International Journal of GEOMATE, Aug. 2023, Vol. 25, Issue 108, pp.233-240
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2023.108.7577
Geotechnique, Construction Materials and Environment

MICROSTRUCTURAL AND PHYSICAL CHARACTERIZATION OF CORDIERITE-MULLITE CERAMICS REFRACTORIES

*Sibpawishkon Sittiakkaranon[1] and Nonthaphong Phonphuak[2]

[1]Faculty of Agricultural and Industrial Technology, Rajabhat Nakhon Sawan University, Thailand, NakhonSawan 60000, Thailand

[2]Department of Industrial Technology, Faculty of Engineering, Rajabhat Maha Sarakham University, MahaSarakham 44000, Thailand

*Corresponding Author, Received: 11 Nov. 2021, Revised: 02 Feb. 2022, Accepted: 28 Feb 2023

ABSTRACT: The morphologies of the synthesized cordierite and mullite samples as well as their physical-mechanical properties were investigated and characterized by x-ray diffraction spectroscopy (XRD). The cordierite and mullite was shown to be successfully synthesized by XRD results and represented phases of mullite cordierite and alumina, indicating the creation of materials having interesting combinations of sample ceramics refractories properties. After sintering at 1300°C and 1350°C temperatures, physical properties, such as shrinkage (varied from 10.1 ~ 13.1% and 10.4 ~ 13.6%), bulk density (range of 2.33 ~ 2.41 g/cm^3 and 2.22 ~ 2.36 g/cm^3), water absorption (varied from 0.07 ~ 5.49% and 0.01 ~ 4.12%), apparent porosity (varied from 0.51 ~ 12.87% and 0.15 ~ 9.15%), flexural strength (range of 37.7 ~ 43.5 MPa and 40.6 ~ 56.9 MPa), thermal expansion coefficients (4.89 ~ 6.60x10^{-6}/°C and 4.72 ~ 6.17x10^{-6}/°C), respectively. The microstructure of cordierite and mullite ceramics refractories in sintered samples, in which consists of short cordierite and mullite grains by SEM imaging. It was found that a new sample sintering at 1350°C. They are most suitable for the manufacture of refractory materials.

Keywords: Refractory, Clay, Cordierite, Mullite

1. INTRODUCTION

Refractory is a material that is able to resist the intense heat without altering the structure, mullite is refractory the stable crystalline phase in the aluminosilicate system. Its chemical composition ranges from $3Al_2O_3.2SiO_2$ to $2Al_2O_3.SiO_2$, mullite formed in refractory materials has a chemical composition $3Al_2O_3.2SiO_2$ with a melting point of about 3362°F (1850°C). It contains about 73.0 percent alumina [1]. It can be produced by sol–gel methods [2] or by a sintering process reaction of mixed Al_2O_3 and SiO_2 mullite materials [3]. It has received significant attention during the last decade as a potential structural material for high-temperature applications, presenting properties including low thermal expansion coefficient, low thermal conductivity, good strength at high temperature, low dielectric constant and chemical stability [4-6] when it was mixed with cordierite to supplement the properties of kiln products. Cordierite is important ceramic constituent of the $MgO-SiO_2-Al_2O_3$ system with the mixture compositions which can be in either 1:1:2 or 2:2:5 ratios. It has excellent properties of low thermal expansion coefficient, low dielectric constant, high chemical mechanical durability and good thermal shock resistance [7-9]. The mixed together in an appropriate ratio, cordierite and mullite will result has fracture strength and good resistance to thermal shock and it can be used products refractory various industrial applications such as kiln furniture, ceramic filters, converter substrates and electrical insulating porcelains, etc. The mullite-cordierite phase can be synthesized from natural raw materials including some of the starting raw materials to form talc, calcined alumina and fly ash [10] talc, kaolinitic clay, and gibbsite [11] kaolin, talc, silica, sepiolite and feldspar [12] and kaolin and talc [13]. The mixed together in an appropriate ratio, cordierite and mullite will result has fracture strength and good resistance to thermal shock and it can be used products refractory various industrial applications such as kiln furniture, ceramic filters, converter substrates and electrical insulating porcelains, etc. The aim of this research was to characterized and investigate crystal formation of cordierite and mullite specimen bodies and to study differences in phase composition, physical and mechanical properties of the ceramic samples to obtain the research results aimed at creating products that can be used in high temperatures by to create mullite and cordierite crystals within the clay body through a single sintering. This simplifies the production of mullite and cordierite crystals used to produce equipment inside the kiln.

In addition, the research was able to create clay bodies in the production of ceramic tiles by adding glass waste or coal ash [14] which are important chemical components in the formation of mullite and cordierite crystals with low-shrinkage and high-strength.

