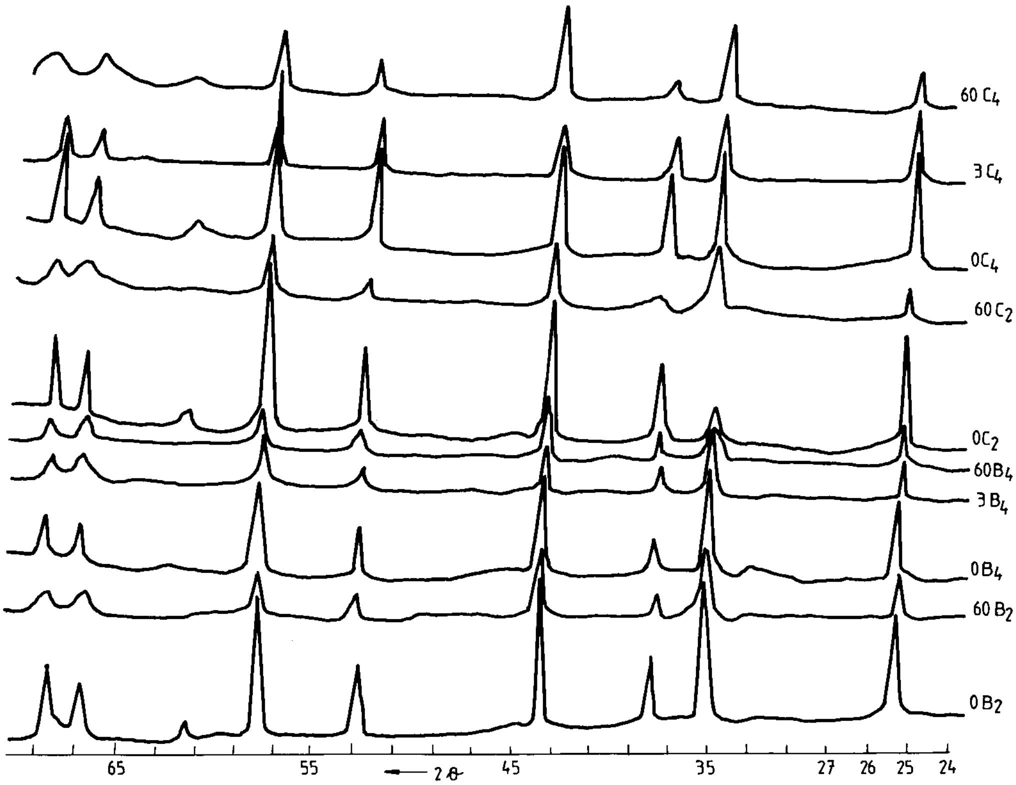

Fig. 5. X-ray diffraction patterns of B and C samples seeded and with and without magnesia addition after heating at 1050°C for 1 h.

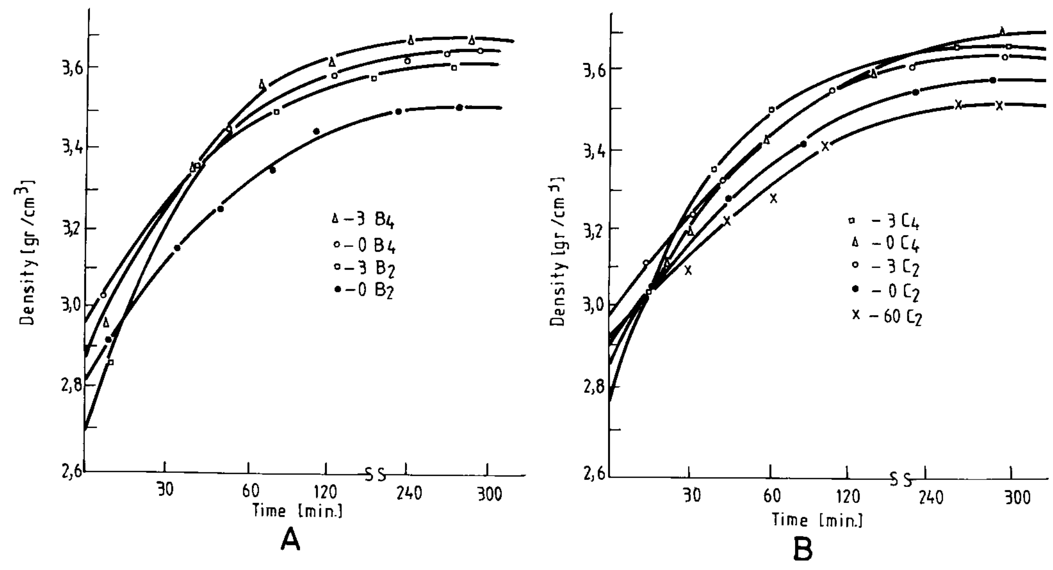

Fig. 6. Plot of density vs sintering time at 1200°C for (A) B samples and (B) C samples.

