EFFECT OF SINTERING AND CORDIERITE ADDITIVES ON THE PHYSICAL AND MECHANICAL PROPERTIES OF MULLITE BASED CERAMICS PREPARED FROM IRAQI RAW MATERIALS

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ABSTRACT

Mullite and cordierite are produced in the laboratory from Iraqi raw materials, have been crushed individually to obtain dense ceramic bodies to a particle size smaller than 45 μ . Five mixtures of cordierite and mullite have been prepared in which cordierite has been added to mullite with the percentages of 30, 40, 50, 60, and 70 %. One hundred and twenty disk samples have been prepared using the semi-dry pressing method, with the pressure of 1000kg/cm². The samples were dried and fired at different temperatures of 1300, 1350, 1400, and 1450 °C, with a soaking time of 2h. Physical evaluation tests (volume shrinkage, water absorption, apparent porosity, and bulk density) in addition to mechanical evaluation tests (compressive strength) have been performed. Samples fired at 1400 °C showed the best rates for the evaluation tests in general, in which the apparent porosity and water absorption for the samples were very low while the rates of density and compressive strength were high. The characteristics of samples fired at 1450 °C were overall poor while samples containing 60 and 70 % cordierite were melted. The best samples in this investigation were proven to be the ones containing 30% cordierite and 70% mullite while samples made out of 40% cordierite and 60% mullite show good mechanical and physical characteristics. The best ideal sample was the one fired at 1400 °C and contained 30% cordierite and 70% mullite.

Keywords: Ceramic; Mullite; Cordierite; Porosity

INTRODUCTION

To use one type of ceramic that has all the properties required in application is not possible. Therefore, there is no preferred type of ceramics that is capable of meeting all of the required engineering specifications. Each type of ceramic has its characteristics. The main advantage of using ceramics is its ability to work in high temperatures and different weather conditions

without any changes occurring in its chemical, mechanical or physical properties (Shyam et al., 2012). These properties depend on the purity of the raw materials used quality of firing and the type of ceramic's constituents (Anggono, 2005). Ceramic contains crystal structures, which are joined together with differing forces, these forces are established during the firing operations due to the chemical reactions occurring between the raw materials of the original structures. Therefore, the properties of the ceramic product depend on the degree of the crystal and amorphous phases in the ceramic. The firing operation plays an important role in determining the crystal structures and the rates of the phases that appear in the final product. Hence, the existence of high percentages of a glass phase or the appearance of any unwanted crystal phase can result in a product with poor properties (Rasteiro et al., 2007).

The need to establish the engineering ceramics industry that has recently been implemented in industrialized countries has achieved rapid development as a result of the increasing number of applications for this type of ceramics. Firstly, must initiate an engineering ceramics industry project in our country, Finally, finding a base that supports the engineering ceramics industry by knowing the best local raw materials that can be used in this field and developing these raw materials. This allows for the diversification and development of the industry through the manufacture of new and more advanced ceramic products. Mullite consists of aluminum silicate $\text{Al}_2\text{O}_3=71.8\%$, and $\text{SiO}_2=28.2\%$, which goes back to the Al_2O_3 - SiO_2 system (Fig .1), that is rarely found in nature on the island of Mull in western Scotland, which was named after mullite (Anggono, 2005).

Fig. 1. Crystallization system Al_2O_3 - SiO_2 (Pask, 1988)

Mullite with the chemical structure of $(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ when crystallized obtains an orthorhombic crystal structure with dimensions of $a=7.5456\text{\AA}$, $b=7.689\text{\AA}$, and $c=2.88\text{\AA}$. From its metallic characteristics, it is colorless, has parallel extinction, a density of 3.20g/cm^3 , specific weight of 3.03, hardness of 7.5 (Moh's hardness scale), and needle shape that gives mullite high strength (Suriyanarayanan et al., 2009). Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) which has the system of $(\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3)$ consists of magnesium and aluminum silicate $\text{MgO}=13.8\%$, $\text{Al}_2\text{O}_3=34.8\%$, and $\text{SiO}_2=51.4\%$ (Grosjean, 1993) (Fig. 2).

