Original Research Article

Lead free Ceramic Cooking ware from Egyptian Raw Materials

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K e y w o r d s Leadless glaze, Ceramic cooking ware, Lead release, Leaching agent, Acetic acid	**A B S T R A C T** Leadless glaze for low temperature firing has been developed. These glazes are composed from frit, 20:30 % and clays 65:80%. Frit based on borax, feldspar and sodium bicarbonate as fluxing agents. The results showed that matt surface of glazed ceramic cooking ware was obtained at firing temperatures in the range 800-950ºC. Increasing the RO, R_2O and R_2O_3 content decreased the melting temperature of the glaze. Thermal compatibility of ceramic cooking ware and glazes are confirmed by measuring coefficients of thermal expansion of body and glaze and thermal shock resistance. the applied ceramic glaze played an important role in lead and zinc release that leached at room temperature after 24 h in acetic acid 4% (v/v). The amount of extracted lead and zinc are less than 1 mg/l compared with uncontrolled one in local market 28 mg/l; while cadmium not determined in all. The results show that the prepared samples passed the national and international standards. Physical and micro-structural characteristics of matured body are evaluated.

Introduction

One of the most important contributions of ceramic technology has been the development of vitreous technology that has ensured the safe use of ceramic and glass foodware. Two general approaches to foodware safety have followed nearly parallel paths during the past 100 years; the careful formulation, control and processing of lead- and cadmium-containing glazes to assure low migration levels and the formulation of a new category of glazes virtually free of the most toxic of the traditional constituents, principally lead.

Pottery is made from clay, mostly formed by the hand while it is still soft and wet then heated in a kiln at high temperatures to change its material quality, making it hard. The clay itself varies from region to region to produce pottery with varying characteristics (Rhodes, 1973).

Pottery used for cooking vessels is normally glazed to produce a non-porous, water-tight surface. The glass-like glaze of good earthenware and ceramics is produced by coating the surface with a carefully prepared frit and heating it to a high temperature in a

kiln. Glazes are applied to clay-based pottery products to provide a shiny, generally smooth surface and seal the clay (Phelps, 1986).

The use of lead in ceramic food ware has an extensive history. According to written accounts and from the analysis of archaeological artifacts, lead has been used in food ware from ancient Egyptian times to the present (Richard and Lehman, 2002).

It is considered to be among the most dangerous metals for human health because it affects the central nervous system, causes anemia and gastrointestinal damage, and is associated with alterations in genetic expression (Schütz et al., 2005 and Lepper et al., 2010).

According to USFDA any dinner-ware should not release Pb more than 3 µg/ml when filled with 4% acetic acid for 24 h at room temperature (Anonymous, 1994).

In Egypt and some other countries, different glazed-clay containers are handmade by pottery wheel and used for the cooking, storage, and consumption of food. These containers can be contaminated with heavy metals, which can derive from the raw materials used in their manufacturing, such as clay or glaze (Wallace et al., 1985; Villalobos et al., 2009).

The problem with the presence of heavy metals in glazed -clay containers lies in the fact that these contaminants can be transferred to food by a leaching process, which is directly related with the physical and chemical conditions of the food, such as temperature and pH (González de Mejía and Craigmill, 1996). PH of most foods is acidic so the leaching is completed by acetic acid.

The basic oxides normally encountered in

glazes the alkali oxides Na_2O and K_2O increase lead solubility, MgO has little effect and CaO decreases solubility. Alumina is very beneficial in reducing solubility whereas boric acid has the reverse effect. Titania (TiO_2) has also been found to have a marked effect on lowering the solubility of lead frits. A level of 1–2% may be used in high lead oxide frits although the coloring effect limits the level of titania that may be incorporated.

Three approaches to leadless compositions have been pursued. Direct substitution of bismuth for lead is the most obvious and produces adequate results. However, bismuth can impart a yellowish color under certain circumstances, the supply of bismuth is limited, the price is high, and the toxicity of bismuth itself may be an issue. A second group of leadless compositions uses zinc and strontium to provide the necessary fluxing. These glazes are glossy and fire well, but color development is poor. A third approach is toward alkali borosilicate [ABS] formulations. These glazes rely on alkali borate fluxing and a typical composition may contain approximately 10% B_2O_3 and 10% (Li, Na, K)$_2$O by weight. The ABS glazes are becoming widely used, particularly on bone china due to the high expansion of the ware, but significant problems remain with its use. Higher firing temperatures are required to produce a smooth glaze surface, the leadless glazes react less aggressively at the body interface, defect rates are higher, and decoration is difficult. A glaze is a thin layer of glass fused onto the surface of clay ware. The glaze holds onto the clay by means of its physical grip on the clay form, but more importantly, by seeping into the surface of the clay and filling some of the open pores (Hamilton, 1977). Continued development should result in increase performance and acceptance of this system

Therefore, sequential leaching of cadmium, zinc and lead into leached solution of glazed cookingware pots from local market and five pots prepared in lab simulating with manufacture plan are evaluated in the present work.

