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Atalla Egyptian Serpentinite for Producing Forsterite and its Thermo-Mechanical Behavior

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Abstract: *The scope of the present work is to study the utilization of some Egyptian serpentinites for producing forsterite. Also, investigate the addition effect of stoichiometrical amount of magnesia and/or alumina sources to form periclase and spinel periclase forsterite on the thermo mechanical properties. To perform this aim, serpentinites masses were collected from Atalla area, which is located in the Central Eastern Desert, Egypt. They were crushed, grinded and passed through 100µm sieve. Mineralogical and chemical studies for the serpentinites were carried out using polarized microscope in addition to XRD and XRF techniques, respectively. Three batches were fired at 1500°C up to five hours. Densification properties of the fired batches were investigated. Mineral composition as well as the microstructure is performed using XRD and SEM, respectively. Also the refractoriness under load as well as the compressive strength was done. It is noticed that, forsterite was produced from serpentinites by adding a calculated amounts of used magnesite, whereas the addition of stoichiometry excess used magnesite and / or alumina source lead to formation of periclase and periclase spinel phases, which increase the refractory quality of the forsterite.*

Keywords: *Atalla Serpentinite, Forsterite, Mechanical Properties, Refractoriness under load.*

1. INTRODUCTION

Forsterite is a mineral of magnesium orthosilicate having formula Mg_2SiO_4 and occurs as a member of the isomorphous series with Fayalite ($2Fe.SiO_2$) in the olivine series. Forsterite melting point is 1890°C, while fayalite melts at 1205°C and hence the melting point of natural mineral is lower if there is solid solution between them (1-3). Forsterite has relatively low thermal conductivity and high temperature creep resistance thus has excellent insulation properties(4-6). For synthesis of forsterite from serpentinites, sufficient amounts of magnesia source materials must be added to convert the low-melting metasilicate serpentine to the high-melting orthosilicate. Forsterite basic refractories must be kept to the MgO-rich side of the forsterite composition to ensure the $MgO–Mg_2SiO_4$ eutectic at 1850 °C (1).

Generally, forsterite refractories can be used in furnace roofs, ceramic kilns as kiln furniture, brick network in the heat exchangers of glass furnaces and rotary kilns of cement industry and kiln for calcinations of lime, dolomite and magnesite (7, 8).

Various composites were developed to improve the physic-mechanical properties, strength, dielectric constant, thermal expansion, thermal conductivity and mechanical performance of forsterite ceramics. The properties are improved through addition of magnesium aluminate spinel, alumina, mullite, and zirconia (9-12).

Different procedures have been performed to prepare forsterite ceramics, including solid-state reaction and sol–gel techniques (13–17).

However, these methods cannot be used to produce forsterite for large-scale industrial applications due to their high cost. Forsterite can be industrially prepared with a large quantity using simple and cheap heat treatment methods based on the solid-state reaction synthesis(17) using MgO–and SiO_2-bearing compounds as precursors. The disadvantage of preparation of forsterite by solid state reaction usually increases grain growth and aggregates particle agglomeration, and consequently leads to a poor sinterability of the forsterite powder.

The aim of the present study is to study the possibility of producing of forsterite bodies from locally occurring serpentinites by adding calculated amounts of used magnesite. Also to study the addition effect of excess of used magnesite and alumina to yield forsterite, periclase forsterite and periclase forsterite spinel on their physical and thermo mechanical properties as well as their microstructure.

2. MATERIALS AND METHODS

2.1. Materials

Materials used for this purpose are locally occurring raw serpentinites, used magnesite bricks powder and aluminum oxide. Serpentinites were derived from Atalla area (Fig. 1), which is located in the Central Eastern Desert, between Lat. 26° 03' -26° 9' 03" and long 33° 33' -33° 36' Egypt. Serpentinite is about 18 km long and has NW-SE trend and the contacts between serpentinite and the adjacent rocks are usually sharp and distinct (18-20). Used magnesite was received from lime kilns of the Egyptian Iron and Steel Company (Helwan, Cairo). Aluminium oxide was bought from El-Gomhoryia Company for chemicals.

