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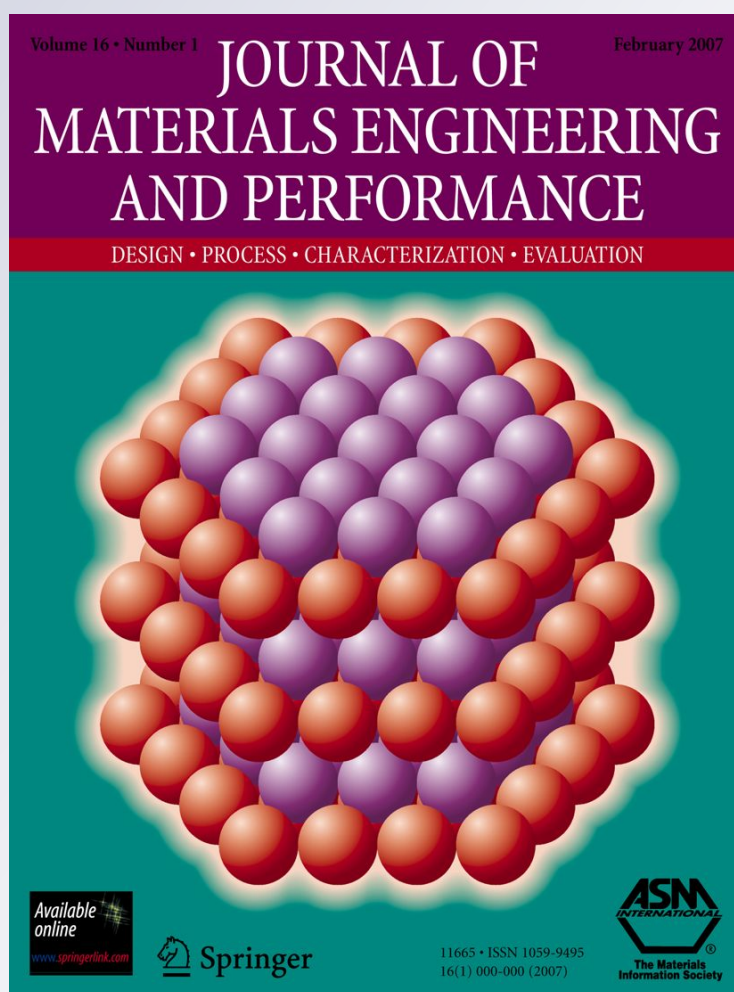
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Andalusite as a refractory material can be transformed to mullite and a silica-rich liquid phase in a temperature range of 1100-1600 °C. In this paper, the influences of MgO and CaO mineralizers on transformation of andalusite to mullite were investigated. Different amounts of MgO and CaO were introduced to andalusite by solution (precipitation) method. Then the precipitated particles were pressed, dried, and fired at 1300, 1400, 1500, and 1600 °C for 2 h. The microstructures of these samples were studied by XRD and SEM. The results showed that the addition of MgO and CaO affected mullitization of andalusite, so that the addition of these oxides increased the amount of mullite formation in andalusite.

Keywords	andalusite, mineralizer, mullite, refractories

1. Introduction

Andalusite and mullite are alumino-silicates with the general formula $Al_{4+2x}Si_{2-2x}O_{10-x}$. When $x = 0$ the sillimanite group is formed. This group includes sillimanite, andalusite, and kyanite (Ref 1-4).

Because of having excellent high temperature volume stability, mechanical strength, thermal shock resistance and creep resistance, the refractories made from andalusite have been used in many industrial fields, such as metallurgical industry, building materials industry, and others (Ref 1-4). Mullite is a solid solution with compositions ranging from $x = 0.25$ ($3Al_2O_3 \cdot 2SiO_2$ known as 3:2 mullite) to $x = 0.40$ ($2Al_2O_3 \cdot SiO_2$ known as 2:1 mullite). Andalusite, theoretically, contains 36.8% silica and 63.2% alumina. However, in commercially available andalusites, the alumina content ranges from 53 to 60%. Small amounts of alkalis, alkali earths, and Fe_2O_3 are inevitably present in the crystal lattice of andalusite (Ref 5, 6). Development of a mullite matrix with various mineralogical based aggregates is highly desirable in commercial aluminosilicate refractories (Ref 2, 7). Andalusite which has good properties can be used for production of mullite in commercial refractories (Ref 3, 4, 7). During heating, andalusite is converted into 3:2 mullite and silica through a topotactical reaction (Ref 8). It has been found that the rate of mullite formation is greatly affected by grain size of the starting material and the impurities that are present (Ref 9).

Typical mullitization process is shown in Fig. 1 (Ref 10). This figure shows that by rising the firing temperature to 1600 °C, the amount of mullite and the glassy phase increases. Andalusite began to decompose noticeably at 1300 °C and the rate of transformation increases at 1400 °C (Ref 9-11). The glass composition shows local variations that may be attributed to the initial distribution of mineral impurities (Ref 10). Wilson (Ref 9) who studied the effect of MgO on mullitization of Kyanite reported some additives can increase the rate of mullite formation from kyanite.

Badiee et al. (Ref 12) studied the effect of CaO, MgO, TiO_2, and ZrO_2 on mullitization of the Iranian andalusite located in Hamedan mines. They found out that the first three of these additives encouraged mullite formation from andalusite; MgO being the most effective and TiO_2 being the least. They observed that the presence of these additives have three main effects; they lower the temperature of liquid formation, increase the amount of the liquid phase and finally decrease the viscosity of the liquid phase; while zirconia shows an inverse effect. In this research, the effect of these additives on reduction of transformation temperature was studied. This reduction can economize the process; as reduction of temperature from 1600 °C to lower temperatures can save energy and increase the life of the furnace.

