Ceramics International 24 (1998) 553–557

PII: S0272-8842(98)00057-6
0272-8842/98 $19.00+.00

Low Temperature Transformation of Alumino-Silicate Gels

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(Received 7 March 1997; accepted 14 May 1997)

Abstract: Polymeric alumino-silicate gel obtained by hydrolytic polycondensation from metal salts of alumina and alkoxide sol of silica is a suitable method for mullite processing. In this work were investigated the effects of the processing variables (dilution, pH, gelling temperature and water content) on the mullite formation. Monophasic gel was synthesized from aluminium nitrate nanohydrate dissolved in absolute ethyl alcohol and silica sol mixture. The gelling is performed at room temperature and at 60°C. Experimentally it was found that temperature for mullite formation depends on the microstructure of the gel. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Mullite ($3Al_2O_3*2SiO_2$) is one of the extensively studied crystalline phase in the Al_2O_3–SiO_2 system. In the classical method of the mullite preparation, kaolinite and related materials are thermally decomposed to mixed oxides at high temperature. The mechanism of mullite formations depends upon the method of combining the alumina- and silica-containing reactants. The reaction between bulk samples of alumina and silica occurs at relative high temperatures (>1550°C) by nucleation and growth at the interface between two phases. The main difficulty in the preparation of mullite is to get a homogenous mixing of Al_2O_3 and SiO_2. Mullite can be obtained through the sol–gel process and can be greatly improved by the control of some reaction conditions particularly by homogeneous mixing of Al_2O_3 and SiO_2 and controlling of the impurities.[1] The so-called sol–gel method allows to prepare very homogeneous and reactive gel which is possible to sinter at low temperature and consequently a submicronic microstructure can be reached. With sol–gel method it is possible to obtain relative high density in green state as a first condition for well densifed ceramics.[2]

Mullite has received much attention during the last decade as a matrix material for high-temperature composite development, as a substrate in multilayer packing in electronic and as an infrared-transparent window especially for high temperature applications. These new interest have sparked extensive studies on the synthesis and processing of mullite by polymer and colloidal sol–gel method. Wei and Halloran[3] studied the phase transformation behaviour in diphasic gels prepared from colloidal boehmite and tetraethyl orthosilicate (TEOS). Based on studies of microstructure evolution and reaction kinetics they concluded that mullite formation occurred by nucleation and growth within the diphasic gel matrix. Microstructure observations suggested that growth proceeded preferentially through the silica phase, since alumina particles were often engulfed by the growing mullite grains. Hoffman *et al.*[4] described several methods of making single phase gels from tetraethyl orthosilicate (TEOS) and aluminium nitrate and showed that even the ethanol content in the precursor solution can change later DTA results. However, despite these early works and many other later studies,[5–7] knowledge of kinetics and mechanism of mullitization is still limited.

Polymeric alumino-silicate gel obtained by hydrolytic polycondensation from metal salts (aluminium nitrate) and alkoxide sol (TEOS) is a suitable method for mullite processing.[8] By this method, alumina and silica can be mixed on a molecular scale and temperature of mullite formation can be significantly lowered.[9] In our studying of the mullite formation by sol–gel method, the hypothesis was that aluminium ions from alcoholic solution of its salts will be incorporated to polymeric silica solutions.[10] In that way it is expected to achieve the lowest temperature of mullite formation, which is the main purpose of this study. In this work we have studied the influence of the structure of alumino-silicates gels on the kinetics of mullite formation. The assumption was that structure of the formed alumino-silicate gel depends on the branching degree of silica network and position of Al-ions in the silica network. The microstructure of the gel was systematically controlled by change of processing parameters (dilution, pH value, gelling temperature and water content). Different gel structure could be designed using well known[11] dependence between the gel structure and sol–gel processing variables. So we expected to get different gel structures from pure polymer to colloidal ones.

