PRODUCTION OF HIGH TEMPERATURE REFRACTORY CRUCIBLES FROM LOCALLY AVAILABLE CLAYS IN NIGERIA

ADAMU A., GIWA Y., & OPOKU, E.V
Department of Industrial Design,
Ahmad Bello University Zaria Nigeria

Abstract
A ceramic bonded refractory crucibles were made by compounding two local natural clays that is 30% Kankara clay (kaolin), 40% Bomo clay (plastic secondary clay) along with 30% fine (600µ) Kankara clay grog. Crucibles were produced after preparation and mixing the materials into throwing clay body, thrown on a potter's wheel, dried and fired in two stages: first, fired for seven hours to 1300°C in a kerosene kiln and then fired again for 3 hours to 1500°C and retained for 2 hours in an electric furnace at the National Metallurgical Development Centre Jos. The result indicated that the body compounded from Kankara clay, Bomo clay and fine Kankara grog can be used as alternative raw material for the production of refractory crucibles.

Introduction
Crucibles are used in high temperature heat treatment in foundry applications such as; metal, bronze and brass casting, coin-minting and ore assaying; in non-foundry applications as in glass and frit making, in laboratories by chemists, as in chemical analysis and ash content determination, as asserted by Martinion & Rehren (2009) and Nnategi, (2012).

One of the important raw materials needed for crucible production is clay (2012) which provides bonding power, sufficient plasticity and strength (Bleininger, 1920) and are available in large deposits in Nigeria. (Garkida, 1998 & Opoku, 2000) 'There is therefore good investment opportunity for the production of crucibles locally. There is also need to develop indigenous expertise in the manufacturing technology to enhance the economic potential of such product' (Nnategi, 2012).

Refractories are materials which are known to withstand high temperature, they are used in the heat furnace, crucibles of shaft furnaces, in retorts, in crucibles, flues and all parts of a metallurgical or chemical plant exposed to the action of heat, and must have the property of withstanding high and changing temperatures, in the action of atmosphere and of the slag without suffering sudden physical or chemical changes (Harvard, 1912).

Crucibles are open-mouth containers made from refractory materials used for heating or melting materials such as metals, glasses and frit powders in foundry and non- foundry applications. Crucibles are of two types; carbon bonded and ceramic bonded crucibles. The ceramic bounded crucibles that are made with refractory clay as a binder gives mullite on firing as the bonding matrix (Aigbodion, et al, 2014 & Rhodes 1957). Mullite ($3Al_2O_3$-$2SiO_2$) as a crystalline phase characterized by needle-like crystals, have many properties such as low thermal expansion and conductivity, excellent creep resistance, high temperature strength, and good chemical stability (Chauki, 2013 & Rhodes, 1957). However, Chauki, (2013) asserted that good resistance of heat and thermal shock is directly connected to refractory performance. The main mineral constituent of kaolin is the kaolinite. Its theoretical formula is $Al_2O_3.2SiO_2.2H_2O$. Kaolinite firing induces numerous complex structure and micro structural transformation leading to the formation of mullite and silica phase, mainly in a vitreous form.

According to Martinion and Rehren (2009), the analytical study of the manufacture and trade of post- medieval crucibles (14^{th} – 19^{th} centuries) by archaeologists, establishes that Hessian (Hess Germany) crucibles structure, revealed from analyzed samples show the use of high alumina (36.9%) kaolinitic clay, mixed with almost pure quartz sand and relatively low alkali oxide, wheel thrown and fired to a very high and prolonged temperature range between 1300^0C and 1400^0C. This extended high temperature also led to the formation of synthetic mullite which is known for its low thermal expansion and the resulting excellent thermal shocks resistance, high creep resistance, high temperature strength, and extraordinary stability in aggressive chemical environments.

Clay is hydrated silicate of alumina which occurs naturally from decomposition of feldspathic rock. The decomposed clay mineral found at a place of formation is called primary or residual clay. This same clay after transported from its first location (place of formation) to another location by the action of rain, wind, glaciers, etc is known as secondary or sedimentary clay (Rhodes, 1957).

In selecting the clay for crucibles no matter the size of the crucibles, properties like plasticity and refractoriness must be put into consideration. The plasticity enables the crucibles to be made to a desired form while the refractoriness allows the clay to be fired without deformation. The tendency for excessive contraction of a plastic clay (used for crucibles) in drying and firing necessitate the addition of non – contracting and infusible material such as fired clay grog, silica, or graphite (Rhodes, 1957 & Davidson, 1921). Davidson (1921) suggested further that fired clay grog is generally used. Tetsui, et al (2010) ascertained that the higher the ratio of the coarse non- contracting material (grog) the greater the thermal shock resistance but the lower the reactivity resistance. Conversely, if the grog is too fine the crucibles body is too dense, and is liable to crack due to the rapid heating and cooling conditions to which it is exposed (Davidson, 1921).

