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MICROSTRUCTURAL CHARACTERIZATION OF Mg-Al SPINEL POWDERS

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Abstract

Mg-Al spinel powders have been prepared by thermal decomposition of a mixture of: A - aluminium and magnesium nitrates; B - aluminium and magnesium hydroxides; and C - aluminium hydroxide and magnesium oxalate.

The initial and the final powders were both characterized by specific surface area measurements, mercury intrusion porosimetry, X-ray diffraction, and scanning electron microscopy. The results showed that the preparation process sharply influences the final microstructure of the spinel powders. In particular while the shape and particle dimensions of the samples prepared by mixture of aluminium and magnesium nitrates are mainly influenced by crushing process, the preparation via mixed magnesium and aluminium hydroxides precipitation permits use of spinel formation temperatures as low as 350°C. Characteristically this powder is very uniform and consists of small particle sizes (0.1 micrometers).

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Introduction

Ceramic materials, tailored for special applications have required more sophisticated material microstructures. The ultimate properties of the product are influenced not only by the sintering conditions but also by the characteristics of the starting powders (Kingery, 1982; Morgan, 1984) and, in this respect, by the preparation process.

The use of aqueous and non-aqueous solutions play a major role in the preparation of ceramic powders, especially in the case of multicomponent materials. Different methods of preparation have been described where the supersaturation is achieved either by solvent removal or by precipitation (Gardner et al., 1986; DeLau, 1970; Thomson, 1974; Amato, 1976; Nagai, 1982). The formation of gels may be considered as an intermediate technique, where the solvent removal takes place after the formation of a colloidal suspension (Dislich, 1986; Haas, 1989; Mazdiyasni, 1985). Often the particles obtained after drying are not the final product and are subsequently thermally decomposed or reacted. The nature of the final product may be determined by either the precipitation or the decomposition processes. Examples of ceramic powders obtained by these methods are many and include:

Single oxides: Al_2O_3, Cr_2O_3, Fe_2O_3, ThO_2, TiO_2, Zr_2O;

Double oxides: $BaO_6Fe_2O_3$, $BaTiO_3$, $CoFe_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$;

Mixed oxides: Al_2O_3-Cr_2O_3, Fe_2O_3-$CoFe_2O_4$; etc.

Material and Method

Sample preparation

Preparation techniques involving liquid phase steps were chosen because of their ability to produce multicomponent powders such as spinels. Three different methods were tested taking into consideration that the reactants should have similar solubilities in water, should precipitate at the same rate and must not give rise to supersaturated solutions.

The powders of the spinel $MgAl_2O_4$ were thus obtained utilizing three different sets of reactants:

A - aluminium nitrate and magnesium nitrate;

B - aluminium nitrate and magnesium nitrate reacted with NH_4OH to give a mixture of aluminium hydroxide and mixed aluminium-magnesium hydroxide.

C - aluminium nitrate and magnesium nitrate reacted
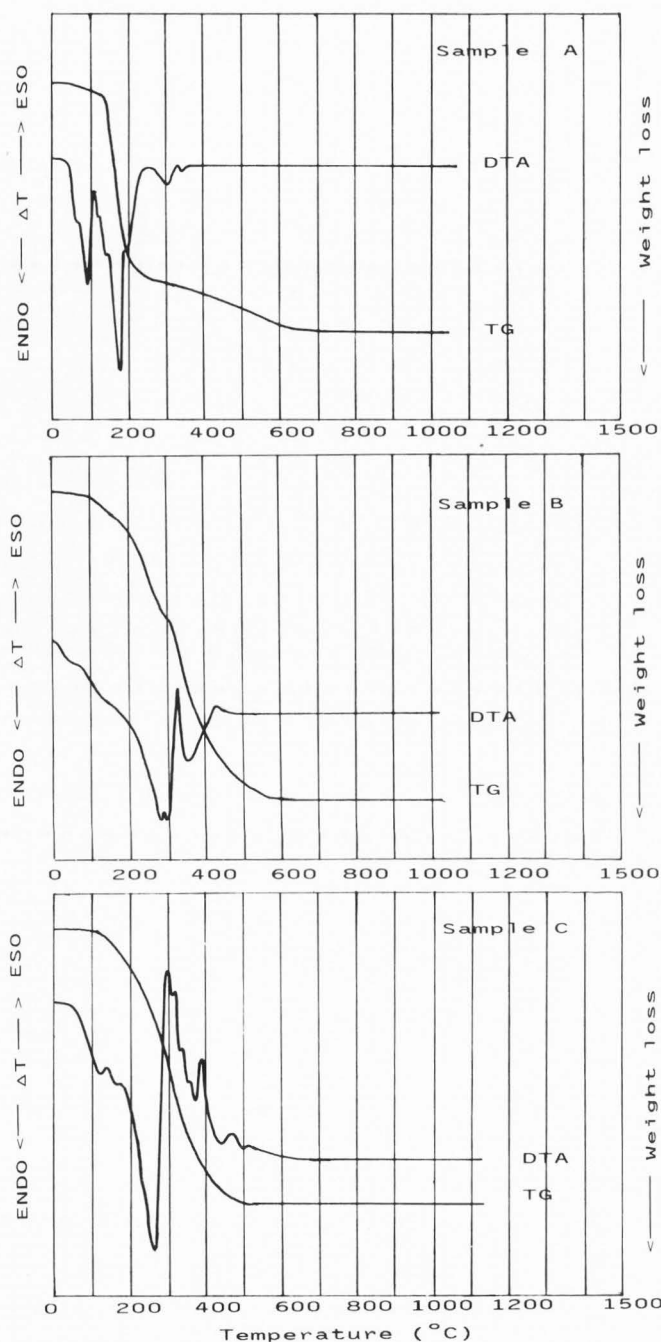
Figure 1 a, b, c. Thermogravimetric analyses of samples A, B and C respectively; heating rate 4°C per min in flowing air.