3.2. *Effect of seeding and magnesia addition on the rate of α-alumina formation and densification*

Although it was known [10,12] that the seeding decreases the temperatures of α-alumina formation (by increasing the number of sites for nucleation), the results of this study confirmed it (presented in Fig. 5). The seeding has a different effect on the nucleation of α-alumina in the B and C doped samples. While the increase of the seed concentration from 2 to 4 wt% almost does not change the rate of α-alumina formation in B samples, it does change in C samples (Fig. 4). The addition of magnesia slightly increases the temperature of α-alumina formation (the rate of nucleation is lower in B than in C samples). This result was not expected, since our previous study showed the opposite effects [16]. This result can only be explained by the original difference in boehmite structure but the mechanism is not clear. In Table 2 are given the results of density measurements, after α-alumina formation. As expected [16], the density increased remarkably during the phase transformation to α-alumina. But still, the density of the C samples seeded and magnesia doped is higher than B samples as in the gel state. In general densities are rather low (as the initial values for sintering) probably because of the low densities of the gels. Besides, the magnesia addition did not improve the densities during the phase transformation to α-alumina.

The effect of seeding, magnesia doping and the boehmite type on sintering behaviour at 1200°C is shown in Fig. 6. The initial density of all samples (seeded, unseeded, magnesia doped and the boehmite type, B and C), as seen in Fig. 6, for B samples is about 65% of theoretical density and for C samples about 70% of theoretical. A drastic increase in the densification rate of doped samples is evident only during the first hour of