Fig. 2. Silica-alumina-magnesia system and the location of cordierite (Chester, 1973)

Cordierite has the hardness of 7-7.5 and specific weight of 2.3. Cordierite can be found in three types, in low temperatures, it crystallizes into β -cordierite that is known as low temperature orthorhombic cordierite if temperature increased turns into hexagonal high temperature cordierite or α -cordierite which is also known as Indialite. There is another unstable phase of cordierite called μ -cordierite that is crystallized from either a melt or can be

prepared from fine materials (Bras et al., 2009; Sembiring et al., 2016). Stable cordierite can be formed in temperatures up to 1460 °C, at this temperature it starts to melt incongruently forming mullite and glass (Hamzawy and Ali, 2006). Sabri (2001) prepared mullite from bauxite mineral and amorphous silica by adding MgCO_3 as a mineralizing material to the mixture and using the mechano-chemical method, the structure of the chemical mixture was close to that of the standard mullite.

Shukur (2002) prepared cordierite from its three oxide constituents; magnesium oxide, aluminum oxide, and silicon oxide, in addition to preparing it from shale rocks. Both double and single firing methods have been used in order to prepare the cordierite. The x-ray diffraction of both firing methods shows that only two samples being investigated contain α -cordierite shows a crystal structure for cordierite glass by turning into μ -cordierite at 968 °C before being changed into α -cordierite at temperatures higher than 1000 °C. α -cordierite shows continuous growth with the increase of the sintering temperatures until it changes back again to μ -cordierite at 1440 °C before it reaches the critical transition temperature that is followed by it melting at 1455 °C. The research aims to assess the local raw materials to study their usability and suitability in producing electrical ceramic insulators, and preparing of ceramic samples consisting of different ratios of cordierite and mullite powder. Studying their physical and mechanical properties and compared with international standards and specifications for electrical ceramic insulators, to this comparison it is determined that the mixtures of these samples can be used in the production of electrical ceramic insulators from local raw materials.

MATERIALS AND METHODS

Preparation of Mixture

To prepare mixture consisting of a mullite and cordierite mix produced from Iraqi raw materials (Urdhuma silica sand, Duekhla Kaolinitic clays tone, alongside other materials pure silica created as by-product of Qaim phosphate manufacturing processes and MgCO_3), crushed cordierite was added to mullite in weight percentages of (30, 40, 50, 60 and 70 %) which were given the symbols of A, B, C, D and E respectively (Table 1) and (Fig. 3). Each mix has been homogenized and grinded individually for 5 h before wetting it by adding 14% water. The mix was homogenized by running it multiple times through a 2 and 1mm sieve respectively. Mixtures have been sealed in nylon bags for 24 h in order to homogenize the moisture in the mixture.

Table 1. Combination of cordierite-mullite mixtures and their incineration temperatures

Mixture (Group)	Sample No.	Firing temperature °C	Cordierite %	Mullite %
A	A1	1300	30	70
	A2	1350		
	A3	1400		
	A4	1450		
B	B1	1300	40	60
	B2	1350		
	B3	1400		
	B4	1450		
C	C1	1300	50	50
	C2	1350		
	C3	1400		
	C4	1450		
D	D1	1300	60	40
	D2	1350		
	D3	1400		
	D4	1450		
E	E1	1300	70	30
	E2	1350		
	E3	1400		
	E4	1450

Fig. 3. Prepared mullite and cordierite powders

Preparation of the Samples

Twenty-four samples are crushed individually to obtain dense ceramic bodies to a particle size smaller than 45μ were prepared from each mixture making the total of 120 samples. The samples, which were pressed using the semi dry pressing method, took the shape of cylindrical disks with the radius of 4cm and the thickness of 0.4cm (Fig. 4).

Fig. 4. Some prepared samples C1, C2, C3, C4, D1, D2, D3, and D4

The cylindrical disks were prepared by a hydraulic uniaxial press type (HERZOG) with the pressure of 1000 Kg/cm² to achieve the highest closing up of particles and to obtain strong and hard samples. Using high pressure can achieve low shrinkage, which results from firing as well as increasing the density of the resulting product.

