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Effect of Simultaneous Additions of Niobia and Magnesia on the Sintering and Microstructure of Seeded Boehmite

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Abstract: Boehmite (γ-AlOOH) was seeded with sub-micron size particles of α-Al_2O_3 and Nb_2O_5 separately and in combination. These compositions were sintered at 1400°C for 100, 500 and 1000 minutes, respectively, to obtain α-Al_2O_3. Further, magnesia was incorporated into these compositions. All the samples were studied for the sintered density and microstructure and the results are discussed. An optimum microstructure and sintered density of 95% of the theoretical value was obtained when niobia and magnesia were added to seeded boehmite.

INTRODUCTION

Sintering of alumina to high densities requires very high temperatures. Several attempts have been made by many researchers in the past to achieve high density at lower temperatures using various methods. They have included fine powder preparation, sol–gel methods and selection of proper sintering aids. In some cases liquid phase sintering helped in obtaining the high density.[1] The transformation of the hydrous and transition phases of alumina have been widely studied.[2] Boehmite has been found to transform to α-Al_2O_3 via the following sequence on heating.

$$\text{Boehmite} \rightarrow \gamma\text{-Alumina} \rightarrow \delta\text{-Alumina} \rightarrow \theta\text{-Alumina} \rightarrow \alpha\text{-Alumina}$$

The final α-phase formed after the $\theta \rightarrow \alpha$ transformation in boehmite is characterised by a coarse non-uniform grain structure with large interconnected porosity. Hence, the sintering of boehmite gels has been found to require high temperatures.[3–5] Messing and co-workers found a novel method to reduce the sintering temperature and also obtain a high density alumina by utilizing the phase transformations taking place in boehmite.[2,6–11] These properties were achieved by seeding (seeding refers to the intentional addition of α-Al_2O_3 particles which act as nuclei for the transformation) the gel with high temperature alpha phase particles.

The present study was aimed at the processing of alumina using powder compacts derived from gels to obtain high density and a controlled microstructure. The amount of seeding and sintering times have been selected as the prime variables. The effect of addition of sintering aids like niobia and magnesia on the transformation, microstructure and density of the seeded boehmite and unseeded boehmite have also been studied.

EXPERIMENTAL PROCEDURE

Materials

The boehmite powder (Condea Chemie GmbH, Hamburg, Germany) (Sol P-3) used had a BET surface area of 300 m^2/g. It also contained 5–7% by weight CH_3COOH for uniform dispersion of the particles in water. The boehmite gave 70 wt% α-Al_2O_3 on transformation. High purity alumina powder (99·97%) (Condea Chemie GmbH, Hamburg, Germany) (APA 0·5) having a median

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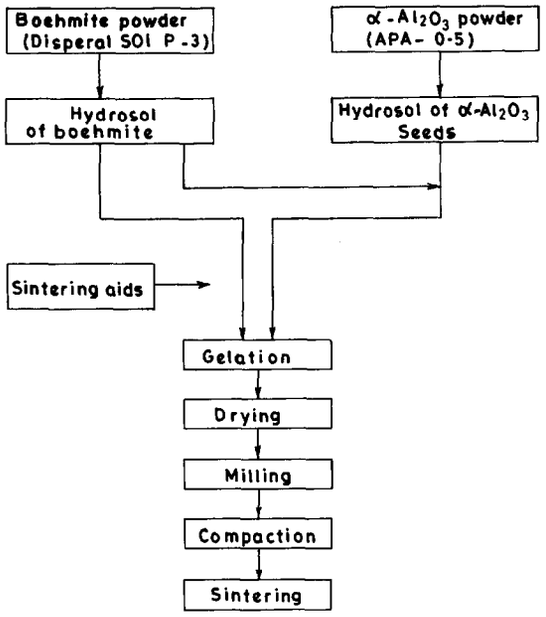


Fig. 1. Flowchart.

particle size of ~0·4 μm was used for seeding the boehmite. The particle size distribution varied from 0·1 to 1 μm. Sub-micron sized niobia (Aldrich Chemical Company Inc., Milwaukee, USA) (99·9% pure) was used and magnesia was added in the form of magnesium acetate (S.D. Loba Chemie, Bombay, India).