2. RESEARCH SIGNIFICANCE

The research focusses on the manufacture of refractory products used in ceramic kilns in industrial plants which includes refractory bricks, posts, slabs and a box sagger. Some of these refractory products are made from a mixture of mullite-cordierite which is sintered twice. The first sintering burns kaolin which creates mullite crystals which are then finely ground and mixed with finely ground cordierite in a ratio of 70:30 to form a product which is then burned a second time. In this study, a single-burn refractory product was developed by sintering mullite and cordierite together to form a crystal structure in a ceramic clay body. This single-burn process will help reduce the amount of fuel used in combustion. A product consisting of kaolin, talc and alumina was sintered in the single-burn refractory product at a high temperature and was analyzed for its microstructure and physical properties to seeking information on crystalline characteristics, mineral composition, thermal expansion and strength values. The analysis allows an assessment of the mullite-cordierite ceramic material as a possible refractory material used in ceramic kilns and other products. The study provides information for further research.

3. EXPERIMENTAL

3.1 Raw Material Synthesis

The raw materials in this experiment were natural clay, talc and alumina powder. The chemical compositions of the synthesized materials were investigated by X-Ray Fluorescence technique (XRF: Mesa-500W, Horiba, Japan) and the phase compositions of clay were identified using X-ray diffraction (XRD: X' Pert PRO MPD, Philips, Netherland).

3.2 Sample Preparation

The raw material ingredients were weighed and mixed in different ratios by various weight percent of alumina (wt.% Al_2O_3). They were rectangular in shape and were formed using a hydraulics press at 150 kg/cm^2 by using 5% water as a binder and used metal molds of around 1 cm x 1 cm x 8 cm. The specimens were given a furnace soaking time at 100°C for 24 h. The sintering process was carried out at a temperatures of 1300°C and 1350°C in air atmosphere with a heating rate of 3°C/min and a soaking time of 1 hour.

3.3 Testing Method

The samples with the addition of different weight percentages of Al_2O3 at 0wt.%, 5wt.%, 10 wt.%, 15wt.% and 20wt.%. The cordierite-mullite phase compositions of samples were identified using X-Ray diffraction (XRD: X' Pert PRO MPD, Philips, Netherland). The physical and mechanical properties of test samples by water absorption, bulk density and apparent porosity of the sintered samples were measured by conventional liquid displacement method based on ASTM C373–88. while the measuring flexural strength was determined by using a universal testing machine according to the standard of ASTM (C02–1161C). The Coefficients of Expansion (COE: DIL 42C, Netzsch, Germany) of the samples were measured as a function of temperature using a dilatometer and analyses of the microstructure of cordierite and mullite were performed by using Scanning Electron Microscopy with X-ray Energy-Dispersive System (SEM and EDS:JEOL JSE-5410 LV).

4. RESULTS AND DISCUSSION

4.1 Raw Material Properties

The starting properties of the cordierite and mullite ceramics were the analyses of the mineral compositions by XRD are shown in (Fig.1). The chemical analysis of the investigated raw materials included clay, talc, and alumina by XRF and loss on ignition are given in (Table 1). It was found that the clay had a high amount of contaminant of 0.79% ferric oxide and by the loss on ignition of 23.53% talc which causes porosity in the clay body.

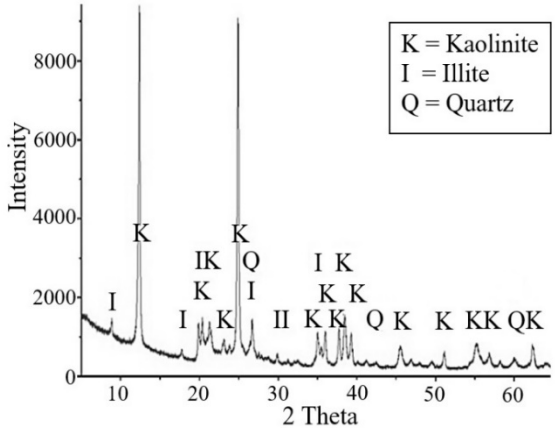


Fig.1 XRD pattern of clay raw materials

4.2 Sample Analysis

In this study, cordierite and mullite ceramics were fired at temperatures of 1300°C and 1350°C and analyzed and tested for physical properties shows in (Fig.2). The samples of 0, 5, 10, 15 and 20wt.% alumina addition had a firing shrinkage 10.1 ~ 13.1% and 10.4 ~ 13.6%, bulk density of 2.33 ~ 2.41 g/cm^3 and 2.22 ~ 2.36 g/cm^3 water absorption 0.07 ~ 5.49% and 0.01 ~ 4.12% and

