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Effect of Cr_2O_3 on the sintering of aluminosilicate precursor leading to mullite formation

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Abstract

Aluminosilicate precursor material for mullite formation was synthesized using wet interaction of the ingredients like aluminum nitrate and silicic acid sol in the aqueous route. The gel was characterized by chemical analysis, measurement of surface area, bulk density and X-ray analysis. Sintering of the gel powder was carried out at different elevated temperatures from 1300°C to 1450°C in presence of Cr_2O_3 as a doping agent. The different physico-mechanical properties of the sintered compacts, such as, volume shrinkage, bulk density, porosity etc. were measured. X-ray diffraction and SEM analysis of the compacts were further carried out to evaluate the degree of sintering of the powder in presence of Cr_2O_3. It was observed that Cr_2O_3 plays a positive role in the formation of mullite at elevated temperature from the aluminosilicate gel precursor. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; D. Mullite; Aluminosilicate gel; Cr_2O_3

1. Introduction

Mullite is the only stable compound of the Al_2O_3–SiO_2 system. Mullite and mullite-containing composites are considered to be very important for high performance applications such as high temperature structural components, infrared transparent windows, substrate for microelectronic package, high temperature protective coating etc.

In the recent years attempts are being made to prepare mullite through the high temperature reaction of synthetic precursor powders. The fine grained and poorly aggregated precursor powders required for achieving high degree of sintering, can no longer be economically prepared in the classical way of mixing and firing oxides and carbonates. Chemical methods are followed presently to generate spherical mono-disperse, sub-micron powders. Single phase or molecularly mixed gels, usually derived from aluminium and silicon alkoxides or other salts by co-hydrolysis or co-precipitation exhibits homogeneity of aluminum and silicon species in the molecular level leading to the attainment of better microstructures of the sintered compacts.

Influence of powder characteristics on microstructure and mechanical properties were studied by various workers [1–5]. Sacks et al. [6] studied on the fabrication of mullite and mullite matrix composites by transient viscous sintering of composite powders. Klaussen et al. [7] worked on the microstructural evaluation mullite derived by sol–gel technique. Li et al. [8] studied on the kinetic mechanism for the mullite formation from sol–gel precursors.

Depending on the synthesis procedure, mullite is able to incorporate considerable amount of impurities. The effect of various impurities on mullite formation by solid-state reactions has been widely investigated. Mackenzie [9] studied the effect of impurities on formation of mullite from kaolinite type minerals. The substitution of chromium into mullite structure has been investigated recently by Schneider and co-workers [10]. They studied incorporation of chromium in mullite annealed at 1650°C, where Cr^{3+} is the only stable oxidation state of chromium. According to them, Cr^{3+} can be incorporated in the mullite structure up to 12 wt% (6.5 mol.%) Cr_2O_3. At lower chromium content, Cr^{3+} substitutes aluminum in the octahedral position, but at higher content incorporation at interstitial lattice sites is preferred. Schneider et al. [10] also pointed out that incorporation of Cr^{3+} in interstitial lattice must be a

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complicated process, which requires removal of Al^{3+} to form tetrahedral and/or octahedral vacancies for excess charge compensations. Cr^{3+} incorporation produces the highest expansion along the *c*-axis followed by expansion along the *a*-axis and *b*-axis of mullite. Murthy et al. [11] performed X-ray study of solid solution of TiO_2, Fe_2O_3 and Cr_2O_3 in mullite. There are no data concerning the influence of chromium ion on spinel formation in Al_2O_3–SiO_2 gels is available.

In the present investigation, powder in Al_2O_3–SiO_2 system having molar ratio as per general mullite composition has been synthesized. Wet interaction of the ingredients in the aqueous route was made to generate particles of very fine size with uniform microstructure. Chromium oxide, which was used as a doping agent in the present investigation, is often used as a nucleating agent for crystallization of spinel in glass ceramics [12]. The effect of Cr_2O_3 on mullitization has been studied in the present work with the object of eliminating the liquid phase during sintering.

2. Experimental procedures

For the synthesis of the hydrogel $Al(NO_3)_3$ of analar quality and liquid sodium silicate (sp. gr. 1.6 and molar ratio of $Na_2O:SiO_2 = 1:3$) were selected. Silicic acid solution was prepared by following the ion exchange technique. Sodium silicate solution (7% w/v) was passed through a column packed with a Dowex-50 cation exchanger maintaining a flow rate of 200 ml/min. The silicic acid thus generated through H-exchanger was stored in a polythene container.