2.2. Methods

Serpentinite samples are collected from the Atalla area, Central Eastern Desert, Egypt. Petrographical study of thin section using transmitted light microscope (TLM) to evaluate the mineral composition as well as the microstructure of the serpentinites raw materials used in this study. Also, chemical and mineral composition of the serpentinites is confirmed using XRF and XRD techniques, respectively. Used magnesite was previously studied for their chemical and phase composition (21). The serpentinites and used magnesite bricks were crushed in a jaw crusher and finely ground in a pilot plant steel ball mill to pass through a 100 µm sieve. Three batched from the serpentinites and used magnesite and/or aluminium oxide were designed to give forsterite, periclase forsterite and spinel periclase forsterite. Each batch was mixed well then semi-dry pressed using 2% PVA solution and one inch square mould at 60kg/cm^2. The shaped briquettes were dried at 110^{o}C over night and fired at 1500 ^{o}C for five hour using one stage firing process technique. The solid phase composition as well as the microstructure of the three batches was carried out using XRD and SEM techniques, respectively. Densification parameters of the fired briquettes in terms of bulk density and apparent porosity were determined according to kerosene displacement method (1, 2). Compressive strength as well as refractoriness under load up to 1500 ^{o}C of the fired briquettes was determined.

3. RESULTS AND DISCUSSIONS

Petrographical study of the serpentinites shows that it is hard, massive, grayish green in color. Microscopically, Serpentinites consists of a mixture of antigorite with subordinate chlorite as its alteration products and opaques. Antigorite occurs as aggregates of fibro-lamellar structures. These aggregates are randomly or preferentially oriented bundles, figure 2. Opaques are represented mainly by magnetite, figure 2.

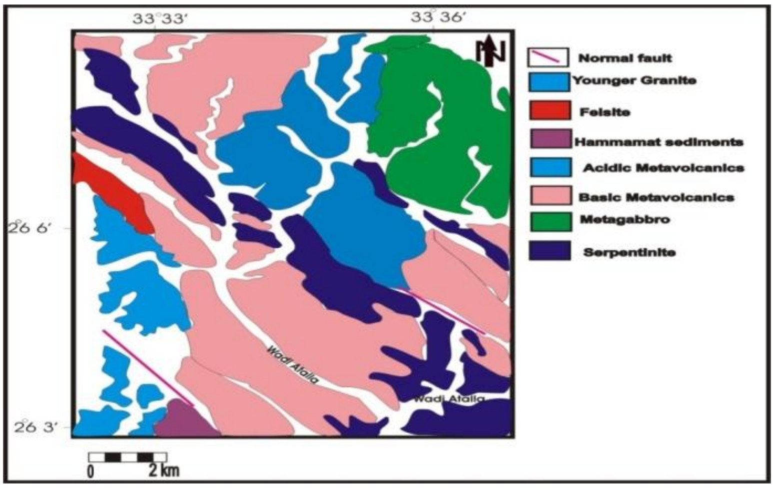


Fig1. *Geological map of Wadi Atalla area modified after Khyamy et al. (2003).*

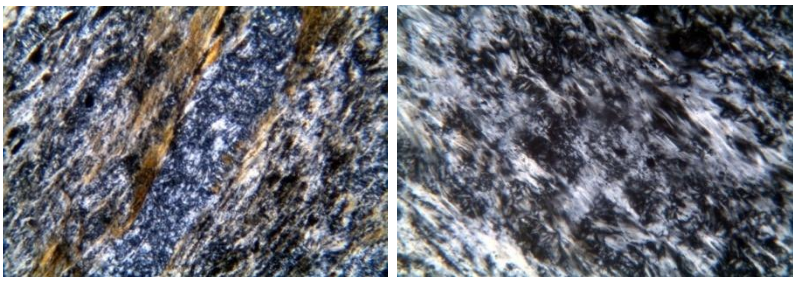


Fig2. *photomicrographs of serpentinites raw materials*

Chemical composition of the used materials is displayed in table 1. It is showed that serpentinites is mainly composed of hydrated magnesium silicate with appreciable amount of iron; the amounts of SiO_2, MgO, FeO and Loss on ignition are 40.79, 36.46, 8.09 and 12.27%, respectively. Lesser amount of alumina and titanium oxide are recorded as 1.17 and 0.05%. Minor and trace amounts of other impurities do not exceed 1% , while the chemical composition of the used magnesite (R) confirms that MgO is the major oxide (93.08%) beside 1.88% of CaO, While Fe_2O_3 and Al_2O_3 are 0.60 and 1.54%, respectively. lesser amount of loss on ignition is detected as 0.58%.

