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# Cordierite–Mullite Refractories

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**Abstract**: This study aims to prepare cordierite–mullite composites to be used as refractories, mainly setters.

The cordierite–mullite percentage was kept constant (70:30%). Mullite and cordierite were added in different proportions either as grog or raw materials, fulfilling the above stoichiometric composition.

To attain the required percent of mullite in the product, a superstoichiometric amount of alumina was added as grog or bauxite. Superstoichiometric addition improved both physical and mechanical properties without affecting the thermal shock resistance.

The effect of added grog percentage on the body properties is discussed.

Best mechanical, thermal and physical properties are achieved with bodies containing 50–70% grog.

## 1 INTRODUCTION

Cordierite–mullite composites have found their application as refractories with recent developments in the fast-firing techniques of ceramic products during the last few decades.

Cordierite supplies resistance to thermal shock, while mullite provides the strength needed.[1-3] Conditions of preparation of composite bodies from cordierite and mullite have been studied by different authors.[4-6] They found that the proper grog gradings for cordierite and mullite were –850, + 224 μm and –850, + 425 μm, respectively.[6] Glass[7] or polyvinylalcohol[5] were used as binder. Grosjean[8] showed that the presence of the cordierite chamotte lowers the reaction temperature and decreases the firing shrinkage.

The present work aims at studying the conditions of production, phase composition and different thermal and mechanical properties of 70:30 cordierite–mullite composite used as tile setter and prepared from local raw materials.

## 2 EXPERIMENTAL PROCEDURE

Raw materials used in this study were: local clay from Tieh District, Sinai; talc from Derhieb District, Eastern Desert; quartz from Aswan; imported bauxite, as well as chemically pure $MgCO_3$, LiF and $AlF_3$. The chemical analyses are given in Table 1. Talc was calcined at 1000°C for 1 h and added as 1:1 mixture of calcined and uncalcined to minimize preferred orientation that leads to lamination in the product with the use of a high percentage of raw talc.

Cordierite and mullite grog were prepared on the basis of their stoichiometric composition, and fired at 1350°C and 1450°C, respectively (Table 2). Once the grog was prepared, the raw constituents were also used to prepare a group of mixes based on the composition 70:30 cordierite–mullite, respectively. The compositions were satisfied by varying the percentage of grog between 0 and 100 of raw constituents (Table 3).

**Table 1. Chemical analysis of raw materials**

| Constituent (oxides) | Clay | Talc | Bauxite |
|---|---|---|---|
| $SiO_2$ | 44·20 | 62·00 | 6·50 |
| $Al_2O_3$ | 37·75 | 1·60 | 87·50 |
| $Fe_2O_3$ | 0·93 | 0·40 | 1·50 |
| $TiO_2$ | 1·85 | — | 3·70 |
| CaO | 0·82 | 0·48 | 0·43 |
| MgO | 0·52 | 30·30 | — |
| $Na_2O$ | 1·15 | 0·32 | — |
| $K_2O$ | 0·72 | 0·11 | — |
| L.O.I. | 13·01 | 4·70 | 0·20 |

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**Table 2. Batch composition of cordierite and mullite**

| Batch (%) | Constituents | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Talc | | Clay | $MgCO_3$ | Bauxite | $SiO_2$ | LiF | $AlF_3$ |
| | C | R | | | | | | |
| Cordierite | 9·38 | 9·38 | 76·60 | 15·24 | 1·90 | 0·57 | 1·00 | 2·0 |
| Mullite | — | — | 55·18 | — | 58·50 | — | — | — |

C: calcined; R: raw.

**Table 3. Batch composition of the different mixes investigated**

| Mix symbol | Mullite grog (%) | Cordierite grog (%) | | Raw (%) | Alumina as bauxite (%) |
|---|---|---|---|---|---|
| | -35,+70 mesh | -20,+35 mesh | -70,+200 mesh | -200 mesh | |
| $G_0$ | — | — | — | 100 | — |
| $G_5$ | 15 | 35 | — | 50 | — |
| $G_7$ | 21 | 49 | — | 30 | — |
| $G_9$ | 27 | 45 | 18 | 10 | — |
| $G_{10}$ | 30 | 50 | 20 | — | — |
| | | Superstoichiometric mixes | | | |
| $G_A$ | 13·64 | 31·82 | — | 45·45 | 9·09 |
| $G_M$ | 26·09 | 30·43 | — | 43·48 | — |

Two mixes representing superstoichiometry of alumina, satisfied by the addition of either calcined bauxite or excessive percentage of mullite grog, were prepared, based on the same composition as above (70: cordierite, 30: mullite, fulfilled by the mix $G_5$).