Materials and Method

Three types of local clays (two of them are red clay from El-Fayoum, and Aswan and the third is kaolin from Aswan-Egypt) used in body and matt glaze preparation. Red clay from Aswan (Aswanlly) is the suitable one without any additives, for body handmade shaping by pottery wheel. Frit composed from Borax, sodium bicarbonate, soda feldspar, calcium carbonate and kaolin. This composition is fritted at $950^{o}C$. Body and coating mixes are extruded separately, as tiles 0.5*5*10 cm, dried then fired between 500 and $1000^{o}C$. Physical properties in terms of firing shrinkage, water absorption, bulk density and apparent porosity were determined according to the ASTM C 326 and ISO 10545-3. Modulus of rapture of matured samples was determined according to the three point standard test specifications. A bending test machine (model MOR /1-M/E) according to ISO 10545-4 1995 was utilized. The average of three specimens was taken. Thermal expansion coefficient for body and mixes of matt glaze was measured using a computerized thermal dilatometer.

Five formulations of coatings glaze were designed based on these clays and transparent frit prepared in the lab. These mixes prepared as suspension slurry with addition 5% kaolin. Green pieces of body prepared by pottery wheel, dried over night in open air, immersed with the coating suspension, dried overnight, single fired in lab kiln at 850–900° C.

The thermal shock resistance test, as per ASTM C 554-77 method, (ASTM International, 2012) of the product and direct heating of the product on a gas cooker were performed to check the suitability. As well as, glazed cooking ware was tested by filling the sample with water and put it in the oven ($350^{o}C$) till vaporization of total water then put it in tap water directly then test cracks by suitable dye. Resistance of surface abrasion which occurred by washing machines or tools is detected by moh scale.

Microstructure of the matured body and vessel was observed by scanning electron microscope (Type X L30, Philips) with EDAX equipment. Specimens were polished, matured body chemically etched using 20 % HF for 10 s, while glazed body thermal etched at $850^{o}C$ for one hour, thoroughly washed, dried and gold sputtered.

Choice of leaching agent Standard tests for release of lead from ceramic ware involves an acetic acid solution as a leaching agent. The pH values of several local foods were compared to 4% acetic acid to ascertain that the acidity of the 4% acetic acid leaching solution proved to be an extreme condition in the use of the ceramic ware. The method used for the leaching of lead from the ceramic ware was a modified combination of the British standard procedure, BS 6748 (BSI, 1986) and that of the American Society for Testing Materials, ASTM C 738.81 (ASTM, 1982) and employed by the United States Food and Drug Administration (USFDA) for screening of Pb release from dinner ware (Wallace et al., 1985).

The samples to be tested were rinsed with distilled water and left to dry. They were filled with 4% acetic acid to within a level no more than 1 mm from the overflow point. The samples were covered with aluminum foil. (It was determined that no lead was leached out from the foil when pieces of foil

were immersed in 4% acetic acid for a period of 24 h at room temperature.) The samples were set aside for 24 h at room temperature (30–32°C). After 24 h, the levels of the acetic acid in the samples were inspected and, if necessary, the samples were filled with fresh 4% acetic acid up to the original level.

The leaching solution was then transferred to polyethylene bottles and analyzed for its lead, cadmium and zinc content by atomic absorption spectrophotometer (Instrument, Gbc 908).

Result and Discussion

The raw materials used to prepare glazed cooking ware pots play an important role in the ultimate product quality. Three types of clays are applied in this study. Red clay from Aswan-Egypt is the most important plastic material, workable, easily hand shaping by pottery wheel so it is the main component of the body without any additive (Konta, 1995).

Frit composed from sodium borate (40%); bicarbonate (25%), soda feldspar (20%), calcium carbonate (5%) and kaolin (10%). This composition is fritted at 800–900°C. Five mixes from matt glaze are prepared based on red clay from Fayoum (50–60%), red clay from Aswan (0–30%), kaolin (0–30%). Five formulations of matt glaze free from lead; are prepared by mixing the prepared transparent frit in the lab with these mixes by 20–35%. These mixes prepared as suspension slurry with addition 5% kaolin. Dried pieces of body prepared by pottery wheel, immersed with the coating suspension, dried again overnight, single fired in lab kiln at 850–900° C.