Figure 2a, b, c. Diffraction patterns of samples A, B and C respectively (dried and calcined).

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with oxalic acid and NH$_4$OH to give aluminium hydroxide and magnesium oxalate.

A. In the first case, 0.5 moles of magnesium nitrate and 1 mole of aluminium nitrate were dissolved in 1 litre of distilled water in such a way to have the molar ratio Mg:Al = 1:2 as in the corresponding spinel. The solution was stirred and evaporated at 60°C. The precipitate was dried at 105°C,
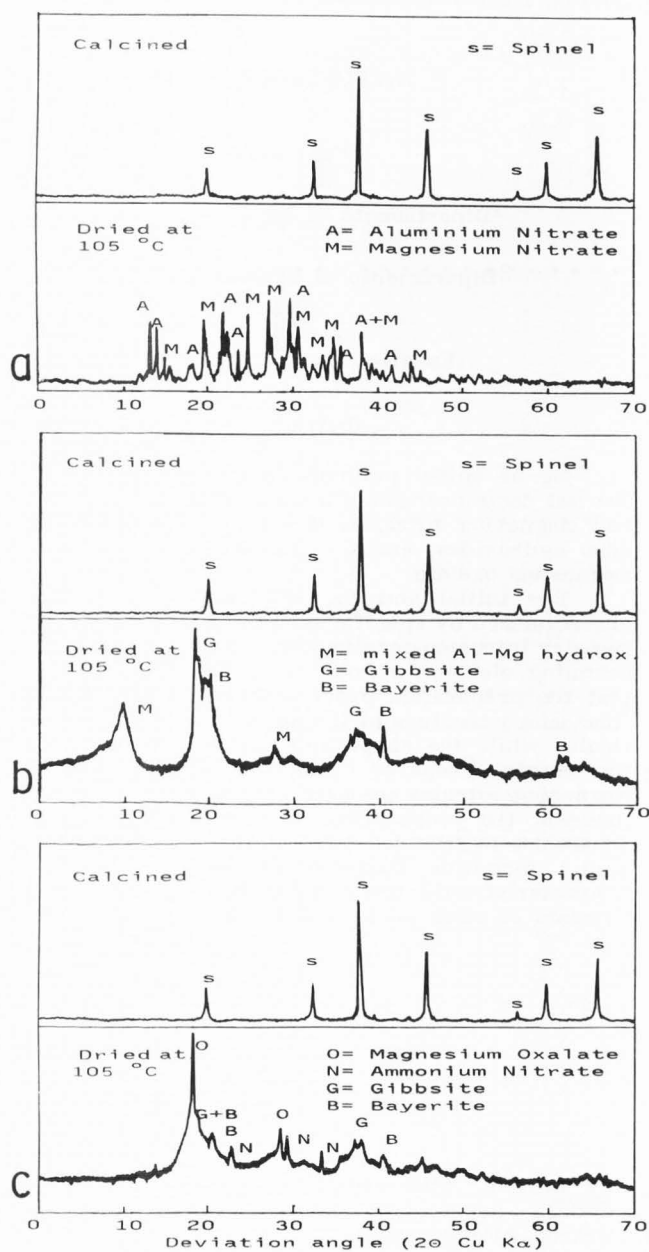
decomposed at 400°C for two hours, crushed, and then calcined at 1100°C for three hours. Milling was performed for 10 minutes in an alumina ball mill with two alumina balls (8000 SPEX Mixer/Mill - mill internal diameter 80 mm, ball diameter 10 mm, mixer/mill action repeated 1200 times per minute).

