

SELF-GLAZED CERAMICS USING CHEMICAL SWELLING OF ZINC-METAL POWDER

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ABSTRACT

Glazing process is considered as a very important step for a lot of unfinished ceramic wares to be suit various technical applications. An attempt was made, in this work, to use a self-glazing process. This includes mixing the necessary raw materials with the some other additives, which has the ability of producing glaze material during firing. Our ceramics were based on kaolin and silica. The promising additive to be responsible for making glaze was zinc metal powder which is known to undergo chemical swelling with dilute solution of sodium hydroxide.

A well crystallized new phase of willemite produces the glaze nature to ceramics fired at high temperatures, causing an increasing in specific gravity of unformed fired powders and decreasing in porosity and water absorption and increasing in the linear shrinkage, apparent solid density and the strength of the fabricated ceramics. This was supported by X-ray and SEM examinations.

INTRODUCTION

Silicate and other oxide compounds have been used as coating materials to protect the base material (metal or ceramics) from the effect of ambient environment or to improve the mechanical or electrical properties of the surface and the appearance of the ware. The term enamel is using for coating on a metal base (steel, cast iron, aluminum, etc.) whereas glazes are similar coatings on the surface of ceramic materials.

A glaze is usually applied in the form of aqueous suspension of powdered mixture that is usually compounded from pre-melted frit (e.g. silicate glass), and other admixture. These components are grounded and mixed in ball mills and applied by various techniques: dipping, pouring, spraying, etc. The subsequent firing of the whole product results in partial fusion of the coating and formation of a thin impermeable layer adhering firmly to the base [1].

The existence of the great variety of glaze types and compositions is a result of diverse requirements for the thermal expansion coefficients, firing temperatures and other properties determined by the nature of the ceramic body to be glazed [2].

An important component of glazing slips is the clay component that has the purpose of adjusting rheological properties of the slip and strengthening the raw coating. Glazing suspensions behave as pseudoplastic materials. They should have a low viscosity and should not settle in the aqueous medium. These properties are provided by the clay component together with suitable electrolytes, which causes the formation of a gel structure from the clay mineral particles.

Adhesion joining between the frit and the body ceramics is created quite readily on firing, because the melted glaze penetrates into pores of the ceramic materials and thus becomes firmly attached to the surface [3].

In previous work [4], controlled porous ceramics were prepared by chemical swelling Al:Zn mixture powders by dilute solution of sodium hydroxide at ambient temperature. Ceramic bodies were formed by semi-dry pressing and by slip-casting forming techniques. The X-ray patterns of the samples showed the presence of the new phases of $ZnAl_2O_4$ namely gahnite Zn_2SiO_4 namely willemite in addition to ordinary phases of the silica, i.e. quartz and tridymite, and they are

more clearly observed with increasing firing temperature. Willemite is known to form a crystalline glass [5], which may be responsible for the decreasing of porosity and permeability, and increasing the linear shrinkage, apparent solid density, specific gravity and mechanical strength under both, compression and impact. In glazing technology it is known that addition of ZnO to the frit creates a matte surface, which is always attributed to the large crystals of willemite that might be grown in glazes. They form large hexagonal plates with the surface [6].

From this point, an attempt was made to examine the ability of chemical swelled zinc metal powder to use as self-glazing in ceramic processing of kaolin and silica.

EXPERIMENTAL

Materials

Kaolin and Silica

Kaolin extracted from Dwekhla as it is pure and low in iron content (white kaolin), and silica as quartz raw material was taken from Al-Ruatba in the western desert of Iraq. They were sieved in a Podemorse sieving machine No. 15104/ England. The fine fractions of particle size less than $-63 \mu\text{m}$ after sieving process were used to prepare ceramic mixes. Table (1) shows their chemical analyses, carried out at the Stat Company for Geological Survey and Mining.