Requisite proportion of silicic acid and Al $(NO_3)_3$ solutions were mixed according to the molar ratio Al_2O_3:-$SiO_2 = 3:2$. The solution was clear having a pH = 2. Gelation was carried out by slowly adding 1:1 ammonia whereby viscosity gradually raised and ultimately set to an enblock gel at pH 8.5–9. The gel was processed properly, dried at 60°C and milled in a pot mill.

With the powders discs of different dimensions were fabricated in a hydraulic press at a pressure of 900 kg/cm^2 without any binder.

The rate of firing of the discs was 10°C/min up to 1000°C and then 5°C/min to the final temperature of heat treatment.

X-ray diffraction patterns of the fired discs were taken with an X-ray diffractometer (Philips PW-1730) using Cu K_α radiation. SEM photographs were taken by S-440 Leo electron microscopy Cambridge, UK.

3. Results and discussion

The precursor aluminosilicate material was synthesized through an aqueous phase interaction, under an optimum condition. The chemical analysis of the ingredients is shown in Table 1.

During the generation of silicic acid, through cation exchange reaction, there was no indication of polymerization in the initial stage. Here silicic acid remained as positively charged colloid. After addition of Al $(NO_3)_3$ solution the pH of the mixture was found to be 5. Two types of reaction occurred simultaneously on addition of ammonia. In the first type, $Al(OH)_3$ was precipitated followed by polymerization of silicic acid through condensation mechanism. The aluminosilicate hydrogel after aging exhibited all the usual characteristics of gel including syneresis, i.e. the expulsion of liquid through capillary force.

The precursor powder so synthesized was found to be of light texture, having the surface area 268 m^2/g, which appears to be significantly high in the inorganic system. The hydrogel contained sufficient amount of water and in order to avoid excessive shrinkage it was calcined at 900°C and milled to fine state of subdivision and mixed with 10% uncalcined material, which acted as bond. Chemical analysis of the powder as shown in Table 2 indicated that the composition lies in the alumina rich zone of the mullite and there was no deviation from the parent batch compositions. The basic idea of keeping the Al_2O_3 content slightly higher than that required for mullite formation was to eliminate the glassy phase as maximum as possible. The uniformity of mixing of $Al(OH)_3$ and silicic acid particles in the molecular level was ascertained because before gelation by addition of ammonia, the silicic acid and $Al(NO_3)_3$ mixture were only in the solution stage. During co-gelation it is evident that distribution of each phase would be uniform. In this system discrete aluminum hydroxide particles should be distributed uniformly in the high molecular weight polysilicic acid gel network.

Table 1
Chemical analysis of the ingredients

Ingredients	SiO_2	Al_2O_3	Na_2O
Sodium silicate	29.64	–	17.52
Aluminium nitrate	–	12.98	–
Batch composition	21.00	79.00	–

Table 2
Physicochemical characteristics of the hydrogel

Composition/properties	
SiO_2	14.43
Al_2O_3	53.00
LOI	32.57
Bulk density (g/cm^3)	0.597
Sp. surface area (m^2/g)	268

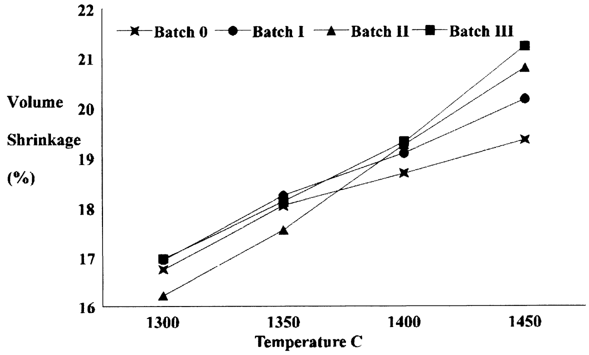

Fig. 1. Volume shrinkage vs temperature curves of samples fired at different temperatures.