Table1. *Chemical composition of the starting materials*

Constituents %	Serpentinite	Used magnesite	Alumina
SiO_2	40.79	1.50	-
TiO_2	0.05	-	-
Al_2O_3	1.17	0.60	100
Fe_2O_3	8.09	1.54	-
MnO	-	-	-
MgO	36.46	93.08	-
CaO	0.09	1.88	-
Na_2O	0.16	-	-
K_2O	0.01	-	-
P_2O_5	0.01	-	-
SO_3	0.21	-	-
F	-	-	-
Cl	0.09	-	-
rC_2O_3	0.035	-	-
CuO	0.033	-	-
NiO	0.015	-	-
SrO	0.02	-	-
V_2O_5	0.047	-	-
ZnO	0.013	-	-
ZrO_2	0.035	-	-
L.O.I	12.27	0.58	-
Total	99.598	99.18	100

Mineral composition of the serpentinites carried out by XRD technique confirms that Antigorite mineral is the major mineral with subordinate amount of chlorite mineral. No other minerals are detected perhaps due to their small amounts, figure 3. Solid phase composition of the used magnesite performed by XRD confirms that the main phase composition is periclase in addition to the very low amount of CMS phase, figure 4.

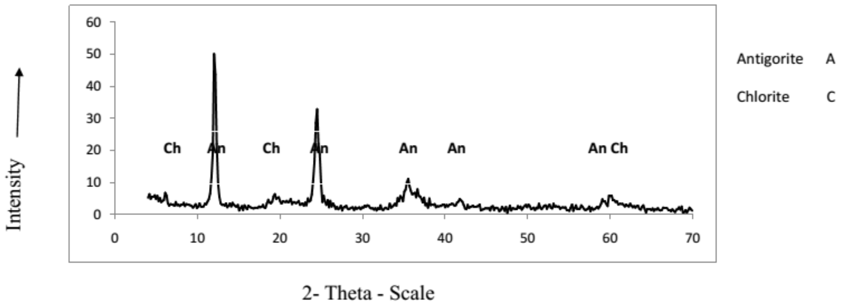


Fig3. *XRD pattern of serpentinites raw materials*

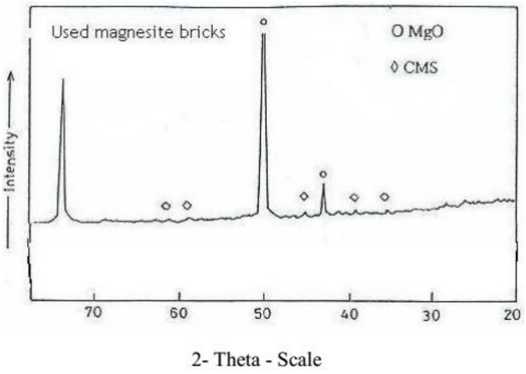


Fig4. *XRD pattern of used magnesite materials*

According to the stoichiometry composition of serpentine mineral and forsterite, the serpentine, $Mg_3SiO_5(OH)_4$, the amount of MgO is 43.48%, while the SiO_2 is 43.48% and H_2O is 13.04%. Whereas the percentage of MgO and silica in forsterite (2MgO. SiO_2) are 57.14 and 42.86%, respectively. So, appreciable amount of magnesia source should be added to increase the magnesia in the batch then fired for forming the forsterite refractory mineral. Three batches were designed to yield forsterite, periclase forsterite and spinel periclase forsterite. Calculated amounts of serpentinites with used magnesite and / or aluminum oxide were mixed to give the three batches, tables (2-4).

Table2. *Calculated stoichiometry composition of forsterite*

Constituents %	Serpentinite 100 gm	20 gm of used magnesite	Total oxides	On calcined basis 100%
SiO_2	40.79	0.3	41.09	38.3846
TiO_2	0.05		0.05	0.046708
Al_2O_3	1.17	0.12	1.29	1.205067
Fe_2O_3	8.09	0.308	8.398	7.845079
MnO	-	-	-	-
MgO	36.46	18.616	55.076	51.44982
CaO	0.09	0.376	0.466	0.435319
Na_2O	0.16	-	0.16	0.149466
K_2O	0.01	-	0.01	0.009342
P_2O_5	0.01	-	0.01	0.009342
SO_3	0.21	-	0.21	0.196174
F	-	-	0	-
Cl	0.09	-	0.09	0.084074
rC_2O_3	0.035	-	0.035	0.032696
CuO	0.033	-	0.033	0.030827
NiO	0.015	-	0.015	0.014012
SrO	0.02	-	0.02	0.018683
V_2O_5	0.047	-	0.047	0.043906
ZnO	0.013	-	0.013	0.012144
ZrO_2	0.035	-	0.035	0.032696
L.O.I	12.27	0.116	12.386	-
Total	99.598	19.836	119.434	100.00