Table (1): Chemical analysis of kaolin and silica

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Trace	L.O.I.
Kaolin%	47.0	35.2	0.75	1.4	0.8	0.25	0.3	0.48	0.92	12.9
Silica %	98.2	0.62	0.06	1.22	0.18	0.61	----	----	----	0.3

Zinc Metal Powder

It is a bluish-white powder. As ordinary obtained, it is tough and moderately hard at room temperature. It has melting point of 419 °C and density 7.1g cm³. Like most other metals [7], it is easily attacked by solution of sodium hydroxide. It forms sodium zincate with liberation of hydrogen gas we believe it is responsible of fluffing the slurry mixture of kaolin and silica.

Specimen Preparation

Many samples composed from different weight percent of kaolin and silica were fabricated using semi dry pressing technique with a hydraulic press type Shimadzu Corporation No. 2666/ Japan. All samples were pressed in cylindrical form having about 25 mm diameter and 5 mm height, using a stainless steel mold. The forming load used was 3 ton because this was found the best pressing load for this type of ingredient (4). The conditions used are shown in Table (2).

Table (2): Conditions of prepared ceramic samples

Mix No.	Kaolin		Silica		Zn		Firing Temperature (°C)
	(wt.%)	Particle size (µm)	(wt.%)	Particle size (µm)	(wt.%)	Particle size (µm)	
GLA ₁	70	63	30	63	---	10	900,1000,1100,1200
GLA ₂	69	63	29	63	2	10	900,1000,1100,1200
GLA ₃	67	63	28	63	5	10	900,1000,1100,1200
GLA ₄	66	63	27	63	7	10	900,1000,1100,1200
GLA ₅	64	63	26	63	10	10	900,1000,1100,1200
GLA ₆	63	63	25	63	12	10	900,1000,1100,1200
GLA ₇	61	63	24	63	15	10	900,1000,1100,1200

Drying and Firing

Samples were dried first at room temperature for 48 hours, then at circulating oven for at least 10 hours. This provides enough time for drying of the samples to prevent vapour evolution into the samples due to the moisture content. The dried samples were fired at four different temperatures, 900, 1000, 1100 and 1200 °C in a Carbolite furnace with two hours soaking time.

Physical Properties

Linear Shrinkage Measurement

Linear shrinkage was calculated by using a micrometer to measure the dimensions of each sample (thickness or diameter) before and after firing. It was calculated as % L.Sh. [8].

Measurements of Porosity and Water Absorption

Since porosity is the main physical property which has to be examined to check whether they are of closed or open pores in the presence of the formed glaze. It was measured by two means. Firstly by using the standard test method (ASTM C20-2000) [9], this method also used to calculate water absorption and the apparent solid density. Secondly, the effective (interconnected) porosity was measured using Helium porosimeter model 3020-062 at Oil

Exploration Company. It is basically depends on gases expansion phenomena according to Boyle's law, whereby a known volume of helium gas at a known pressure expanded into an unknown volume, the resultant equilibrium pressure is measured and the unknown volume can be measured [10].

Specific Gravity Measurement

The specific gravity of ceramics is a function of their chemical and mineralogical compositions, and it varies with the degree of calcinations and its determinations used to control the products [4,11]. Specific gravity is measured by pycnometer method, in the physical chemistry laboratory, which includes powdering the ceramic material; drying at 110 °C. It is being the ratio of the density of a material to that of water.

Mechanical Properties

The investigation of mechanical properties of samples was essential for their use in various applications. The fracture strength in compression and impact and hardness are among the primary properties examined.

Brazilian Disc Fracture Test

This type of test is commonly used when conventional tensile is difficult to carry out due to the brittle nature of the test material [12].

This test was performed on fired discs having about 24.9 mm diameter and 5 mm height, using compression test device Instron 1195 at the University of Technology. The samples were fixed between upper and lower plates to start compression at a rate of cross-head speed 5 mm/min until failure. Then, fracture strength in MPa was determined.

Impact Strength Test

The impact strength was measured by Izod system. In this method a pendulum arm was dropped through definite arc onto the centre of a specimen to break it, an alternative test procedure is to increase the pendulum energy incrementally until the specimen fractures. This has an advantage that the incidental energy losses are minimized, and its residual energy is measured by its rise on the other side [13].