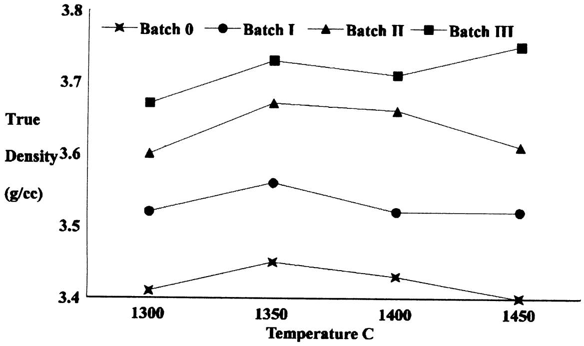

Fig. 2. True density vs temperature curves of samples fired at different temperatures.

The mineralizer Cr_2O_3 was added after thorough dispersion of the gel in acetone in three different percentages as shown in Table 3. The pressed pellets after sintering in normal atmosphere exhibited shrinkage as shown in Fig. 1. The initial shrinkage might be due to loss of residual water followed by solid state interaction leading to the formation of the stable crystalline phases. It is to be noted here that the original precursor powder was completely amorphous as tested by XRD analysis (figure not shown). Sintering was assisted in the compacts by mass transfer followed by crystallization and liquid formation, if any, as a result of which considerable shrinkage (as high as 20%) in the sintered compacts were noticed.

True density is one of the parameters related to phase transformation and the experimental value was an average of the density of the different phases like mullite and corundum in the multi-component system. In each case maximum density was achieved at 1350°C (Fig. 2). True density was found to increase with the Cr_2O_3 content. The shrinkage and true densities are two completely different properties. The former is related to textural factors, e.g. expulsion of gel water, particle orientation, pre generation and orientation. True density is related to ultimate phase composition and is determined experimentally by grinding the sintered compacts. This might be the reason for the apparent contradiction of the data shown in Fig. 1 (volume shrinkage increased with temperature) and Fig. 2 (density became maximum around 1350°C).

The true density values of the sintered batch mixture were higher than the theoretical density of traditional mullite ($3Al_2O_3{\cdot}SiO_2$). This can be explained by the fact that in the batch composition SiO_2:Al_2O_3 mole ratio was 1:2.1 (Table 2) instead of 1:1.5 in the traditional mullite. The comparatively high percentage of Al_2O_3 is responsible for high density.

Table 3
Batch composition of the samples

Batch no.	Al_2O_3–SiO_2 hydrogel	Cr_2O_3
0	100.00	0.00
I	98.50	1.50
II	97.75	2.25
III	97.00	3.00

Like true density bulk density values were also found to increase with the sintering temperature as well as with the mineralizer content (Fig. 3).

XRD patterns of the samples seeded with different proportions Cr_2O_3 fired at 1450°C have been represented in Fig. 4.

Mullite formation was noticed with all the samples. It is interesting to note that there was no other crystalline phase even though the Al_2O_3 content was slightly higher than the traditional mullite. This might be due to the formation of Al_2O_3 rich mullite as evidenced through the density values.

In the diphasic solution gel system, mullite formation occurs at relatively low temperature by nucleation and growth within the amorphous alumina saturated silicious phase. Microstructure development for doped samples sintered at 1450°C was studied by SEM and the micrographs have been shown in Fig. 5 (a–c). It was observed that the existence of porosity was common in all the samples and grain boundaries were more or less sharp, especially with highest Cr_2O_3 containing sample.

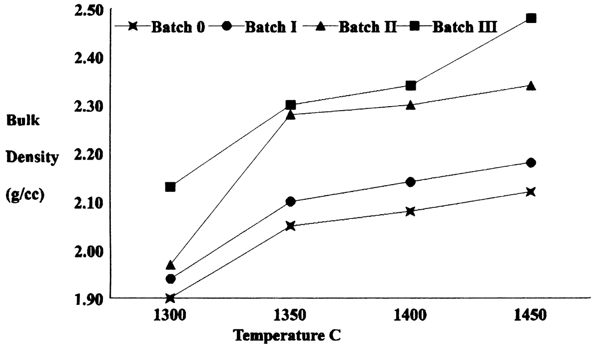

Fig. 3. Bulk density vs temperature curves of samples fired at different temperatures.