Table3. *Calculated stoichiometry composition of periclase forsterite composites*

Constituents %	Serpentinites 100 gm	30 gm of used magnesite	Total oxides	On calcined basis 100%
SiO_2	40.79	0.45	41.24	35.275
TiO_2	0.05		0.05	0.042768
Al_2O_3	1.17	0.18	1.35	1.154734
Fe_2O_3	8.09	0.462	8.552	7.315029
MnO	-		0	0
MgO	36.46	27.924	64.384	55.07142
CaO	0.09	0.564	0.654	0.559405
Na_2O	0.16	-	0.16	0.136857
K_2O	0.01	-	0.01	0.008554
P_2O_5	0.01	-	0.01	0.008554
SO_3	0.21	-	0.21	0.179625

F	-	-	0	0
Cl	0.09	-	0.09	0.076982
rC_2O_3	0.035	-	0.035	0.029938
CuO	0.033	-	0.033	0.028227
NiO	0.015	-	0.015	0.01283
SrO	0.02	-	0.02	0.017107
V_2O_5	0.047	-	0.047	0.040202
ZnO	0.013	-	0.013	0.01112
ZrO_2	0.035	-	0.035	0.029938
L.O.I	12.27	0.174	12.444	0
Total	99.598	29.754	129.35	99.99829

Table4. *Calculated stoichiometry composition of spinel periclase forsterite composite*

Constituents %	Serpentinite 100 gm	40 gm of used magnesite	Alumina	Total oxides	On calcined basis 100%
SiO_2	40.79	0.6	-	41.39	30.262927
TiO_2	0.05	-	-	0.05	0.036558259
Al_2O_3	1.17	0.24	10	11.41	8.342594759
Fe_2O_3	8.09	0.616	-	8.706	6.365524099
MnO	-	-	-	0	
MgO	36.46	37.232	-	73.692	53.8810248
CaO	0.09	0.752	-	0.842	0.615641086
Na_2O	0.16	-	-	0.16	0.11698643
K_2O	0.01	-	-	0.01	0.007311652
P_2O_5	0.01	-	-	0.01	0.007311652
SO_3	0.21	-	-	0.21	0.153544689
F	-	-	-	0	-
Cl	0.09	-	-	0.09	0.065804867
rC_2O_3	0.035	-	-	0.035	0.025590781
CuO	0.033	-	-	0.033	0.024128451
NiO	0.015	-	-	0.015	0.010967478
SrO	0.02	-	-	0.02	0.014623304
V_2O_5	0.047	-	-	0.047	0.034364764
ZnO	0.013	-	-	0.013	0.009505147
ZrO_2	0.035	-	-	0.035	0.025590781
L.O.I	12.27	0.232	-	12.502	-
Total	99.598	39.672	10	149.27	100

Table 2 shows the calculated stoichiometry composition of forsterite synthesis from serpentinite and used magnesite. 100gm of serpentinite added to 20 gm of used magnesite were mixed to give about 38.35 and 51.45% of silica and magnesia, respectively. On basis of 100% of silica and magnesia recalculation, it gives 42.73 and 57.27%, respectively. These ratios are closed to the stoichiometry composition of forsterite. Part of Fe_2O_3 and Al_2O_3 are participating within the forsterite structure while the other part are forming liquid phase with the other impurities at high temperature. On increasing the amounts of the used magnesite to 30 gm, the ratio of SiO_2 and MgO became 35.275% and 55.07142%, respectively. On recalculation of silica and magnesia to 100%, the percentage of SiO_2 and MgO are 39.04 and 60.96%. On basis of stoichiometry composition of forsterite, the percentage of silica 39.04 is combined with 52.05% of magnesia to give about 91.0% of forsterite. The excess of magnesia expected to form periclase phase. Increasing amount of used magnesite to 40gm per 100gm of serpentinites lead to raise MgO to 53.88% and decreasing of SiO_2 content to 30.26%. All of SiO_2 is depleted with 40.35 % amount of MgO to form forsterite and part of the excess of MgO is reacted with the Al_2O_3 to form magnesium Aluminates spinel and periclase. The total iron detected in the batch is participating as ferrous and/or ferric as solid solution in the structure of both forsterite and spinel.

