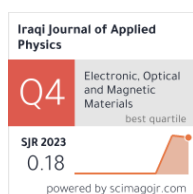


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Structural and Mechanical Properties of Porcelain Prepared from Iraqi Raw Materials with Non-plastic Clay Additives

Porcelain is one of the most important technical ceramics, but the shrinkage in dimensions after firing resulting from plastic clays is one of the shortcomings that manufacturers suffer from. Therefore, this work aims to reduce shrinkage by adding non-plastic powder (fired kaolin (Grog): prepared by firing plastic clay up to 1100°C) and extend their effect on some other properties of porcelain. The composition of hard porcelain is: 60 wt.% kaolin, 20 wt.% flint and 20 wt.% potash feldspar as Iraqi raw materials. Non-plastic clay was added to the porcelain by 25, 30, 35 and 40 wt.% instead of kaolin. Forming the samples by axial pressing into discs then fired at 1300°C. FE-SEM images showed the emergence and increasing of the mullite phase as a result of the porcelain firing with the addition of fired clays. XRD analysis confirmed the presents of mullite phase in addition to the cristobalite phase. Increasing the non-plastic clay from 25 to 40 wt.% led to a significant decrease in linear shrinkage from 12.6 to 5.4%, increased the porosity from 12.2 to 15.1%, decreased the bulk density from 2.25 to 2.16 g/cm³, this clearly affected the decrease in the diametral strength from 23.26 to 10.48 MPa. The results obtained determined the possible application range for construction, to include thermal insulation, wall tiles and decoration.

Keywords: Porcelain; Kaolin; Flint; Feldspar; Grog; Diametral Strength

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1. Introduction

Porcelain is one of the most important technical materials that using in many different fields such as pottery industries, enamels, dental industry, electrical industries and construction materials [1]. Porcelain differs and is better than whiteware ceramics due to the properties shown in table (1) [2]. Porcelain is mixed ceramic material consist of three raw ceramic materials: kaolin, flint and feldspar. The difference in the weight percentage of these components makes porcelain wide-ranging in terms of applications [3]. Hard porcelain is common type of porcelain consist of 50 wt.% of Kaolin, 25 wt.% of flint and 25 wt.% of feldspar, as shown in Fig. (1) [4-6]. The most common uses of porcelain include household, laboratory and industrial [7,8]. Medically, porcelain has proven to be very successful in dental applications, including: inlays, onlays, veneers, crowns and artificial teeth [9,10]. While vitreous porcelain used as coating material for decoration both exterior and interior like supermarkets and swimming pools as well as art ware, chemical ware, kitchen ware, table ware and tiles [11,12]. The processes of firing porcelain components lead to the formation of the refractory mullite phase ($\text{Al}_6\text{Si}_2\text{O}_{13}$) with quartz and glass phases that give porcelain transparency and surface smoothness. Hard porcelain is resistant to high temperatures due to the high sintering temperature, which ranges from 1250 to 1450 °C [13]. This gives it good mechanical properties (high flexural strength $>35 \pm 2$ MPa) and low water absorption ($<0.5\%$) [14].

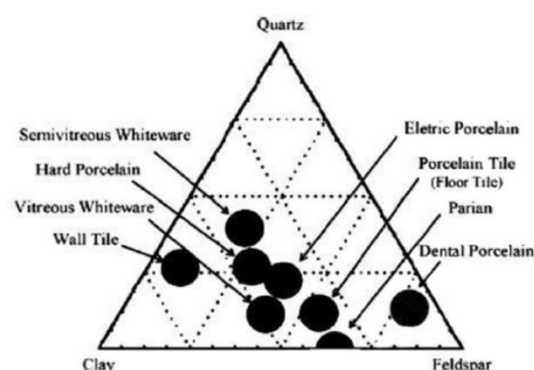


Fig. (1) Triple diagram of porcelain types [4]