Preparation method

The experimental procedure for the specimen preparation is shown in the flowchart (Fig. 1). The boehmite sol was obtained by adding boehmite to water (14 g of powder in 86 g water) under intensive stirring for 15 minutes. α-Al_2O_3 particles were dispersed in water by adjusting the pH at 4 using acetic acid. The α-Al_2O_3 sol was obtained by vigorous stirring using a magnetic stirrer and an ultrasonic vibrator. Different mixtures of α-Al_2O_3 and boehmite sol were prepared by varying the wt% of α-Al_2O_3 (with respect to boehmite on a dry weight basis). Niobia and magnesia (equivalent amount of magnesium acetate) additions were made at this stage. All the additions discussed are in weight percent, unless specified. The magnesia and niobia are added with respect to the alumina. The sols were gelled by heating them on a hot plate at 80–90°C for 3 h. The gels were dried in an electric oven to remove the moisture present. The dried powders were milled in a planetary ball mill for 2 h, using an alumina vessel and alumina balls to give fine powders. The compositions prepared are listed in Table 1.

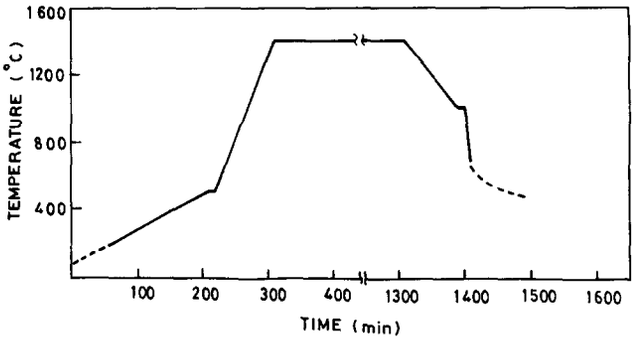


Fig. 2. Heating schedule.

The compositions were compacted in an hydraulic press uniaxially in a OHNS die (15 mm dia × 8 mm height) at a pressure of 100 MPa. The compacts so prepared were fired in a high temperature furnace using $MoSi_2$ super kanthal heating elements in ambient air, with a PID controller. The samples were heated from room temperature to the sintering temperature as shown in Fig. 2. The samples were sintered at 1400°C for 100, 500 and 1000 min, respectively.

The densities of the samples were found by the Archimedes technique. The fractured surfaces were coated with gold for observing under the scanning electron microscope. (Cambridge Instruments model Steroscan 90).

RESULTS AND DISCUSSION

Figure 3 shows the variation of density with the wt% of α-Al_2O_3 in boehmite (compositions A–D). The density values plotted are the average of a minimum of three sample measurements. The density of the unseeded sample was found to be 62% of the theoretical value. It was observed that the density of the powder compacts increased drastically to 75% of theoretical density (Th.D) when 1·5% seeds of α-Al_2O_3 were added to boehmite. This was obtained for a sintering time of 100 min.

The density further increased to 83% when the amount of seeds was raised to 5% α-Al_2O_3.

Table 1. Compositions of samples (by weight %)

Sample	A	B	C	D	E	F	G	H	I	J	K	L	M
Alumina	—	1·5	5	10	—	—	5	5	5	5	5	5	5
Niobia	—	—	—	—	1	2·5	0·5	2·5	2·5	2·5	2·5	2·5	2·5
	—	—	—	—	—	—	—	—	0·15	0·25	0·35	0·45	0·55

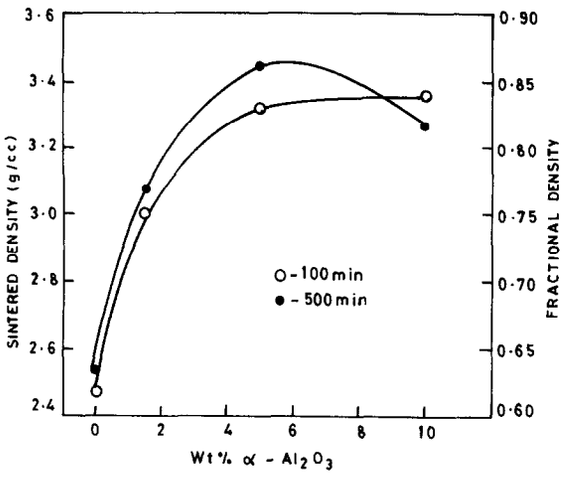


Fig. 3. Density vs wt% α-Al_2O_3 in boehmite compacts at 1400°C for 100 and 500 min.