Solid phase composition of the fired batches up to 1500°C for five hours is illustrated in figure 5. Forsterite is the only phase recorded in the first batch, while periclase and forsterite phases are the two batches detected the second batch designed to form these phases. In the third batch, three phases are shown, namely spinel, periclase and forsterite phases. The solid phase composition carried out by XRD ensure the petrographic studies displayed for the raw materials as well as the stoichiometry phase composition designed to form these phases.

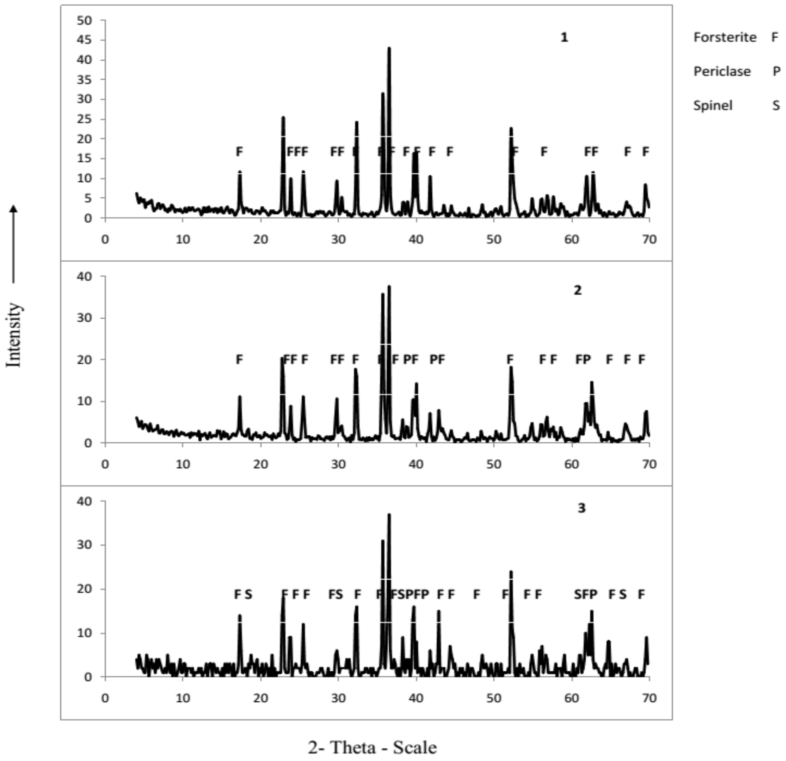
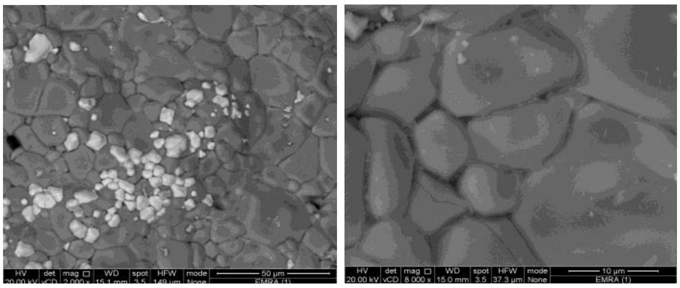
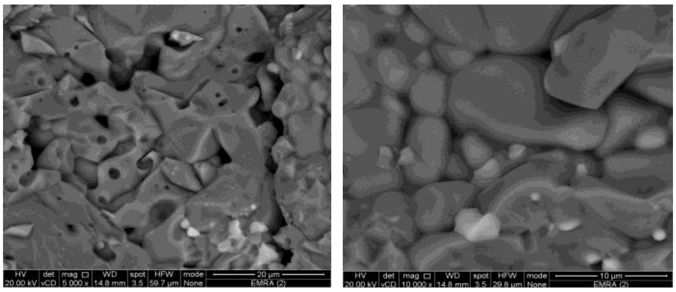