Drying and Firing

The samples have been dried at 105 °C for 24 h using an electric oven in order to get rid of the added water slowly to prevent cracking due to fast evaporation and to give strength to the pressed samples in order to handle the samples easily. The samples were fired at temperatures of 1300, 1350, 1400, and 1450 °C using a specific firing program with temperature rise rate 50 °C / h and soaking time of 2 h. Later, the samples were taken out of the furnace after 24 h. Shut down the furnace to give the metallic phases enough time to react and crystallize. The firing stage is considered the most complicated and most important stage because it involves a number of physical and chemical operations that give the ceramic body strength and toughness. The firing stage was performed at the Geological Survey Laboratories, Iraq. After the firing stage is complete, a number of evaluations tests were conducted for the resulting samples. These tests include; physical tests (volume shrinkage after firing, apparent porosity, water absorption, and bulk density) and mechanical tests (compressive strength).

RESULTS AND DISCUSSIONS

Cordierite and Mullite Preparation

Cordierite and mullite ceramics were prepared from Iraqi raw materials as a first part of the research project. The x- ray diffraction pattern for mullite and cordierite is presented in Fig. 5. Mullite and cordierite have been separately crushed using a porcelain ball crusher before each powder was sieved using a 45 µ sieve. Powders were later stored in nylon sealed bags.

Fig. 5. X- ray diffractograms a. cordierite, and b. mullite

Physical Properties

Volume shrinkage

Table 2 and Fig. 6 shows the results of the volume shrinkage tests for samples that were fired at 1300, 1350, 1400, and 1450 °C, samples can be sorted into five groups which are: A, B, C, D, and E.

Table 2. Volume shrinkage values for samples fired at 1300, 1350, 1400, and 1450°C

Group	Firing Temperature oC			
	1300	1350	1400	1450
A	6.28%	12.00%	11.97%	10.00%
B	6.20%	11.80%	11.90%	11.54%
C	6.15%	11.68%	11.62%	12.00%
D	6.00%	11.49%	11.43%	15.40%
E	5.51%	11.09%	12.12%	14.32%

Fig.6. Samples volume shrinkage with the firing temperature change

The results show that all samples of these groups display a low volume shrinkage when fired at 1300 °C. Volume shrinkage was between 5.51 and 6.28 % because disappearance of the liquid glass phase between the two materials particles (cordierite and mullite) which works to bring them closer together (Li et al., 2020).

When the firing temperatures for the groups A and B is between 1300-1400 °C, an increase in the volume shrinkage for the samples. With the increase of temperature to 1450 °C, we can notice a slight decrease in the volume shrinkage for both groups A and B, which was due to the increase of the firing temperature to more than 1350 °C, the structure of cordierite starts to partially break down that helps the sintering process as well as the appearance of the liquid glass phase which reduces the volume of pores and blocks them that leads to the increase in volume shrinkage for the ceramic samples (Tabit et al., 2018).

With the increase of temperature to 1450 °C, according to Hodge (1985), the temperature of 1355 °C is the lowest temperature at which the stable liquid phase forms below the melting point of cordierite in the MgO-AL₂O₃-SiO₂ system, but by increasing the temperature to 1450 °C, the cordierite melts accompanied by an increase of the volume of both closed and opened porosities. The quantity of the glass phase that formed from the melting of cordierite in the two groups wasn't enough to fill all the porosities. The existence of closed porosities poses a resistance to the volume shrinkage.

Sample of groups C, D, and E has a high increase in the percentage of volume shrinkage with the increase of the firing temperature from 1300 to 1450 °C where it was 6.15-12 %, 6 -15.40 %, and 5.51-14.32 % respectively. It should be pointed that the samples of the groups E and D underwent warping at 1450 °C, due to this, the volume shrinkage for the samples is not accurate. Because with the firing temperature increases, the particle closeness increases due to the sintering process, as well as the emergence of the liquid phase, which closes a certain percentage of the pores, and this depends on the amount of glass material formed, which depends on the components of the samples, their type, the size of their particles and the temperature (Norton, 1974). When these samples are cooled, the liquid glass freezes, the particles in the samples are joined together, the porosity ratio decreases and the volumetric shrinkage ratio of the samples increases (Tabit et al., 2018).