2. Experimental Procedure

Andalusite (55 μm, Kerphalite KF, from Damrec Co., in France), magnesium nitrate, and calcium chloride (high purity above 98%, Negar Chemical Company, Iran) and ammoniac 24% were used as raw materials. The chemical composition of the andalusite is shown in Table 1.

In this research, CaO and MgO were added to andalusite by precipitation method. Andalusite was mixed with water soluble salts of magnesium (magnesium nitrate) and calcium (calcium chloride) to form hydroxides of magnesium and calcium. Then by heating these hydroxides, they were converted to magnesium

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and calcium oxides. This transformation occurs at 350 and 580 °C for magnesium and calcium oxides, respectively (Ref 13). Badiee et al. (Ref 12) studied the effect of CaO, MgO on mullitization of the Iranian andalusite located in Hamedan mines by wet mixing method.

To obtain the optimal conditions for precipitation, a series of experiments were conducted, so that to obtain the most suitable pH and temperature for transformation. The amounts of precipitate obtained 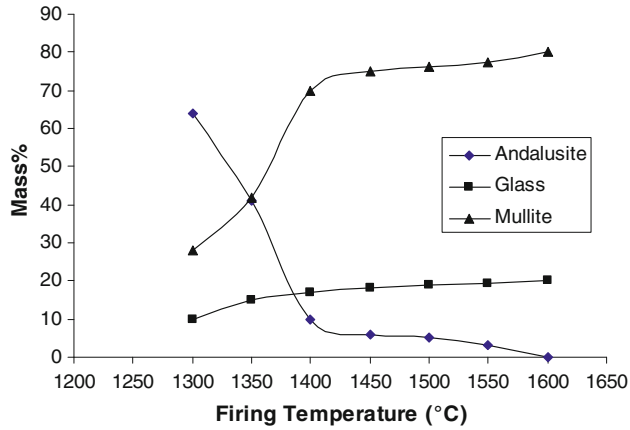for various pH within 10.2-11.25 range at two temperatures (i.e., 15 and 40 °C). Different pH obtained by adding various amounts of ammoniac to solutions of either magnesium nitrate or calcium chloride in water. The codes and

Fig. 1 Percentage mass change of mullite and glass content with increasing the firing temperature (Ref 7)

Table 1 Chemical composition of the andalusite

Composition of andalusite	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
(wt%)	60.0	38.4	0.5	0.15	0.05	0.07	0.07	0.16

Table 2 Codes and compositions of different samples produced (wt%)

Sample code	Andalusite (wt%)	MgO (wt%)	CaO (wt%)
A	100	…	…
AM1	99.5	0.5	…
AM2	98.5	1.5	…
AM3	97.5	2.5	…
AC1	99.5	…	0.5
AC2	98.5	…	1.5
AC3	97.5	…	2.5