Clay

In considering the behaviors of clays used in the crucible body during firing, Bleininger, (1920) emphasized that two criteria must be critically observed; firing temperature and softening point. It has been established that all clays that vitrify below 1400^0C have a decisive control of drop in porosity, resulting in the increase in shrinkage. Clay which immediately over - fire upon attaining the state of maximum density should not be used, except the use of refractory grog which raised the firing limit of such clay. It was clarified further that clays in connection with the above stated criteria, can be classified into three district groups:- First groups; clays that become dense at about 1150^0C and exhibiting no sign of over firing at about 1400^0C can be used for the manufacture of graphite crucibles used in brass melting. Second groups:- clays that become dense around 1275^0C and not over fired at 1400^0C or higher are suitable for crucibles used in steel melting. When these clays do not over fire before 1425^0C, they too become valuable for glass refractories. Third groups; clays which have good strength, but do not vitrify at low temperatures, becoming dense only at 1425^0C or higher, overfiring at about 1450^0C or higher are particularly useful for the glass industries. The clay which become dense as low as 1150^0C to 1300^0C, and over fire just above 1300^0C, or having no well-defined range, are considered unsuitable. (Bleininger, 1920)

The two different clays used in this study are Kankara kaolin (primary clays) sourced from Kankara town of Katsina state in Nigeria, and bomo clay (plastic secondary clays) from Bomo, Zaria, in Kaduna State of Nigeria. Table 1 shows the chemical analysis of Kankara kaolin from three different sources and studies conducted by previous researchers with similar elemental compositions. The physical properties of such clay are clearly stated on Table 2.

Methodology

The two clays used in this study; Kankara kaolin and Bomo clay were separately prepared in the same way. They were both slaked with water and sieved through 200 Tyler mesh sieve (75µ) in reference to Nwobi, (2006.) In the case of Bomo clay, the resultant slurry was first stirred and allowed to settle, decanted the fine clay (suspended) particles and discarded the free silica that settled at the bottom of the container. The top water from both sieved clay was dewatered after they completely settled and poured on a plaster trays to dewater it before drying. The grog was prepared by mixing the raw Kankara kaolin with small quantity of water to a stiff consistency, molded into balls and dried.

In order to achieve a maximum density, grog mixture must be graded into coarse, medium and fine particles in such a way that smaller particles fill the voids between larger ones giving a good particle size distribution (Kirkpatrick, 1918 and Meena, 2011). When combined into clay bodies, grog reduce firing shrinkage and provide greater stability in application (Elngar, et al 2009).

It was established by Kirkpatrick (1918) that from the result of the quenching test, bodies containing larger size of grog withstood the test best because coarse grog is slowly vitrifying than the fine grog which is rapidly vitrifying in bodies. Kirkpatrick (1918) further states that the right proportion of the ratio of grog sizes can only be determined by experiment and suggested the range between 20 to 80 mesh in order to get the strongest bodies.

The grog size used in this study was under mesh 30 (600µ) which is within the range suggested above and produced by firing the processed and dried kaolin balls as mentioned above to about 1300^0C and then crushed and sieved through 30 mesh in two different ways; i. With all the fractions that is coarse, medium and fine ii. Only the coarse fraction, sieved through 30 mesh (600µ) retained on 50 mesh (300µ).

Crucible Body Composition

Grading of grog and other body constituents to achieve maximum density and minimum warpage is an indispensable trend in the refractory industry. The manufacture of white-ware using triaxial bodies of feldspar, quartz and kaolin is an example of three component system of coarse, medium and fine particles.

Hugil, and Rees, (1930) in Meena, (2011) suggested a batch composition of 45:10:45 (coarse, medium and fine) in formulation of batch composition in refractories. In contrast, Karisson and Spring, (1970) also in Meena, (2011) worked with fire clay grog of irregular shapes, suggested their best composition of 40:30:30 for such three component system. Thus the latter composition was adopted with some variation on the said compositions to arrive at 6 crucible body composition used in this study are as in Table 4.

Mixing Procedure

Each composition was prepared by the following steps done by Nwobi, (2006) with slight adjustment:

Step 1: each material from body 1-5 was weighed separately according to its percentage weight (% wt), then 1000g of dry material was slaked with 750g of water for about 20 hrs.

