PHASE TRANSFORMATION DURING THE HEAT TREATMENT OF SOL–GEL MULLITE

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Abstract

The mechanism of mullite formation depends upon the method of combining the silica and alumina-containing reactants. In this work, the effects of the processing variables (dilution, pH, gelling temperature and water content) on mullite formation were investigated.

Monophasic gel was synthesized from aluminium nitrate nanohydrate dissolved in an absolute ethyl alcohol and silica sol mixture. The gelling was performed at room temperature and at 60°C. It was found experimentally that the temperature of mullite formation depends on the microstructure of the gel. The lowest temperature of mullite formation (970°C) was observed when the mullite gel was prepared at low pH (pH=1), low water content and high gelling temperature.

Keywords: aluminium ions, aluminosilicate gel, mullite, silica solution, sol–gel

Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is one of the extensively studied crystalline phases in the system Al_2O_3–SiO_2. The mechanism of mullite formation depends upon the method of combining the alumina- and silica-containing reactants. During the past decade, the most attractive method for mullite preparation has been the sol–gel process. The main difficulty in the preparation of mullite is to attain a homogeneous mix of Al_2O_3 and SiO_2. Via the process variables, it is possible to change the microstructure on the nanometric scale and hence to change the kinetics of the mechanism of mullite formation. The sol–gel method allows the preparation of a very homogeneous and reactive gel which can be sintered at low-temperature and consequently yield a submicronic microstructure. With the sol–gel method, it is possible to obtain a relatively high-density gel, one of the conditions for well-densified ceramics [1]

Mullite obtained after sol–gel processing has received much attention as a matrix material for high-temperature composite development, as a substrate in multilayer packing in electronics, and as an infrared-transparent window, especially for high-temperature applications. Various types of sol–gel method have been described [2–5] for making a single-phase gels, using tetraethyl orthosilicate (TEOS) and alumina precursors of different types. However, despite these early works and many other studies, knowledge concerning the kinetics and mechanism of mullitization is still limited.

The application of polymeric gels obtained after the hydrolytic polycondensation of metal salts (aluminium nitrate) and an alkoxide sol (TEOS) is a suitable method for mullite processing [6]. By this method, alumina and silica can be mixed on a molecular scale and the temperature of mullite formation can be lowered considerably [4]. In our study of mullite formation by the sol–gel method, the hypothesis was that aluminium ions from alcoholic solution could be incorporated into the polymeric silica sol from the starting of tetrahedral and octahedral coordination [7]. This is expected to furnish the lowest temperature of mullite formation, which was the main purpose of this study. In this work, we have studied the influence of the processing variables on the microstructure of the gel and the kinetics of mullite formation. The microstructure of the gel was systematically controlled via changes in the processing parameters (dilution, pH, gelling temperature and water content). Different gel structures could be designed by using the well-known [8] dependence between the gel structure and the sol–gel processing variables.

Experimental procedures

Sample preparation

Polymeric gel with the stoichiometric composition of mullite (Al:Si=3:1) was obtained by dissolving 10.2 g aluminium nitrate nonahydrate in absolute ethyl alcohol, followed by mixing, at room temperature, with 2 ml 99% tetraethyl orthosilicate (TEOS). The pH of this solution was about 1. The water used for the hydrolysis of the TEOS was the bonded water in the aluminium nitrate nonahydrate. This bonded water was 3 to 27 mol of water per mol of TEOS, but when the pH was increased by the addition of ammonia solution, the quantity of water was increased up to 140 mol of water per mol of TEOS (Table 1). The majority of the samples were gelled at 60°C and only one (A-7) was gelled at room temperature (Table 1). The gels obtained were dried at 110°C during 2 days and then calcined at 600°C for 2 h. Some of the

Table 1 Notations and processing variables of starting sols

Sample	pH	Gelling temp./ °C	R ratio mol water/ mol TEOS	Dilution mol Al-nitrate/ mol alcohol	Gel appearance
A-1	1	60	27	0.06	transp.
A-2	1	60	27	0.08	transp.
A-3	1	60	27	0.05	transp.
A-7	4.5	20	83	0.04	opaq.
A-12	4	60	65	0.03	opaq.
A-15	4.5	60	75	0.04	opaq.
H-9	1	60	27	0.06	opaq.
H-1	1	60	3	0.03	opaq.

samples were heat-treated up to 1050 or 1300°C for 2 h. The experimental conditions for gel preparation are given in Table 1.