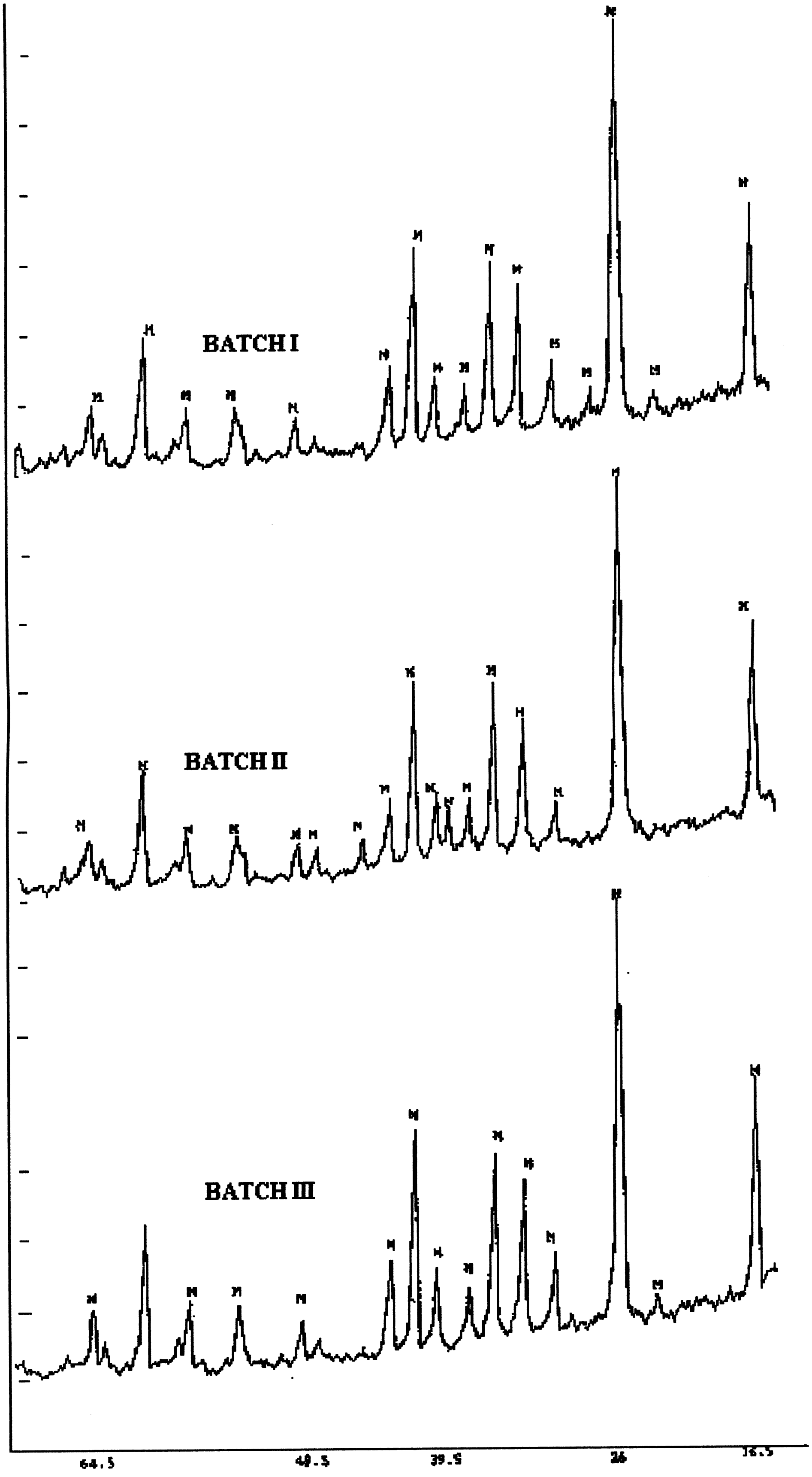

Fig. 4. XRD diagram of sintered compacts of batch I, II and III fired at 1450°C.