Fig. 3 X-ray diffraction patterns of sample A (andalusite with no additives) heated at (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, and (d) 1600 °C (A: andalusite, M: mullite)
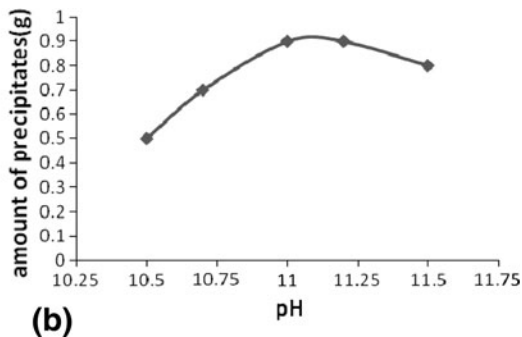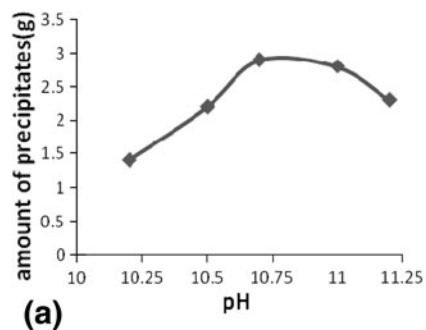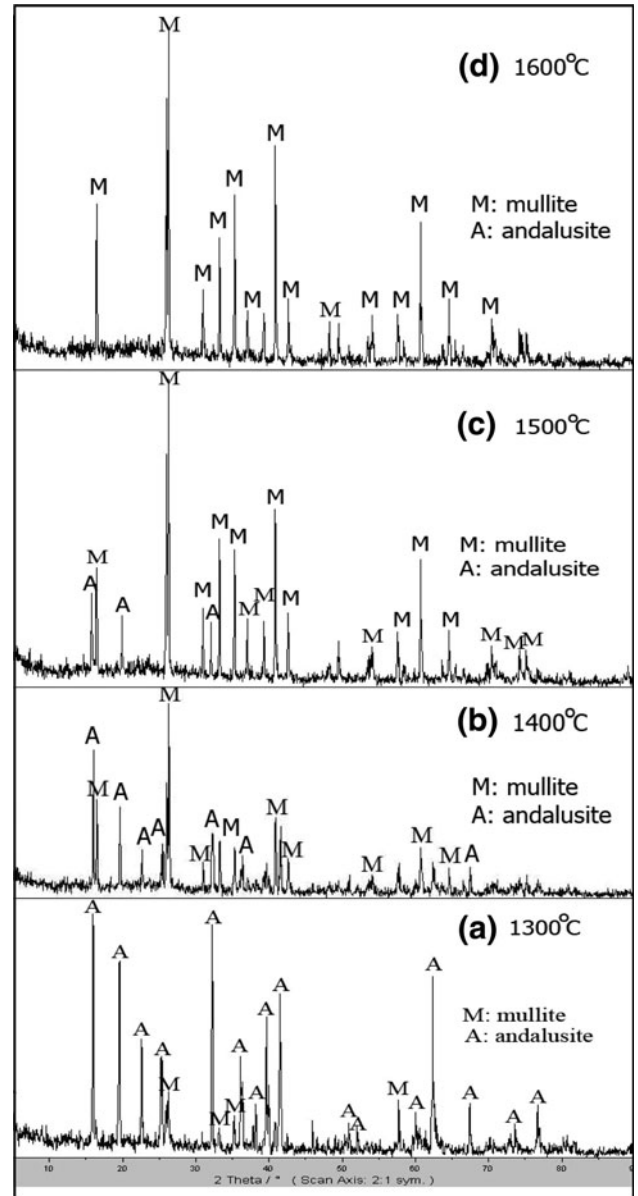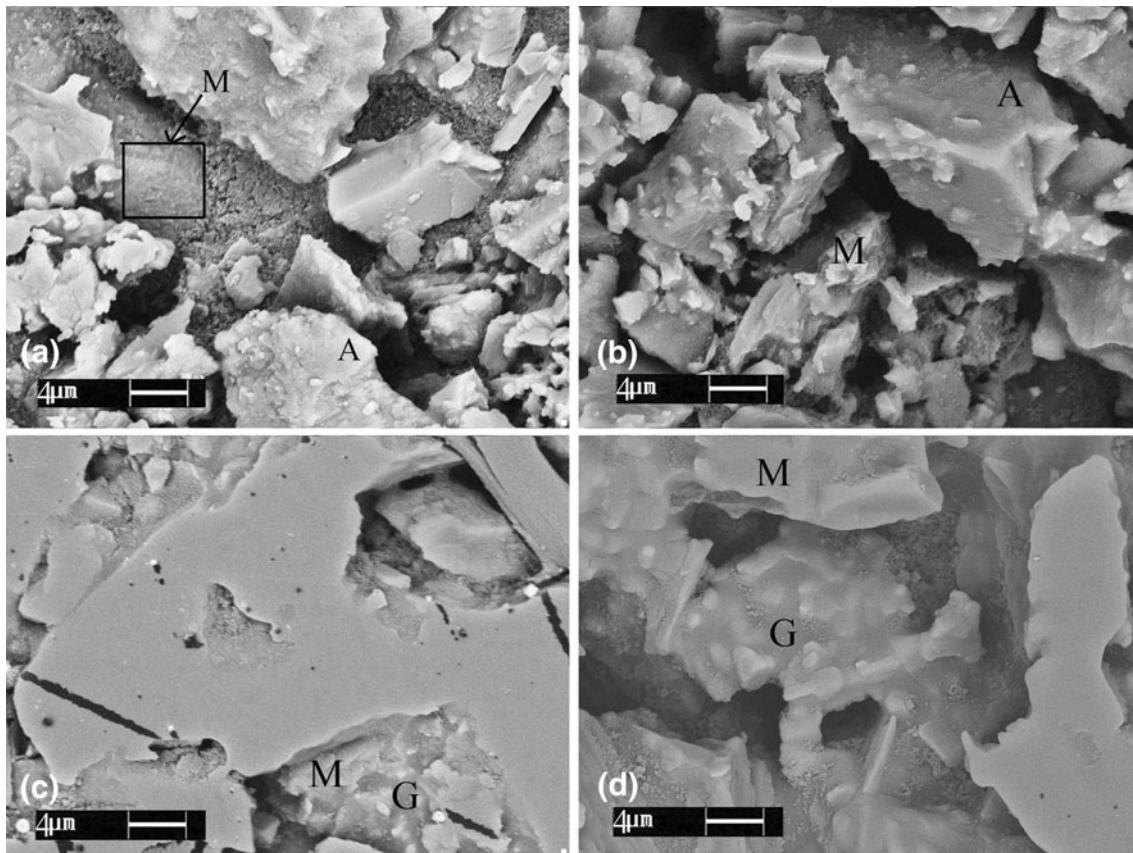

Fig. 2 Effect of pH on the amounts of precipitates obtained from (a) magnesium nitrate and (b) calcium chloride in 15 °C water

Fig. 4 Backscattered electrons SEM micrographs of sample A at (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, (d) 1600 °C (fired for 2 h) (A: andalusite, G: glassy phase, M: mullite)

compositions of the samples produced in this research are shown in Table 2. Samples were prepared in the form of disks having a diameter of 21.6 mm and thickness of 5 mm. Each batch of the samples includes five pieces. These samples were compacted in a unidirectional die with a pressure of 55 MPa, dried and then fired at 1300, 1400, 1500, and 1600 °C for 2 h. For phase characterization of the samples, x-ray diffraction (XRD) technique was used, using a German Seifert PTS3003 diffractometer (Cu K$_\alpha$) with a scanning speed of 0.05 s^{-1}. The amount of mullite formed from andalusite was evaluated on the base of peaks heights of XRD patterns. The most intensive peak of mullite, andalusite, occurred at $2\theta = 26.27$ and 15.95, respectively.