Rambaldi et al. (2014) have studied the physical properties of different commercial porcelain stoneware. It was concluded that there is a clear effect of surface glazing on the types of porosity. Although the open porosity of the glazed sample decreased, but the closed porosity increased. This explains the decrease in mechanical properties of glazed porcelain in some cases despite the decrease in open porosity [15]. Lerdprom et al. (2016) have used kaolinite, albite and quartz as raw materials to prepare porcelain by pressing method. After the drying process, sintering was performed at different rates and direct sintering up to different temperatures (1150, 1175 and 1200°C). The effect of different sintering rates on the properties of porcelain was studied. It was found that direct sintering gives the highest bulk density compared to different sintering rates, while there is a clear decrease in water absorption. Sintering at a temperature of 1200°C

gave higher crystallization of porcelain through the emergence of mullite phase. The diametral strength decreased in the case of direct sintering compared to other sintering rates. In general, the maximum value of the diametral strength was 32 ± 4 MPa [16]. Akpinar et al. (2017) have prepared porcelain tile from 50 wt.% kaolin, 25 wt.% silica and 25 wt.% feldspar. Calcium borate was chosen as the flux, and was added in different proportions to the porcelain mixture. The samples were formed by slip casting, and then sintered at different temperatures 1250-1300°C. It was found that the linear shrinkage increased with increasing flux addition. While the porosity and water absorption decreased significantly to low values (<2% and <1%, respectively). In contrast, the flexural strength values increased to 33 MPa. Mullite and quartz were the main phases shown in the x-ray diffraction (XRD) pattern, and their appearance increased as the sintering temperature increased [17]. Alwikutty (2020) has replaced feldspar with fly ash (0-25 wt.%) in the porcelain tile and measured physical, mechanical and microstructure properties. It was concluded that 5 wt.% of fly ash at a sintering temperature of 1250°C is the best percentage and obtained the highest strength and hardness with good density and mullite content [18]. Nor Izam et al. (2023) have compared between glazed, unglazed ceramic and porcelain tile with industry technique, physical and shape properties. It is concluded that porcelain tiles are superior to glazed and unglazed ceramic tiles based on these comparisons [19].

Porcelain raw materials have been modified for the last years by using additive materials to enhance the mechanical properties and moderate percentage of porosity. In this research a non-plastic clay (grog), as additive material, have been add to the porcelain composition as replacement with specific weight percentage of kaolin with attempted to lowering the linear shrinkage, dimensional inaccuracy, reasonable mechanical strength and required porosity in the porcelain for tile applications.

This work and the results obtained from it are an incentive to invest in local raw materials and employ them in the ceramic industries, most notably porcelain products, at a low cost.

2. Experimental part

2.1 Raw Materials

Iraqi raw materials were used for the preparation of hard porcelain (60 wt.% kaolin ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$), 20 wt.% flint (SiO_2) and 20 wt.% potash feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$)). Kaolin was taken from Alduejlh Zone in Iraq while the flint and potash feldspar were taken from western desert of Anbar Province. The chemical compositions of these Iraqi raw materials are shown in table (2).

2.2 Porcelain preparation

Powder metallurgy technique was used to prepare porcelain specimens. Fine particles sizes of Kaolin and Nonplastic clay (grog) were used. The non-plastic clay was prepared by firing kaolin at a temperature of 1100°C to lose the plasticity property that characterizes clays. Micro Potassium feldspar and Flint, with various weights percent of kaolin and nonplastic clay (grog) that were used, illustrated in table (3). To reduce the effect of moisture and powder agglomeration, all powder was dried at 100°C for 2 hours. Ceramic powders were mixed with each other according to the required weight percentage for 6 hours using ball mill mixer with alumina balls of 14mm in diameter, and the speed of rotation was 250 rpm. All mixtures were sieved and the coarse powder was re-grinded again until the particle size of 75 μm was achieved. A uniaxial cold press technique was used to press 5 specimens from each mixed powder by using steel cylindrical mold under force of 10 tons of a hydraulic press to form green compact with thickness of 5 mm and diameter of 10 mm.