An improvement in the density values was observed on increasing the sintering time to 500 min, except for 10% seeds. Density values remain similar to those obtianed at 500 min sintering even after sintering for 1000 min. These points are not plotted in the figure for clarity. An optimum density of 86% Th.D was obtained for 5% seeds and 500 min sintering. Boehmite compacts on sintering at 1400°C for 100 min showed a vermicular microstructure (Fig. 4(a)) with very large grains. The $\theta \rightarrow \alpha$ transformation is a nucleation and growth type of process where the nucleation of the new α-phase in the θ matrix has been found to be difficult. After transformation the growth was found to occur rapidly. Because of the limited number of nucleation sites the volume transformed per nuclei was high, thus leading to the formation of a coarse microstructure with low density. The addition of α-Al_2O_3 seeds eliminated the nucleation step by providing a large number of heterogeneous nucleation sites for the $\theta \rightarrow \alpha$ transformation. An increase in the seed concentration led to a decrease in the grain size (volume transformed per nuclei is lowered as seed concentration increases) (Fig. 4 (b) and (c)). The formation of fine grain structure with distributed pore phase between α-Al_2O_3 grains led to higher sintered density as compared to unseeded boehmite. The slight decrease in the density at 10% seed concentration may be due to the decreased control of the seed dispersion in the matrix. The trends observed in the microstructural and density variations of the powder compacts were in agreement with the findings of Kumagai and Messing[2] for boehmite gel monoliths.

The seeded powder compacts gave a maximum density of 86% of the theoretical value. This low density may be due to porosity inhomogeneity caused by the formation of agglomerates during the compaction stage as stated by Dynys and Halloran.[12] The temperature adopted is not sufficient for completing the sintering as the self-diffusion of Al^{3+} is low in α-Al_2O_3. The diffusion rates can be increased with the help of sintering aids. TiO_2 and Ta_2O_5 have been found to be very effective in increasing the diffusion rates during

(a)