apparent porosity 0.51 ~ 12.87% and 0.15 ~ 9.15%, respectively. In general, firing shrinkage of the clay occurs because of the loss of water and organic matter in the clay body after high temperature burning, there are causing the clay particles to move closer and causing clay shrinkage. The addition of alumina to the clay caused the percentage of shrinkage to decrease as the amount of alumina increased at both temperatures. It is predicted that the added alumina has some parts that do not react with the clay and talc because the alumina itself is a heat-resistant material. It has a high melting point at 2053°C [15] high purity and the inserted alumina has a large particle structure and has very little change in particle size, with 0.17% loss on ignition shown in (Table 1) which makes alumina result in a lower shrinkage when added in higher quantities, thus creating more gaps and pores between the edges. Therefore, the increase of alumina content causes the percentage of shrinkage to decrease as shown in (Fig.2 (a)). On the other hand, it increases the sample bulk density shown in (Fig.2 (b)). Additionally as the amount of alumina increased, it clearly made increases in porosity and water absorption, as shown in (fig.2 (c) and (d)). The results of the addition of 20% alumina sintered at 1300°C were the highest, at 12.87% apparent porosity and 5.49% water absorption, and when sintered at 1350°C had the effect that both results were reduced 9.15% apparent porosity and 4.12% water absorption. Thus it is deduced that the alumina added to the clay and sintered at 1300°C and 1350°C temperatures contains some alumina, contributing to the crystalline, cordierite and mullite structure. It also contains a higher amount of free alumina, which is a major contributor to higher gaps and porosity. This is due to the large size of the alumina and little structural change for both sintering temperatures, the gap between the grain is increased, with the gap and porosity caused by the loss of on ignition of the 23.53% talc and the 10.73% clay shown in (table 1). The mixture becomes a crystal structure of the cordierite and mullite crystals. The crystal structure of the cordierite has a high porosity which creates gaps and pores within the sample. And when sintered at a temperatures of 1350°C, the sample contracted

Table 1 Chemical analysis (wt.%) and particle size of raw materials

Compositions (wt.%)	Raw materials		
	Clay	Talc	Alumina
SiO_2	48.55	40.38	0.04
Al_2O_3	31.23	-	99.50
K_2O	1.67	-	-
CaO	0.10	1.17	-
MgO	-	34.18	-
Na_2O	-	-	0.29
Fe_2O_3	0.79	0.71	0.02
LOI	10.73	23.56	0.17