The respective chemical analyses of the raw materials and suggested matt glazes are given in Table 1&2. Silica content in clayed materials and feldspar is ranged 50:56% and 60:70% respectively, as main source of SiO_2 in batches; which exist in ceramic bodies as residual quartz particles, although finer ones dissolve into the inter-particle glass and glass forming oxide in glazes. Alumina is 18:30% as resistant of tendency during firing due to its refractoriness property.

The high iron contents (10%) in the clay (Table 1) act as coloring agent gives the reddish color of the clay-based products after firing as shown in Figure 1 that represent the produced pots in this study. In clays and glazes, that containing significant organic matter, the Fe_2O_3 converts to FeO which is very powerful flux as early as 900°C (Romero and Rincón, 2002). A color is red for all samples, getting darker for increasing temperature due to the high concentration of iron oxides content (Swapan and Kausik, 2005). Velde (1992) confirmed that red clay mineralogical, is of the kaolinite group with gibbsite, goethite, and quartz as accessory minerals.

The source of alkaline earth oxides in the studied formulations; (RO as 2:3 %) is mainly from limestone as CaO; MgO%, and alkali oxides (R_2O as 5:8%) as Na_2O from feldspar and borax and K_2O is traces from feldspar and clay. These oxides are the strongest common flux and affect across all temperature ranges from 900–1300°C having big role in glaze formulations (Casasola et al., 2012). Calcium oxide in small amounts is the principle flux in medium and high temperature glazes; beginning its action in the glaze around 1100°C. It improves hardness, stability, resistance to leaching and expansion properties of silicates of soda and potash. In non-lead mixes it can also help reduce crazing (Ghosh et al., 2013).

Na_2O works well with boric oxide in low temperature lead-free glazes. In glazes, boric oxide reduces melting temperature and improves glaze/body fit as shown in microstructure thermal etched cross section of body/glaze double layer (Fig. 5). It enhances glaze appearance and can improve chemical and mechanical durability. Sodium borate is used to produce low viscosity frits for ceramics, as source of Na_2O as flux and B_2O_3 which has dual effect as a flux and network former (Torres et al., 2006,2005). Mix 3 and 5 have the highest content of boric oxide which is related to content of transparent frit based on borax in glaze composition.

The physical properties of the ceramic cooking ware body were determined in firing range till maturation as illustrated in Figure 2. The higher alkali and alkaline oxides contained in the body clay could induce early vitrification and increase the firing shrinkage (Bender and Händle, 1982). The loss of ignition (LOI) of the bulk samples (about10 wt. %) are associated with the presence of clay minerals, hydroxides and organic matter (Baccour et al., 2009; Milheiro et al., 2005).

Relationships within the firing characteristics such as bulk density, firing shrinkage, water absorption, and apparent porosity of both extruded body clay and matt glaze mixes are shown in Figure 2 and Table 3; a function of firing temperatures. The bulk density and firing shrinkage increased with an increase of the firing temperature for all samples till maturation then reversed.

It can be seen that the higher the firing shrinkage, the lower the water absorption. The greatest tendency of this correlation was found above 1000^oC for all the samples due to a more significant liquid phase formation.

During the liquid phase formation, the liquid surface tension and capillarity force help to bring particles close together and reduce the porosity (Monteiro and Vieira, 2004; Swapan and Kausik, 2005).

An increase of the bulk density and fired shrinkage and decrease of water absorption of ceramic cooking body which appeared above 1050^oC is due to the formation of the glassy phase of the sample at this temperature, as clearly seen in Figure 2. The densification behavior of the red clay mixture is influenced by the sources of flux materials such as K_2O (3.9%); Na_2O and Fe_2O_3, which favor the formation of a glassy phase.

The densification behaviors of extruded matt glaze as bodies are determined with different temperatures as shown in Table 3. Density and water absorption are the factors affected. Matured bodies have the highest density and lowest water absorption. The order of densification is related to mix content of silica, alumina and fluxing agents as $(RO+R_2O+R_2O_3)$. The earliest matured one is mix 5 which has lowest silica; 53% and highest fluxing agents 26%. While the latest mixes are 1 and 2 that have silica 55-56% and fluxing agents 20-22%. The alumina content in closed values in all mixes 20–23%.

Leaching of ceramic cooking pots is achieved by 4% acetic acid due to acidity of common cooked foods (Norita et al., 1995). Concentration of heavy metals in prepared ceramic cooking ware compared with market one is illustrated in Table 4. The market ceramic cooking ware is out of the control where Pb is 28 mg/l.