The percentage of mullite was calculated from the most intensive peak of mullite at $2\theta = 26.27$ for (210) planes, named I100M, and the most intensive peak of andalusite at $2\theta = 15.95$ for (110) planes, named I100A, where 100M and 100A are the height of peak 100 of mullite and andalusite, respectively (Ref 14). For each sample, the amount of mullite was determined by x-ray quantitative analysis, using eskolaïte (Cr$_2$O$_3$) as internal standard and reference mullite samples with known 3/2 mullite amounts. The relative error of the measurements is estimated to be maximally 5%.

The microstructure of the samples was investigated by LEO 440I Scanning Electron Microscope made in UK; and chemical analysis of the samples was identified by an Energy Dispersive Spectroscopy (EDS) made in Oxford UK. Some samples were etched in 5 vol% HF acid before studying their microstructures under microscope.

3. Results and Discussion

3.1 Optimization of the Precipitation Conditions

Figure 2 shows the amounts of precipitates for different pH values. One may conclude from this figure the optimum pH values which lead to the conditions for obtaining maximum precipitates from magnesium nitrate and calcium chloride are at pH 10.7 and 11.1, respectively. When pH is low, the lack of (OH)$^-$ causes a reduction in the rate and the amount of precipitation and when pH is high, ammoniac resolves precipitates again.

In order to see the effect of temperature on the amount of precipitations that can be obtained during the precipitation process, the experiments were carried out at 15 and 40 °C. These temperatures were chosen because 15 °C is the temperature in which ammoniac is stable, and 40 °C is the maximum temperature above which ammoniac evaporates. The rate of precipitation was more at 15 °C for both magnesium nitrate and calcium chloride than that of 40 °C.

3.2 Andalusite Without Any Additive

Figure 3 shows the XRD patterns of sample A (i.e., andalusite without additives) heated at 1300, 1400, 1500, and 1600 °C. X-ray diffraction patterns in this figure indicate that at 1300 and 1400 °C, the rate of mullite formation was slower than that happened at 1500 °C. At this temperature some unreacted andalusite was observed. At 1600 °C, nearly all of
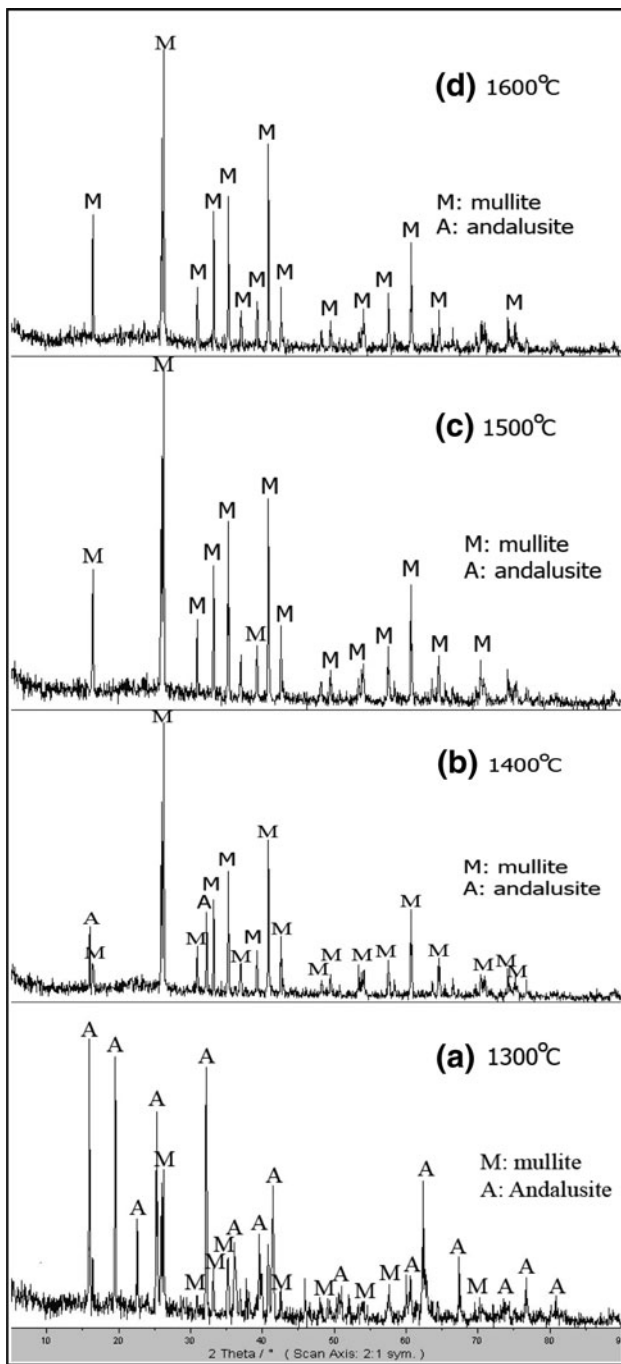
Fig. 5 X-ray diffraction patterns of sample AM2 (andalusite with 1.5% MgO) heated at (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, and (d) 1600 °C (A: andalusite, M: mullite)

Fig. 6 Backscattered electron micrographs of sample AM2 at (a) 1400 °C, (b) 1500 °C, and (c) 1600 °C fired for 2 h (A: andalusite, G: glassy phase, M: mullite)

the andalusite transformed to mullite. This shows that when no additive was present, substantial mullite formation can occur, at a temperature of at least 1600 °C (Ref 15).

Formation of mullite from andalusite is divided into two steps according to Schneider (Ref 16), i.e., below and above 1400 °C. At temperatures below 1400 °C formation of mullite and silica may occur at energetically favored sites of the andalusite lattice, such as grain boundaries, cleavage planes, and other more-dimensional lattice defects.

