

# EFFECT OF COPPER IONS ON MULLITE FORMATION FROM ALUMINOSILICATE PRECURSOR

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Submitted August 1, 2009; accepted February 12, 2010

**Keywords:** Mullite, Copper ions, Aluminosilicate powder, Chemical preparation, Sintering, Microstructure

*Aluminium nitrate and silicic acid were used for the synthesis of aluminosilicate precursor powder of mullite by colloidal process. Copper ions were used in different concentration as sintering additive to the synthesized precursor powder. The compacted powder mixes were sintered at different elevated temperatures. The influence of copper ions on the sintered samples was investigated by the measurement of different physico-mechanical properties, like bulk density, porosity, flexural strength and fracture toughness. The microstructure and phase analysis of the sintered masses were carried out by scanning electron microscopy and XRD analysis. It was observed that copper ions exhibited positive effect on the densification and development of mullite phase in the sintered compacts.*

## INTRODUCTION

Due to its favourable technical properties, mullite has achieved outstanding importance as a material for both traditional and advanced ceramics. These properties include low thermal expansion and thermal conductivity, good stability, high melting point, superior chemical resistance and creep resistance [1]. Owing to these qualities mullite can be widely used in the production of heat resistant materials in heat insulation, ceramics, composites, computer chips etc. [2,3] Mullite has a molecular formula  $Al_2[Al_{2+2x}Si_{2-2x}O_{10-x}]$ . It is basically a non-stoichiometric compound where x denotes the number of missing oxygen and atoms per unit cell, varying between 0.17 and 0.59 [4]. Recently synthesis of mullite using chemically synthesized precursors has gained a lot of importance where the precursors are converted to mullite in a low temperature range from  $\sim 850^\circ$  to  $\sim 1350^\circ\text{C}$  [5-7]. Mullite synthesized by this method is known as 'chemical mullite' [8]. The importance of these preparation methods has increased within the last few years. Different transition metal oxides have been shown to have favourable mineralizing effect on the formation of mullite ceramics from the precursor materials. Ferriera da Silva [9] observed that presence of manganese ion can induce mullitization at lower temperature from  $Al_2O_3$ - $SiO_2$  gel. Martisius and Giraitis [10] observed that copper oxide as an additive

can decrease the transformation temperature of kaolinite to mullite by  $200^\circ\text{C}$ . Kong et al [11] observed that  $V_2O_5$  accelerated the mullite phase formation, while  $Nb_2O_5$  and  $Ta_2O_5$  inhibited the mullitization. Baudin and Moya [12] observed that addition of  $TiO_2$  under the solubility limit enhanced the initial sintering and grain size in mullite whereas an amount in excess of that limit inhibit sintering and drastically increased the total porosity and mean pore size. Nass et al. [13] investigated the influence of chromium on homogeneity of gels and on mullite formation at  $980^\circ\text{C}$  by DTA coupled with quadrupole mass spectrometry, SEM, EDX and TEM analysis and observed that difference in chromium content affected the crystallization path of mullite. Mitra et al [14] observed that  $Cr_2O_3$  played a positive role in the formation of mullite at elevated temperatures from the aluminosilicate gel precursor. Copper oxide is one of the most effective additives for reducing the temperature for the conversion of kaolinite to mullite [15,16]. The effect of copper oxide addition results in an exothermal reduction of the transformation temperature by some  $50$ - $70^\circ\text{C}$  [15]. According to Spokauskas [15], copper oxide reacts with kaolinite at  $800^\circ\text{C}$  by forming a quartz-type phase. At a higher temperature it decomposes, amorphous  $SiO_2$  and quartz crystallizes to cristobalite and finally mullite is formed. Segnit and Gelb [16] also affirmed that the high temperature transformation of kaolinite to mullite in the presence of copper oxide

took place by the intermediate simultaneous formation of a quartz-type phase and a spinel type phase  $\text{CuAl}_2\text{O}_4$ . Other researchers also related the formation of mullite at lower temperature to the formation of copper aluminate spinel [17]. Bagchi et al [18] studied the influence of copper ions on the synthesis of nano-crystalline mullite at a low temperature and observed that activated crystal lattice of copper catalyzed the reaction between alumina and silica to form mullite at a much lower temperature of 600°C.