According to USFDA any dinner-ware should not release Pb more than 3 µg/ml, when filled with 4% acetic acid for 24 h at

room temperature (Anonymous, 1994). European directive 84/500/EEC relating to ceramic articles intended to come into contact with food stuffs are illustrated in Table 5 (Carrington et al., 1996; WHO, 2011).

Glaze ceramic materials are considered polycrystalline solids containing a residual glassy phase and possess a valuable combination of the favorable properties of both glasses and ceramics. Dissolution of vitreous materials is a complex process which depends on solution condition (the solution used is 4% acetic acid) as well as the composition and microstructure of the vitreous materials. The easily released components in solutions are the basic oxides consisting of the monovalent (Na, K) and divalent (Ca, Mg) cations which occupy modifier positions in the structure (Eppler et al., 1983).

Sodium removal involves the ion exchange mechanism with H^+ or H_3O^+ from leaching solution and is accompanied with the easily soluble borate phase. Addition of alkaline earth ions generally decreases glaze durability, but much less than alkalis. Hence, substitution alkaline earth for alkali on a mole-for-mole basis will be to improve the durability. Addition of alumina is particularly beneficial in increasing acid resistance of glasses and glazes. In the presence of alkali and/or alkaline earth oxides, alumina takes over a function similar to boric oxide forming tetrahedral coordinated by oxygen ions taken from the alkalis and alkaline earths (Rado, 1969).

The phase microstructure is an important factor in these changes. Microstructure of phase separated vitreous materials fall into three categories is explained by Tomozaw (1979). A: Both phases have interconnected, continuous structures, when their volume proportions are approximately equal: (b) the more durable phase (usually SiO-rich) is dispersed in a continuous matrix of the less durable phase (usually rich in B_2O_3 and glass-modifying components); (c) The less durable phase is dispersed in a continuous matrix of the more durable phase. The durability of a glaze is less related to ($RO+R_2O+B_2O_3$)-rich. The all samples are acceptable due to decrease the lead release in acid leachate, so it is recommended that fabrication of leadless glaze special for ceramic cooking ware based on alkali and alkaline earth oxides.

According to these explanations of glaze durability mechanisms we can explain the results obtained from studied pots. The release content of lead and zinc is higher in pots that used glaze has more boric acid content. Also, the summation of RO, R_2O_3 and B_2O_3 is important factor in glaze durability where the glaze that has 12–13% (mixes 1,2 and 4) less durable than that has 16–17% ; mix 3 and 5, as shown in Table 2.

Thermal compatibility of a ceramic body and glaze in a glazed ceramic product is of great importance in ceramic engineering to fabricate defect free glazed ceramic products (Tite et al., 2001; Sudarman Upali Adikary and Sanjeewani Thakshila Jayawardane, 2013). Lack of compatibility between them causes defects in ceramic fabrication (Ziman, 1967). Glaze is a glassy material and can bear compressive stresses much better than the tensile stresses. Hence when matching, the glaze is kept in a state of slight compression. Thermal shock resistance is another important property that should be considered during the fabricating of glazed ceramic cookware. The ability of a material to resist sudden temperature changes is known as its thermal shock resistance. Thermal shock occurs when a substrate is exposed to temperature extremes

in a short period of time. Under these conditions, the substrate is not in thermal equilibrium, and internal stresses may be sufficient to cause fracture. The thermal stresses depend on the different factors including geometrical thermal boundary conditions and physical parameters, such as coefficient of thermal expansion, modulus of elasticity, thermal conductivity, and mechanical strength.

The term cookware refers to the commonly found pots used in the kitchen for the purpose of cooking. Thermal shock resistance is an important factor for cookware as they are directly in contact with an open flame. Red clay, which is the major raw material of the traditional pottery industry in Egypt, is available in many parts of the country. Hence a glazed red clay product with enhanced thermal conductivity will be better for cookware.

Thermal expansion is affected with chemical composition of tested materials. Ceramic cooking ware body is mainly red clay and its thermal expansion coefficient, (TEC) α is $86.636*10\text{-}7/C^o$ at 600^oC. While their values ranged from 83 to 110 for the prepared matt glazes. The highest value is $110*10\text{-}7/C^o$ at 600^oC which is attributed to the high content of Na_2O and B_2O_3. (Wannagon et al., 2011).

The body is compatible to all glazes as shown in Figure 3 and Table 6 due to closed values of TEC where all glazed pots pass the difficult condition of thermal shock resistance of cooking ware pots.

The resistance of abrasion and action of washing machines of kitchen tools and ceramic cooking pots is considered. This property is measured in view of Moh's scale (Table 7) where its value ranged from 3 to 4 which indicate to suitability of this cooking ware in kitchen tools.

