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Preparation and properties of ceramics from magnesium spinel by sol–gel technology

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A dense electroinsulating ceramic was prepared at lower temperature (1400–1450 °C) compared to the solid phase synthesis. The synthesis of the spinel was carried out at 1000 °C reaching over 97% spinel by applying the sol–gel method and the inclusion of one of the components as a soluble salt. Combinations of additives like B_2O_3 and TiO_2 were included as alcoholates during the process of hydrolysis. These additives caused an intensification in the course of the process of spinel-formation.

1. Introduction

The noble (magnesium) spinel is an important high-refractory electroinsulating and constructional material with application in metallurgical, electrotechnical, radiotechnical and chemical industry.

Depending on the dispersity of the initial materials, the type and the quantity of the additives, the magnesium spinel is prepared by solid phase synthesis in the 1000–1600 °C temperature range. Ceramics based on magnesium spinel sinter in the 1450–1800 °C temperature range [1–11].

Sol–gel technology is regarded as a prospective method for the synthesis of $MgAl_2O_4$ and ceramics have been obtained on this basis as well [12–16].

The aim of the present investigation was the study of spinel formation and the preparation of ceramics by using a variation of sol–gel technology. In this case, a soluble salt was used as one of the components and the other was introduced as alcoholate. In order to obtain dense ceramics with good electrotechnical and physicomechanical characteristics, it was necessary to introduce new combinations of additives as metal alcoholates.

2. Experimental procedure

$Mg(NO_3)\cdot 6H_2O$, $Al(OC_4H_9)_3$, $B(OCH_3)_3$ and $Ti(OC_4H_9)_4$ (reagent grade) were used as the initial raw materials for the synthesis of $MgAl_2O_4$.

The technological scheme for the synthesis of the spinel and the preparation of the ceramics is presented in Fig. 1.

100 ml distilled water with pH < 3, preheated to 50 °C and intensively stirred were added to 1 ml $Al(OC_4H_9)_3$. The additives of B_2O_3 and TiO_2 in the ratio of 2:1 mass % were added as alcoholates: $B(OCH_3)_3$ and $Ti(OC_4H_9)_4$. These additives were chosen because of their effective influence during the process of solid phase synthesis [11]. Under these conditions the hydrolysis continued for about 60 min. This process is followed by the heating of the mixture in a water bath up to 70–90 °C and an addition of $Mg(NO_3)_2\cdot 6H_2O$ (the necessary stoichiometric quantity for the preparation of magnesium spinel). In order to accelerate gelation 1 N HNO_3 was added in a quantity ensuring 0.3 mol HNO_3 per 1 mol AlOOH. The gelation was performed in about 10–15 min. The gel was dried at 80–100 °C and was thermally treated in the 1000–1100 °C range as tablets were pressed at $P = 100$ Pa. As experimental specimens, spinel ceramics were prepared from the spinel synthesized in accordance with the technological operations shown in the scheme. The specimens were sintered at 1400–1450 °C with a time delay of 2–3 h up to the preparation of ceramics with zero absorption.

The changes taking place in the gel during the thermal treatment were observed with the help of X-ray phase analysis (apparatus Dron UM-1, Nickel-filter, CuK_α radiation), infrared spectroscopy (apparatus "specord" M80 in the 400–4000 cm^{-1} range).

The quantity of the prepared spinel was determined by chemical methods. The quantity of $MgAl_2O_4$ formed is determined by the amount of free MgO in the specimens. Its determination was performed by the following operations. After preliminary titration and determination of CaO content in the specimen, another aliquot part of the solution was titrated in order to determine the total CaO and MgO content with 0.05 M solution of EDTA at pH ~ 10 and methyltimolblue indicator. The percentage of MgO corresponds to the difference between the determinations. With the help of the methods developed, the systematic error was deduced and the accuracy was increased [17].