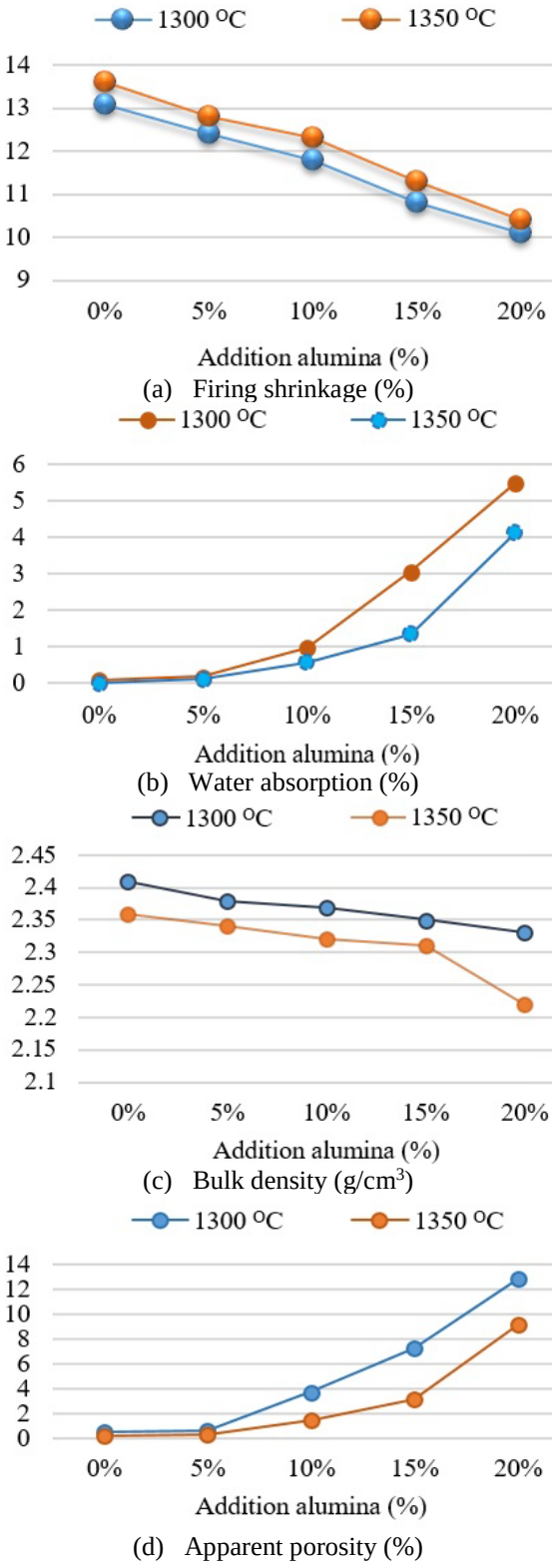


Fig.2 Physical properties of samples sintering at 1300°C and 1350°C (a) firing shrinkage, (b) water absorption, (c) bulk density and (d) apparent porosity

at higher values. The crystals of the cordierite, mullite and free alumina became closer to each other, and the gap and pore size were reduced, thus reducing strength is related to physical properties and sintering temperature, with the more gapped and porous samples having lower density, lower shrinkage and higher water absorption, resulting in low flexural strength values. From the analysis of the increased alumina content ceramics, it reduced the strength. In the sample sintered at 1300°C it produced a maximum flexural strength of 43.5 MPa at 0% alumina addition and a minimum of 37.7 MPa at 20% alumina addition. When sintered at 1350°C temperature, the flexural strength was increased to 56.9 MPa and 40.6 MPa, respectively as shown in (Fig.3). This is because when sintering at 1350°C there is an increase in cordierite and mullite reaction and the higher the mullite content the higher the internal strength. This is because mullite has a needle-shaped structure that is overlapping and connected. This mechanical bonding occurs during firing, giving the ceramic texture a