During heating three kinds of processes take place: decomposition, phase transformation, and sintering with partial melting, with both decomposition and phase transformations affect development and extent of the subsequent sintering (Baccour *et al.*, 2008).

Scan electron microscope (SEM) images of matured clay at 1150 ^{o} C, that used in this study as cooking ware reveal particles of submicrometre size (Fig. 4). Micrograph (A) reveals general view of matured clay; homogenous texture, higher densification behavior and fewer pores. Grains of primary mullite formed from clay-rich relics, have particle size 600-800nm and are clearly seen in Figure 4d. Types of mullite formed in clay-based ceramics were recently reviewed by Lee et al. (Lee W et al 2008). After firing at 1150^oC, this is the maturation firing temperature for cooking ware clay regarding its physical properties (Tarvornpanich, 2005, 2007)

The microstructure was found to comprise primary (grains) and secondary (needle-like) mullite, partially dissolved quartz with solution rim, glassy phase and cracks especially around quartz particles. Needle-like, elongated shape mullite is more developed and longer than Secondary mullite that formed from molten feldspar or flux particles was also detected as shown in Figure 4C. The interaction between two layers; body and glaze during the preparation of glazed cooking ware is illustrated in Figure 5.

The results of our study indicate that the amount of lead and zinc that migrate into food from ceramic cooking ware vessels constitutes a significant public health concern. Furthermore, our work demonstrates that vessels of this type are commonly available and in use in the local community despite years of accumulated

knowledge about the risks they pose. There is clearly disconnects between academic and community knowledge with respect to the hazards of ceramic cooking ware. The prepared glazed pots tested in our study were used for cooking in homes. We must warn the local community from harmful local clayed cookingware using due to high lead migration to the cooked foods which reach 28 mg/l. lead release in the prepared pots in this study is less than 1 mg/l and are suitable for safe use in cooking. These ceramic cookingware are confirmed by WHO as well as thermal shock and abrasion resistant leading to their suitability for safe use.

Table.1 Chemical analyses of raw materials, %

Oxide	Red clay (Aswan)	Red clay (Fayoum)	Kaolin	Soda feldspar	Lime stone
SiO_2	55.35	55.75	49.93	66.4	0.45
TiO_2	1.51	1.93	1.98	0.41	0.02
Al_2O_3	21.69	18.02	31.30	19.0	0.23
Fe_2O_3	8.19	10.65	4.88	0.75	0.05
MnO	0.10	0.03	0.10	0.03	0.00
MgO	0.16	1.45	☐0.01	0.12	0.70
CaO	2.05	1.22	0.18	0.60	54.15
Na_2O	0.77	1.15	0.06	10.9	0.05
K_2O	1.21	1.21	0.10	0.32	0.08
P_2O_5	0.17	0.17	0.12	0.03	0.06
Cl^-	☐0.01	0.75	☐0.01	0.06	0.35
SO_3^{--}	☐0.01	0.89	☐0.01	0.18	1.05
LOI	8.57	6.51	11.10	0.97	42.55

Table.2 Chemical composition of matt glaze mixes, %

Oxide	Body	Mix1	Mix2	Mix3	Mix4	Mix5
SiO_2	55.35	56.4	54.90	52.80	56.43	52.70
TiO_2	1.51	1.72	1.91	1.76	1.78	2.00
Al_2O_3	21.69	19.81	23.40	21.28	19.32	19.80
Fe_2O_3	8.19	9.26	8.17	7.91	9.55	8.00
MgO	0.16	0.92	0.88	0.91	1.06	0.90
CaO	2.05	2.10	1.48	1.82	2.00	1.94
Na_2O	0.77	5.14	4.96	7.31	5.20	7.73
K_2O	1.21	1.14	0.76	0.80	1.15	0.85
B_2O_3	-	3.51	3.54	5.41	3.51	6.08
$RO+R_2O_3+B_2O_3$	**-**	**12.81**	**11.62**	**16.25**	**12.92**	**17.05**

Table.3 Relation between physical properties of extruded matt glaze and firing temperature