The grain size of mullite grog fraction is chosen to be between -35 and +70 mesh, while cordierite grog has two fractions, -20: +35 and -70: +200 mesh.[6]

The composite bodies were fabricated into discs, 2 cm in diameter and 0·5 cm thick, and rectangles of 7 × 0·5 × 1 cm by the semi-dry press method under a pressure of 30 kN using molasses as a binder. They were dried and then fired between 1200° and 1400°C with a temperature interval of 50°C.

Bulk density and apparent porosity were determined according to the ASTM-C20-74. Reversible linear thermal expansion was determined with a heating rate of 5°/min up to 1000°C using an automatic dilatometer.* Cordierite and mullite phases were semiquantitatively followed up by XRD using $CaF_2$ as an internal standard. A universal testing machine** was used to perform the flexural test. The thermal shock resistance test was carried out according to the ASTM (C–554) general method, and then test specimens were subjected to flexural test. The underload test was carried out on selected specimens to determine the range of their application and to spot the temperature of the start of deformation.

## 3 RESULTS AND DISCUSSION

All mixes under investigation represent one and the same stoichiometric composition. The difference lies in the processing of the ingredients. The addition of various percentage of the two grogs, namely cordierite and mullite, to the raw mix affected, to a great extent, the properties of the fired bodies.

The fired bodies are generally highly porous; the apparent porosity varied between 30 and 44%. Therefore bulk density values lie between 1·53 and 1·94 g $cm^{-3}$ (Fig. 1). The increase in grog content from 0 to 100% decreased the bulk density at all firing temperatures, while the addition of a superstoichiometric proportion of alumina (in the form of calcined bauxite or mullite grog) improved bulk density. Higher bulk densities were obtained at 1400°C for all bodies containing grog. This may be attributed to the dissociation of cordierite into mullite + liquid.

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*Orton automatic dilatometer.

**Instron 1128.

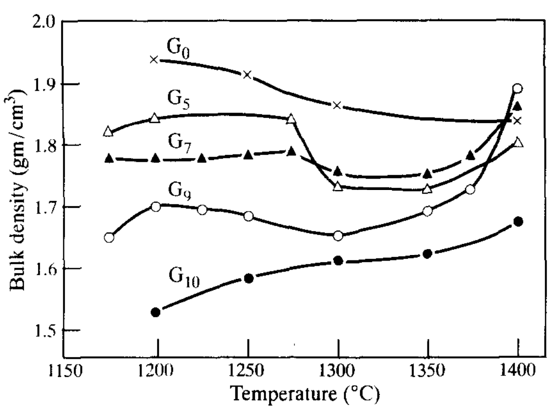

Fig. 1. Change in bulk density with firing temperature.

Addition of excess alumina, i.e. superstoichiometric proportion in the form of calcined bauxite or mullite grog, improved bulk density, mechanical strength and refractoriness underload of mix $G_c$.

Although the bodies are designed to achieve 70: 30 cordierite–mullite composition, this mullite proportion was not achieved (Table 4). The percentage of mullite represents that added as grog, although part of the mullite grog participated in the crystallization of cordierite. Accordingly, the percentage of mullite recorded was in some cases less than that started with.

The raw mix composition ($G_0$) favored the crystallization of cordierite at the expense of mullite. The early formed mullite at 1250°C gave way to cordierite crystallization, reaching 70% at 1350°C.

The reversible linear thermal expansion coefficient lies in the same range, between 1·77 and 1·79 $\times 10^{-6}/°C$, except for the superstoichiometric mix containing excess mullite, which showed a higher value of 2·103 $\times$ $10^{-6}/°C$ (Table 4). The approximately constant content of cordierite phase in the former mixes and mullite phase in the latter are the responsible factors for such behaviour.

MOR of the different bodies containing grog was relatively low. Porosity is responsible for these low values (Fig. 2).

**Table 4. Coefficient of reversible linear thermal expansion and phase composition of different bodies**

| | Firing temp. (°C) | $\alpha$ (× $10^{-6}$/°C) | Phase composition (%) | | |
|---|---|---|---|---|---|
| | | | C | M | Cr |
| $G_0$ | 1350 | 1·79 | 70 | 9 | 10 |
| $G_5$ | 1300 | 1·785 | 70 | 15 | 3 |
| $G_7$ | 1250 | 1·77 | 71 | 21 | — |
| $G_9$ | 1250 | 1·77 | 71 | 20 | — |
| $G_{10}$ | 1250 | 1·78 | 70 | 20 | — |
| $G_A$ | 1350 | 1·769 | 72 | 20 | — |
| $G_M$ | 1350 | 2·103 | 72 | 23 | — |

C: cordierite; M: mullite; Cr: cristobalite.