2 EXPERIMENTAL PROCEDURES

2.1 Sample preparation

Polymeric gel with the stoichiometric composition of the mullite (Al:Si = 3:1) was obtained by dissolving 20.4 g aluminium nitrate nanohydrate in absolute ethyl-alcohol and by mixing, at room temperature, with 4 ml 99% tetraethyl orthosilicate (TEOS). The pH value of this solution was about 1. In order to increase the pH value the water solution of NH_4OH (25%) was added. The quantity of water used for hydrolysis of TEOS was from the bonded water in aluminium nitrate nanohydrate. That bonded water was 27 mol of water per mol of TEOS, but in the case when the pH value was increased by adding of ammonia solution the quantity of water was increased up to 130 mol of water per mol of TEOS (see Table 1). The solutions for gelling were placed in a water bath, some of them at 60°C and some them at room temperature (Table 1). The obtained gels were dried during two days at 110°C and then calcined at 600°C for 2 h. Some of the samples were heat treated up to 1100 and 1300°C for 2 h. Experimental conditions for gel preparation are given in Table 1.

2.2 Characterisation methods

The X-ray powder patterns of the specimens were obtained on a Philips X-ray diffractometer (PW 1050, 51) with Ni-filtered Cu–Kα radiation operating at 30 kV and 30 mA, They are used for 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 the sample powder, (heat treated at different temperatures) for the investigation.

DTA and TG analysis was performed on powder samples on a MOM derivatograph Q-1500 D at a heating rate of 10°C min^{-1} in air in order to determine the temperature of the mullite crystallization and the structural change during heating.

Microstructures of the non-crystalline and crystalline materials were investigated by the SEM. A scanning electron microscope (JEOL-SM35) was used to reveal the microstructure of the material obtained at different heat-treatment conditions. For SEM observations the samples were coated with silver coating.

3 RESULTS AND DISCUSSION

3.1 Gel appearance

Polymeric gel, obtained by the mixing of TEOS and aluminium nitrate nanohydrate could be transparent or opaque, depending on the pH value, the gelling temperature and the water content. The results in Table 1 show that gels change the

Table 1. The notations and processing variables of the starting sols

Sample notation	pH	Gelling temperature (°C)	R-mol ratio of water to TEOS	Dilution mol ratio Al-nitrate to alcohol	Gel appearance
A-1	1	60	27	0.06	Transparent
A-2	1	60	27	0.08	Transparent
A-3	1	60	27	0.05	Transparent
A-5	2	20	110	0.25	Opaque
A-7	4.5	20	83	0.04	Opaque
A-10	7.5	20	130	0.025	Opaque
A-11	1	20	27	0.06	Transparent
A-12	4	60	65	0.03	Opaque
A-15	4.5	60	75	0.04	Opaque

appearance depending on the processing variables. At higher pH values and water content (samples A-7, A-12, A-15) gels were opaque. At lower pH values (samples A-1, A-2, A-3, A-11) gels were transparent. This difference can be explained by the size of structural species in the gels. At higher pH value and the water content the structure of gel is more network-like[11] and it causes the gel to be opaque.[11] But at lower pH value and water content, silica structure is more chain-like[11] and the gels were more transparent (Table 1).

3.2 Results of thermal and structural analyses

TGA results (heating rate 10°C min^{-1} up to 1000°C) of some of the gels are given in Fig. 1. As is obvious from Fig. 1, the gels drastically change the weight in the temperature interval 150–300°C mainly by losing water. The lowest weight of loss has the gel A-3 (55%) and the highest one has the gel A-7 (83%). This difference in the quantity of weight loss could be related to the quantity of bonded water during the gelling. The weight loss is mainly related to the water loss and removal of organics in the polymer silica network. So the gels with high content of water have high loss of water (samples A-7 and A-15). Minimal water losses result with the gel with minimal water content (sample A-3, with 27 mol of water per mole of TEOS).

All the samples were first heated up to 600°C (heating rate 2.5°C min^{-1}) for 2 h. XRD results show that at so low a temperature after calcination the samples were non crystalline (XRD results are not presented). This result is expected since it is too low temperature for the mullite formation or any solid state reaction in the system.