After specimens prepared by powder metallurgy technique, they were fired to be sintered at temperature of 1300 °C by a Nabertherm GmbH furnace (Germany) (heating range 30-3000°C), the firing program shown in Fig. (2).

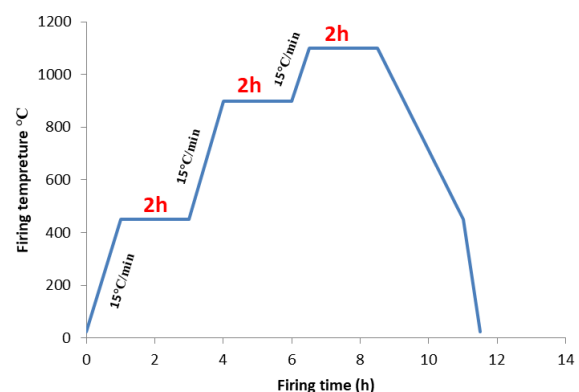
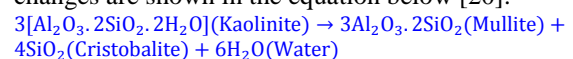


Fig. (2) Firing program

2.3 Characterization and testing

On first heating, the kaolin lost chemical water and the impurities such as organic and others, these changes are shown in the equation below [20]:



Shrinkage was measured by taking the specimens dimensions before and after firing by using the Vernier caliper. Total linear shrinkage after firing of ceramic specimens as a percentage of plastic length was calculated according to ASTM C326 by the following equation [21]:

$$\text{Linear Shrinkage (L.S)} = \frac{L_0 - L}{L_0} * 100\% \quad (1)$$

where L_0 is plastic length of test specimen (before firing) and L is fired length of test specimen

Archimedes method was achieved to determined bulk density and open porosity by using distilled

water. The measurement of density was done by dividing the mass of material in air by its buoyancy (reduction in weight) when suspended in a water.

The density of a material is [22]:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \quad (2)$$

There are three volume expressions in common use as follows [23]:

1- Apparent volume or bulk volume: which are the volume of the solid component, open pores and closed pores, determined by the difference between the soaked mass (S) and the immersed mass (I) of the soaked piece.

2- True volume: The solid component volume was done by milling it into smaller pieces till it become powder form, into which all pores are destroyed and using "Density Bottle" method.

3- Apparent solid-volume: The closed pores and solid component volume only, is determined from the difference between the dry weight (D) and the immersed weight (I) of the piece.

The densities and porosity expressions are [23]:

$$\text{Apparent (or bulk) density } (\rho_b) = \frac{\text{mass}}{\text{apparent volume}} = \frac{D}{S-I} \quad (3)$$

$$\text{Percentage apparent porosity} = \frac{\text{open pore volume}}{\text{total volume}} * 100$$

$$A.P\% = \frac{S-D}{S-I} * 100 \quad (4)$$

Motivated by the wishing to use compressive forces to induce tensile failures, as well as the demand to study the surface area and volume effects, the specialists have devised a number of ingenious in direct tension test, one of these methods is diametral compression; this method solve the common problem of precise machining of an ordinary machine materials.

Loading configuration is an important factor in the diametral compression disk (Fig. 3), this simple theory described the stress distribution under a uniform diametric load on a disk-shaped specimen predicts a uniform tension field at the center of the disk [24]:

$$(\text{Diametral Strength}) \sigma_D = \frac{2F_{Max}}{\pi R d} \quad (5)$$

where F_{max} is the applied load (N), R is the disk diameter and d is the thickness of disk [24]

The stress field in the transverse direction is highly dependent on the width of load application and becomes highly compressive. The disk test has therefore been used to attempt to study biaxial stress failure response [25].

The x-ray diffraction patterns of compact porcelain specimens were obtained using a Shimadzu XRD-6000 diffractometer, using Cu radiation at a frequency of 2 deg/min, voltage of 40kV, current of 30mA, and wavelength of 1.54060Å, and scanning range of 5-90°.