Temp,^{O}C	Property	M1	M2	M3	M4	M5
500	WA,%	14.87	14.05	15.41	15.38	14.54
	BD,gm/cm^3	1.75	1.83	1.75	1.80	1.80
	AP%	25.96	25.66	26.98	27.62	26.22
600	WA,%	14.46	14.88	14.52	14.51	13.66
	BD,gm/cm^3	1.79	1.64	1.73	1.80	1.77
	AP%	25.95	24.46	25.20	26.11	24.20
700	WA,%	12.27	13.17	12.48	11.71	8.41
	BD,gm/cm^3	1.91	1.79	1.76	1.80	1.93
	AP%	23.47	23.53	21.96	21.08	16.20
800	WA,%	7.72	12.21	10.35	10.81	0.70
	BD,gm/cm^3	2.04	1.85	1.86	1.88	2.45
	AP%	15.76	22.58	19.23	20.29	21.28
900	WA,%	1.89	2.83	0.48	1.97	4.71
	BD,gm/cm^3	1.94	2.02	2.24	2.19	1.99
	AP%	3.66	5.73	1.07	3.23	19.37
950	WA,%	1.19	1.17	0.62	1.81	0.33
	BD,gm/cm^3	2.27	2.29	2.23	2.22	2.11
	AP%	2.68	2.68	1.37	2.12	0.69
1000	WA,%	3.32	0.15	6.91	5.50	7.49
	BD,gm/cm^3	1.89	2.06	1.65	1.67	1.61
	AP%	4.39	0.31	11.44	9.20	12.06

Table.4 Concentration of heavy metals in prepared ceramic cooking ware compared with market one

mg/l	Market pot	1	2	3	4	5
Zn	**0.199**	0.133	0.084	0.122	0.104	0.116
Cd	**n.d**	n.d	n.d	n.d	n.d	n.d
Pb	**27.55**	0.028	0.173	0.462	0.242	0.546

Table.5 European Directive 84/500/EEC relating to ceramic articles intended to come into contact with food stuffs

Category	Specifications	Pb level
Flatware	Internal depth ≤ 25mm	0.8 mg/dm^2
Small hollowware	Volume <3L	4mg/L
Large hollowware	Volume >3 L	1.5 mg/L

Table.6 Thermal expansion coefficient as α value at 600oC, of ceramic
cookingware and matt glaze

TEC/600°C $\alpha* 10^{-7}$	Body	Mix 1	Mix 2	Mix 3	Mix4	Mix5
	86.63	82.70	96.20	79.80	109.35	110.16

Table.7 Moh's Scale of ceramic cookingware pots as abrasion resistance indicator

Sample no	1	2	3	4	5
Moh,s scale	3.5	3.0	3.5	3.25	3.5

Fig.1 Photograph of studied pots in this research (unglazed body and glazed pots 1,2,3,4 and 5)