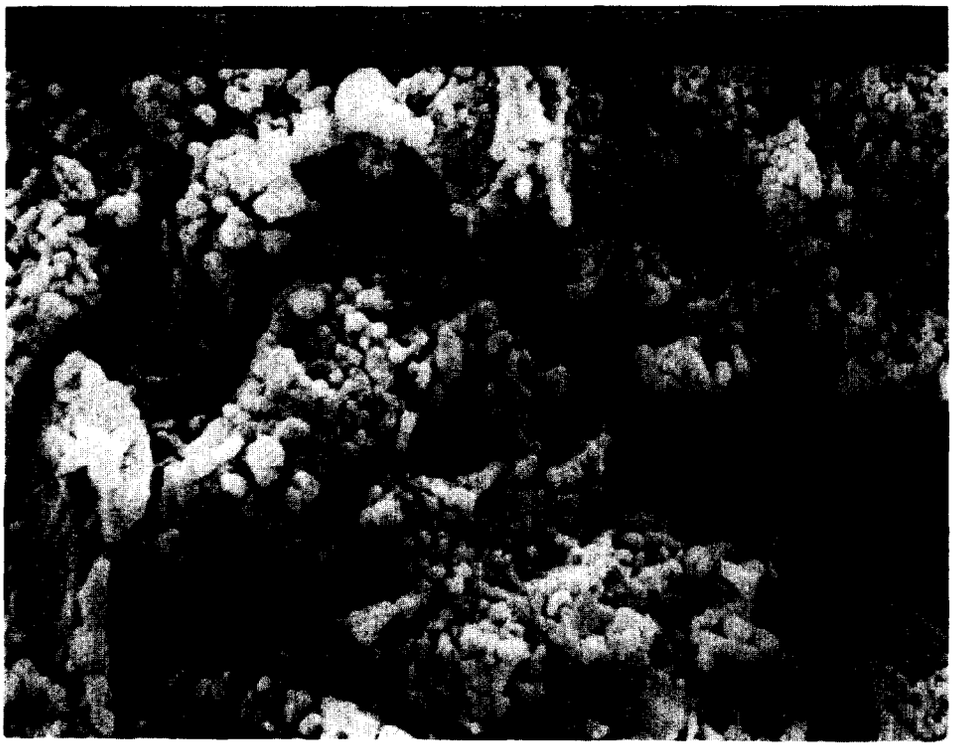
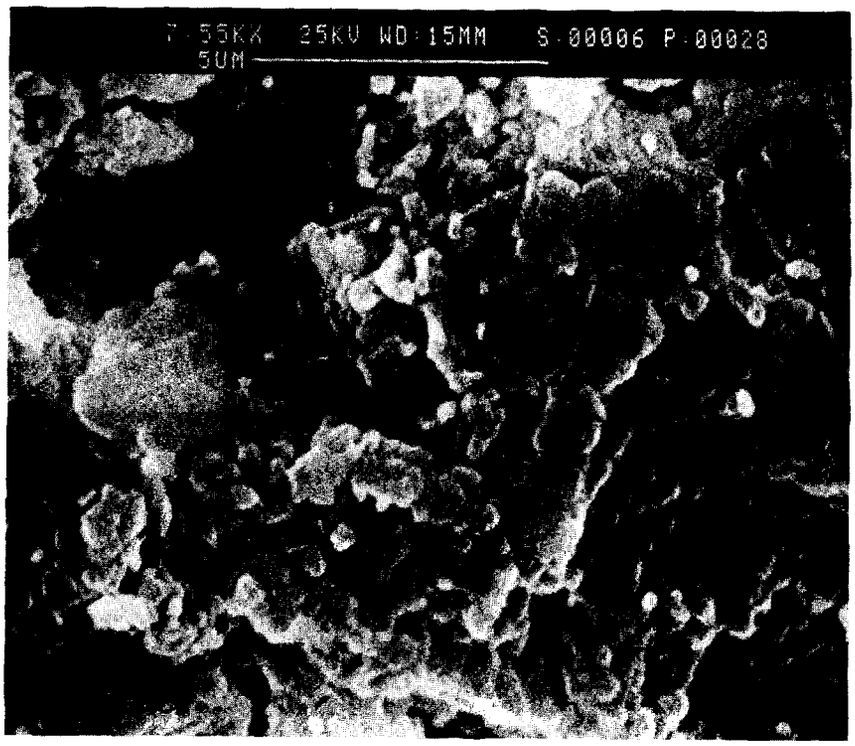


Fig. 4. SEM of fracture surface boehmite samples seeded with (a) 0%, (b) 2·5% and (c) 5% α-Al_2O_3, sintered at 1400°C for 100 min.

(b)



(c)