Field-emission scanning electron microscopy (FE-SEM) was performed using a FEI Inspect f50 FE-SEM instrument to introduce the morphology of the fracture surface for the specimen.

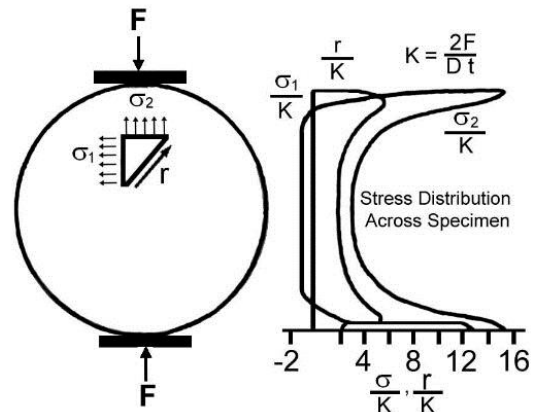


Fig. (3) Analysis of diametral stress [19]

3. Results and Discussion

The XRD patterns of the prepared porcelain samples are shown in Fig. (4). It is noted that the firing process was completely done, as well as all the phase transformations of the porcelain components were achieved. The main phases are mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and silica (SiO_2) with its phase's quartz and cristobalite. These crystalline phases are dominant, with some amorphous compositions of the glassy phases resulting from the reaction of flux oxides and are present in the raw materials, forming the glassy phase during firing.

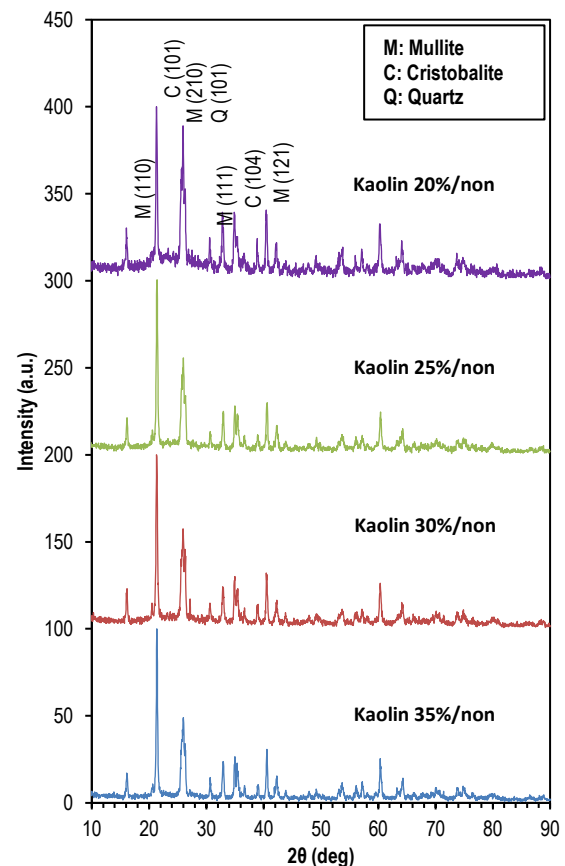


Fig. (4) XRD patterns of porcelain with different Kaolin (wt.%) / non plastic clay (wt.%) ratio

Quartz is considered a natural raw mineral, found in the form of crystalline structures in the original raw materials. This compound transforms into other phases such as tridymite and cristobalite during the firing process. Part of the quartz combines with alumina to form mullite, and the remainder remains in the form of free silica in the cristobalite phase. An increase in the percentage of mullite after firing the raw materials is matched by a decrease in cristobalite, and this determines the amount of alumina in the clay. There was no significant change in the percentage of cristobalite, because it requires high temperatures (more than 1400°C) to appear sharply and transform all the quartz into cristobalite. The basic cristobalite phase appeared at the diffraction angle $2\theta=21.28^\circ$ in the crystal plane (101). As for quartz, it was seen at the diffraction angle 25.92° and the crystal plane (101). The main mullite phase appeared at the diffraction angle 25.56° and in the crystal plane (210). In general, the mullite phase increased in appearance with the addition of non-plastic clays.