Fig.2 Effect of firing temperature on shrinkage, water absorption, bulk density and apparent
porosity of cooking ware body
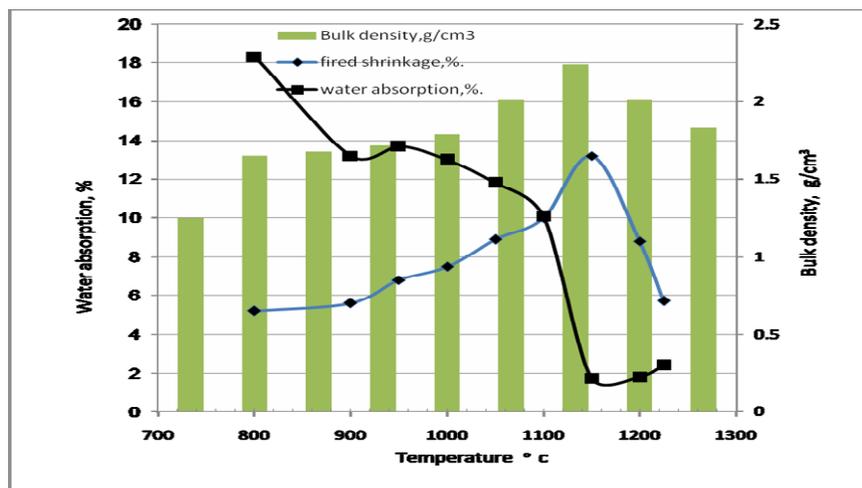
**Figure.3** Thermal expansion of matt glazes with body of cooking ware
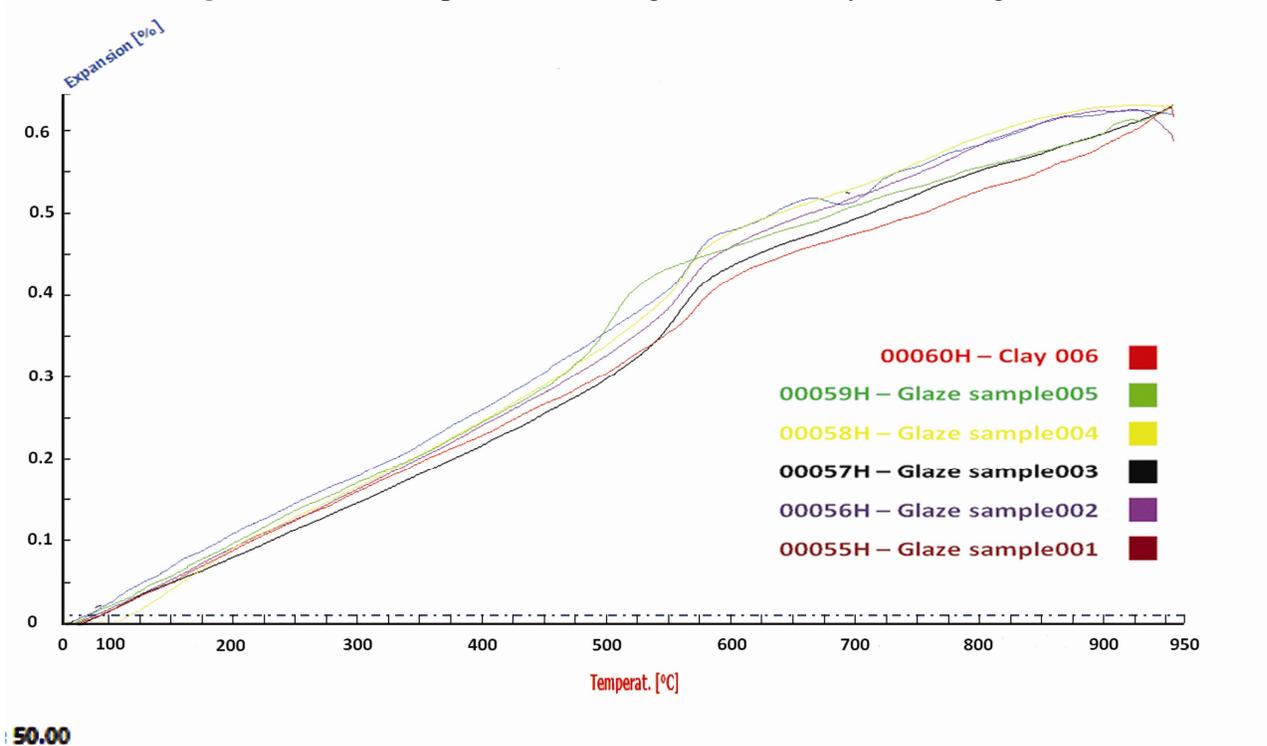
Fig.4 A: SEM of general view of matured clay at 1150oC which reveals compact structure and minimum porosity; B: SEM images reveal particles of micro size, grains of primary mullite, needles of secondary mullite particles and residual quartz; C: secondary mullite which is elongated shape grows from the clay–flux oxides containing and residual quartz; D: primary mullite grains formed from clay-rich relicts, has particle size 600-800nm