Fig5. *XRD pattern of the three fired batches at 1500oC for five hours*

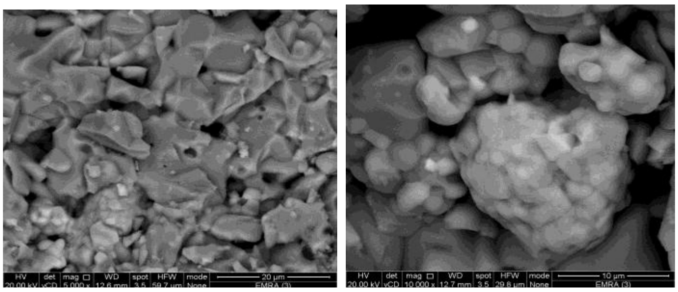
The microstructure and microchemistry of the fired batches were studied using SEM and EDAX point analysis as revealed in figures 6&7, respectively. Batch no 1 shows fine, medium and coarse of interlocked grains, gray in colour, subhedral to rounded crystals of forsterite, point analysis no. 1. Very few amounts of pores are observed between the grains. White bright grains of forsterite contain some iron and alumina in solid solution within the magnesium silicate structure of forsterite is noticed between the rich in magnesia type, gray, point analysis no. 2. Batch no. 2 shows rounded to sub rounded of forsterite gray in colour. The size of the grains is varying in size from fine to very fine. Bright grains of ferroan forsterite are dispersed within the gray type. Small amount of liquid phase are observed between the forsterite grains, point no. 3. More amounts of pores with different sizes are observed in the ground mass. Small rounded grains of periclase grayish in colour are seen between the forsterite grains. Pore sizes and amounts are increasing in the batch no 3 where as spinel is appear beside the solid solution of forsterite and periclase.



Batch 1 (1) *(2)*

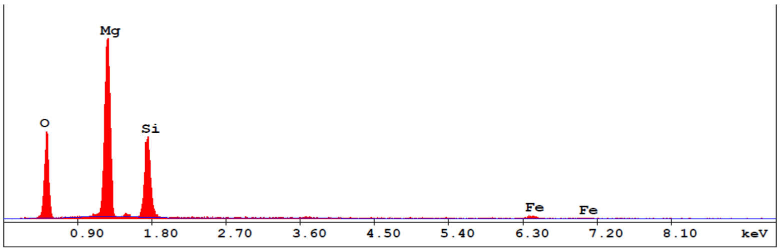


Batch 2 (1) *(2)*

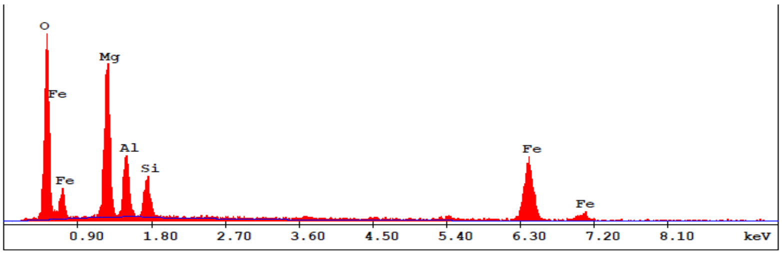


Batch 3 (1) *(2)*

Fig6. *SEM of the prepared batches fired at 1500OC for 5 hours*



Point no. 1



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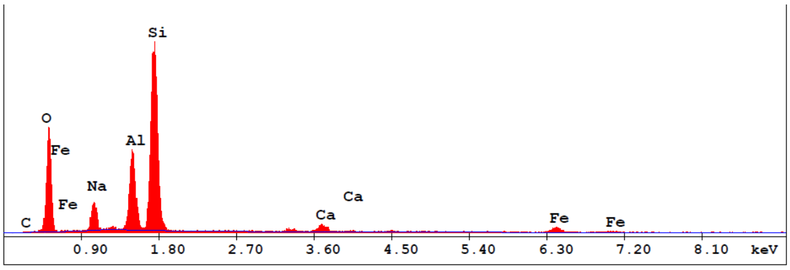

Point no. 3

Fig7. *EDAX analysis of the prepared batches fired at 1500OC for 5 hours*

Densification properties of the fired batches are illustrated in table 5. It shows that the bulk density of the forsterite batch is 3.26 g/cm^3, while that of the periclase forsterite and g/cm^3 spinel periclase forsterite are 3.12 and 3.27 g/cm^3, respectively.

Apparent porosity has reverse relation to the bulk density and the linear shrinkage. The apparent porosity of the forsterite batch is %, while these of periclase forsterite 20% and 21% g/cm^{3}spinel periclase forsterite are 20 and 21 %, respectively.