Microstructure Characterization

Scanning Electron Microscope (SEM)

Examination by the scanning electron microscope was performed using "Joel, JSM-6400 SEM". The samples were ground and polished, then coated with gold (6 min) to a thickness of (480 Å) by using "Jeol-JFC-1100E Ion Sputter" at working pressure of 10^{-1} Pa (10^{-3} torr). This test was carried out at the University of Technology

X-rays Diffraction

It was performed for the fired samples using X-ray vertical diffractometer type TW 1050, Fe K α for $\lambda=1.937$ Å, power 40/20 KV/mA. The selected specimens were milled using mortar and pestle. A line pattern is obtained from the chart containing the characteristic reflections from each mineral present. From the d-spacing and relative intensity of diffracted line, (considering the highest peak represents 100% of intensity), we can identify the phases formed in the each specimen according to the ASTM files.

RESULTS AND DISCUSSION

In processing of self-glazing ceramics based on kaolin, the starting point was to use a mix of kaolin and silica in such ratio to produce a ceramic body having high strength and lowest level of porosity. Thus, the prepared mix was based on porcelain whiteware. It has the classic components of kaolin, silica and feldspar [5]. The feldspar was excluded from this ingredient because it forms a glassy phase at high temperature which might interfere with the aim of this work, mix GLA₁, Table (1), was found to be the best mix to start with [10]. A high content of the clay component in the mix is necessary for ware, which is to have superior

mechanical strength, and simultaneously favorable forming properties.

The apparent porosity and water absorption properties are very correlated to each other, and their measurement allows the evaluation of a body for a specific purpose [5]. In this work, porosity was measured by two methods, by Archimedes and Helium porosimeter. The later method had slightly higher porosity values than that measured by Archimedes method using standard (ASTM C20-2000) [9]. This was attributed to that the small particles sizes of gas, which permit to diffuse in, narrow pores [14]. However, we will discuss these results only, and they are shown in Fig. (1).

It can observe from Fig. (1 A) that at zero wt.% addition the porosity of the ceramic body decrease with increasing firing temperature. This can be attributed to the natural glazing process occurs during firing [15]. This might come from two sources, firstly is by the melting action of some impurities present in the raw materials which may act as fluxes and hence decreasing the porosity of the fired body. The chemical analysis of the raw materials showed the presence of such impurities, especially in kaolin like K_2O , Fe_2O_3 , CaO , MgO , etc. Table (1). Secondly, the resulted silica liquid formed during firing helps to bind the different particles together by occupying of the spaces or

voids present between ceramics particles leading to decrease in the porosity, and this consider good starting step in the faith of this work.

Addition of Zn-metal powder enhances more decreasing in the porosity level of ceramic body. This was absolutely true for all wt.% used for samples fired at 1100 and 1200 °C, and the level of porosity decreasing up to less than 3% for the later firing temperature, Fig. (1). While firing at lower temperature less than 1100 °C (i.e.1000 and 900°C), showed that the first few additions caused an increasing in porosity but it start to decline again at addition of Zn powder from 10wt% and more. This was true for water absorption property, which was measured by standard method of ASTM, Fig. (1B). The lowest water absorption value which was less than 2%, was obtained with ceramic samples had 15 wt.% of zinc metal powder, mix GLA₇, and fired at 1200 °C.

The above behaviour can be attributed to the formation of new phases as samples were examined by X-ray diffractometer, Fig. (2). The X-ray diffraction patterns of the ceramic samples prepared from kaolin and silica having 5% and 15% of Zn-metal powder are shown in Fig. (2 B and C). The new phases namely gahnite ($ZnAl_2O_4$) and willemite ($ZnSiO_4$) can be observed in addition to the quartz and

tridymite. The presence of these two newly phases can not be seen in X-ray diffraction patterns of the ceramic samples had no Zn metal powder in their origin mixes, i.e. had kaolin and silica only (GLA₁), and fired at the same temperature, Fig. (2 A). It is worth to mention here, using fine silica particles which to increase the rate of reaction and the transformation to the new phase's [14]. Of course it is undesirable to use coarse silica, as it is increase the porosity [10,15], which is in contrast with the line of this work.