B. In the second case, an aqueous solution of the same composition was dropped into an aqueous solution of NH$_4$OH at pH 10 and 60°C, then filtered. The product obtained was dried at 105°C, crushed, decomposed at 400°C for two hours and then calcined at 1100°C for three hours.

C. In the third case, the same aqueous solution of the nitrates was first reacted with a 1.5 M

Table 1: Specific surface area, particle size and porosimetry data for the three spinel powders.

Sample	Heating Temperature °C	Specific Surface BET (m²/g)	Particle Size SEM (micrometers)	Porosity (%)	Porosimetry Pore Radius (micrometers)	Particle Size (micrometers)
A	400	10	-	-	-	-
	1100	3.8	1-100	36	0.03-3* 6-30	0.2-10* 60-300
B	400	250	-	-	-	-
	1100	17	0.1	55	0.005-50	0.05-300
C	600	205	-	-	-	-
	1100	17.5	0.1	46	0.008-50	0.05-200

*Two ranges

solution oxalic acid and then NH_4OH added to pH = 9.5. The solution was stirred at 60°C for one hour, then filtered. The product obtained was dried at 105°C, decomposed for two hours at 600°C, crushed in the ball mill and finally calcined at 1100°C for three hours.

In the three cases, precipitation temperature, pH, and decomposition temperature were selected to optimize synthesis process. In particular pH was selected in order to minimize the solubility of the precipitated compounds, while the decomposition temperatures were chosen on the basis of the results of X-Ray Diffraction (XRD) of the three different products, previously heated at different temperatures.

Sample characterization

X-Ray Analyses: Diffraction patterns were obtained with a D500 Siemens diffractometer, utilizing Cu K_α at 40 kV and 30 mA. The 2-θ scanning rate was 1°/min.

Thermogravimetric analyses (Thermogravimetry (TG), Differential Thermogravimetry (DTG), Differential Thermal Analysis (DTA)): The equipment was a TA1 Mettler thermoanalyser, heating rate at 4°C/min, the samples were maintained in air flow, from room temperature up to 1000°C.

Specific Surface Area (BET) measurements were carried out with a Carlo Erba Sorptomatic Series 1900 using nitrogen as adsorbate gas.

Porosimetry: Carlo Erba mercury intrusion porosimeter series 2000 was used assuming a contact angle mercury-spinel of 151.9°.

Scanning Electron Microscopy (SEM): The equipment employed was a Philips Model 505 SEM. The samples were prepared for the observation by dispersion in iso-amyl-acetate by ultrasonic stirring (5 minutes). The dispersion was deposited on aluminium stubs and then coated with gold. The acceleration voltage was kept at 25 kV. The working distance ranged between 4 and 7 mm. The microphotographs were taken at three magnifications: 1000X, 10000X and 40000X.

Results and Discussion

The results of the thermal analysis are shown in Fig. 1 a, b, and c, respectively, for dried samples A, B and C. It is possible to ascertain the different modes of decomposition, which allowed the proper temperature of decomposition to be chosen.

Sample A melts around 90°C and decomposes mainly around 180°C; the second small endothermic peak is due to the final decomposition of magnesium nitrate.

Sample B decomposes in more steps involving loss of water from the mixed Mg-Al hydroxide and from Al hydroxide, a solid state reaction occurs between Mg and Al dehydration products. The decomposition is completed just over 400°C.

The decomposition process of sample C involves the loss of water from Al hydroxides and a two step decomposition of magnesium oxalate that ends near 500°C.

X-ray analyses were carried out on samples dried at 105°C and calcined (Fig. 2, a, b, c). The comparison of diffraction patterns with ASTM and JCPDS files demonstrates that final product is a spinel ($MgAl_2O_4$) phase regardless of material processing, while the initial materials were a mixture of magnesium and aluminium nitrates in the sample A; a mixture of gibbsite, bayerite and mixed magnesium hydroxide in samples B; and a mixture of magnesium oxalate, bayerite and gibbsite containing traces of ammonium nitrate in sample C.

The dimensional distributions of pores and particles from porosimetry measurements are shown in Figures 3-5. The calculations were performed by the Carlo Erba software. Sample A (Fig. 3) shows a double distribution of pores, which indicates two types of porosity: the intraparticle porosity centred around a dimension of 0.5 micrometers and the interparticle porosity ranging between 6 and 30 micrometers. A double particle size distribution occurs: one mode comprises particles with dimensions between 0.2 and 10 micrometers, the other mode comprises particles between 60 and 300 micrometers.

In the case of sample B (Fig. 4) the pore size distribution appears to be markedly flattened between 0.005 and 50 micrometers. Also the particle size distribution appears to be uniform, ranging between 0.05 and 300 micrometers with a weak prevalence of particles around 2-3 micrometers.