Characterization methods

The X-ray powder patterns of the specimens were obtained on a Philips X-ray diffractometer (PW 1050, 51) with Ni-filtered CuK$_\alpha$ radiation operating at 30 kV and 30 mA. They were used for the identification of the crystalline phases and also for the qualitative assessment of crystallization. Care was taken to use the same sample holder, with the same volume of sample powder, heat-treated at different temperatures for the investigation. DTA and TG analysis was performed on powder samples on a Q-1500 D derivatograph (MOM) at a heating rate of 10°C min^{-1} in air in order to determine the temperature of mullite crystallization and the structural change during heating.

Results and discussion

Thermal analysis

The TG results (heating rate 10°C min^{-1} up to 1000°C) on some gels are given in Figs 1 and 3. According to the DTA data (Fig. 2, endothermic peak at 275°C), the mass loss in the region 150–300°C corresponds to the removal of residual organic content and nitrate [8]. It may be seen from Fig. 3 that gel A-3 has the lowest mass loss (55%) and gel A-7 the highest (83%). This difference in mass loss could be related to the loss of nitrate and the removal of organics from the polymer silica network. The gels with added ammonia solution give the highest mass loss (samples A-7 and A-15). The minimum mass loss is that of the gel with only a small quantity of water, a low pH, without ammonia solution and with the lowest dilution (sample A-3, R=27, Table 1). These preparation conditions (small R, low pH and low dilution)
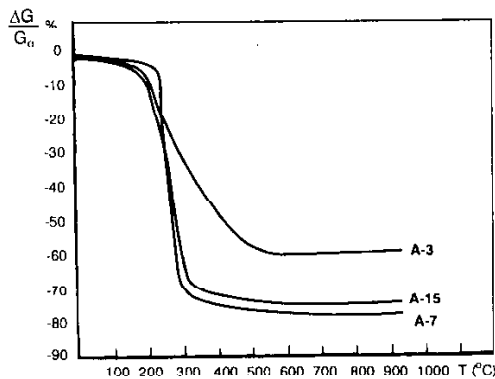

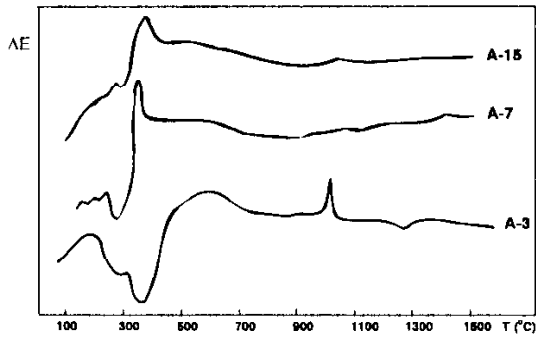**Fig. 1** Mass loss (%) from mullite gels (A-3, A-7 and A-15), determined by TG

Fig. 2 DTA traces of mullite gels (A-3, A-7 and A-15) detailed in Table 1

lead to the formation of a silica network which retains a smaller quantity of organics during drying than the gel with added ammonia solution (samples A-7 and A-15).

The DTA results on mullite formation for some samples are presented in Fig. 2. The DTA traces generally contained two peaks. The endothermic peak at 275°C can be attributed to the combustion of nitrate and organic substituents [9]. The exothermic peak at 980°C indicates the temperature of mullite formation [4, 5]. According to Fig. 2, mullite formation is obvious from the sharp peak in the sample prepared at low pH and water content (A-3). In the samples prepared at higher pH and water content, the peak at 980°C is small and rather broad (Fig. 2, samples A-7 and A-15). In this case, the rate of mullite formation is reduced [5, 10]. This confirms that the rate of mullite formation depends on the gel microstructure.

Figures 3 and 4 present TG and DTA results on gels H-1 and H-9. For gel H-1, the quantity of water for hydrolysis is reduced, at only 1 mol H_2O ($R=3$). It may be seen from Fig. 4 that gel H-1 underwent a greater mass loss (52.8%) than did gel H-9 (48.4%). These results can be explained in that, in the acid-catalysed silica sols, the ethoxide content determined from combustion analysis decreases with increasing R.
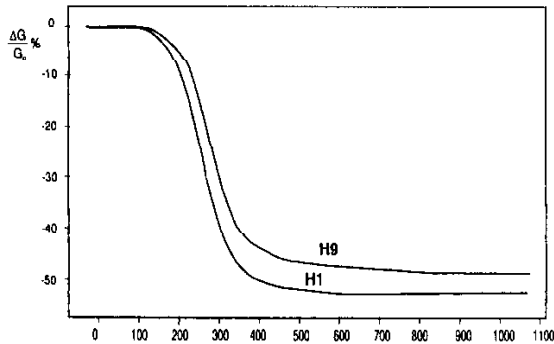