A well-crystallized willemite phase is clearly observed as a major constituent at high temperature, Fig. (2 C). Increasing the content of Zn metal powder leads to increase the formation of the willemite phase at high temperature. This new phase is known to form a crystalline glass [5], which it may for decreasing of porosity and its correlated property, water absorption of all tested ceramic samples, GLA₂ to GLA₇.

In the same way, measuring of specific gravity of unformed fired mixture powder of mix GLA₁, mix GLA₃ and mix GLA₇ gave another proof for the formation of a glassy phase of high specific gravity in the later two mixes which are not present in the initial component, i.e. GLA₁, Fig. (3).

Examining the surface of the resulting ceramics, which we believe it contains mainly the developed willemite phase, had a smooth glassy surface. Evidence came from SEM micrographs. The image of open pores and the pores were closed due to the new phases which appeared at high firing temperature, are shown in Fig. (4). The formation of this glazing layer was positively reflected on the other physical properties and on the strength of the ceramic bodies.

The linear shrinkage and apparent solid density were found to increase with increasing the formation of those newly phases, i.e. with increasing both addition wt.% and firing temperature, because of the enhancement of sintering which causes better densification and reduction of ceramic body volume causes [16]. Results obtained are shown in Fig. (5 A) for linear shrinkage and in Fig. (5 B) for apparent solid density.

The strength of the fired samples, under compression and impact, was found to decrease at the lower addition of zinc metal powder then increase as additives wt.% rises at (900, 1000, 1100 °C), whereas they are always increasing for samples fired at 1200 °C even with lowest addition of Zn metal powder, Fig. (6). This was directly proportional to the formation of new phases, which appears as glazing layers not

only on the surface but also in whole body. This explains why the impact strength was behaved similarly to other properties.

CONCLUSIONS:

- 1- The possibility of manufacturing self-glazed ceramics from Iraqi kaolin and silica was achieved by chemical swelling of zinc powder.
- 2- The porosity was minimized to the lowest level (less than 3%).
- 3- The formation of the new phase, willemite found to be responsible for the glazing of the ceramic body.

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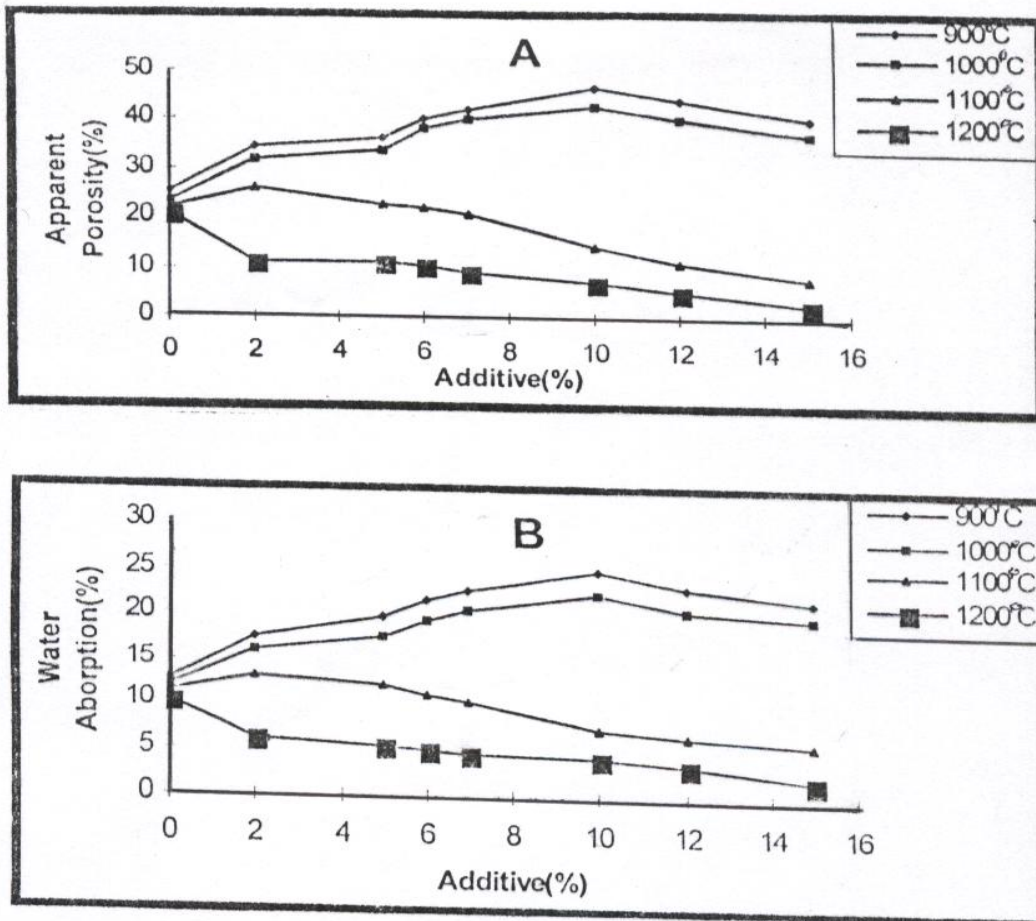