The same characteristics are shown by sample C (Fig. 5) which presents a flattened pore size distribution between 0.008 and 50 micrometers. Particle size evaluated from pore distribution data ranges between 0.05 and 200 micrometers. Specific surface area, pore sizes, total porosity and particle sizes are summarized in Table 1.

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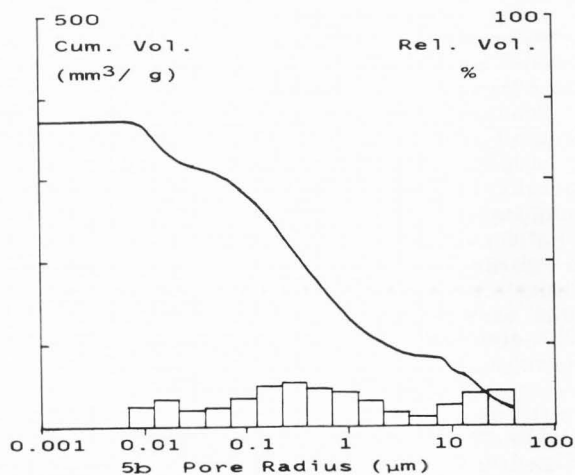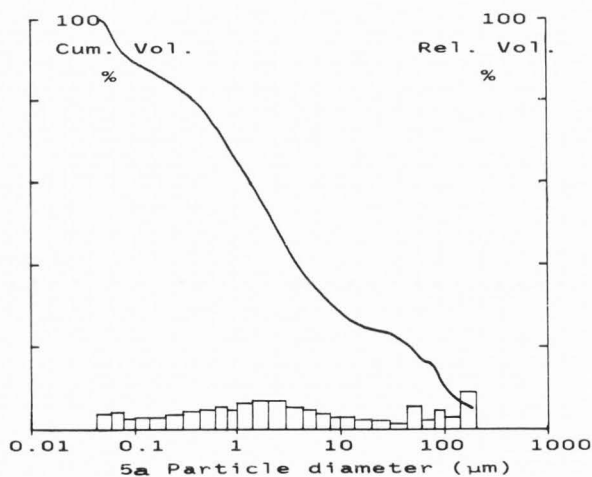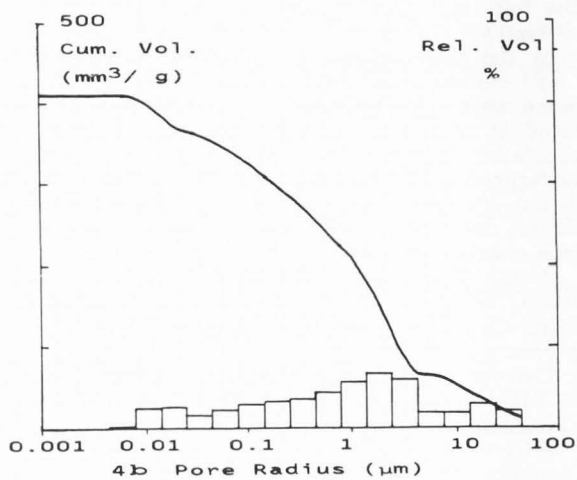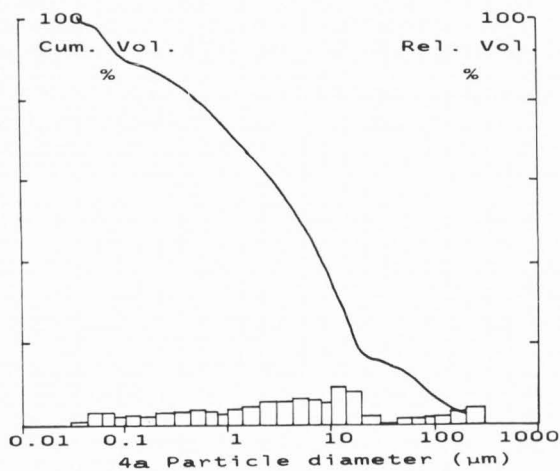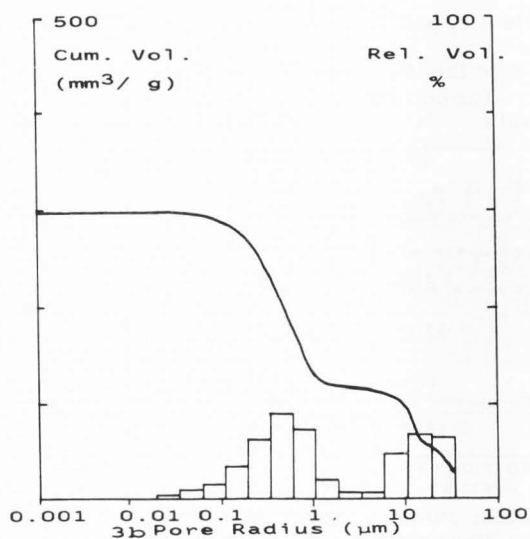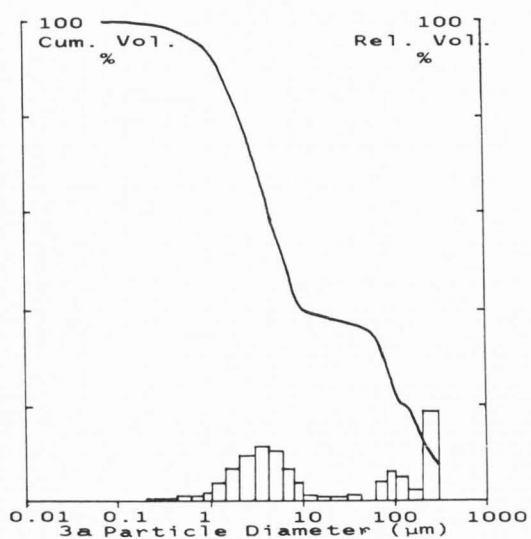