At temperatures above 1400 °C formation of mullite is said (Ref 12) to occur in the liquid phase. Therefore, according to
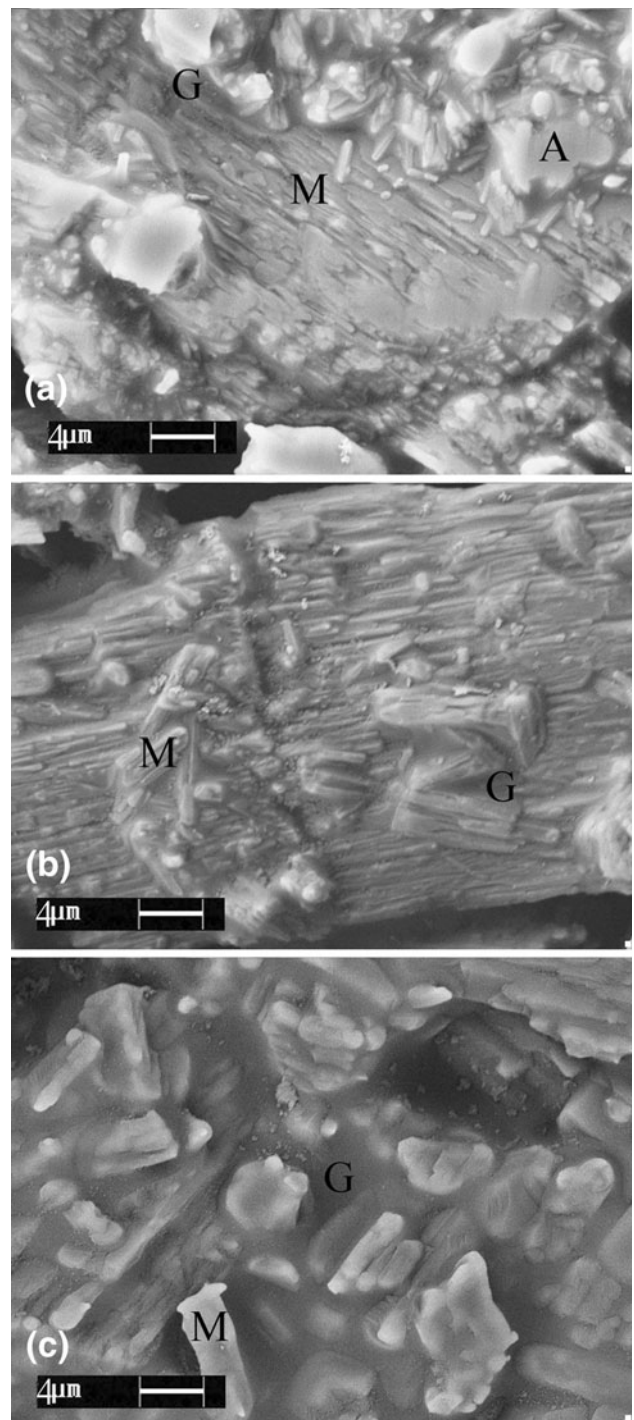
the above mechanism of formation, transformation of andalusite to mullite at 1500 and 1600 °C occurred in liquid phase (Fig. 4c, d), while this transformation at 1300 and 1400 °C (Fig. 4a, b) occurred in solid phase.

Formation of liquid phase in transformation of andalusite to mullite which occurs at 1590 °C (i.e., eutectic point) can be confirmed from the phase diagram of Al_2O_3-SiO_2 (Ref 17). However, in this study formation of liquid phase occurred at

1400 °C when additives, such as MgO and CaO were added to andalusite, see Fig. 5. The mechanism of the transformation is discussed below.
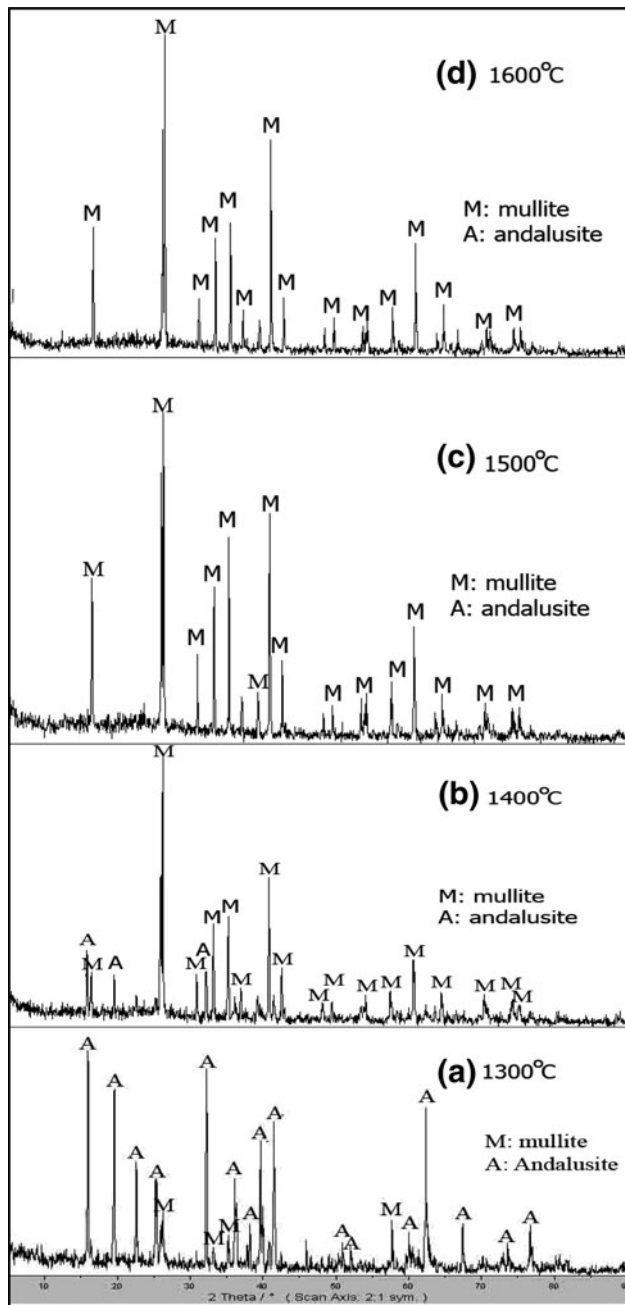