The following properties of the ceramics obtained were investigated: the density of hydrostatic pulling; the band strength (ZP-400, GDR); the coefficient of thermal extension, with the help of a quartz dilatometer in a 20–700 °C temperature range; the coefficient of heat conductivity by the Pyk and Stalhane method; the electrical properties; the dielectric permittivity (Verlustfaktor-messgerat TYP 1033 GDR; the

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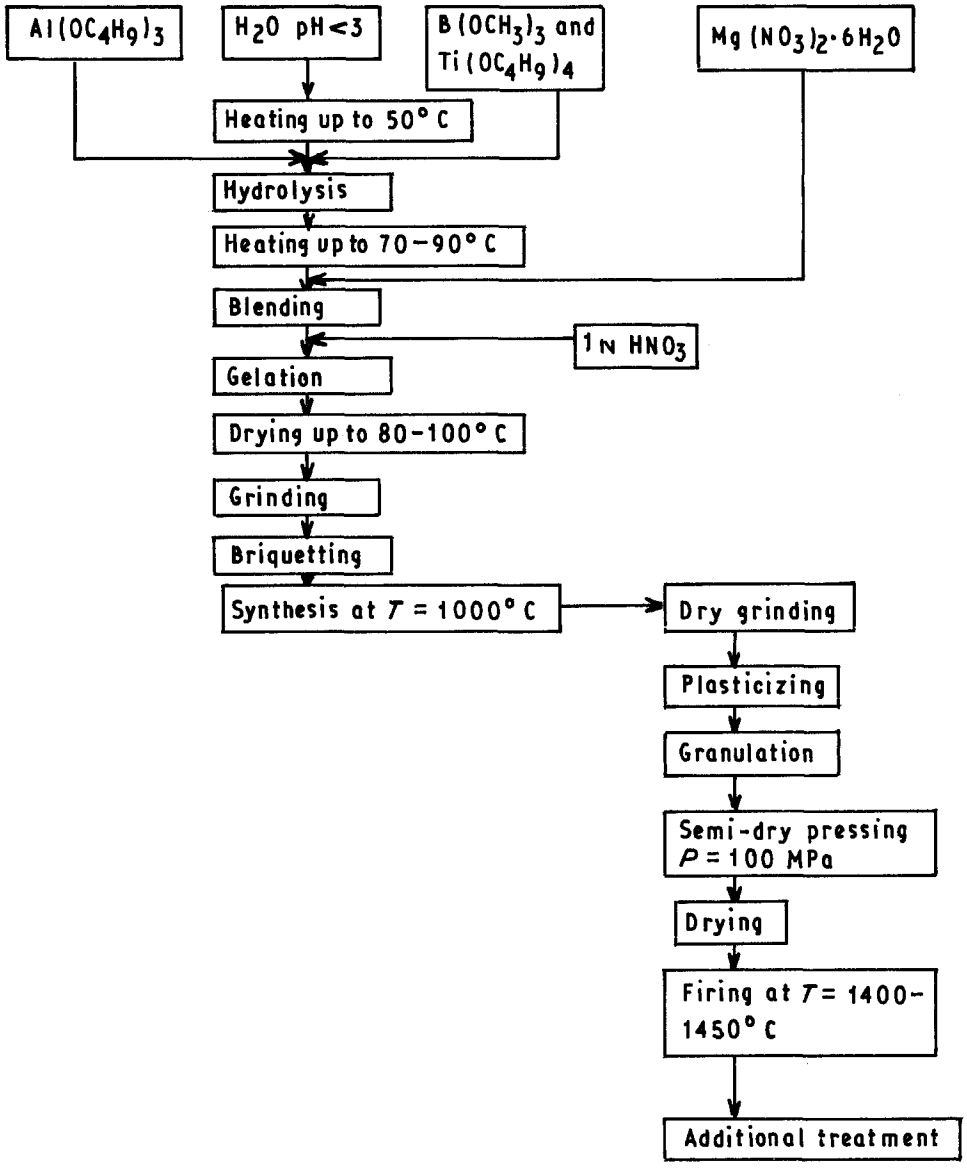

Figure 1 Technological flow chart for the synthesis and preparation of ceramics based on $MgAl_2O_4$.

dielectric losses (Verlustfaktormessgerat TYP 1033 and Tesla BM 238); and the specific bulk resistance (meggaometer Tesla BM 238, CSSR).

3. Results and discussion

The results of the X-ray phase analysis of the thermally treated gels are presented in Fig. 2. Up to 500–600 °C, the specimens are röentgenoamorphous. Intensive crystallization of the gels begins at 900 °C, when the magnesium spinel crystallizes from the amorphous phase ($d = 0.467$, 0.284, 0.244 and 0.202 nm). With increasing temperature the intensity of these bands increases considerably, which is an indication that the quantity of the spinel formed is increased.