Figures 3, 4 and 5. Particles (Figs. 3a, 4a, and 5a) and pore (Figs. 3b, 4b, and 5b) distribution of calcined samples A, B, and C respectively.
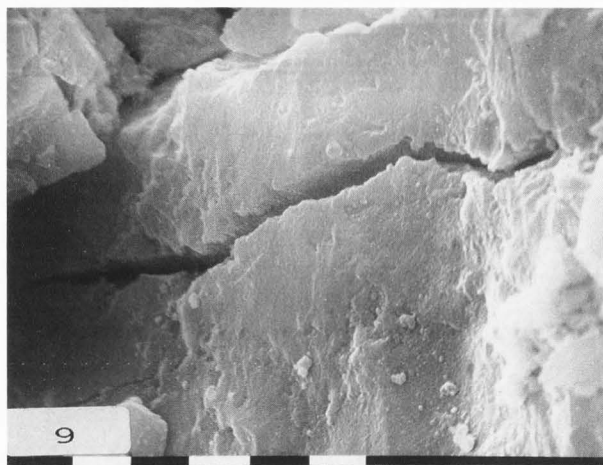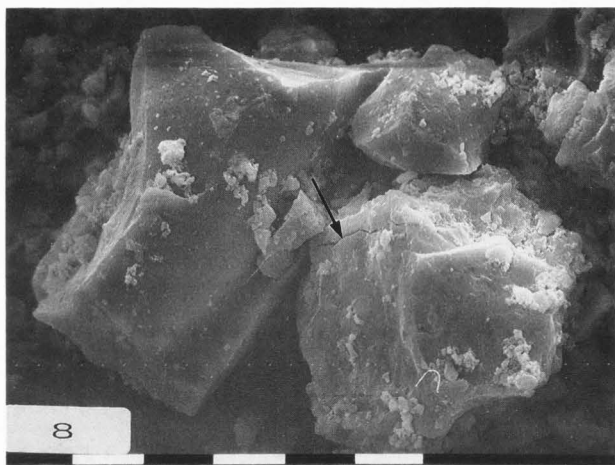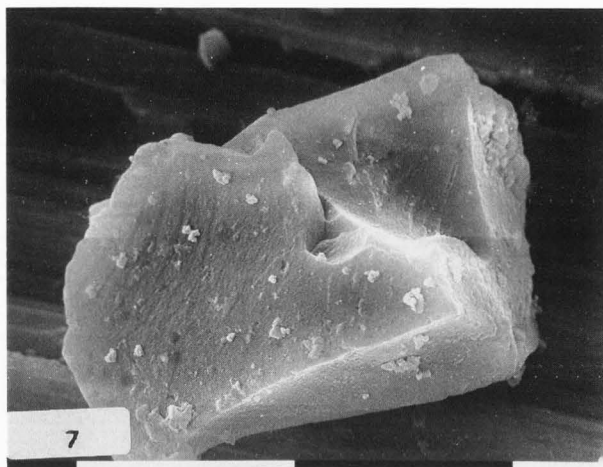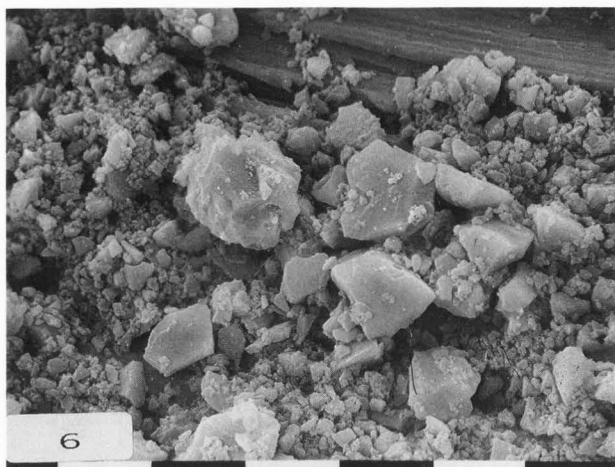
Figures 6 - 9. Sample A calcined and mill crushed. **Figure 7.** Magnified view of a particle showing sharp fracture edge due to comminution. **Figure 8.** Fracture edge and fracture line (arrow; magnified view **Figure 9**) propagating inside the bulk of particles. Scale bar = 10 micrometers (Figs. 6-8); 1 micrometer (Fig. 9).