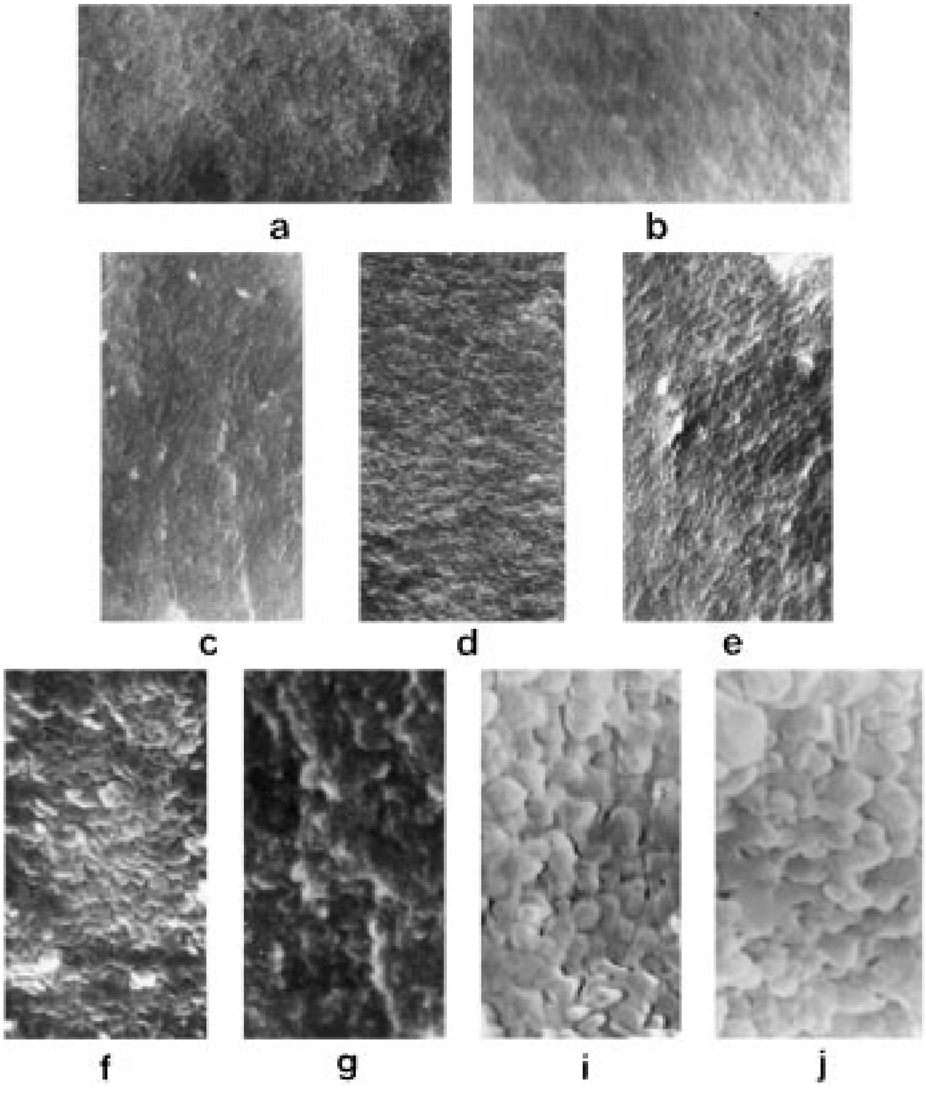

Fig. 7. SEM micrographs of (a) gel $0C_2$; (b) gel $3C_4$; (c) (d) (e) after heating at 450°C for 2 h, $3B_4$, $0C_4$ and $3C_4$, respectively; (f) (g) after heating at 1050°C for 1 h, $3B_4$, $60C_4$, respectively; (i) (j) after sintering at 1200°C for 3 and 5 h, $3C_4$, $60C_4$, respectively.

sintering. The addition of 300 ppm of magnesia in the B and C samples increases the densification rate so that the density of these samples exceeds the density of undoped samples [Fig. 6(A) and (B)] (at the beginning of sintering the density of undoped samples was higher). However, the density of sample with a high concentration of magnesia doping such as 6000 ppm [Fig. 6(B), curve: ×-60 C_2] cannot reach the density of an undoped sample even after a very long sintering time. This is probably the result of too low an initial density, which could not be compensated for by magnesia doping.

After sintering for about 1 h there is no considerable increase in the density (Fig. 6). After this sintering time the differences in the densification rates of undoped and doped samples disappear. The final density (after sintering for 300 min in these experiments) of the doped C samples is higher than the B ones. But still, the final densities of B and C samples is not as high as was expected [16]. Recently, after research done on this subject, Messing et al. [14,19] admitted that pressureless sintering of sol–gel alumina cannot attain high density (as earlier stated [12]) by sintering at 1200°C unless assisted by pressure.

The sequence of the microstructural development in boehmite gels during the phase transformations (at 450 and 1050°C) and sintering at 1200°C, is presented in Fig. 7. Gel microstructures of C seeded and doped samples [Fig. 7(a) and (b)], are fine grained structures (scale of structure is somewhat finer after addition of magnesia) [Fig. 7(b)]. After forming of γ-alumina at 450°C, B samples have a very fine scale structure (similar to gel structure, not shown in Fig. 7), Fig. 7(c), and C samples undoped and doped are on a somewhat coarser scale but still similar to gel microstructure [Fig. 7(d) and (e)]. Drastic change in the microstructural development is seen after phase transformation at 1050°C [Fig. 7(f) and (g)]. Just-formed α-alumina has a uniform, fine scale grainy nanoscale structure, and in B samples [Fig. 7(f)] is on a finer scale than in C samples [Fig. 7(g)]. During the sintering at 1200°C, grain size (in both B and C samples) does not increase until the density of the samples is less than 92% of theoretical density. After interconnected pores transform to close pores (especially in sample B), the grain growth is observed [Fig. 7(i) and (j)]. Even when the grain growth is measurable the microstructure is still uniform on a nanoscale. Addition of magnesia to the alumina cannot inhibit the grain growth but only decreases the grain growth rate in respect of the densification rate.

4. Conclusions

The effect of the boehmite type, seeding and magnesia addition on microstructural evolution and sintering of boehmite alumina was investigated. Experimental results showed that the original boehmite structure and magnesia doping has the major role in phase transformation and sintering of gel-derived alumina. Seeding of alumina gels in the investigated concentration range (2–4%wt), does not exhibit any important difference in the gel processing, but the role of seeding is beneficial, as was already known (in lowering the phase transformation temperature, enhancing densification rate and refining the microstructure and subsequent densification behaviour). Addition of magnesia to boehmite gels changes the microstructure and properties from the gelling level and keeps that tendency to the α-alumina sintering level; it has a specific and different peptization role for B-and C-boehmite: magnesia changes distinctly the local B-boehmite structure (decreases the interlayer distance) and decreases the density and grain size of both B and C-boehmites. The addition of magnesia slightly changes the temperature and rate of α-alumina formation and its grain size. Besides, the addition of magnesia increases the densification rate of both boehmites, B and C, but more C than B-boehmite. By increasing the magnesia addition, the grain size of alumina decreases, meaning that magnesia retards the grain growth rate of alumina. By sintering of alumina at so low a temperature (1200°C) even after the addition of magnesia, alumina cannot reach a very high density.

It is obvious that new, ingenious ideas in the sol–gel processing of alumina are necessary in order to get high density alumina. Further research in this field can bring the solution to the achievement of high density in sol–gel processing.

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