In the present investigation the effect of copper ion on the crystallization of mullite from aluminosilicate precursor powder was investigated by assessing the microstructure and mechanical properties of sintered products from aluminosilicate gel precursor derived from inorganic salts.

## EXPERIMENTAL

The aluminosilicate hydrogel was synthesized by the interaction of aluminum nitrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] and liquid sodium silicate (sp. Gr. 1.6 and molar ratio of  $\text{Na}_2\text{O} : \text{SiO}_2 = 1:3$ ). Both the chemicals used were of analar grade and their chemical composition is given in Table 1. Silicic acid was prepared by ion exchange from sodium silicate using Dowex-50 cation exchanging resin in a column exchanger. 7 % (w/v) sodium silicate solution was used as the feed with a flow rate of 200 ml/minute. 5 % (w/v) silicic acid solution and 10 % (w/v)  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution were mixed together stoichiometrically to attain a molar ratio of 3:2 for  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the mix. The pH of the solution was 2. To the solution 5 % (w/v) copper sulfate solution was added in

Table 1. Chemical composition of the components (wt.%).

Components	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$
Sodium silicate	30	–	17
Aluminium nitrate	–	13	–
Batch composition	27	73	–

Table 2. Physicochemical properties of the hydrogel.

Composition (wt.%)	Properties
$\text{SiO}_2$	18.00
$\text{Al}_2\text{O}_3$	48.00
Ignition Loss	34.00
Bulk density ( $\text{g}/\text{cm}^3$ )	0.27
Sp. Surface area ( $\text{m}^2/\text{g}$ )	70

Table 3. Batch composition of the samples (wt.%).

Batch No.	$\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ Hydrogel	Copper Oxide
1	100	0
2	99	1
3	98	2
4	97	3

different ratios to obtain 1, 2 and 3 wt.% CuO in the final product (Table 3). To the mixed solution 1:1 ammonia solution was added slowly with stirring. The viscosity of the solution increased gradually and ultimately complete gel formation took place at pH of 9. The gel was filtered, washed thoroughly, dried at 80°C followed by calcination at 800°C for a period of 2 hours. The calcined gel was properly pulverized in a pot mill and characterized by chemical analysis, and measurements of surface area and bulk density. The results are given in Table 2. The powder mixtures were compacted at 100 MPa. The samples were fired in an electrically heated muffle furnace at three different final temperatures 1400, 1500 and 1600°C, with 2 hours of dwell time in each case. Bulk density and apparent porosity of the sintered samples were measured following the procedures described in specification BS 1902, Part 1A, 1966. The flexural strength of the sintered samples were determined from a three point bending strength with a span of 30 mm and a loading rate of 0.5 mm/min. Fracture toughness was determined by using an indentation micro-crack method with a load of 5 kg. [19]. XRD pattern of the samples was taken with a Rigaku X-ray diffractometer with  $\text{CuK}_\alpha$  radiation (Miniflex, Japan). Scanning electron microscopic investigation of the samples was carried with FEI Quanta microscope (US).

## RESULTS AND DISCUSSION

When silicic acid was mixed with  $\text{Al}(\text{NO}_3)_3$  solution, the mixed solution became acidic. With the addition of ammonium hydroxide non-simultaneous formation of the gels aluminium hydroxide and polysilicic acid took place and therefore, the formed aluminosilicate gel was di-phasic in nature. In this system discrete aluminium hydroxide gel particles was likely to be distributed uniformly in the high molecular weight polysilicic acid gel network [14, 20].

Compared to the solid state mixing, the solution mixing of the additive generated better homogeneity in the composition by molecular level mixing and the additive copper ions is expected to be distributed uniformly in the gel precursor. Silicic acid after being generated by ion exchange process, did not show any tendency of polymerization as it is a positively charge colloid.