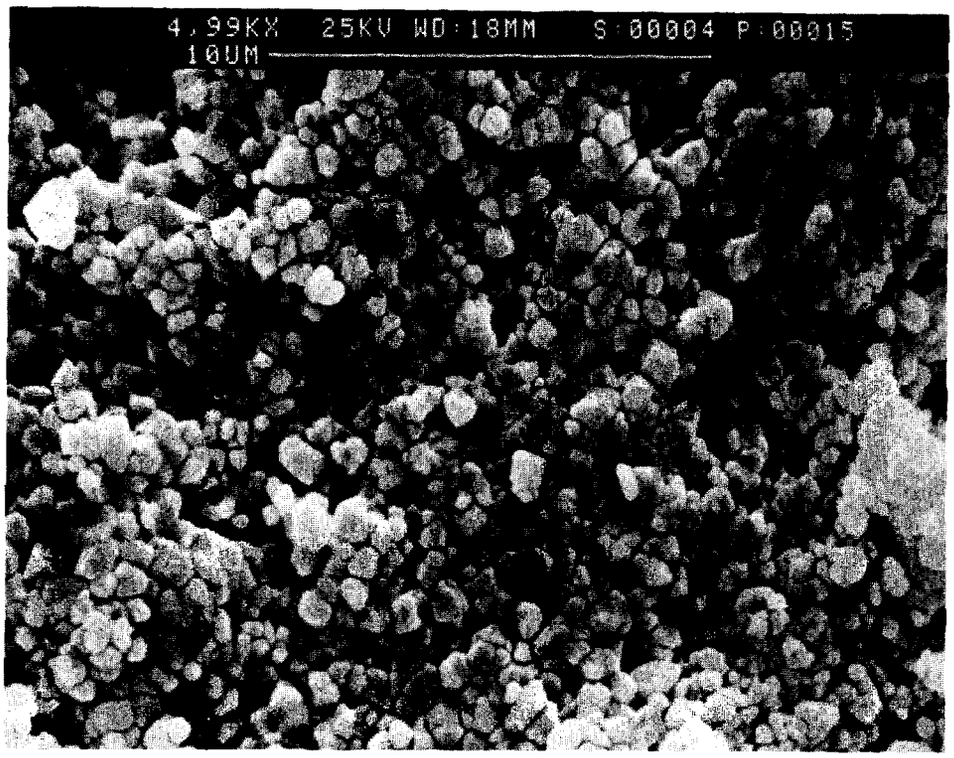


Fig. 4—*Contd.*

sintering.[13,14] Suryanarayana *et al.* have reported that the enhanced diffusion in alumina doped with niobia gave higher density at relatively lower temperatures than that of pure alumina.[15] The addition of 1% niobia (sample E) to boehmite led to an increase in the sintered density up to 81·2% for 100 min soaking. This value further increased to 87% by increasing the soaking time to 500 min. This behavior is due to the action of niobia as heterogenous nucleation sites which resulted in the formation of smaller grains as compared to boehmite (Fig. 5). The higher density observed is due to the enhanced diffusion caused by the presence of niobia in the matrix. The addition of niobia results in the defect formation where each niobium ion occupying the aluminum ion site

results in corresponding aluminum vacancies. This led to the enhanced diffusion and faster densification. Further addition of niobia, i.e. 2·5% (sample F) to boehmite led to a drop in the density values to 75%. This behavior may be due to grain growth being more dominant than densification. The observed density values are higher than that for the same composition prepared by solid state sintering, although the trend is similar to the results observed by Suryanarayana *et al.*[15]

In order to enhance the diffusion rates 0·5% niobia was added to seeded boehmite (sample G). This composition resulted in 79% Th.D, which was less than that of seeded boehmite (sample C).