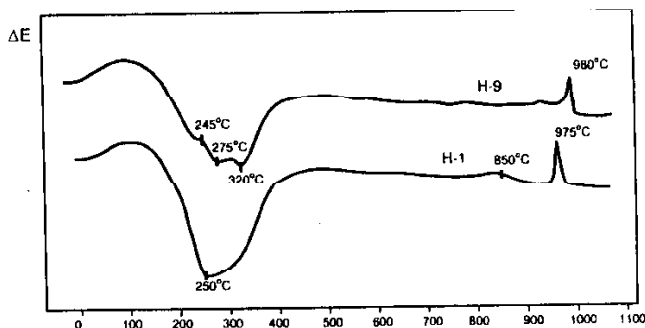**Fig. 3** Mass loss (%) of mullite gels (H-1 and H-9), determined by TG

This removal of organic substituents by heat treatment contributes to the mass loss. Thus, gel H-1, with smaller R ($R=3$), undergoes a greater mass loss than that for gel H-9.

According to Scherer [8], incomplete hydrolysis and reesterification contribute to the retention of organic groups in the final dried gels (this is the case with gel H-1). Both factors promote a more open structure containing excess free volume. We presume that this open structure provides a possibility for redistribution of the aluminium ion with tetrahedral and octahedral coordination during heating, and also gives better conditions for mullite formation. This hypothesis is supported by the result shown in Fig. 4, where the temperature of mullite formation for gel H-1 (975°C) is seen to be somewhat smaller than that for gel H-9 (980°C).

Structural analysis

All the samples were first heated up to 600°C (heating rate 2.5°C min^{-1}) for 2 h. The XRD results revealed that at this low temperature the samples were non-crystalline after calcination (XRD data are not presented). This result was to be expected, since this temperature is too low for mullite formation or any solid-state reaction in the system. XRD analysis (Fig. 5) was used to characterize the phases formed during heat treatment at 980°C (evident from DTA). The DTA results (Fig. 2) demonstrated only one exothermic peak between 980 and 1300°C, meaning that only one crystalline phase is formed. The results (Fig. 5) of the XRD analysis of sample A-3 (heat-treated at 1100°C) showed the presence of the mullite phase. At the same time, no other phase was detected. The mullite phase present at 1100°C in samples A-3 and A-12 is formed at almost the same rate. The quantity of mullite is somewhat higher in sample A-3 than in sample A-12 only because the pH values of the sols were different (the pH being lower in A-3 than in A-12) [11]. This difference in pH probably leads to the different numbers of direct –Al–O–Si– bonds, which is caused by the redistribution of the aluminium ion to tetrahedral and octahedral sites. This result indicates that the rate of mullite formation obviously depends on the processing parameters of the gel formation, i.e. the gel microstructure. At the same time, from
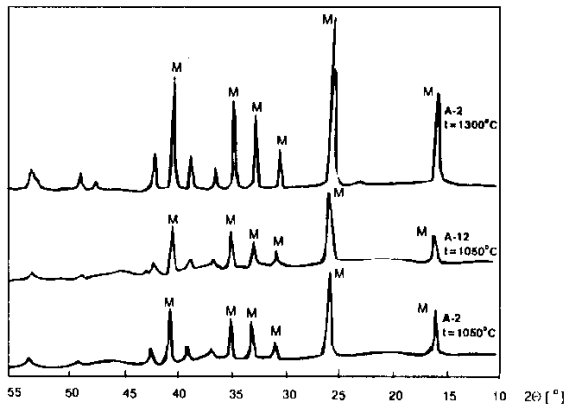
Fig. 5 XRD analyses of gels transformed at 1050 and 1300°C; *M*=mullite

Fig. 5 it is evident that the rate of mullite formation (peak intensity) increases with increase of the temperature of heating.

Conclusions

The results of this study have demonstrated that the microstructure of the aluminosilicate gel influences mullite formation. The lowest temperature of mullite formation (970°C) was observed for the mullite gel prepared at low pH and high gelling temperature (60°C). The degree of sol dilution does not markedly influence the rate of mullite formation. Higher pH, higher water content and lower gelling temperature (20°C) all decrease the rate of mullite formation. These findings confirm the assumption that the processing parameters of mullite sol preparation determine the gel microstructure and influence the rate of mullite formation.

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