In order for mullite to be formed the samples had to be heat treated up to a much higher temperature (temperature interval between 980 and 1300°C). DTA results of mullite formation for some samples were presented at Fig. 2. Mullite formation from gel is obvious on 980°C from the sharp peak in the sample prepared at low pH value and water content (A-3). In the samples prepared under higher pH values and water content, the peak at 980°C is small and rather broad (Fig. 3, samples A-7, A-15). In this case, the rate of mullite formation is reduced. This fact confirms expectations that the rate of mullite formation depends on the gel microstructure. The content of the formed mullite is the highest in the gels prepared at low pH value, higher gelling temperature and low content of water (sample A-3).

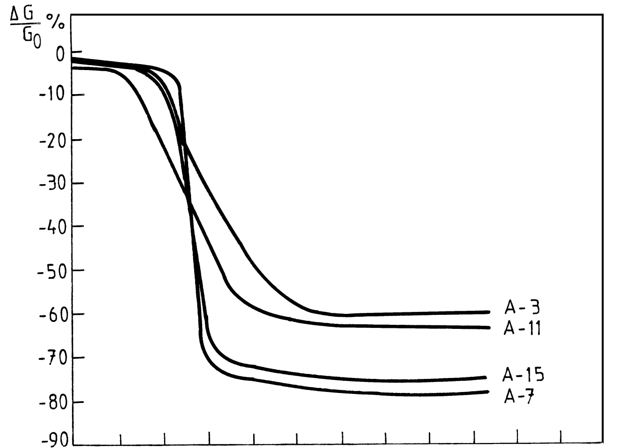


Fig. 1. Weight loss (%) determined by TGA.

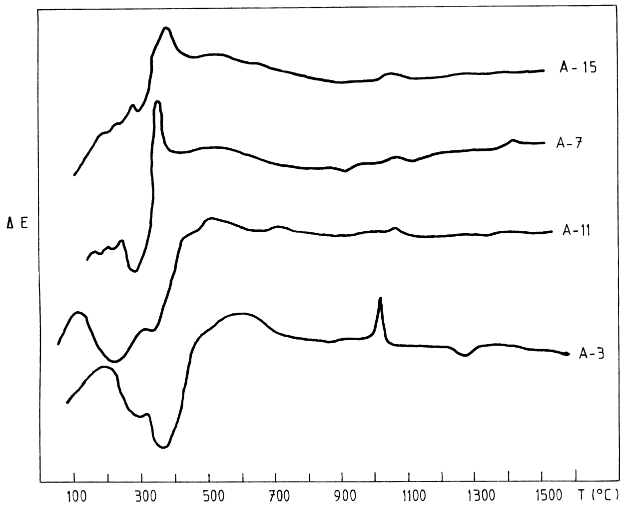


Fig. 2. DTA traces of mullite gels presented by Table 1.

The rate of mullite formation was tested as a function of alcohol dilution too(the samples A-1, A-2, A-3, Table 2). DTA results presented in Table 2 show that degree of alcoholic dilution does not remarkably change the temperature of mullite formation. Somewhat lower temperature of mullite

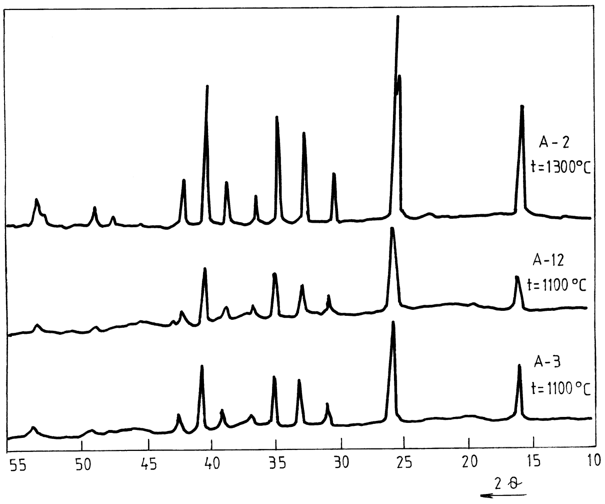


Fig. 3. XRD analyses of gels transformed at 1100°C and 1300°C.