A

B

C

D
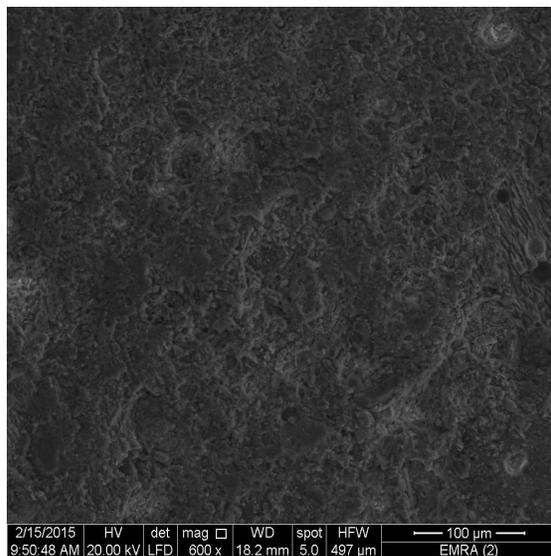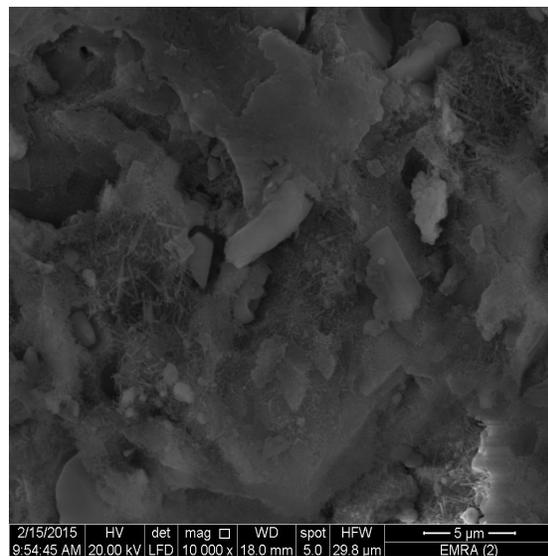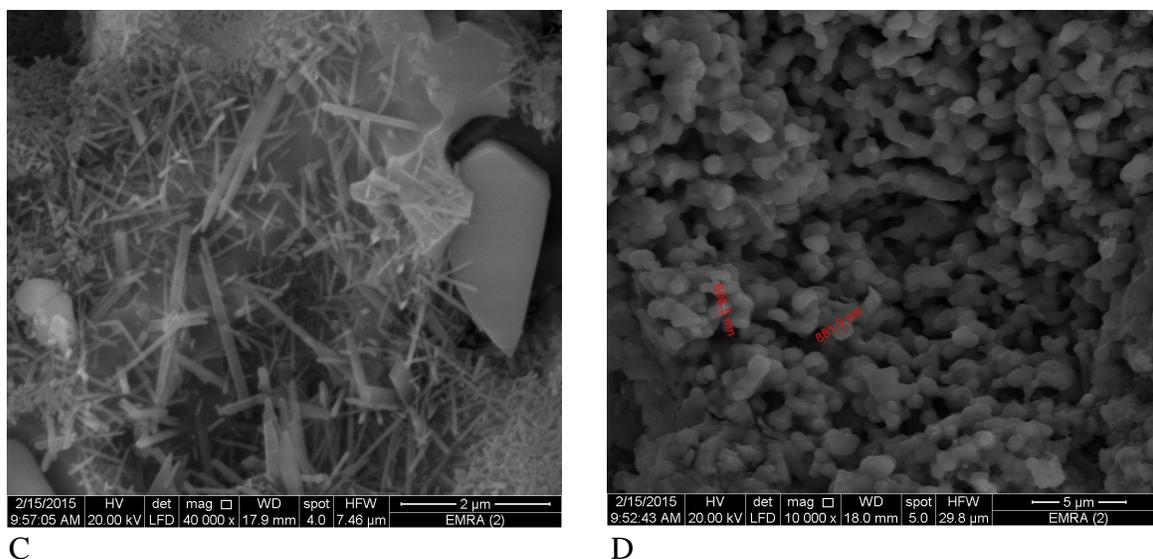
Fig.5 micrograph explains double layer interactions between cooking ware body and coating glaze
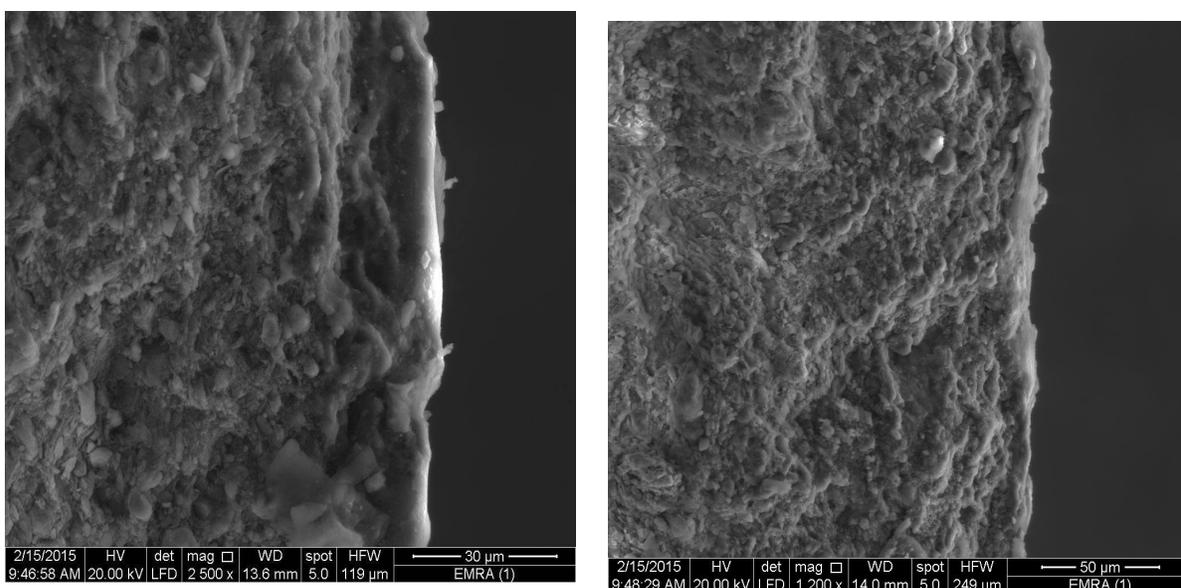
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