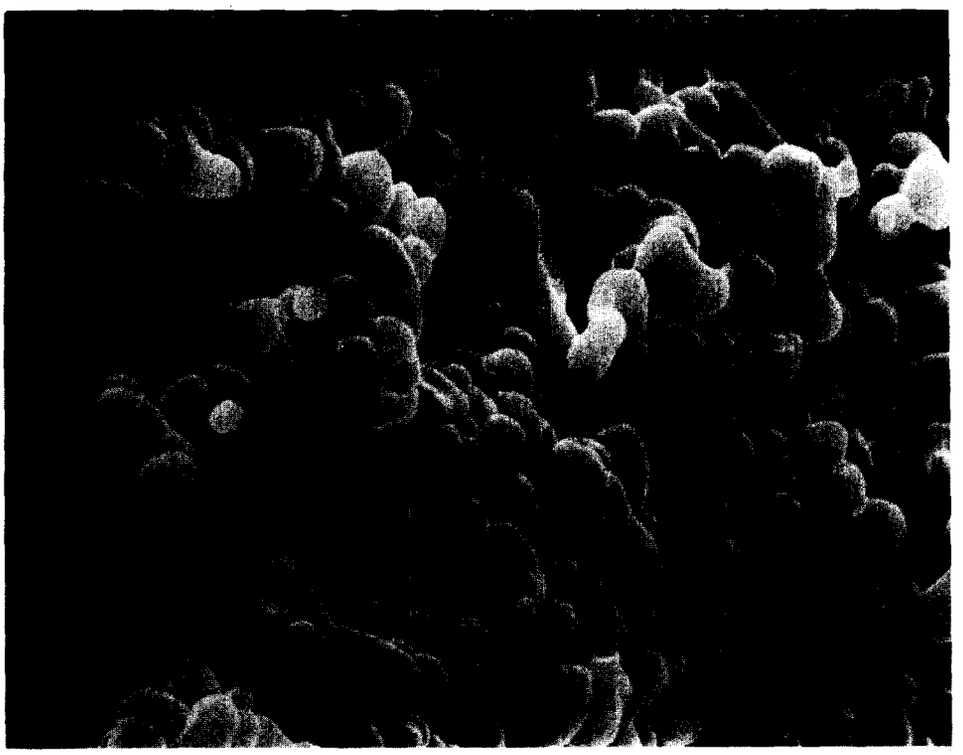


Fig. 5. SEM of fracture surface boehmite with 1% niobia and sintered at 1400°C for 100 min.

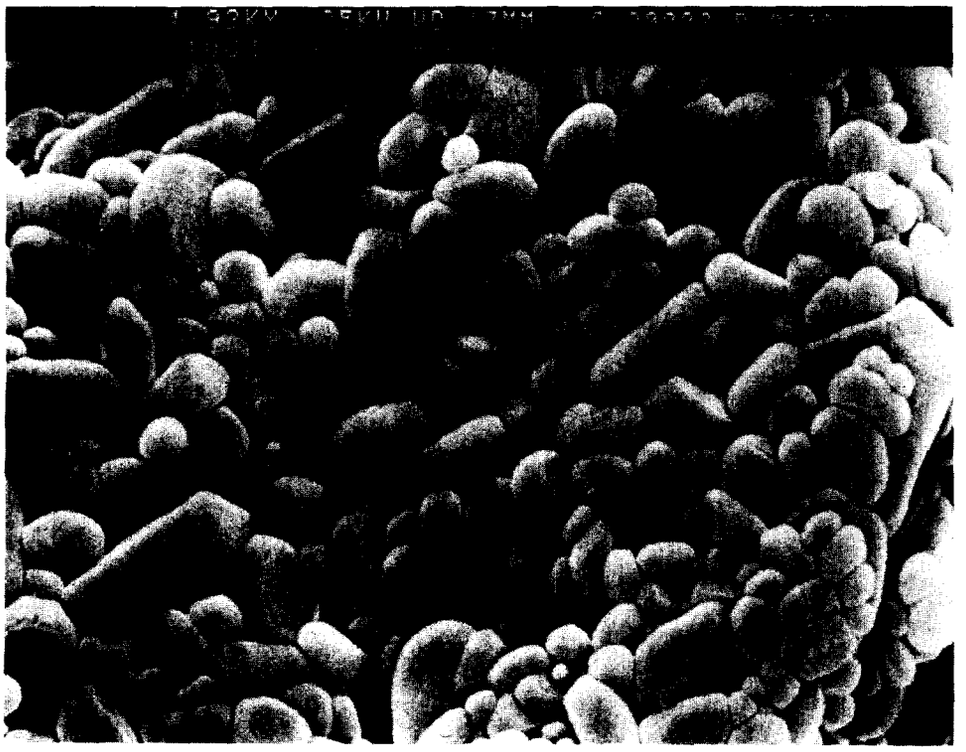


Fig. 6. SEM of fracture surface of 5% seeded boehmite with 0·5% niobia and sintered at 1400°C for 100 min.

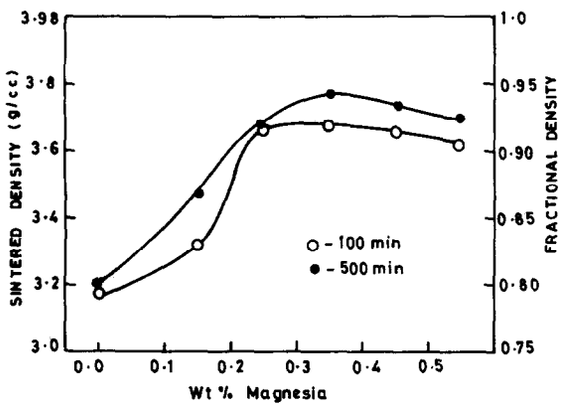


Fig. 7. Density vs wt% magnesia in boehmite with 2·5 wt% niobia and 5wt% α-Al_2O_3 seed at 1400°C for 100 and 500 min.