Linear shrinkage is evidence of the progress of the process of transformation and granular growth after the firing process. Kaolin is the main cause of linear shrinkage due to the significant change in structure during firing. It is also a result of the appearance of glassy phases that merge the grains with each other. Figure (5) shows a clear decrease in shrinkage with increasing addition of non-plastic clays (grog). This behavior is logical, because fired clay does not suffer from shrinkage when added to porcelain mixtures. Perhaps one of the most important reasons for adding grog is to reduce the shrinkage resulting from plastic clay [26].

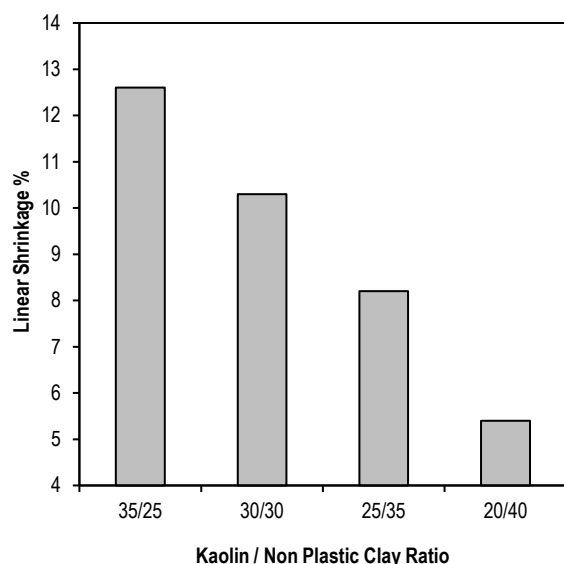


Fig. (5) Linear Shrinkage of porcelain with different kaolin (wt.)/non plastic clay (wt.%) ratios

Most ceramic bodies that suffer from high shrinkage experience significant dimensional deformation and thus loss of homogeneity. The

decrease in linear shrinkage was from 12.6% for samples 35 kaolin/25% non-plastic clays to 5.4% for samples 20% kaolin/40% non-plastic clays. Decreasing shrinkage may be matched by a decrease in density provided the mass loss remains constant. From the results of the raw material component analysis tables, it is possible to determine the raw material causing shrinkage, because raw materials that contain higher percentages of silica do not suffer from significant shrinkage, and therefore both raw materials (kaolin and flint) participate in shrinkage.

Figure (6) shows the change in apparent porosity results with an increase in the percentage of adding non-plastic fired clays. The reason for this can be attributed to the lack of fusion of plastic clays with non-plastic clays. There are also pre-existing pores in the structure of the added non-plastic clays. In general, the apparent porosity increased from 12.2% to 15.1% when the percentage of adding non-plastic clays increased from 25 to 40 wt.%. The increase in porosity was not significant, as the percentage increase was 23.8%. The effect of porosity will be reflected in other properties, and in any case, increased porosity should not be considered a weakness, unless there is a serious deterioration in the mechanical properties. It is important to note that porosity is required for thermal insulation purposes and construction requirements.

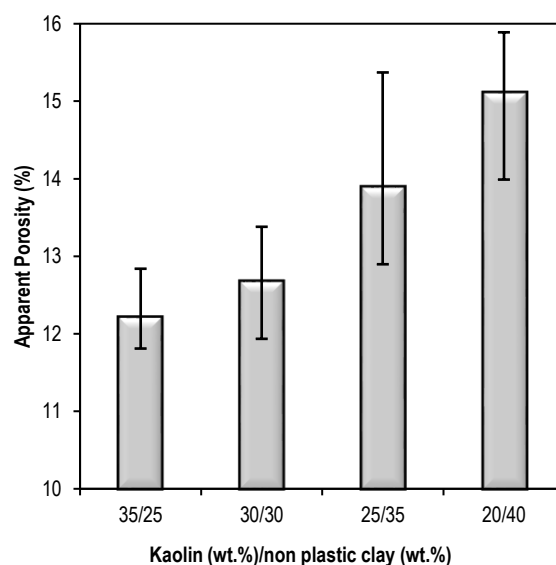


Fig. (6) Porosity of porcelain with different kaolin (wt.)/non plastic clay (wt.%) ratio