Fig. 7 X-ray diffraction patterns of sample AC2 (andalusite with 1.5% CaO) heated at (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, and (d) 1600 °C (A: andalusite, M: mullite)

3.3 Effect of MgO

Various XRD patterns of sample AM2 (andalusite with 1.5% MgO) heated at 1300, 1400, 1500, and 1600 °C are shown in Fig. 5. When the spectra in this figure compared with those presented in Fig. 3 one can see that this additive had a pronounced effect in lowering the temperature of mullite formation. In other words, the andalusite peaks in these samples disappeared at 1500 °C, while all the andalusite peaks did not disappeared in the samples without additive at this temperature, Fig. 3. Effect of MgO in lowering the temperature of mullite formation to 1300 °C was probably due to the fact that it reduces the liquid formation temperature which results to an increase in the diffusion rate (Ref 15). However, according to Al_2O_3-SiO_2 diagram, eutectic point is at 1590 °C, but when a small amount of MgO is added (i.e., 0.5, 1.5, 2.5 (wt%)) to this compound eutectic point lowers to 1440 °C.

MgO can increase the amount of liquid phase according to Badiee (Ref 8, 12). MgO can also reduce the viscosity of liquid which has an increasing effect on diffusion rate. In addition, MgO dissolves into the structure of andalusite at high temperature; therefore it can form some defects which may encourage the diffusion rate (Ref 18). The XRD patterns presented in Fig. 5 show that I100M at 1600 °C is less than that of 1500 °C. This might be due to an increase in the amount of glassy phase as the result of MgO increase. Thus, it seems until 1500 °C MgO can increase the intensity of peak 100M, but after that it has an opposite effect on transformation of andalusite to mullite.

Figure 6 shows SEM micrographs of sample AM2 (with 1.5% MgO). This figure indicates the present of glassy phase at 1400 °C. Thus, one can say that MgO lowered the temperature of andalusite transformation to mullite.

The microstructure at 1500 °C shows the composite made of mullite and a glassy phase. At 1600 °C, growth of mullite crystal and rise in the amount of glassy phase were observed, see Fig. 6. Therefore, it is reasonable to assume that the effect of MgO on viscosity of liquid phase caused the growth of mullite crystal at 1600 °C.

EDS analysis of points M and G shown in Fig. 6(c) indicates the present of element Mg in mullite phase. One should note that the sizes of Mg and Al atoms are very close to each other. This means that Al atoms can be replaced by Mg atoms, thus one may say that MgO can cause an improvement in mullite formation on this way. In fact Mg increases the amount of Al in liquid phase so that formation of mullite can occur with more ease.

Figure 7 shows the XRD patterns of samples AC2 (andalusite with 1.5% CaO) which were heated at 1300, 1400, 1500, and 1600 °C. These spectra show that addition of CaO had a pronounced effect on mullite formation from andalusite. So, the andalusite peaks in these samples disappeared at 1500 °C not at 1600 °C as it had been reported by Badiee (Ref 12).

Table 3   The amount of mullite determined by x-ray quantitative analysis

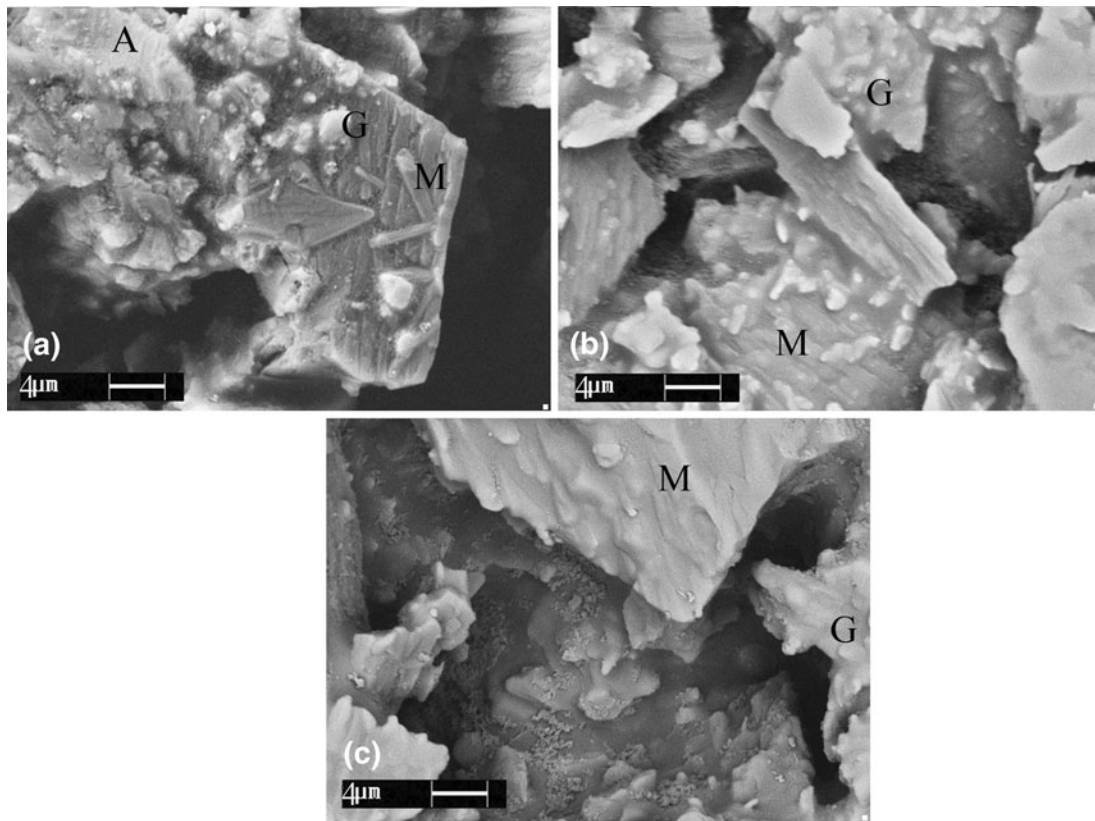| sample	A	AM1	AM2	AM3	AC1	AC2	AC3
Measured amount mullite (mass%) at 1300 °C	9	14	16.3	18.1	12.5	15.8	17.9
Measured amount mullite (mass%) at 1400 °C	29.5	45.3	48.1	49.5	44.5	46.7	48
Measured amount mullite (mass%) at 1500 °C	72.3	80.5	79.2	78	80.2	78.9	77.3
Measured amount mullite (mass%) at 1600 °C	81.4	79	78.2	77.1	78.5	77.8	76