The SEM observations point out a distinct morphological difference between samples A, B and C, not completely in accordance to the variation in the pore size distribution given by mercury intrusion measurements. The main differences between SEM observations and porosimetry measurements occur in powder A, which consists of very compact particles distributed over a wide size range (between 1 and 100 micrometers). The particles are generally irregularly shaped and have sharp edges due to comminution (Figures 6-7). Figures 8 and 9 show fracture lines propagating inside the bulk, but do not reveal neither intraparticles pores nor any fine microstructure. The morphology of sample A may be understood by considering low melting points (respectively 73.5°C and 90°C) of $Al(NO_3)_3$ and $Mg(NO_3)_2$, so that, during the first decomposition step the salt mixture became fused. Further decomposition leads to the formation of a bulk sponge which is then crushed by milling. These observations do not agree with measurements of porosity, but are in agreement with the low value of surface area. The comparable low

values of surface areas of samples heated at 400°C and 1100°C are also in agreement with this model.

Figure 10, from sample B, confirms the presence of particles with different sizes. Higher magnifications, however, show that all the particles are agglomerates (more or less sintered, due to the calcination temperature) of submicron particles, whose size is around 0.1 micrometers (Figure 11). The sintering of the agglomerates allows the abrupt lowering of surface area to be understood. The morphology of this powder may thus be explained by the process of decomposition of the agglomerate formed during the precipitation of the hydroxides.

Sample C (Figures 12 and 13) is also made up of particles sized around 0.1 micrometers. These particles underwent sintering during calcination according to the marked diminution of surface area. In this case, the flakes of $Al(OH)_3$ encapsulate the magnesium oxalate. The particles were disaggregated by gases (CO and CO_2) that evolve strongly during decomposition of the oxalate.

A comparison between particles sizes as
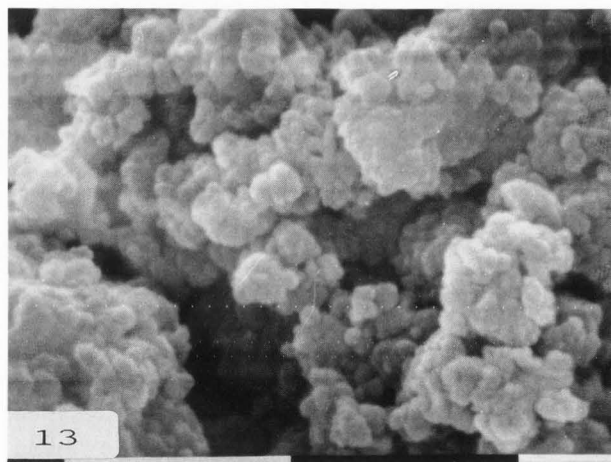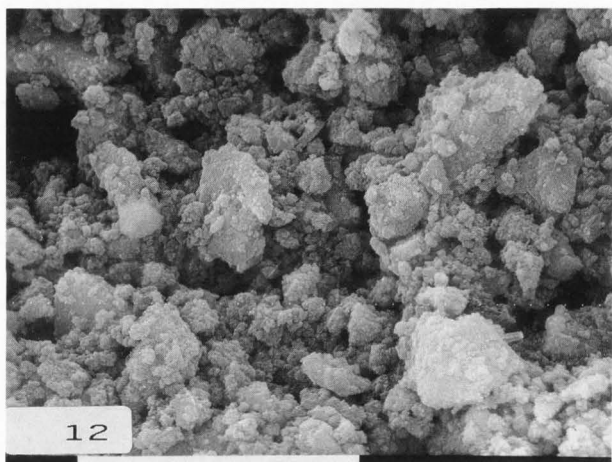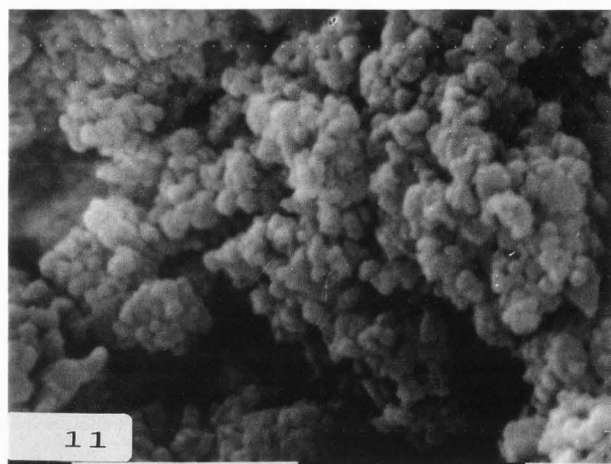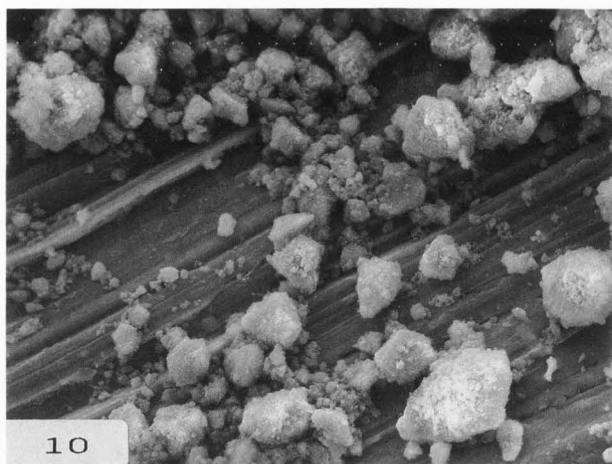
Figures 10, 11. Sample B, calcined and mill crushed; **Figure 11** shows a high magnification image of an agglomerate shown in Figure 10 revealing its fine microstructure.
Figures 12, 13. Sample C, calcined and mill crushed; **Figure 13 shows** a high magnification image of micro particles which form agglomerate shown in Figure 12.
Scale bars = 10 micrometers (Figs. 10 and 12) , and 1 micrometer (Fig. 11 and 13)