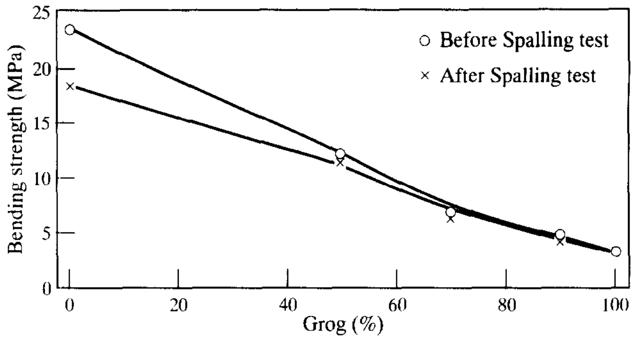

Fig. 2. MOR of different mixes before and after spalling test.

Bodies high in grog withstand 50 cycles without showing a conspicuous change in strength, while bodies containing a high percentage of raw materials were detrimentally affected. The crystalline phases that developed, especially cristobalite, played a role in minimizing the spalling resistance (Fig. 2). Superstoichiometric mixes showed a drop in strength recorded after 50 cycles of thermal treatment, 30 and 39% for $G_A$ and $G_M$, respectively (Table 5).

**Table 5. MOR of superstoichiometric mixes**

| Mix symbol | MOR (MPa) | |
|---|---|---|
| | Before spalling | After spalling |
| $G_A$ | 15·00 | 10·45 |
| $G_M$ | 17·60 | 10·70 |

Underload test results (Figs 3 and 4) indicated that selected samples $G_7$ and $G_9$ resist deformation during testing up to 1225 and 1300°C, respectively. The $T_a$ temperature for mixes $G_A$ and $G_M$ was shifted to its higher temperature of 1325 and 1400°C, respectively, compared with that of the original mix $G_5$. The increase in percentage of mullite, either added as grog or as a result of the reaction of added alumina with the siliceous matrix, is responsible for their improvement of refractoriness and mechanical strength.

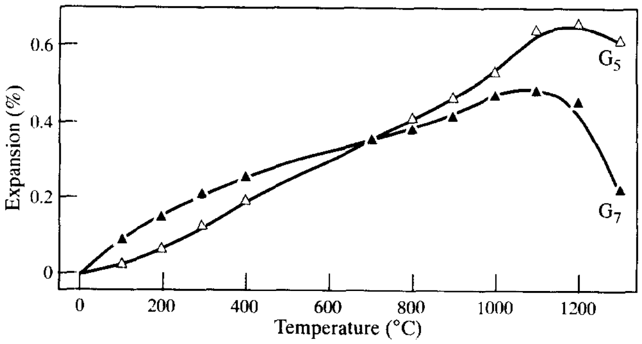

Fig. 3. Refractoriness underload of mixes $G_5$ and $G_7$.

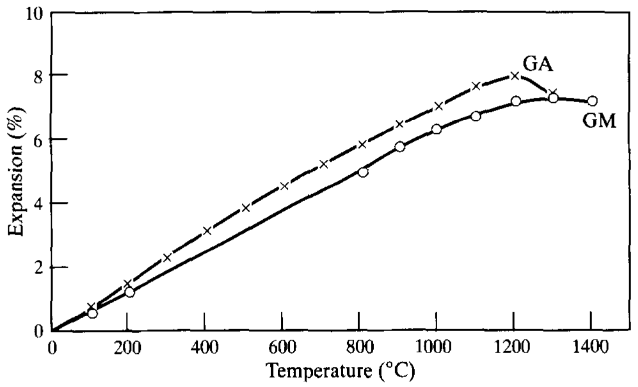

**Fig. 4.** Refractoriness underload of superstoichiometric mixes.

SEM of mixes fired at 1250°C (Fig. 5) showed grains of mullite grog preserved in their original size as identified from the fine microstructure formed of 0·3 μm mullite crystals. Cordierite prisms crystallizing out as a reaction product at the mullite grog grain boundaries, due to the diffusion of $Mg^{2+}$ ions from the neighboring cordierite grain or from the matrix, are shown in Fig. 6. SEM of products of mixes containing raw proportion showed a matrix formed of well crystallized prismatic shaped cordierite, 5–12 μm in size.