Table5. *Densification properties of the fired batches at 1500oC for five hours*

Batch no.	Bulk density g/cm^3	Apparent porosity %	Linear shrinkage	CCS Kg/cm^2	Ta ^{o}C
1	3.26	5	9.6	740	1450
2	3.15	20	7.2	700	1500
3	3.27	21	6.3	500	1500

Linear shrinkage decreased from the forsterite batch to record 9.6% through the periclase forsterite batch to give 7.2% and finally the spinel periclase forsterite to be 6.3%, this lowering in the shrinkage attributed to that liquid phase formed increasing from the forsterite to the spinel forsterite batch.

Compressive strength of the fired batches based mainly of the densification properties of the fired batches as well as their mineral constitution. Forsterite batch show highest density and shrinkage as well as lower porosity. So it shows the highest compressive strength than the other two batches as illustrated in table 4. The compressive strength recorded for the forsterite is 740kg/cm^2, while that of the periclase forsterite and spinel periclase forsterite are 700 kg/cm^2 and 500 kg/cm^2, respectively. This is owing to high liquid phase content decrease from the forsterite batch to spinel periclase forsterite batch.

Refractoriness under load of the fired batches is carried out for the three designed batches to detect the thermal behavior and the maximum operating temperature. The maximum temperature could the sample bear is depend on the solid and the liquid phases composition formed in each batch at 1500^{o}C, figure 8. The maximum bearing temperature under load of 2kg/cm^2 (Ta) for the forsterite, periclase forsterite and spinel periclase forsterite are 1450 ^{o}C, 1500 ^{o}C and 1500 ^{o}C, respectively. This mainly due to the additional formed periclase and spinel refractory phases, to the essential forsterite refractory phase. This confirms that the addition of periclase and spinel refractory phases improve the refractory quality of the forsterite ceramic body.

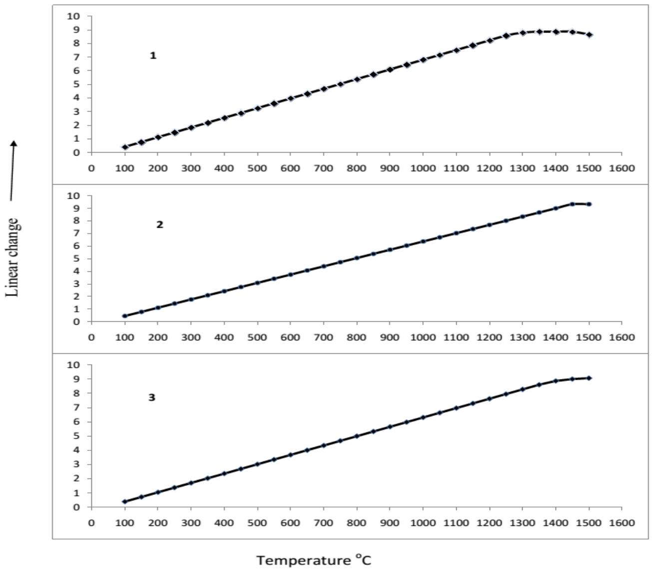

Fig8. *Refractoriness under load of the prepared batches fired at 1500OC for 5 hours.*

These ceramic bodies are recommended to apply in lining of permanent layer of iron and steel ladles and the brick network in the heat exchangers of glass furnaces.

4. CONCLUSION

- Three batches were designed from serpentinites and used magnesite as well as aluminum oxide to synthesis forsterite, periclase forsterite and periclase spinel forsterite refractory phases.
- Mineral composition of the used magnesite and serpentinites show that the used magnesite is composed of periclase and CMS phases, while serpentinites are consisted of antigorite and chlorite.
- Phase composition and the microstructure of the fired batches at 1500^{o}C for five hours confirm that forsterite and periclase forsterite as well as spinel periclase forsterite refractory phases are formed.
- Densification properties show that the bulk density of the three batches range from 3.15 to 3.27g/cm^3, while porosities are and shrinkage 9.6, 7.2 and 6.3%, respectively.
- Compressive strength of the three batches decrease from forsterite 740kg/cm^2 to periclase forsterite 700kg/cm^2 and spinel periclase forsterite 500kg/cm^2.
- Refractoriness under load confirms that the additional phases of periclase and spinel improve the refractoriness of the forsterite to 1500^{o}C.
- These ceramic bodies are recommended to apply in lining of permanent layer of iron and steel ladles and the brick network in the heat exchangers of glass furnaces.

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