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measured via SEM and as calculated by porosimetry is made in Table 1.

In summary, SEM observations show that morphology of sample A particles is a function only of the crushing parameters. Samples B and C are characterized by highly agglomerated particles which, during calcination, lose a major part of the surface area and of the interparticle porosity.

Conclusion

X-ray diffraction analysis showed that the same phase MgAl$_2$O$_4$ was obtained with all three processes described above. BET and porosimetry measurements revealed differences in surface area, particle size distribution and porosity among the three products. SEM analysis confirmed an important difference between sample A and samples B and C, but showed morphological aspects of sample A which do not agree with the presence of intraparticle porosity

given by mercury intrusion measurements. The obtained difference in microstructure is in agreement with the different precipitation processes and different decomposition mechanism. The preparation of sample A involves a melting step. For this reason the obtained particles are characterized, according to SEM observations, by absence of intraparticles porosity and a size distribution determined by the crushing process. Shapes and sizes of samples B and C are very different. In these cases, once again, the SEM observation allowed us to explain the results of BET and porosimetry measurements, showing that both samples consist of clusters made of agglomerate particles with dimensions less than 0.1 micrometers and intraparticle porosity.

The different morphologies observed between sample A and sample B are important in selecting the preparation method in order to obtain the Mg-Al spinel at low temperature, and to tailor its reactivity in relation to its final application.

Aknowlegments

We are grateful to Mr. Pietro Italiano, microstructure line manager of Carlo Erba Instrumentation, for his kind collaboration that allowed us to obtain BET and porisimetry measurements.

References

Amato I, Baudrocco F, Martorana D (1976) Evaluation of freeze-drying and spray-drying process for preparing transparent alumina, Mater. Sci. Eng., 26, 73-78.

DeLau JGM (1970) Preparation of ceramic powders from sulfate solutions by spray drying and roasting, Ceram. Bull. 49, 572-574

Dislich H (1986) Sol-gel: Science, processes and products, J. Non-Cryst. Solids, 80, 115-121.

Gardner TJ, Sproson DW, Messing GL (1986) Powder synthesis for electronic ceramics by evaporative decomposition of solutions, Ceram. Int. 12, 3-7.

Haas PA (1989) Gel processes for preparing ceramics and glasses, Chem. Eng. Prog., 85, 44-52.

Kingery DW (1983) Powder preparation, Mat. Sci. Mon.: Ceramic Powder: Preparation, Consolidation and Sintering, 16, 3-18.

Mazdiyasni KS (1985) Metal alkoxy-derived powders, 30th Sagamore Army Mater. Res. Conf. Proc. 1983 (Innovations Mat. Proc.), G. Bruggeman (ed.), Plenum Press, New York, pp. 285-336.

Morgan PED (1984) Avoing ceramic problems by the use of chemical techniques, in Mat. Res. Soc. Symp. Proc., Pub. by Elsever Science Publishing, 32, 213-226.