As for the bulk density, it decreased with increasing addition of non-plastic clay. Figure (7) shows the decrease from 2.25 to 2.16 g/cm³ when the addition of non-plastic clays increased from 25 to 40 wt.%. The decrease in density is related to the increase in porosity, and the percentage decrease in density was small, approximately 4%. Not affecting density significantly means obtaining products with good condensation. Understanding density helps

control porosity, which is very important in filter and membrane applications. Ceramics with low density and porosity are also linked to the ability to manufacture and the completion of subsequent operations, the most important of which is glazing.

Mechanical properties were achieved using the diametral fracture method suitable for disc models. Engineering analyzes of stresses acting on the sample when applying diametral stress, it was found that 79% is tensile stress and the remainder is compressive stress [27]. Therefore, this test is considered an indirect tensile test, and it is important because it identifies the failure zones in ceramics, which are represented by a decrease in tensile strength compared to compression. Figure (8) shows the decrease in diametral strength with increasing percentage of non-plastic clay added.

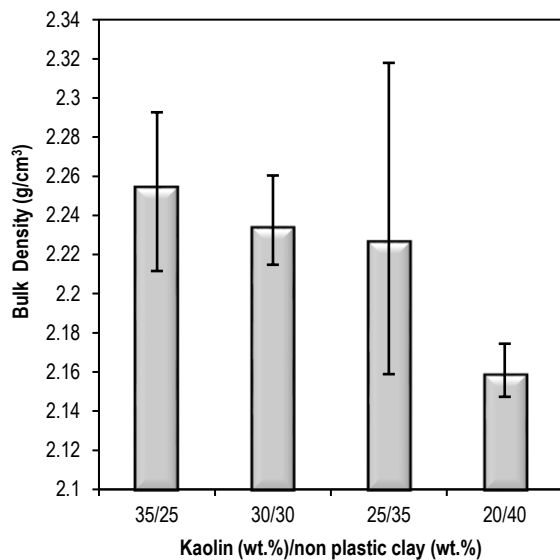


Fig. (7) The bulk density of porcelain with different kaolin (wt.)/non plastic clay (wt.%)

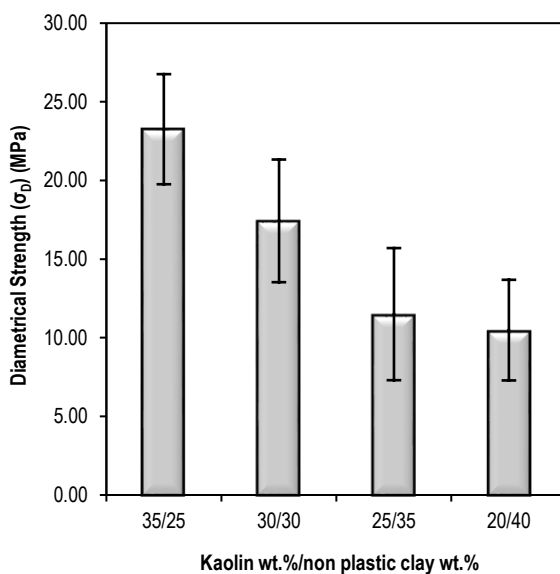


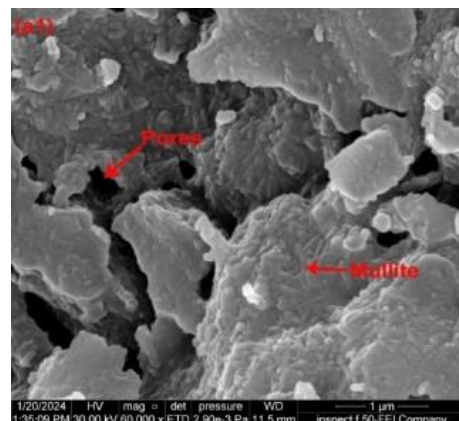
Fig. (8) The diametral strength of porcelain with different kaolin (wt.)/non plastic clay (wt.%) ratio