Fig. (1): Effect of wt.% Zn metal powder on: (A) Apparent porosity and (B) Water absorption, of self-glazed ceramics fired at different temperatures.

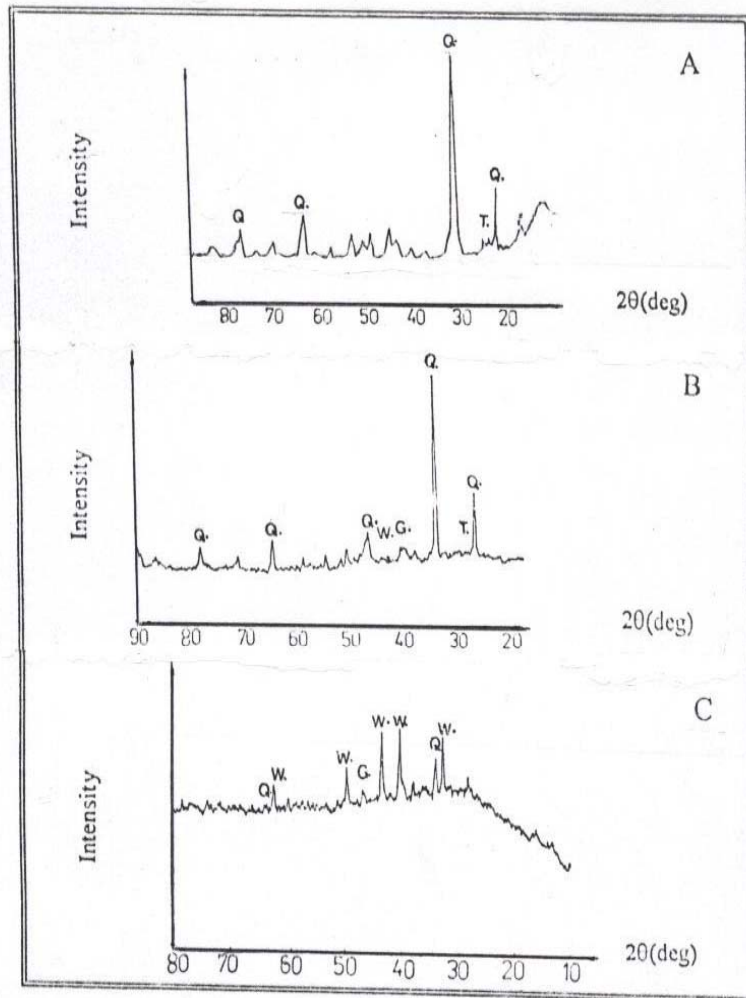


Fig. (2): XRD Patterns of ceramics fired at 1100 °C; (A) with no additive, (B) 5% Zn metal powder, (C) 15% Zn metal powder; where Q=Quartz, T=Tridymite, G=Gahnite and W=Willemite