The precursor powder is expected to have considerable surface activity as it had a very low bulk density ( $0.27 \text{ g}/\text{cm}^3$ ) and a considerably high surface area ( $70 \text{ m}^2/\text{g}$ ). As the hydro-gel contained significant amount of water (34%) it was calcined at 800°C to prevent excessive shrinkage during sintering. The composition of the aluminosilicate was intentionally kept slightly in the alumina rich zone of the mullite to minimize the formation of glassy phase after sintering. After synthesis no deviation was observed from the parent

batch composition in the synthesized material. Mullite formation in diphasic aluminosilicate gel is controlled by dissolution-precipitation reactions, where  $\text{Al}_2\text{O}_3$  species dissolve in the co-existing  $\text{SiO}_2$  liquid until a critical  $\text{Al}_2\text{O}_3$  concentration is reached [21, 22].  $\text{Al}_2\text{O}_3$  particles act as the nuclei for mullite formation and higher  $\text{Al}_2\text{O}_3$  concentrations can induce random mullite nucleation in the bulk of the  $\text{SiO}_2$ -rich phase. Therefore,

the dissolution velocity of  $\text{Al}_2\text{O}_3$  into the  $\text{SiO}_2$  liquid is the rate limiting step for the nucleation and subsequently growth of mullite crystals.

Aluminosilicate lattice is basically composed of  $\text{AlO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra. At high temperature (around  $1050^\circ\text{C}$ )  $\text{CuO}$  decomposes to  $\text{Cu}_2\text{O}$  [10]. This result in the formation of  $\text{Cu}^+$  which has higher diffusivity and consequently reactivity towards alumina

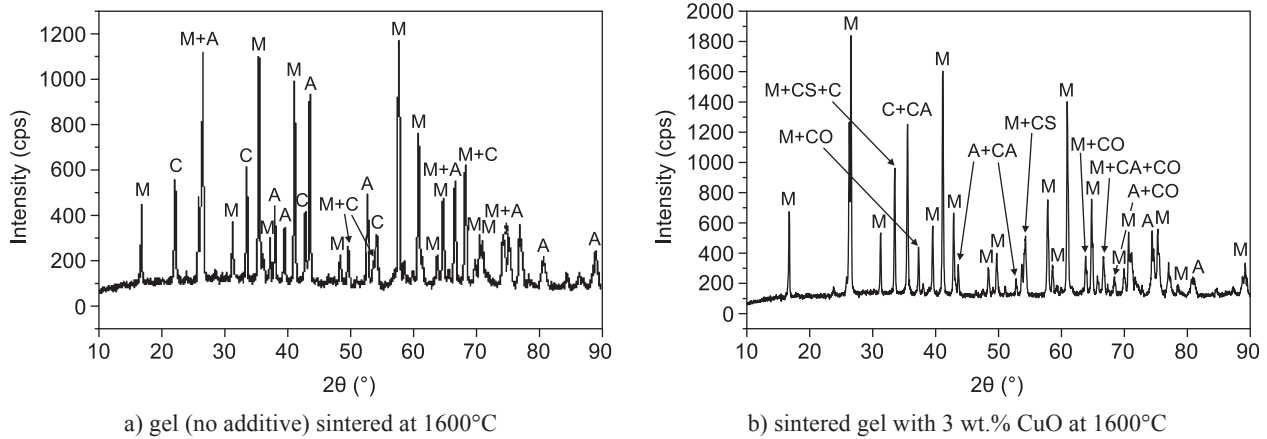


Figure 1. XRD Diagram of the gel.