high mechanical strength and good heat resistances. Mullite provides the strength needed, while cordierite supplies resistance to shock. The presence of cordierite also lowers the reaction temperature and decreases the firing shrinkage. Both mullite and cordierite were added in different proportions either as grog or raw material [16]. Sintering at 1350°C found higher cordierite and mullite content than sintering at 1300°C by the X-ray diffraction pattern of the XRD form of the ceramic sample. Mullite and cordierite are the main components and we also found a small amount of alumina is shown in (Fig.4). Considering the peaks in the main graph of mullite cordierite and alumina, the increase in 0 ~ 20% alumina results in increased mullite and alumina at both temperatures. This may be due to the presence of added alumina contributing to the formation of mullite and cordierite crystals. As 5% and 10% alumina added the cordierite amount increased. As both chemical compositions contain alumina, they support their crystallization.

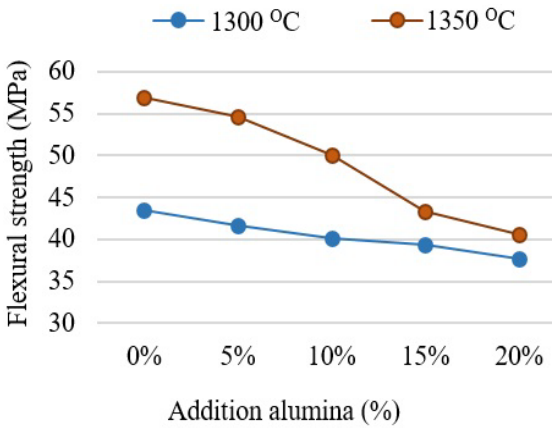


Fig.3 Flexural strength of samples sintering at 1300°C and 1350°C

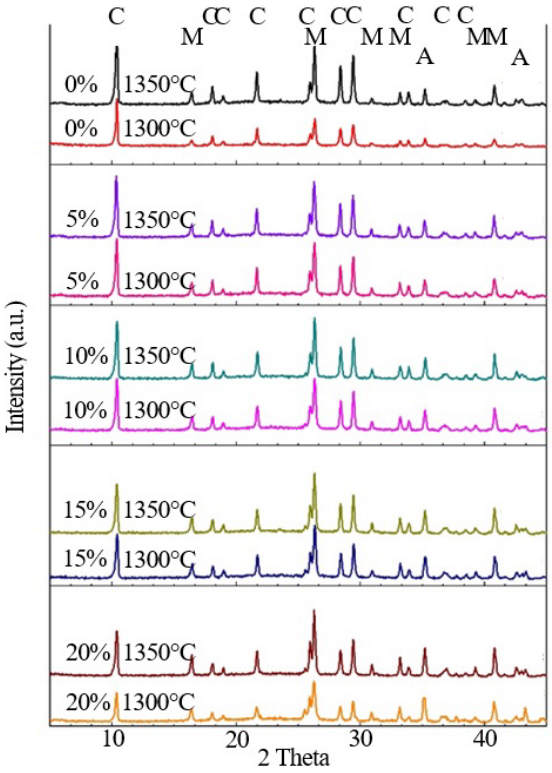


Fig.4 XRD patterns of the investigated ceramic samples after sintering at 1300°C and 1350°C