Cordierite added to these groups (50, 60, and 70) % respectively which is the reason for the increase in the liquid glass phase that works on filling a large portion of the porosities between the particles, therefore the porosity is reduced and then undergoes verification at high temperatures causing a reduction in its apparent porosity and an increase in its density hence an increase in its shrinkage (Gonzales et al., 1992). We notice that the highest shrinkage rate for the samples was for the samples containing 30% mullite and 70% cordierite for all firing temperatures. The smallest volume shrinkage rates were for samples containing 30% cordierite and 70% mullite.

Water absorption and apparent porosity

Fig.7, Table 3, and Table 4 illustrates the relation between water absorption and apparent porosity in different firing temperatures where the percentage of cordierite remains constant. On the basis of these percentages, we can split samples into 5 groups. It is noticed that all samples A, B, C, D, and E that contain 30, 40, 50, 60 and 70 % cordierite respectively display a high apparent porosity as well as high water absorption at 1300 °C. These high readings due to the firing temperature were not sufficient for the sintering process between the ceramic

particles, therefore the low quantity of the liquid glass phase which was not enough to fill the opened and closed porosities between the particles that caused to have a high percentage of apparent porosity as well as high water absorption rates (Warrir et al., 1989). With the increase of the firing temperature from 1300-1350 °C, a sudden, considerable decrease occurs in the porosity and the water absorption for all groups A, B, C, D and E. then a slight increase when the firing temperature is increased to 1450°C for groups A, B, and C.

Fig. 7. The relationship between water absorption and apparent porosity of samples with the firing temperature change

Table 3. Water absorption values for samples fired at 1300, 1350, 1400, and 1450 °C

Group	Firing Temperature °C			
	1300	1350	1400	1450
A	9.86%	0.91%	0.90%	1.16%
B	10.05%	1.07%	0.978%	1.16%
C	10.46%	1.46%	1.10%	1.28%
D	11.49%	1.58%	1.17%	1.01%
E	11.71%	1.97%	1.60%	1.00%

Table 4. Apparent porosity values for samples fired at 1300, 1350, 1400, and 1450 °C

Group	Firing Temperature °C			
	1300	1350	1400	1450
A	22.30%	2.71%	2.08%	2.29%
B	22.32%	2.71%	2.08%	2.50%
C	22.61%	3.73%	2.48%	2.89%
D	23.21%	3.90%	2.70%	2.25%
E	24.15%	4.73%	2.90%	2.00%

This was due to the fact that with the increase of the firing temperature, the particles get closer with one another due to the sintering process in addition to the creation of the liquid glass phase that works on filling the spaces between the pores in the ceramic samples which causes its percentages to decrease (Grim, 1971). The decrease in porosity directly leads to the decrease in water absorption and with the increase of the firing temperatures, the cordierite starts to fuse and causes an increase in the percentages of closed and opened porosities that directly leads to the increase in the water absorption percentages for samples (Li et al., 2020). The samples of the groups E and D show significant decrease in the percentages of apparent porosities and water absorption with increase of the firing temperature from 1300-1450 °C. Due to the sintering process the particles close together in addition to creating a liquid glass phase, which works on filling the porosities and reduce their proportions, and then vitrification occurs at high temperatures that increases its surface tension, decreases the apparent porosity and decrease the water absorption.

Bulk density and apparent porosity

The relationship of the bulk density and apparent porosity with the change of burning temperatures by the stability of the proportions added from the cordierite are presented in Fig. 8 and Table 5. Note that all samples indicated with A, B, C, D, and E are characterized by a gradual increase in the bulk density with an increase in the burning temperature from 1300 - 1400 °C, ranging from 2.05- 2.69 g /cm³ for all samples. This is due to the fact that with the burning temperature rising to more than 1350 °C, the crystalline structure of the cordierite

begins to break down (softening), and this works to obtain the sintering process between the particles of the cordierite and the mullite, the two main components of the samples, as well as increasing the amount of liquid glass phase (cordierite glass and glass) which closes a certain percentage of the pores of these samples (depends on the proportion of the cordierite in the samples), depending on the amount of the formed glass material which in turn depends on the amount and type of components of the burnt substance, the size of their particles, and the firing temperature (Norton, 1974; Sknath and Rakesh, 2014).