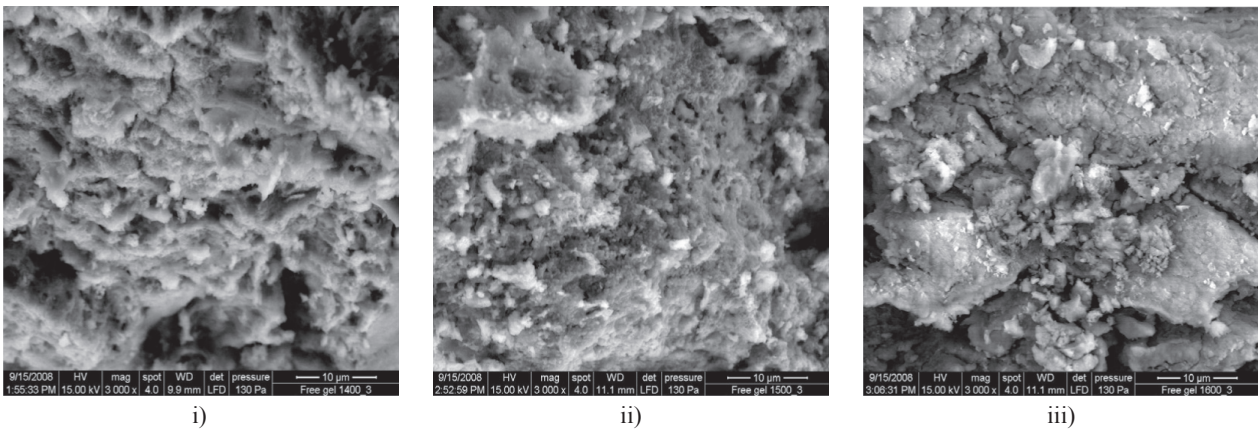


Figure 2a. Scanning Electron Micrograph of the sintered gel samples (no additive) (i): sintered at  $1400^\circ\text{C}$  (ii) sintered at  $1500^\circ\text{C}$  (iii) sintered at  $1600^\circ\text{C}$ .

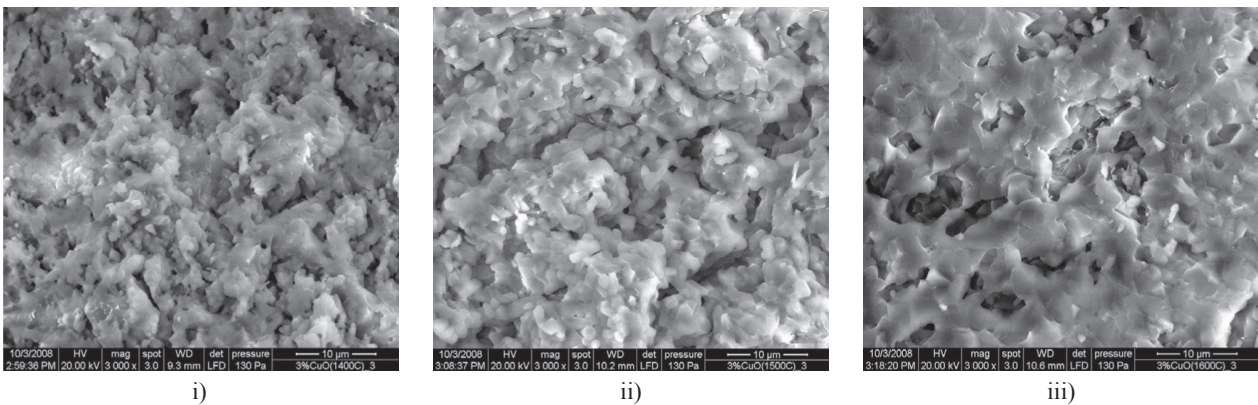
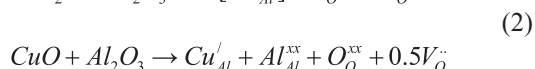
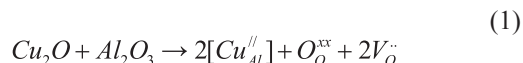


Figure 2b. Scanning Electron Micrograph of the sintered gel samples with 3%  $\text{CuO}$  additive (i): sintered at  $1400^\circ\text{C}$  (ii) sintered at  $1500^\circ\text{C}$  (iii) sintered at  $1600^\circ\text{C}$ .