Thomson J, Jr. (1974) Chemical preparation of PLTZ powders from aqueous nitrate solutions, Cer. Bull. 53, 421-424, 433.

Discussion with Reviewers

M. Patel: A peak around 440-460 °C is expected in DTA curves to show the thermal change of the hydroxides (Serry and Naga, "Silicates industriels" LII (3-4) 41-46, 1987). The authors have not found such peak; why? In TGA, the weight losses are in these temperature ranges. XRD: Fig.2, is it Bayerite or Boehmite?
Authors: As far as observation on thermal analysis results are concerned, and in particular the differences with respect to the results obtained by Serry and Naga, it is important to underline that DTA curves presented by those authors refer to single magnesium hydroxide and aluminium hydroxide obtained starting from ores and not from single solution of pure magnesium and aluminium nitrates; the precipitation pH was different and also the precipitated product was different. In particular, according to our precipitation procedure a mixture of mixed magnesium-aluminium hydroxides and aluminium hydroxide was obtained.

The results of DTA can be explained with the decomposition mechanism of mixed hydroxides as proposed by Bratton (R.J.Bratton, "Ceramic Bulletin", Vol.48, No 8, 1969) who obtained the same DTA curve. The absence of the endothermic peak can be explained by the contemporary exothermic effect due to the spinel formation.

As far as the point concerning the form in which aluminium hydroxide is obtained (Bayerite or Boehmite) once again we have to underline that the crystallographic phase of aluminium hydroxide depends on the starting salts and precipitation parameters. Starting from chloride solution Bratton obtained mainly gibbsite (See reference of Bratton above). D. Beruto et al. (D. Beruto, R. Botter, G. Giannetti, M. Giordani, G. Gusmano, E. Proverbio, E. Traversa, Proc. 1st Europ. Ceram. Soc. Conf., 18-23 June, 1989, Maastricht) obtained mixture of gibbsite and bayerite or boehmite by changing starting salts, pH and precipitation temperature.

R.St.C. Smart: The important results in this paper are the differences in decomposition processes and resulting structure from the A, B and C preparations. Please comment on the advantage and disadvantage of the final products in ceramics technology.
Authors: The results presented in the paper clearly show that morphology, geometry and reactivity of the intermediate and final product are deeply affected by the preparation method. This can strongly influence the final properties of the Mg-Al spinel. Changing the precipitation procedure it is possible to lower the sintering temperature and in this way to tailor porosity and grain size. Thus the microstructure of the sinterized spinel can be designed in view of the final application, for example as active element in a humidity sensor device.

G. Bonifazi: Results reported in the paper demonstrate the importance of the process on the morphology of the particles, anyway it seems that all the sample are characterized by a high degree of agglomeration or by nonuniform distribution of the particle size. Do the authors not think that much more attention should be given to the drying phase?
Authors: The process of drying usually increases the degree of agglomeration and cause a strong adhesion to take place, but it is during the precipitation process that single particles take their size and shape and more particles stick togheter. The process of drying if properly designed, can save the structure of the wet precipitates.

In addition to what you suggest, the size and shape of particles, as well as the adhesion between particles (mainly in the case of preparation of coprecipitates or mixed hydroxides), can be influenced by other precipitation parameters such as type of anions, pH, temperature, aging, etc. Tests on all these parameters and effect of different drying techniques are in progress in order to optimize the morphology (shape and size distribution) of the particles.

G. Bonifazi: It is well know that the results of particles size analysis are greatly influenced by the techniques employed. It is not surprising that mercury intrusion porosimetry cannot give information on the fine microstructure of the particles due to high pressure collapse of the structure. On the other hand SEM can give this information but cannot give detailed and statistically reliable information on the size distrubution of the particles. Would you not think that the use of SEM image analysis could greatly help in obtaining complete information on the morphological characteristics of the powders?
Authors: Usually the analysis of SEM images is not considered a satisfactory method for characterizing porous bodies. Surface texture, in fact, is not necessarily linked with three dimensional distribution of

pores in the bulk. However, when the particle sizes and shapes are to be determined, BET and mercury intrusion methodologies are indirect techniques as well.

As far as the analysis of images is concerned, it is necessary to develop:

1. a dedicated software for shape and size distribution calculations; and

2. a proper technique of sample preparation.

Both these aspects are being developed in our department. It is expected that a more comprehensive characterization of powder samples will be possibled. In fact, our first results show an excellent degree of correlation between BET and shape/size distribution obtained by the means of computerized image analysis. These results will be presented in a further work when completed. It should also be pointed out that image analysis will be a very valuable technique, since the equipment to perform BET are very expensive and the duration of each measurements is very long.

In our SEM image analysis procedure, images coming from the SEM are digitally recorded and subsequently analysed. It is possible to read the images in DOS compatible computers, lowering the cost of the overall equipment.