Fig. 8. The relationship between bulk density and apparent porosity with the firing temperatures change

Table 5. The bulk density values for samples fired at 1300, 1350, 1400, and 1450 °C

Group	Firing Temperature °C			
	1300	1350	1400	1450
A	2.22%	2.64%	2.67%	2.49%
B	2.26%	2.57%	2.67%	2.47%
C	2.17%	2.55%	2.60%	2.18%
D	2.11%	2.55%	2.55%	2.08%
E	2.05%	2.44%	2.53%	1.98%

When these samples cool, the liquid glass phase solidifies, and the particles are bounded together, their porosity decreases, the bulk density of the samples increases. When the burning temperature increases to 1450 °C for the samples of the groups A, B, C, D, and E, a decrease in the bulk density was observed. Temperature of the cordierite were increased from 30-70%, increases amount of the porous (open and closed) resulting from the melting of cordierite, and the amount of the liquid phase (cordierite glass and glass) was not sufficient to fill all these pores, so the percentage of porosity of the samples increased, which leads to a decrease in the bulk density. Therefore it is noted that the lowest value of the bulk density was for the samples containing 70% of the cordierite.

Mechanical Properties

Compressive strength

Fig. 9 and Table 6 illustrates the relationship of compressive strength and the firing temperatures with the constancy of the added proportions of the cordierite. It is noted that the samples A, B, C, D, and E all have a gradual increase in the compressive strength with an increase in the burning temperature from 1300 – 1400 °C. The values ranged between 61.5 - 69.2 kg /cm³ for all samples. When the firing temperature rises to 1450 °C , a decrease in the values of compressive strength is observed. The increase in the firing temperature from 1300 – 1400 °C, The crystalline structure of the cordierite of the samples begins to collapse (softening), the sintering process occurs, an increase in the the particles close together, and appearance of a liquid phase that reduces the size of the pores and closes them. After solidification on cooling, the density increases, and the samples become more tough and strong, and their compressive strength increases.

Fig. 9. The relationship between compressive strength with the firing temperatures

Table 6. The compressive strength for samples fired at 1300, 1350, 1400, and 1450 °C

Group	Firing Temperature °C			
	1300	1350	1400	1450
A	69.00%	93.30%	96.20%	90.50%
B	67.40%	90.10%	94.30%	90.10%
C	65.10%	89.80%	94.30%	98.60%
D	63.70%	88.40%	92.10%	86.60%
E	61.50%	87.50%	89.80%	80.30%

CONCLUSIONS

1. Physical and mechanical evaluation tests showed that the samples with constant firing temperature and an increase in the percentage of cordierite (30-70)%. Decreased in density, volumetric shrinkage, and compression strength, but the porosity and water absorption increases.
2. The burnt samples at a temperature of 1450 °C with a cordite percentage (60-70 %). An increase in volumetric shrinkage and a decrease in porosity and water absorption are observed.
3. When the percentage of cordierite in the samples is constant and increase the burning temperature from 1300 – 1450 °C. A decrease in the apparent porosity, water absorption, increased density, volumetric shrinkage ratio and compressive strength were observed for the samples.
4. By compared the results of samples (physical and mechanical), it was found that the best ceramic samples for all added percentages of cordierite, with firing temperature 1300, 1350, 1400, and 1450 °C, are samples with the symbol A1, A2, A3 and A4, respectively, it contains 30% cordierite and 70% mullite.
5. It has been verified that the optimal sample for all study samples is symbol A3; it contains 30% cordierite and 70% mullite, and burns at a temperature of 1400 °C.
6. Adding 30 and 40% cordierite to mullite and burning their samples at temperatures of 1350, and 1400 °C, improves the physical and mechanical properties of the samples.
7. Using 50, 60 and 70% cordierite in the cordierite and mullite samples may weaken the physical and mechanical properties of the samples.

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