Fig. 8 Backscattered electron micrographs of sample AC2 at (a) 1400 °C, (b) 1500 °C, and (c) 1600 °C fired for 2 h (G: glassy phase, M: mullite)
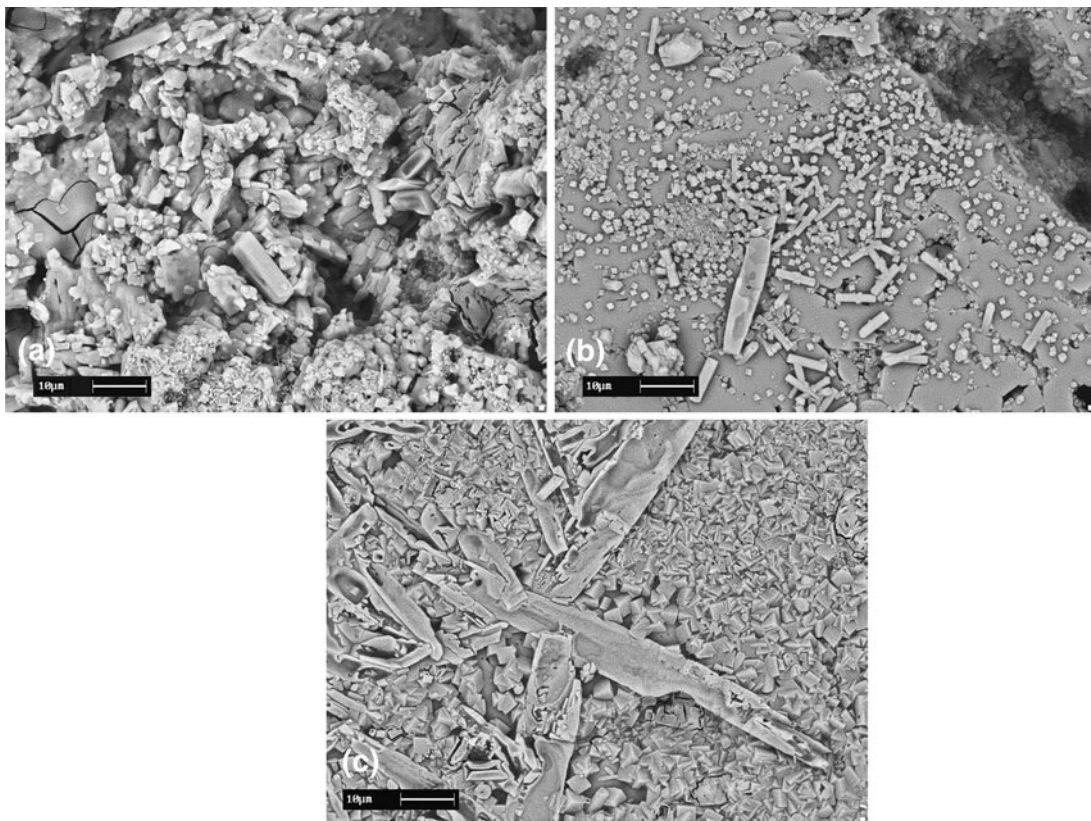