Chemical analysis of the specimens treated at different temperatures shows that the percentage of spinel increases with increasing temperature attaining 96–97% at 1100 °C, as the quantity of the free MgO < 1% (Fig. 3).

The same trend of increasing spinel content in the specimens was observed with increasing the delay time at constant temperatures (Fig. 4).

The results from the X-ray phase analysis were also confirmed by infrared spectroscopy (Fig. 5). Bands at 1425, 1525, 1630, 3450 cm^{-1} on the infrared spectrum at 500 °C were found. The former two bands correspond to γ_{NO_3} vibrations, present because of the inadequate decomposition of the nitrates.

The band at 3450 cm^{-1} corresponds to the valence vibrations of the constitutional water [18]. The area and the intensity of this band diminishes with rising temperature during the process of treatment of gels. The band at 1630 cm^{-1} is assigned to the deformation vibration of water molecules (δ_{H_2O}) [18]. Its appearance at high temperature up to 1100 °C was most probably caused by the water absorption during the pelletization of the specimens with KBr.

Above 500 °C the bands assigned to the γ_{NO_3} disappear and new ones (690–525 cm^{-1}) are found. Their intensity and area increase with the rising temperature. These bands correspond to the existence of

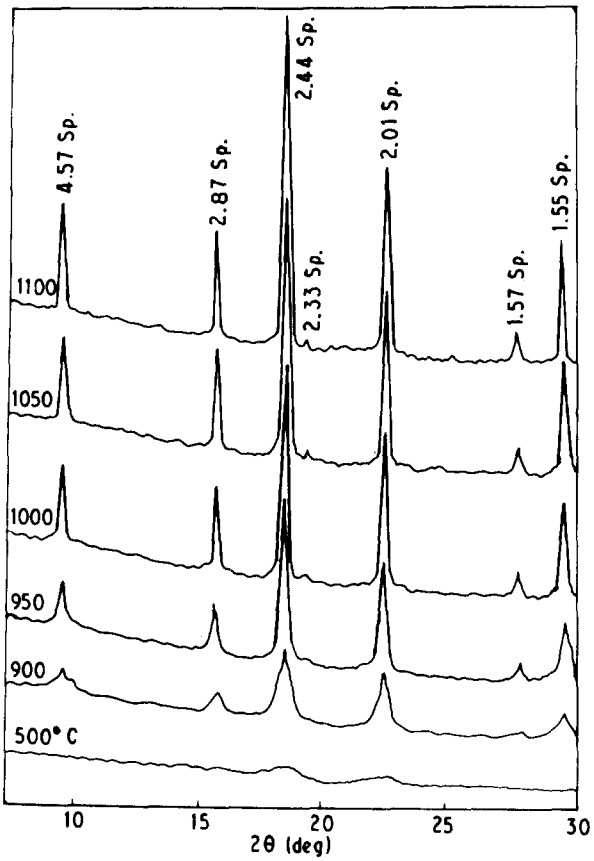

Figure 2 Diffractograms of the spinel synthesized at different temperatures.

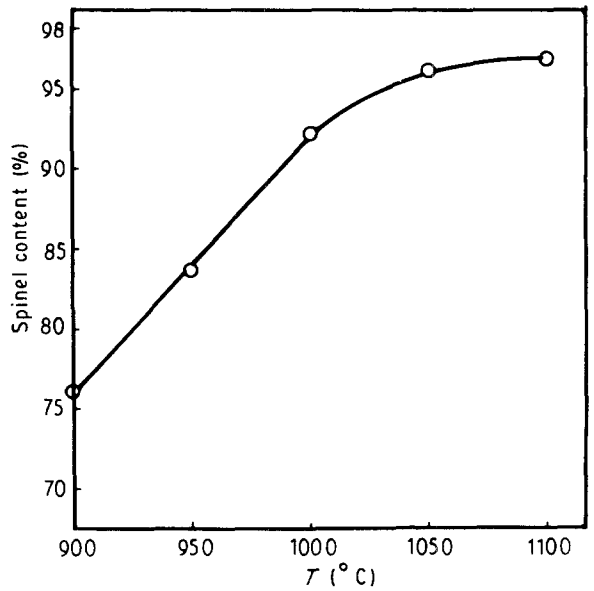

Figure 3 Spinel content versus temperature of the synthesis.