Table 2. The effects of the dilution on the temperature of mullite formation

Sample notation	Dilution mol ratio of Al-nitrate to alcohol	Temperature of mullite formation (°C)
A-1	0·06	977
A-2	0·08	981
A-3	0·05	970

formation exhibits the sample A-3. This result can be explained in the manner of Yoldas[5] by the stronger bonds –Al–O–Si– in the polymer silica structure under high dilution. This Yoldas model holds only for the mullite formation from the polymer gel. It can be seen (Table 2) that the highest diluted (sample A-3) has the lowest temperature of mullite formation (970°C).

XRD analysis was used for characterisation of the phases that have been formed during the heat treatment at 980°C (what is evident from DTA). DTA results (Fig. 2) have shown that between 980 and 1300°C exists only one exothermic peak, meaning only one crystalline phase is formed.

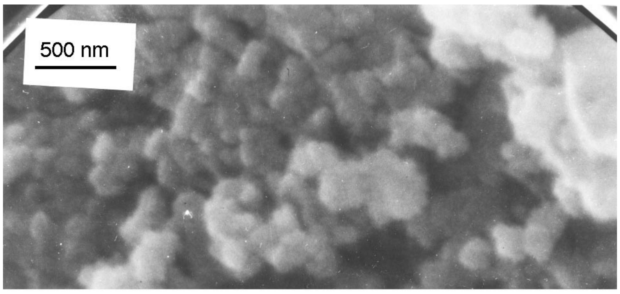
The results (Fig. 3) of the XRD analysis of the samples A-3 (heat treated at 1100°C) have shown existing mullite phase. At the same time it has not detected another phase.

The mullite phases present at 1100°C in the samples A-3 and A-12 are formed at almost the same rate. The quantity of formed mullite is somewhat higher in the sample A-3 than in sample A-12 only because the pH value of sols were different (pH being lower in A-3 than in A-12). This difference in the pH probably leads to the different number of the direct –Al–O–Si– bonds which are responsible for the mullite formation. This result shows that the rate of mullite formation obviously depends on the processing parameters of the gel formation meaning the gel microstructure. At the same time from Fig. 3 it is evident that the rate of mullite formation (peak intensity) increases with the temperature of heating. The rate of mullite formation at 1300°C in respect to 1100°C is about double (Fig. 3) what is expected.

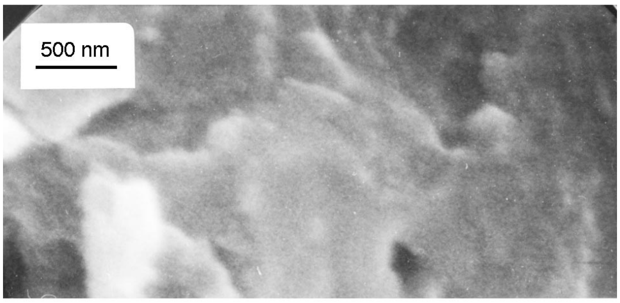
3.3 Results of the microstructure analysis

The microstructure of heat treated samples A-3 and A-11 were further investigated by SEM. Figure 4 shows a micrograph of a fresh fractured surfaces of mullite materials after heat treatment at 1100°C for 2 h.

The microstructure differences (Fig. 4(a) and (b)) are only in the scale of the nucleated mullite. Even though the temperature of mullite formation was almost the same the microstructure scale of mullite is different, probably only because of different parameters of mullite gel preparation (Table 1) which caused the different scale of the nuclei growth.



(a)



(b)

Fig. 4. SEM micrographs of samples A-3 (a) and A-11 (b) obtained after heat treatment at 1100°C for 2 h (white bar = 500 nm).

4 CONCLUSION

The results of this study showed that the microstructure of alumino-silicate gel has influence on the mullite formation. The lowest temperature of the mullite formation (970°C) results from the mullite gel preparation under low pH value, water content and high gelling temperature (60°C). The degree of sol dilution does not show a remarkable effect on the rate of the mullite formation. The higher pH value, water content and low gelling temperature (20°C) decrease the rate of mullite formation.

So, the assumption that the processing parameters of mullite sol preparation determine the gel microstructure and that it has effect on the rate of mullite formation, was confirmed.

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