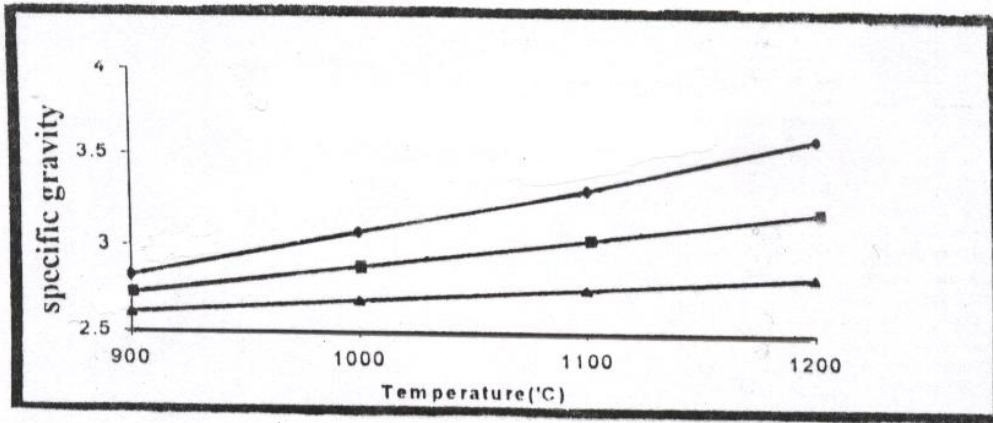


Fig. (3): Effect of firing temperature on specific gravity of unfired fired powders; (○) no additive, (◻) 5% Zn powder, (◻) 15% Zn powder.

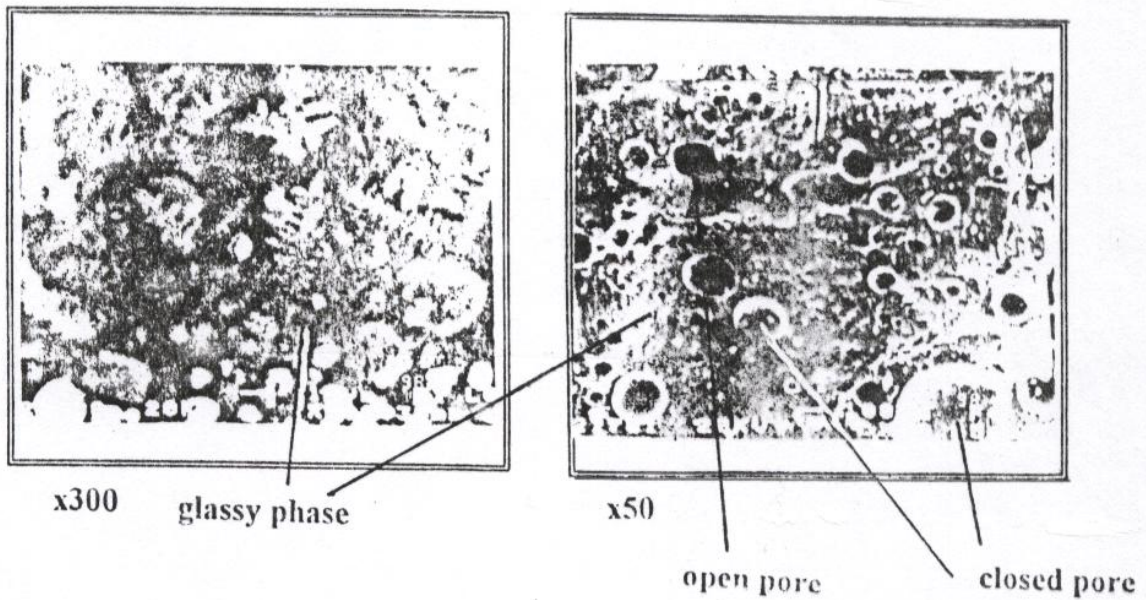


Fig. (4): SEM micrographs of some prepared self glazed ceramics.