sublayer. Therefore the formation of copper aluminate is accelerated. The cationic radius of both  $\text{Cu}^{2+}$  (87 pm) and  $\text{Cu}^{+1}$  (91 pm) are more than cationic radius of  $\text{Al}^{3+}$  (53 pm) [23]. Therefore, substitution of  $\text{Al}^{3+}$  by both of these ions causes lattice expansion. In the XRD pattern of the sintered sample trace of copper aluminate with spinel phase was observed (Figure 1b). It indicates that  $\text{CuO}$  improved the solubility of aluminum oxide in the silica matrix. Trace of copper silicate was also detected in the diffractogram. It indicates that copper oxide ( $\text{Cu}_2\text{O}$ ) also interacted with the  $[\text{SiO}_4]$  tetrahedron and deformed the tetrahedral layer, thereby improving its activity towards aluminum oxide. Therefore copper ion actually forms a complex with the alumina and silica sublattices. The substitution of  $\text{Al}^{3+}$  by both  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  results in anionic vacancy in the oxygen sublattice, which also contributed to the faster rate of mullitization in presence of the additives. The defect reactions can be represented in the following way,



From the defect reactions it is evident that Cu (1+)

brings more anionic vacancy in the oxygen sublattice of  $\text{Al}_2\text{O}_3$ . Therefore mullitization rate is expected to increase above  $1050^\circ\text{C}$ , the temperature above which  $\text{Cu}^{2+}$  is converted to  $\text{Cu}^{1+}$ .

From the XRD diagrams of both the sintered samples with and without additive, it is apparent that copper oxide promoted the formation of mullite as the intensity of the mullite peaks increased significantly in the samples with additives (Figure 1). At the maximum sintering temperature ( $1600^\circ\text{C}$ ) under the experimental condition the approximate amount of mullite in the sample without additive was about 79 %, whereas in samples with 3 % copper oxide, it was about 87 %.

From the SEM photographs of the samples, it is apparent that mullite formation has been promoted by copper oxide additive (Figure 2). Mullite has a strong tendency to grow anisotropically if the grain formation occurs without constraint [24]. But with the increase in the sintering temperature the grain size was reduced, indicating copper oxide imposed more restriction on grain growth at higher temperature. For the batch containing 3 % additive, the average grain size as calculated using Scherrer's equation [18] was  $3.6 \mu\text{m}$  at  $1400^\circ\text{C}$ ,  $2.59 \mu\text{m}$  at  $1500^\circ\text{C}$  and  $2.26 \mu\text{m}$  at  $1600^\circ\text{C}$ .

The variation in bulk density and apparent porosity

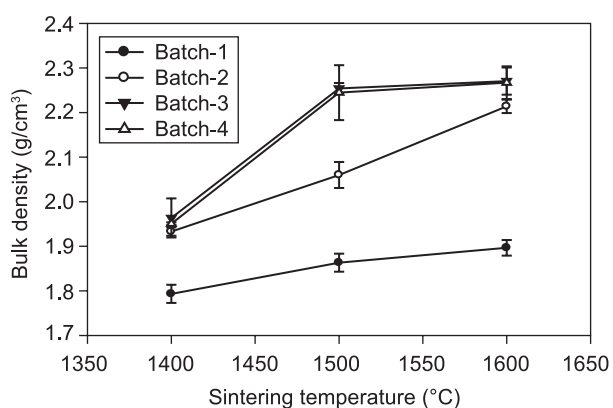


Figure 3. Variation in bulk density with sintering temperature.

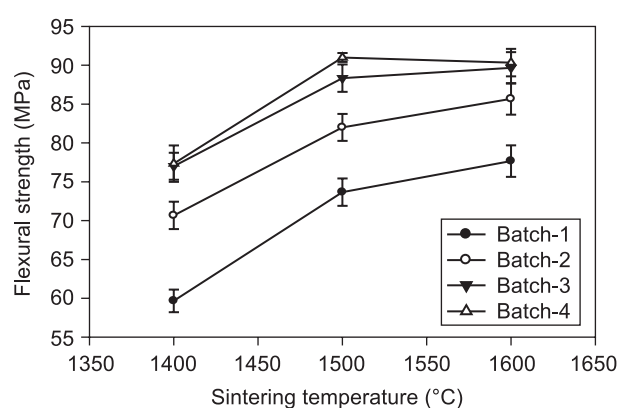


Figure 5. Variation in flexural strength with sintering temperature.