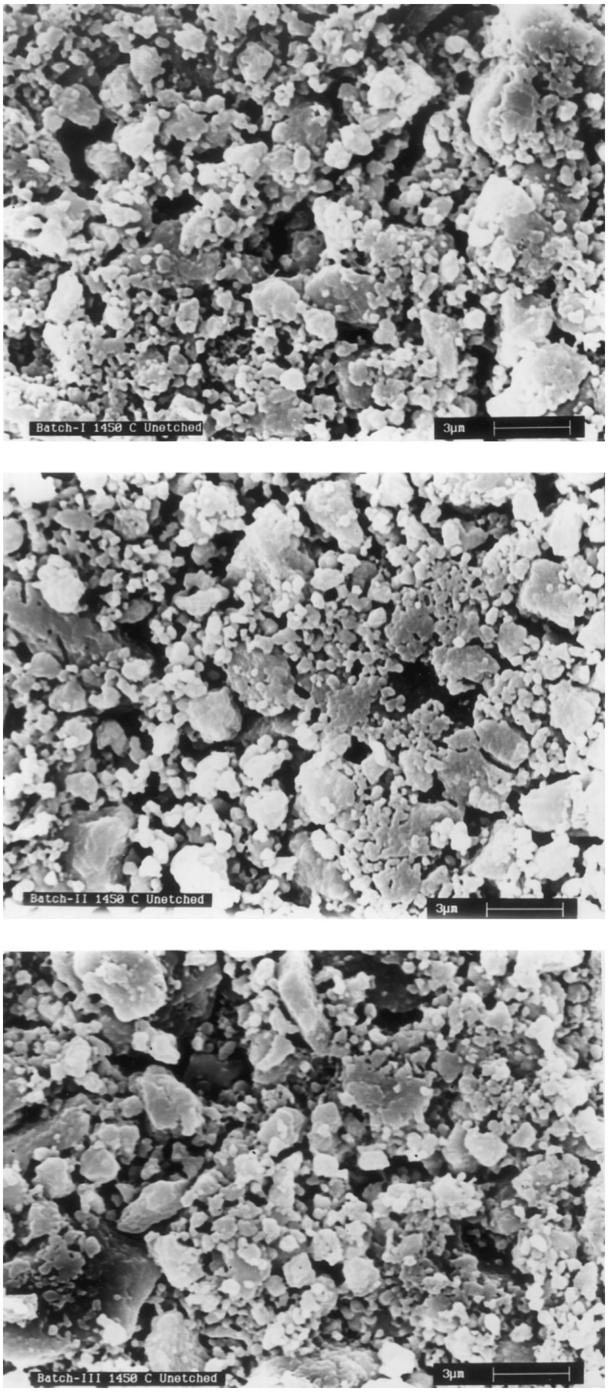

Fig. 5. SEM photomicrograph of sintered compacts of batch I, II and III fired at 1450°C.

The absence of needle-shaped mullite in the microstructure might be due to the absence of sufficient amount of liquid phase and more refractory nature of the doped oxide. The grains retained equiaxed morphology and there was positive variation in grain sizes. Numerous fine particles were observed both at intra- and inter-granular locations, which seems to be alumina cores with residual silica coating. The inhomogeneity that was observed in the microstructure was mainly due to phase separation. The grain development was dependent upon the concentration of sites for mullite growth. Coarsening of the microstructure was also observed in the batch-I and II during transformation to mullite. The grain development was consistent with nucleation of mullite at a relatively low number of sites followed by growth throughout the interconnected siliceous phase. Particles could become entrapped intragranularly by the growth of large individual mullite grains through the interconnected siliceous matrix.

After the initial phase separation, clustering of alumina rich phase probably took place. Chromium incorporation into the regular octahedral position is generally preferable. In this particular condition of sintering Cr^{3+} is the only oxidation state of chromium and moreover it was taken in Cr^{3+} state. Al(Cr)–Si spinel was expected as an intermediate product. It is also expected that Cr_2O_3 did not enter into the mullite lattice but a part co-exists in the amorphous matrix.

4. Summary and conclusions

Aqueous interaction of silicic acid sol and aluminium nitrate at pH 8.5 develops aluminosilicate precursor powder for mullite of high surface area. Chromium oxide acts as a positive doping agent for the development of mullite from this aluminosilicate gel at high temperature. Sintering temperature plays a positive role in the formation of mullite and other crystalline phases as indicated by the volume shrinkage and true density value. High values of density were achieved at a relatively lower temperature, i.e. 1450°C indicating the activity of the gel. In XRD diagram only mullite was observed as the crystalline phase in all the batches in spite of the slightly higher alumina content in the batches suggesting the formation of high alumina mullite in the batches. The absence of needle-shaped mullite in the microstructure was related to the absence of sufficient amount of liquid phase and more refractory nature of the doped oxide. The inhomogeneity in the microstructure was related to the phase separation in the sintered products and chromium oxide was thought to be present in the amorphous matrix without entering into the mullite structure.

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