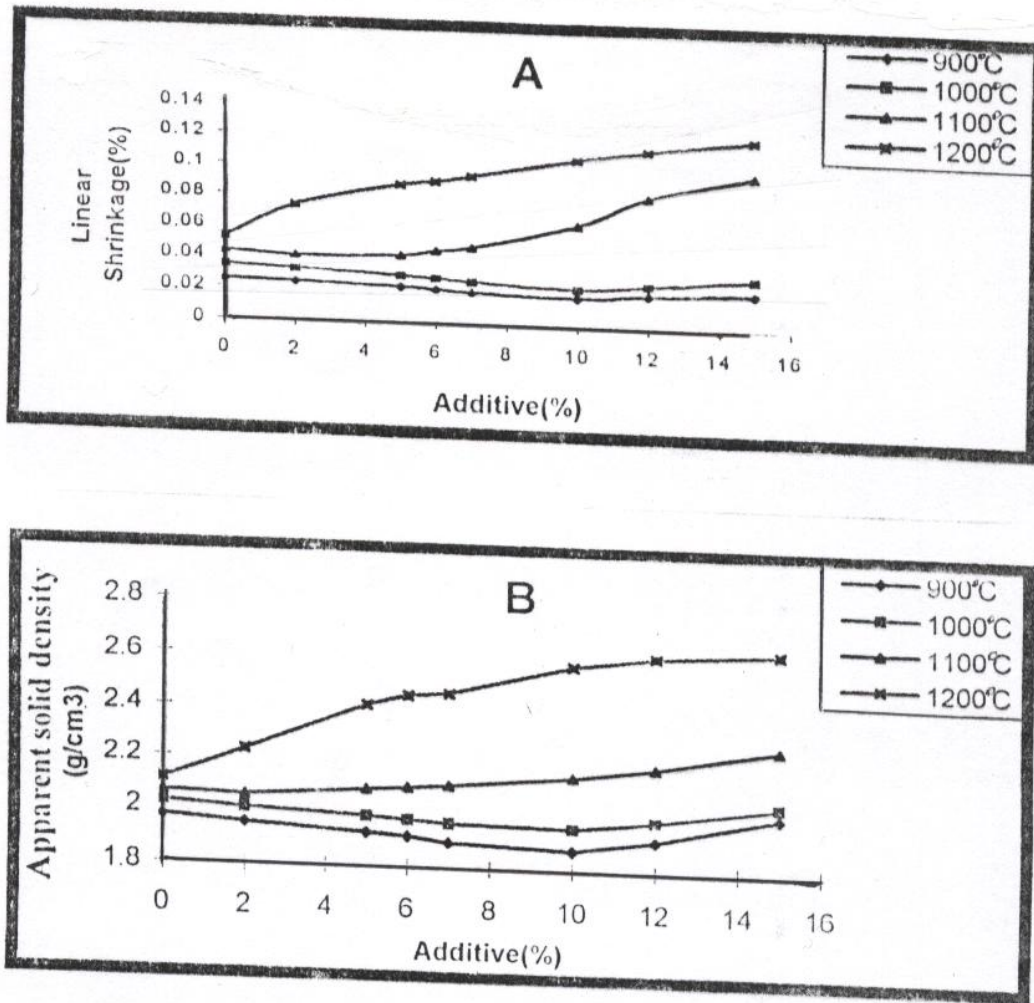


Fig. (5): Effect of wt.% Zn metal powder on: (A) Linear shrinkage and (B) Apparent solid density, of self-glazed ceramics fired at different temperatures.