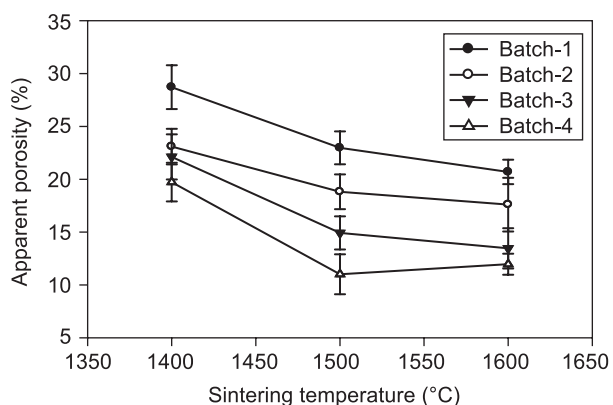


Figure 4. Variation in apparent porosity with sintering temperature.

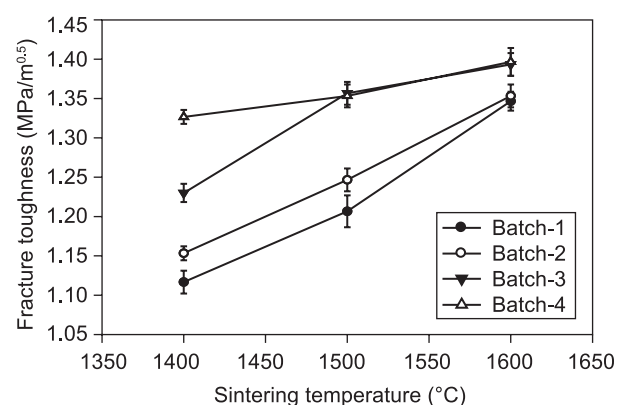


Figure 6. Variation in fracture toughness with sintering temperature.

of the samples with sintering temperature has been shown in Figures 3 and 4. From the figures it is clear that copper oxide exhibited a positive effect on the densification of the mullite ceramics. The melting point of copper (II) oxide is about 1200°C and that of copper (I) oxide is 1235°C. During re-crystallization of mullite if copper oxides came out of the crystal structure, it would form a liquid phase. This might be a reason for the enhanced densification of the samples at elevated temperatures. In the SEM micrographs of the samples some amorphous phase also noticed (Figure 2). After sintering temperature 1500°C, the densification effect was not much significant.

The flexural strength and fracture toughness (Figures 5 and 6) of the samples also increased in the presence of copper oxide additive. It can also be related to the improved densification of the samples in the presence of copper (II) oxide additive. The additive in the liquid form reduced the stress surrounding the pores in the samples by displacing the gasses. It might be a reason for the improvement in the mechanical strength [25]. The formation of more interlocked crystalline phases in the presence of copper oxide additives can be another reason for the improvement of the mechanical strength. A small amount of highly viscous silica or aluminosilicate glass can exist at the grain boundaries, which would minimize the contribution of grain boundary sliding to the fracture stress.

### CONCLUSION

Mullite ceramics was synthesized from the biphasic aluminosilicate gel precursor by the colloidal interaction of silicic acid and  $\text{Al}(\text{NO}_3)_3$  solution. The gel powder possessed very low density ( $0.27 \text{ g/cm}^3$ ) and high surface area ( $70 \text{ m}^2/\text{gm}$ ). Copper oxide was used as sintering additive for the processing of mullite ceramics. Copper oxide promoted the formation and sintering of mullite as a function of sintering temperature. The mechanical properties of the sintered masses were also improved significantly due to improved microstructure and favourable phase compositions.

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