AlO_6 groups building up the magnesium spinel, which is the only crystalline phase in accordance with the X-ray studies at this temperature.

The prepared spinel ceramics are mechanically very good and satisfy the requirements for electroinsulating materials. It is worth noting that, by the sol–gel technology, the spinel synthesis and the preparation of the investigated ceramics were performed at lower temperature and, at these conditions, the mechanical

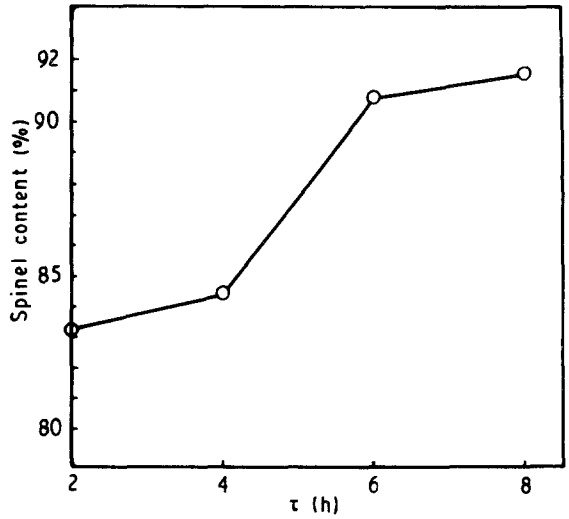

Figure 4 Variation of spinel content at 950 °C with different time delays.

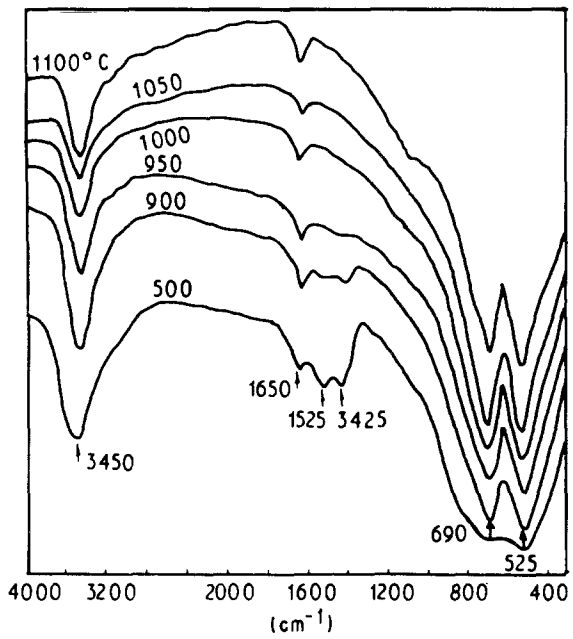

Figure 5 Infrared spectra of the spinel synthesized at different temperatures.

TABLE I Properties of ceramics from magnesium spinel by sol–gel and solid phase synthesis

Properties	Sol–gel technology	Solid phase synthesis [11]
Temperature of synthesis of spinel (°C)	1000	1250
Temperature of sintering of ceramics (°C)	1400–1450	1450–1480
Density (g cm^{-3})	3.43	3.44
Bending strength (mPa)	210–280	160–190
Coefficient of thermal extension (10^6 $°C^{-1}$) from 20–700 °C	8.2	8.4
Dielectric permittivity at 20 °C	7.3	8.0
Coefficient of heat conductivity (W m^{-1} K^{-1}) from 20–100 °C	6.3	4.7
Dielectric losses (tan $\delta \times 10^4$, 20 °C, 1 MHz)	4.8	1.9
Specific bulk resistance (Ω cm) at 20 °C	10^{13}–10^{14}	$> 10^{14}$

characteristics were improved, and the rest were within the limits for this material (Table I).

4. Conclusions

The investigation carried out and the results obtained lead to the following conclusions.

1. Synthesis of the spinel is carried out at 1000 °C, reaching over 97% spinel, by applying the sol–gel method and the inclusion of a soluble salt as one of the components.

2. Combinations of additives like B_2O_3 and TiO_2 were included as alcoholates during the process of hydrolysis. These caused an intensification in the course of the process of spinel-formation.

3. A dense electroinsulating ceramic was prepared at a lower temperature (1400–1450 °C) compared to solid phase synthesis.

4. The spinel ceramic has improved mechanical properties and retains the necessary electrical and thermal characteristics.

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