But when 15 ~ 20% alumina was added, cordierite amount was reduced, possibly due to the formation of cordierite crystals. Talc was a structural component that was completely reacted during the addition of 5 ~ 10% alumina. This is different from the mullite that can still produce more crystals according to their structure and chemical composition. Morphology of the ceramic samples used in this study by scanning electron microscope (SEM) analysis crystal structure at 20,000 magnification finds crystals of cordierite and mullite. The crystals mullite were shaped as overlapping needles with their particle size smaller than 5 microns, and the crystals of cordierite have a cotton ball shape and a porous sheet and their particle size is smaller than 2 microns. The mullite crystallization content increased when sintered at 1350°C as shown in (Fig.5). They have confirmed elements of mullite and cordierite crystals in samples with 10% added alumina sintering at 1350°C. Through Energy dispersive spectrometer (EDS) by spectrum 1 is crystal of mullite shown in (Fig.6 (a)) and spectrum 2 is crystal of cordierite shown in (Fig.6 (b)). The samples were tested for thermal expansion, and found that the COE curve of the all-ceramic samples showed low thermal expansion [17] during the heating period from room temperature to 1200°C. It was found that the thermal expansion of the sintered ceramic sample at 1350°C was between 4.72 ~6.17x10^{-6}/°C. Lower values than the firing at 1300°C, with values between 4.89 ~ 6.60x10^{-6}/°C and the

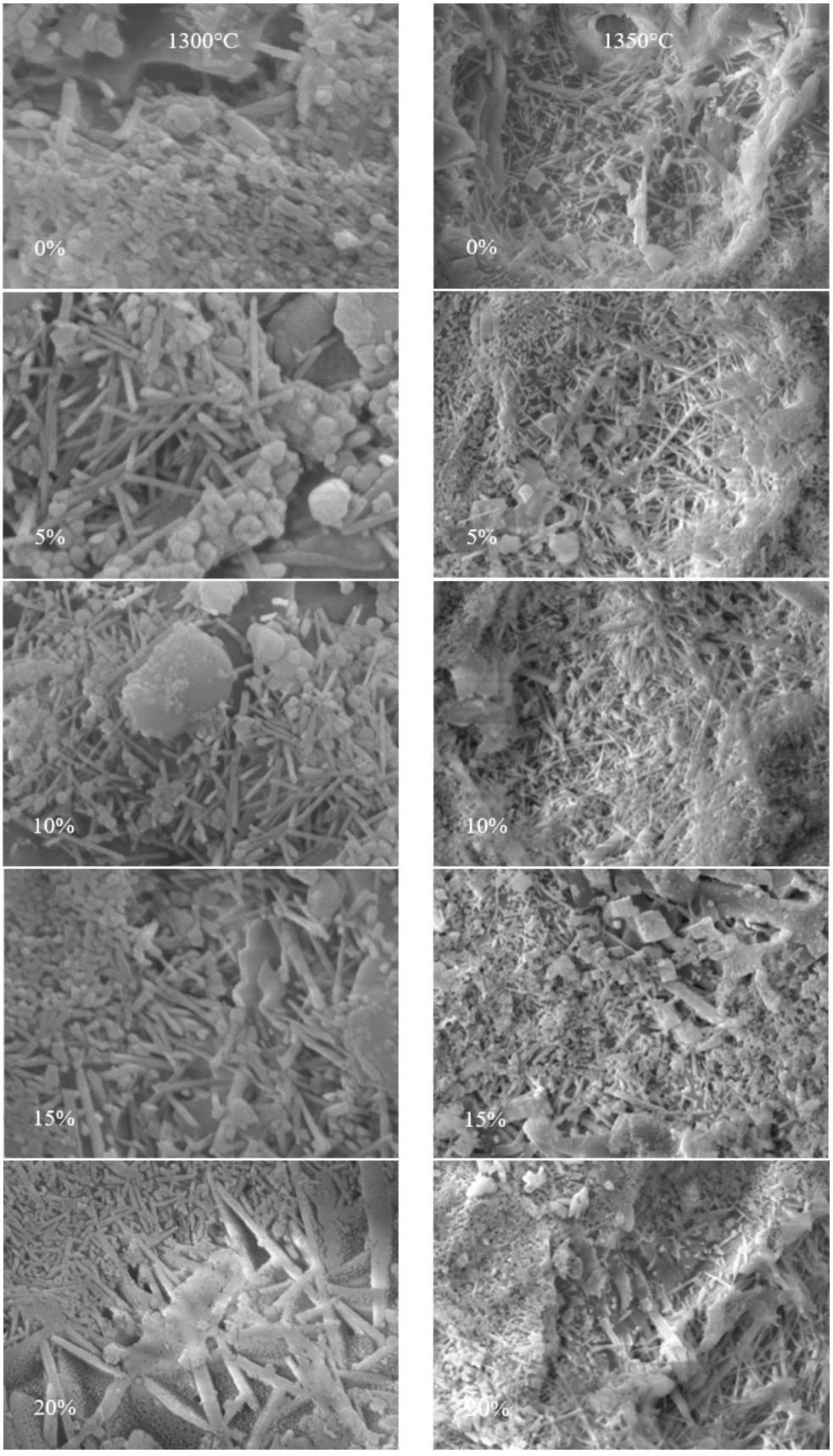
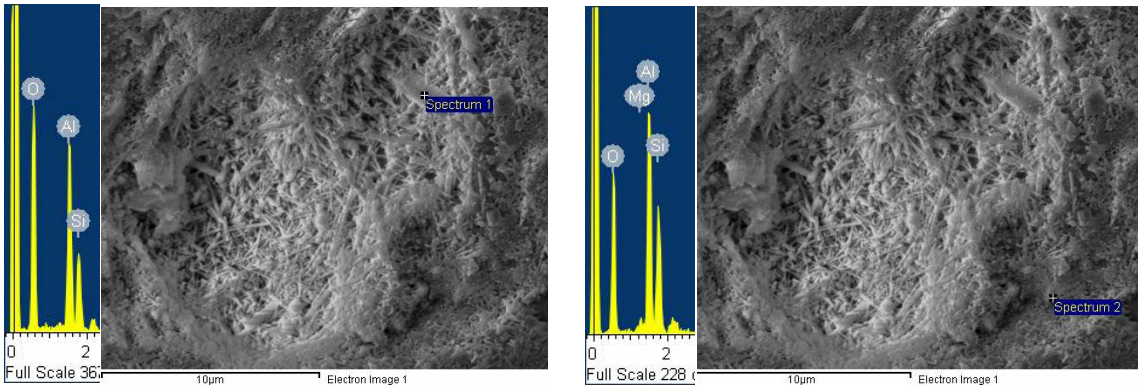