In general, porosity is considered one of the most important reasons for the decrease in mechanical properties. The decrease in diametral strength from 23.26 MPa to 10.48 MPa when adding grog from 25 to 40 wt.%, respectively. This means a decrease in diametral strength by 55%. Figure (9) shows a photograph of the samples after fracture, and it shows that the sample was split into two halves approximately. This is evidence of the homogeneity of the samples, while the fragmentation in the middle of the sample is due to the brittleness of the samples and the high fracture stress.



Fig. (9) Shape of the diametral stress of the samples

The FE-SEM images are shown in Fig. (10), and the mullite phase clearly appears, which a needle-like structure is resulting from the transformation of clay sheets as a result of firing. Other structures that appear with mullite result from glassy phases, and these phases differ from each other in terms of thermal expansion coefficients. This difference leads to the emergence of microscopic cracks in the structure of the samples, and this may be one of the reasons for the decrease in fracture strength. The pores are also shown in the images and their shape is irregular due to the variety of raw materials. It is important to mention that the needle structures of mullite may help improve the mechanical properties in a way similar to the reinforcement of composites with short crystalline fibers (whiskers).



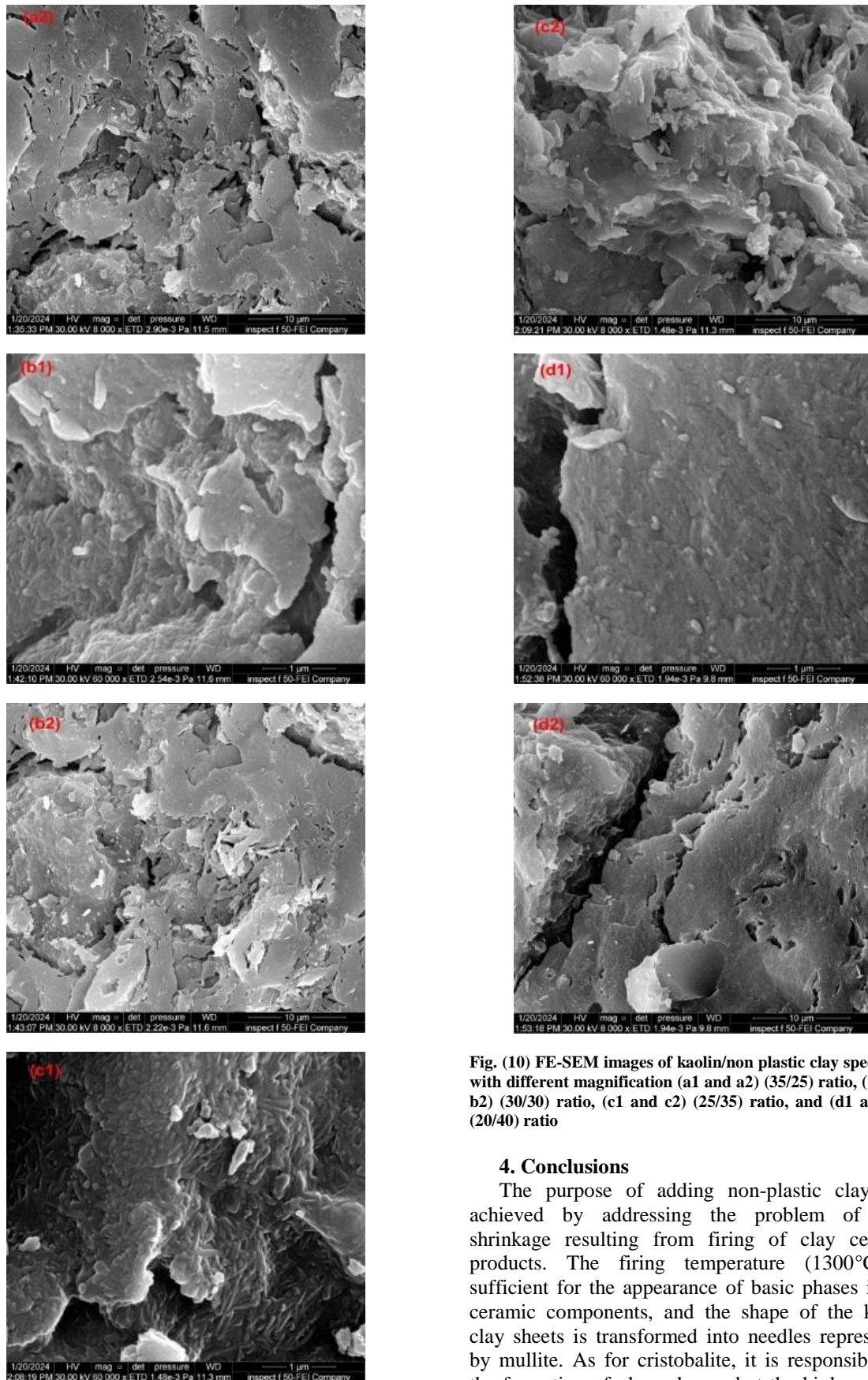


Fig. (10) FE-SEM images of kaolin/non plastic clay specimens with different magnification (a1 and a2) (35/25) ratio, (b1 and b2) (30/30) ratio, (c1 and c2) (25/35) ratio, and (d1 and d2) (20/40) ratio

4. Conclusions