It can be said from this that the presence of niobia, along with alumina, causes grain growth to be more predominant than densification (Fig. 6).

Magnesia has been used by many researchers to inhibit the grain growth and enhance densification in alumina. To incorporate this effect in the seeded boehmite, and also to utilize the faster densification observed due to higher niobia content, composition I was prepared and sintered under similar conditions as the previous samples. As shown in the Fig. 7, the density of sample I is more than sample H. On increasing the magnesia content the density value increased and attained a maximum of 91% at 0·35% magnesia. No further increase in density was observed, even after increasing the magnesia up to 0·55%. But when the sintering time was increased to 500 min, the maximum density observed was 95% for sample K. The microstructure of sample K reveals uniform fine grains (Fig. 8). These results follow the operative mechanism discussed by Wanqui *et al.*[14] who used magnesia, along with tantalum oxide, to improve the densification in α-Al_2O_3. Wrobleska[16] also observed that magnesium niobate helps in improving the densification at low temperatures. The present method of preparation yielded almost similar densities at 1400°C sintering and a fine grained microstructure.

CONCLUSIONS

Boehmite, on transformation to α-Al_2O_3 and subsequent sintering, resulted in a coarse, non-uniform grain structure with low density (62% Th.D).

Optimum density (86% Th.D) and a fine microstructure (<1 μm) were obtained for boehmite seeded with 5% α-Al_2O_3 particles. Niobia additions to boehmite resulted in a maximum density of 87% Th.D, although addition of niobia to seeded boehmite has not contributed for improving density beyond 80% Th.D. Combined additions of 2·5% niobia and 0·35% magnesia to boehmite seeded with 5% α-Al_2O_3 resulted in 95% Th.D.

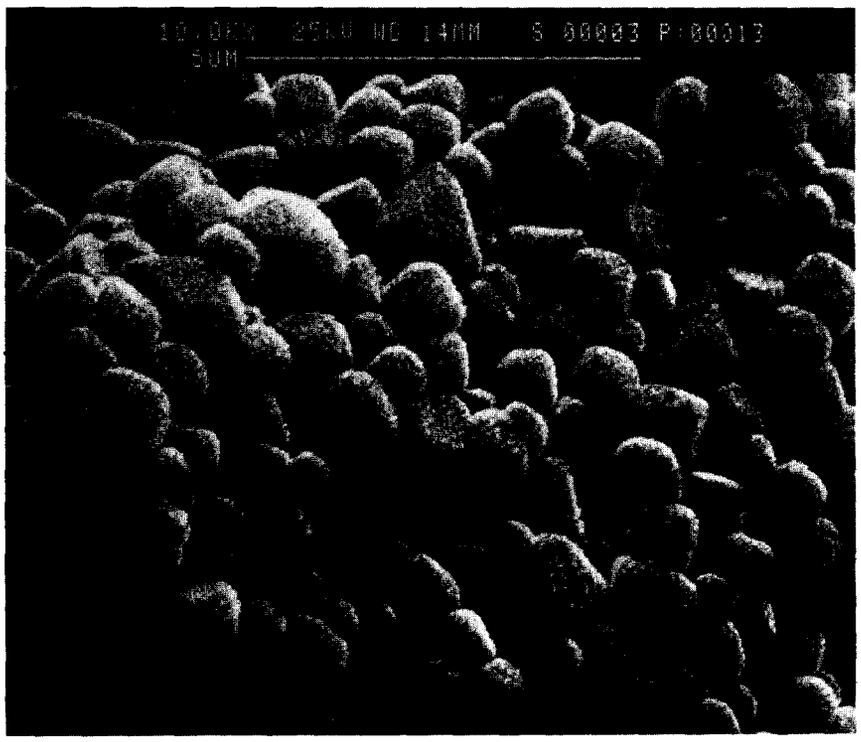


Fig. 8. SEM of fracture surface of 5% seeded boehmite with 2·5% niobia and 0·35% magnesia, sintered at 1400°C for 100 min.

In general, sintered density was found to improve on increasing the sintering time from 100 to 500 min. No observable change in density was seen on further increasing the sintering time to 1000 min.

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