Fig.5 SEM micrographs of the investigated mullite and cordierite crystals samples after sintering at 1300°C and 1350°C



(a) crystal mullite (b) crystal cordierite

Fig.6 EDS micrographs of the investigated cordierite and mullite ceramic samples 10% added alumina sintering at 1350°C

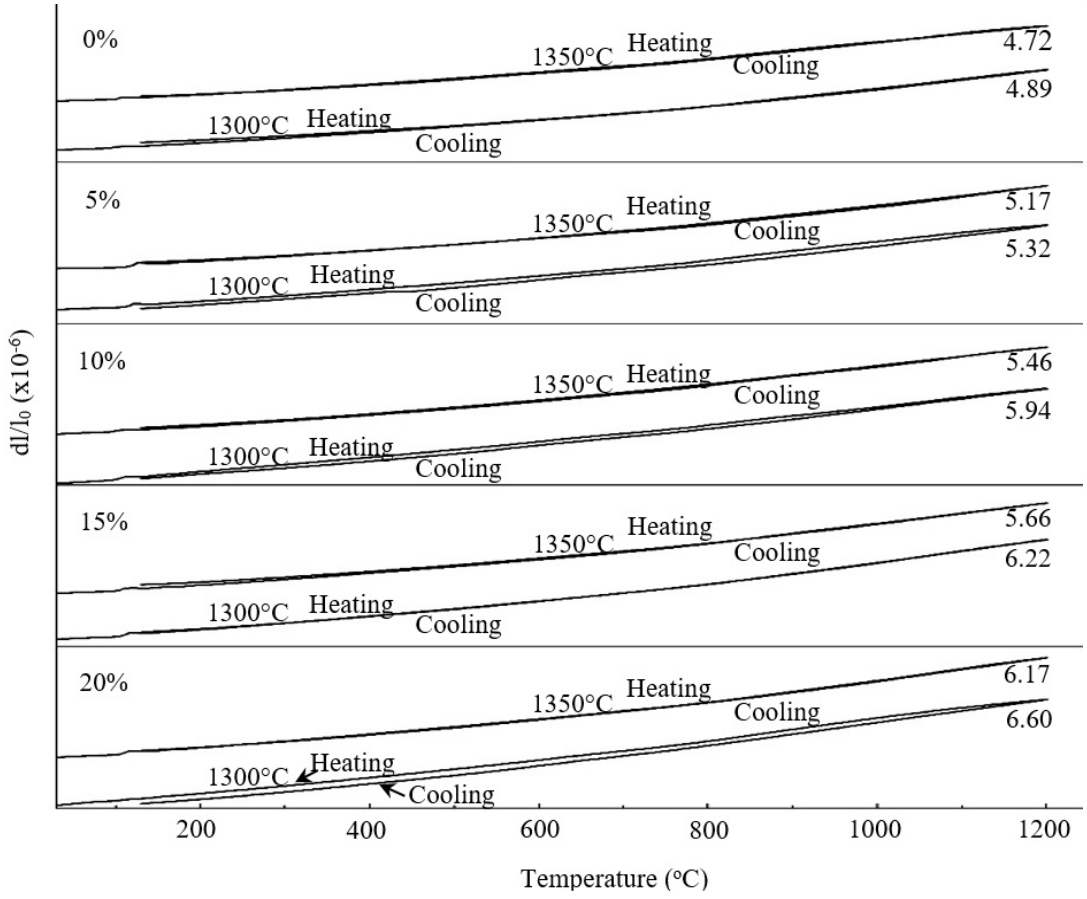


Fig.7 COE curve of the investigated cordierite-mullite ceramic samples after sintering at 1300°C and 1350°C

expansion due to heat tended to increase as the content of alumina increased. It can be predicted that the excess alumina contained in the samples of crystal cordierite and mullite structure which has a melting point that is higher than the temperature of sintering at 1350°C. So that when heated, it will expand more by proportion with the increased amount of alumina. Considering the heating and cooling graph of the sample sintered at 1300°C and 1350°C, showing expansion during heat increase and graph showing sample contraction during heat decline, it is a graph which overlaps the same line, because when the sample is cooled, it shrinks back to its original position at room temperature. This demonstrates that it has thermal elastic properties and a low coefficient of thermal expansion which it helps to support for properties of thermal shock resistant as well [18,19,20]. This is different from the sample sintered at 1300°C, as shown in (Fig.7).

5. CONCLUSIONS

This research is a study of the characteristics of cordierite and mullite ceramics from mixing clay, talc and alumina raw materials and by varying alumina added at 0%, 5%, 10%, 15% and 20% and sintering at 1300°C and 1350°C, the XRD results indicated graph main phases of crystals of mullite and crystals of cordierite. All the samples were evaluated for their mineralogical, microstructure, physical and mechanical properties. It was found that, when the amount alumina increases, it increased the amount of mullite crystals formation but the number of cordierite crystals formed was decreased, and this has an influence on bulk density and a decrease in flexural strength but higher water absorption, porosity, and thermal expansion coefficients. In particular this indicates that flexural strength is controlled by the continuous mullite microstructure and porosity. The significant characteristic of mullite crystals is that they are found in the shape of needles and cordierite in the shape of cotton balls and a porous sheet from image SEM. This shows that alumina can react with clay and talc raw materials formed into a crystal structure cordierite and mullite at 1300°C and 1350°C, even if it has a melting point which is higher, and can form mullite and cordierite crystals This can be achieved within the ceramics body with a single firing, which reduces the cost of producing ceramics made from mullite and cordierite materials It can be used to produce ceramic refractories as cups and plates ceramics that are well used in microwave ovens, sagger or kiln furniture.

6. ACKNOWLEDGMENTS

The authors also would like to gratefully thank to Rajabhat Nakhon Sawan University for financial support.

7. REFERENCES

[1] Schneider H., Fischer RX. and Schreuer J., Mullite Crystal Structure and Related Properties, Journal of the American Ceramic Society, Vol. 98, 2015, pp. 2948-2967.

[2] Lu Z., Tian G., Wan W., Miao K. and Li D., Effect of In Situ Synthesised Mullite Whiskers on the High-Temperature Strength of Al_2O_3 - Based Ceramic Moulds For Casting Hollow Turbine Blades. Journal of Ceramics International, Vol. 42, 2016, pp. 18851–18858.

[3] Zhao X., Liu Q., Yang J., Zhang W. and Wang Y., Sintering Behavior and Mechanical Properties of Mullite Fibers/Hydroxyapatite Journal Ceramic Materials, Vol. 11, 2018, pp.1859-1867.