The purpose of adding non-plastic clay was achieved by addressing the problem of high shrinkage resulting from firing of clay ceramic products. The firing temperature (1300°C) is sufficient for the appearance of basic phases in the ceramic components, and the shape of the kaolin clay sheets is transformed into needles represented by mullite. As for cristobalite, it is responsible for the formation of glass phases, but the high porosity negatively affected the mechanical properties. From the values obtained for density, porosity and diametral strength, it is clear that this type of

ceramic is not considered hard porcelain, and therefore the applications will be for thermal insulation purposes and building materials represented by unglazed porcelain for decorative purposes. Adding 30% by weight of non-plastic clay is not recommended if porcelain is used in applications requiring high tolerance to mechanical strength.

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Table (1) Comparison between ceramic and porcelain [2]

Property	Major compound	Firing Temperature	Strength	Absorbency	Opacity	Thickness	Texture
Whiteware Ceramic	Clay	Lower (800- 1300 °C)	Strong	10% (without glaze)	Higher	Thicker	Coarser
Porcelain	Mixed of clay, flint and feldspar	Higher (1200- 1400 °C)	Very strong	0%	Lower	Thinner	Smoother

Table (2) Chemical composition of Iraqi raw materials

Raw materials	Oxide wt%										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	Na ₂ O ₃	K ₂ O	SO ₃	Loss on ignition %
Kaolin	43.57	42.20	0.32	Nil	0.76	Nil	Nil	Nil	Nil	Nil	13..06
Potassium feldspar	67.00	18.00	0.14	--	0.26	0.03	2.10	--	11.00	0.002	0.46
Flint	42.05	38.70	0.88	2.20	1.50	1.00	0.1	0.1	0.15	0.03	11.90

Table (3) The specimens names, and the composition of raw materials for each specimen

Specimen No.	Kaolin wt. %/Non plastic clay wt. %	Composition wt. %			
		Kaolin	Non plastic clay	Potassium feldspar	Flint
1	35/25	35	25	20	20
2	30/30	30	30	20	20
3	25/35	25	35	20	20
4	20/40	20	40	20	20