Fig. 9 Backscattered electron micrographs of the etched samples (a) A, (b) AM2, (c)AC2 at 1600 °C fired for 2 h
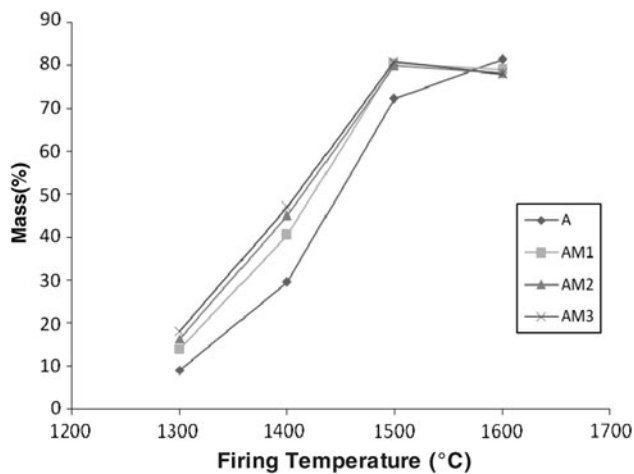
Fig. 10 Percentage mass change of mullite as a function of firing temperature for samples A, AM1, AM2, and AM3
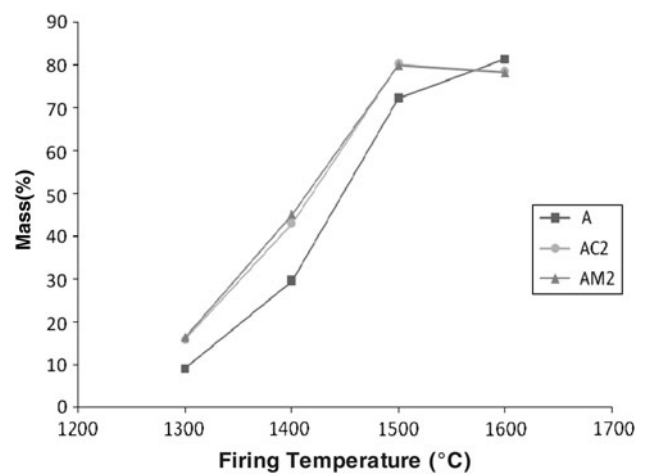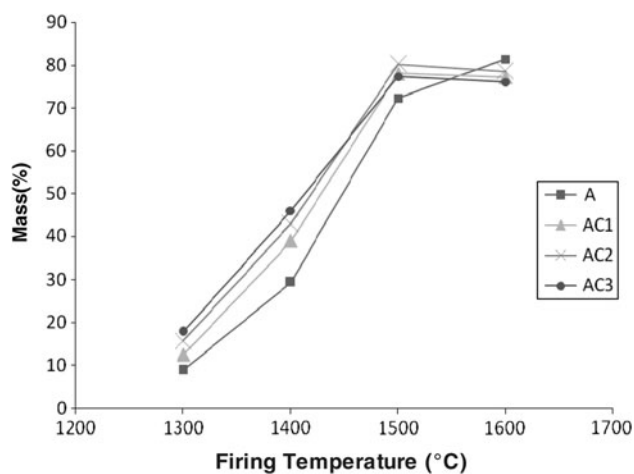

Fig. 11 Percentage mass change of mullite as a function of firing temperature for samples A, AC1, AC2, and AC3

The amount of mullite has been shown in Table 3. The effect of MgO and CaO is confirmed in the table. This table shows MgO has a better effect than CaO and especially in 1400 °C formation mullite from andalusite have been improved and in 1500 have been completed by addition MgO and CaO.

Micrographs in Fig. 8 show the microstructure of AC2 sample (with 1.5% CaO). Similar to the effect of MgO addition to andalusite, addition of CaO caused the formation of glassy phase at 1400 and 1500 °C. A mixture of mullite and glassy phase can be observed at these temperatures on XRD patterns. At 1600 °C the growth of mullite crystals in addition to an increase in the amounts of glassy phase can be observed. So CaO had a similar effect to that of MgO, but to a lesser extent. EDS analysis of points M and G shown in Fig. 8(c) shows a little amount of Ca has been solved in mullite. This might be due to the larger difference in the atomic size of Ca and Al relative to that of Mg and Al.

Figure 9 shows backscattered electron micrographs of the etched samples. As observed in this figure, the sizes of mullite grain in samples with additives are bigger than those of the sample without additive. This figure also shows the amount of mullite grain increased due to addition of these additives which caused reduction in viscosity and melting point of andalusite.

Fig. 12 Percentage mass change of mullite as a function of firing for samples A, AM2, AC2

The plots of the amount of mullite versus temperature for MgO and CaO are shown in Fig. 10 and 11, respectively. These plots helped to investigate the reaction rate. These plots show at temperatures below 1400 °C, transformation of andalusite to mullite was slow and above 1400 °C was rather fast. These results are similar to those obtained by Majdic and Schneider (Ref 16) and Badiee (Ref 12). In addition, it seems evident that MgO and CaO had a positive influence in accelerating the formation of mullite; and these additives caused a change in mullite formation rate to lower temperatures. At 1300 °C MgO and CaO did not have a pronounced effect on mullite formation rate, but at 1300-1400 °C they were very effective. At 1400 to 1500 °C, the effect of MgO and CaO was less than that of 1300 to 1400 °C. This was perhaps due to the increase in the amount of liquid phase. Negative effects of these additives on the formation mullite may be equal to their positive effect on the decrease of viscosity.

To compare the effect of additives CaO and MgO on mullite formation, the graph of the amount of mullite versus temperature was plotted in Fig. 12 for the samples having 1.5% of either MgO or CaO. As observed in this figure, MgO proved to be more effective than CaO in mullite formation. This might be due to the higher diffusion rate of Mg in andalusite with respect to that of Ca (Ref 18).

4. Conclusion

The effect of CaO and MgO additives on mullitization of andalusite was studied. It was concluded that by addition of CaO and MgO to andalusite, the formation rate of mullite from andalusite increases. MgO and CaO reduced the temperature of mullite formation by at least 100 °C but the amount of additives did not have much effect on the quantity of mullite formation while it reduced the temperature of formation by 50 °C wet mixing method (Ref 12). MgO proved to be more effective on formation of mullite than CaO. Furthermore, by addition of these additives the rate of growth of mullite grains increased.

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