[4] Hamidouche M., Bouaouadjd N., Olagnon C. and Fantozzi G., Thermal Shock Behaviour of Mullite Ceramic, Journal of Ceramics International. Vol. 29, 2003, pp. 599-609.

[5] Schneider H. S., Schreurer J. and Hildmann B., Structure and Properties of Mullite, Journal of the European Ceramic Society, Vol. 28(2), 2008, pp. 329-344.

[6] Ghassemi Kakroudi M., Pourmohammadie Vafa N., Shahedi Asl M. and Shokouhimehr M., Effects of SiC Content on Thermal Shock Behavior and Elastic Modulus of Cordierite–Mullite Composites, Journal of Ceramics International, Vol. 46 (15), 2020, pp. 23780–23784.

[7] Yu W., Cao S., Wang J., Zhang Z., Han J., Liu C. and Ruan J., Crystallization Mechanisms of Cordierite Glass-Ceramics With "Surface-Center" Crystallization Behavior, Journal, Journal of the European Ceramic Society, Vol. 41 (13), 2021, pp. 6708–6721.

[8] Romero A.R., Elsayed H. and Bernardo E., Highly Porous Cordierite Ceramics From Engineered Basic Activation of Metakaolin/Talc Aqueous Suspensions, Journal of the European Ceramic Society, Vol. 40 (15), 2020, pp. 6254–6258.

[9] Goren R., Gocmez H. and Ozgur C., Synthesis of Cordierite Powder From Talc Diatomite and Alumina, Journal of Ceramics International, Vol. 32, 2006, pp. 407-409.

[10] Ohsato H., Varghese J., Kan A., Kim J.S., Kagomiya I., Ogawa H., Sebastian M.T. and Jantunen H., Volume Crystallization and Microwave Dielectric Properties of Indialite/Cordierite Glass by TiO_2 Addition, Journal of Ceramics International, Vol. 47 (2), 2021, pp. 2735–2742.

[11] Tamborenea S., Mazzoni A. D. and Aglietti E. F., Mechanochemical Activation of Minerals on The Cordierite Synthesis, Thermochim. Acta, Vol. 411, 2004, pp. 219-224.

[12] Acimovic Z., Pavlovic L., Trumbulovic L., Andric L. and Stamatovic M., Synthesis and Characterization of The Cordierite Ceramics From Nonstandard Raw Materials For Application In Foundry, Journal of Materials Science Letters, Vol. 57, 2002, pp. 2651-2653.

[13] Xu X., Xu X., Wu J., Lao X., Zhang Y. and Li K., Effect of Sm_2O_3 on Microstructure, Thermal Shock Resistance and Thermal Conductivity of Cordierite-Mullite-Corundum Composite Ceramics For Solar Heat Transmission Pipeline, Journal of Ceramics International, Vol. 42 (12), 2016, pp. 13525–13534.

[14] Yuan Q., Mohajerani A., Kurmus H. and Smith J. V., Possible Recycling Options of Waste Materials in Manufacturing Ceramic Tiles, Conf. on GEOMATE, Feb, 2021, Vol. 20, Issue 78, pp. 73-80.

[15] Wiley-VCH Verlag GmbH & KGaA Co., Weinheim, Ceramic Material Classes, Ceramics Science and Technology, ISBN: 978-3-527-31156-9, Vol. 2, 2010, pp.4-7.
[16] Yu P.C., Tsai Y.W., Yen F.S., Yang W.P. and Huang C.L., Thermal Characteristic Difference Between α-Al_2O_3 and Cristobalite Powders During Mullite Synthesis Induced by Size Reduction, Journal of the European Ceramic Society, Vol. 35, 2015, pp. 673–680.
[17] Costa Oliveira F. A. and Fernandes C. J., Mechanical and Thermal Behaviour of Cordierite-Zirconia Composites, Journal of Ceramics International, Vol. 28, 2002, pp. 79-91.
[18] Donald Askeland R. and Phule Pradeep P., The Science and Engineering of Materials, Cengage Learning, 2010, pp. 843-845.
[19] Sittiakkaranon S., Thermal Shock Resistance of Mullite-Cordierite Ceramics from Kaolin, Talc and Alumina Raw Materials, Materials Today, Proceedings Vol. 17, 2019, pp 1864–1871.
[20] Alves Hugo P.A., Silva Jaquelígia B., Campos Liszandra F.A., Torres Sandro M., Dutra Ricardo P.S. and Macedo Daniel A., Preparation of Mullite Based Ceramics From Clay–Kaolin Waste Mixtures, Journal of Ceramics International, Vol.. 42, 2016, pp. 19086-19090.