The results of distribution of pores, pore volume, pore surface area measured by the Hg porosimeter for the end members of the studied series ($G_0$ and $G_{10}$) indicate a great variation in the size of pores developed. In spite of displaying nearly the same total pore area of 0·722 and 0·78 $m^2/g$, respectively, the pore size and pore distribution differ conspicuously. $G_0$ showed maximum pores of capillary size, while $G_{10}$ revealed a better distribution of pores with a median pore size of 2·2 μm (Table 6). The superstoichiometric mix, $G_A$, has a good distribution of pores of median size (3·07 μm), but its pore area percentage was relatively low. It represents about 1/7 of that of the original mix (Table 6).

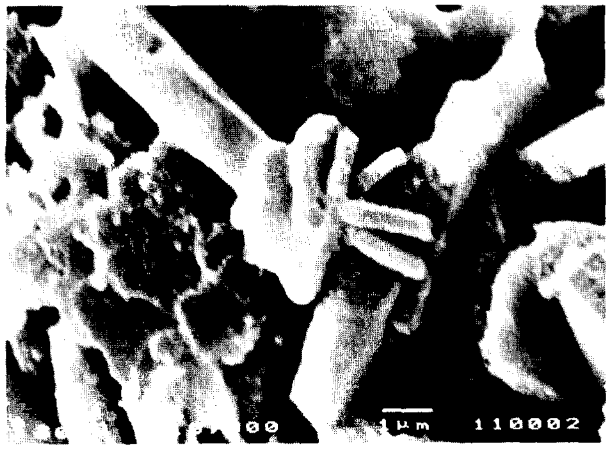

**Fig. 5.** Fine grained mullite crystals occurring in patches with prismatic well crystallized cordierite. (× 10000).

**Fig. 6.** Prismatic well developed crystalline cordierite uniform in size with different orientation. (× 10000).

**Table 6. Pore size distribution, pore volume, pore surface area and density**

| Measurements | Results | | |
|---|---|---|---|
| | $G_0$ | $G_{10}$ | $G_A$ |
| Total intrusion volume | 1·1836 cc/g | 0·0228 cc/g | 0·0691 cc/g |
| Total pore area | 0·7222 $m^2/g$ | 0·7844 $m^2/g$ | 0·1008 $m^2/g$ |
| Median pore diameter | 6·7897 μm | 2·2697 μm | 3·0768 μm |
| Average pore diameter | 1·0170 μm | 0·1162 μm | 2·2437 μm |
| Bulk density | 1·6255 $g/cm^3$ | 1·5566 $g/cm^3$ | 1·6464 $g/cm^3$ |
| Apparent porosity | 2·3172% | 1·6136% | 1·8579% |
| % capillary | 32·7766 | 2·3983 | 7·9943 |

The above results show a correlation with the mechanical behaviour of these mixes; poor mechanical strength and high thermal shock resistance. According to Ravaglioli and Krajewsky[9,10] the mechanical strength and thermal shock resistance oppose each other. They are affected by pore size, shape and distribution from different concepts. So, porosity leads to low mechanical strength, but on

**Fig. 7.** Well developed prismatic cordierite crystals and acicular fine grains of mullite. (× 7500).

the other hand, to better shock resistance. Rasch[11] recorded that fine porosity is advantageous. Thus, not less than 50% of the total pores should lie between 0·5 and 5 $\mu$m, and not more than 20% should be greater than 20 $\mu$m. Lachman *et al.*[12] attributed the presence of fine porosity to the utilization of raw talc. Meanwhile, Rasch[1] and Nakahara *et al.*,[13] recorded the presence of eutectic liquid phase at the contact of talc particles with alumina giving the fine pores which reduce the apparent porosity.

## 4 CONCLUSIONS

The raw mix favoured the crystallization of cordierite rather than mullite. The proportion of raw mix is responsible for the proportion of porosity in the capillary range that decreases the spalling resistance.

In order to improve the mechanical strength, spalling resistance and physical properties, there is an optimum range of added grog ranging between 50 and 70% cordierite. Otherwise it negatively affects the mechanical strength. The percentage of mullite detected represents that added as grog.

Superstoichiometry of alumina, added in the form of mullite grog or calcined bauxite, improved both the physical and mechanical properties, without affecting the spalling resistance. Mullite addition also raised the mechanical properties and refractoriness underload of the mixes (high temperature bearing capacity).

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