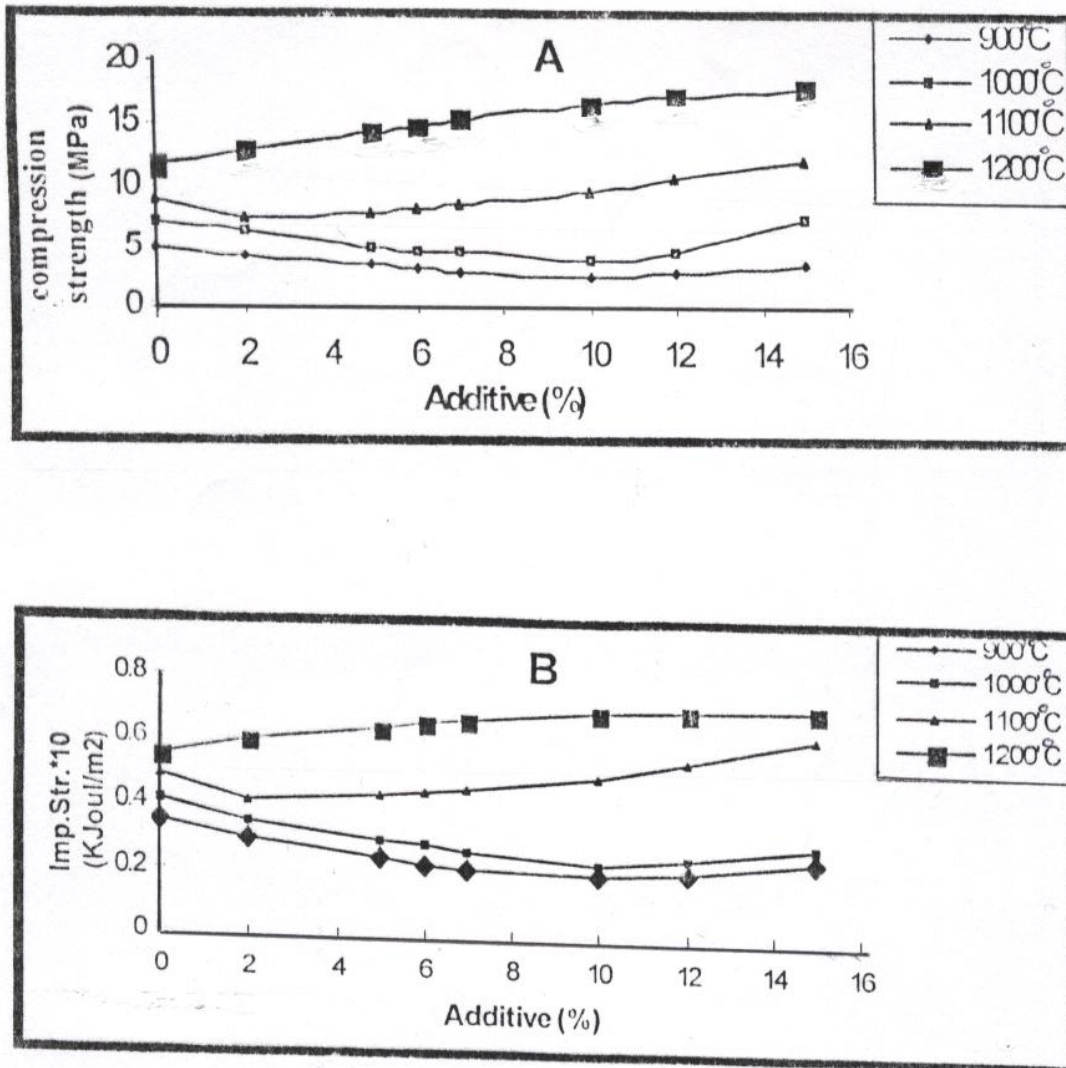


Fig. (6): Effect of wt.% Zn metal powder on: (A) Compressive strength and (B) Impact strength, of self-glazed ceramics fired at different temperatures.

الخلاصة

تعتبر عملية التزجيج خطوة مهمة في عملية إنتاج المواد السيراميكية، ليتلاءم المنتج السيراميكي مع مختلف التطبيقات التكنولوجية. لقد تم في هذا العمل محاولة إجراء عملية التزجيج الذاتي لخليط من الكاؤولين والسليكا بإضافة نسب وزنيه مختلفة من مسحوق معدن الزنك، الذي من المعروف بأنه يسبب في انتفاخ العينة السيراميكية نتيجة لتفاعله معها، و مكوناً طور ويلمايت (willemite) أثناء عملية الحرق.

أن مادة ويلمايت معروف عنها تواجدها في حالة زجاج بلوري مؤدية إلى تزجيج كل الجسم السيراميكي. تم التأكد من ذلك بسبب الزيادة في الوزن النوعي للمسحوق المحروق غير المشكل، وكذلك النقصان في مسامية وامتصاصية الجسم السيراميكي المحروق و الزيادة في معامل التقلص، كثافة الصلب الظاهرية و في المتانة. دعمت النتائج بفحوصات الأشعة السينية والمجهر الإلكتروني الماسح.