Step 2: the slaked mixture was well mixed, blended and screened using 600µ Tyler mesh sieve to provide an intimate mixture.

Step 3: the thick slip from the above clay body mixture was dewatered by pouring it into a plaster mold. The plastic clay was then removed from the mold, kneaded and stored in a closed damp container.

Step 4: the clay body from each sample was used to produce some crucible samples using throwing method.

Physical Property Test

Below are some physical property test conducted on the five crucible bodies. They are as follows:

1. Drying Shrinkage
2. Firing Shrinkage
3. Water Absorption
4. Thermal Shock Resistance
5. Determination of Refractoriness

Drying Shrinkage

To measure the drying shrinkage of the crucible bodies, the following formula (Achilam, 2010) was adopted:

$$\frac{\text{Plastic Length} - \text{Dry Length}}{\text{Plastic Length}} \times 100$$

Firing Shrinkage

The firing shrinkage formula (Ibid, 2010) was calculated thus:

$$\frac{\text{Dry Length} - \text{Fired Length}}{\text{Dry Length}} \times 100$$

Water Absorption

The water Absorption test was conducted using this formula (Ibid, 2010):

$$\frac{\text{Saturated Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Thermal Shock Resistance

Water quenching test for thermal shock resistance of crucibles were done by heating the crucible to redness and plunge in cold water. (Singer & Singer, 1963)

Determination of Refractoriness

Refractoriness determination involve firing crucible to highest possible temperature to see its resistance to excessive fusion or luquid formation. (Garkida, 1998)

The five crucible bodies were fired in a kerosene kiln for 7hrs to 1300^0C with a very good stability and then fired in an electric furnace at National Metallurgical Development Centre Jos, to 1500^0C for 3 hrs and retained for 2hrs with no sign of loosing shape.

Result and Discussion

Kankara kaolin and Bomo clay were prepared by slaking with water and sieving both with Tyler mesh sieve (75µ). Bomo clay was levigated after sieving and remove the free silica resulted in improved refractoriness of the clay Ibid, (1998). Grog was also prepared by mixing Kankara Kaolin with water, moulded, dried and fired to 1300^0C, crushed and sieved with 600µ Tyler mesh (0.6mm) with the fine powder. Again coarser fraction was obtained by sieving through 600µ and 300µ, having grog agregate between 0.6 to 0.3 mm.

Five crucible bodies were compounded with varying amount of clays and grog sizes. Each body was thrown on the wheel, but out of the five samples, body 1, 2 and 3 demonstrated a reasonable plasticity for throwing. As a rule, the higher the percentage of ball clay in the body constituents, the better throwability of the body. Likewise, the higher and coarser the percentage of grog the poorer and shorter the throwability of the body. The body samples were tested to determine the following; physical properties, namely drying and firing shrinkage, water absorption (See Table 5). Thermal properties such as thermal shock resistance and refractoriness of the crucibles. In testing the refractoriness, the five bodies were fired for seven hours to 1300^0C in kerosene kiln, and then in an electric furnace to 1500^0C for 3 hours.

Conclusion

Out of the five bodies formulated; body 1, 2 and 3 exhibited reasonable degree of plasticity for throwing. The remaining bodies 4 and 5 found to be unsuitable for throwing due to the too much amuont of coarse grog in the body constituents which rendered them non-plastic. Physical property tests were carried out, firing shrinkage as high as 6.6% and as low as 4.2 % and water absorption as high as 0.51% and as low as 0.37% were recorded. All the five bodies showed excellent thermal shock resistance as they were withdrawn from the kiln at about 1300^0C and plunged in water with niether cracking nor shattering. The results indicated that the body compounded from Kankara clay, Bomo clay and fine Kankara kaolin grog can be used as alternative raw material for the production of refractory crucibles in Nigeria.

Table 1 Analysis of Kankara Kaolin from three different sources:

Compound	Formula	1st Source (wt %)	2nd Source (wt %)	3rd Source (wt %)
Silica	SiO_2	44.55	47.30	46.48
Alumina	Al_2O_3	31.45	36.80	36.40
Iron Oxide	FeO	1.07	0.71	1.09
Magnesia	MgO	0.87	0.16	0.87
Lime	CaO	0.28	0.08	0.73
Sodium Oxide	Na_2O	0.17	0.05	0.00
Potassium Oxide	K_2O	0.03	1.01	0.10
Excess water	H_2O+	12.03	-	-
Chemical water	H_2O	9.06	-	-
Titanium Oxide	TiO_2	0.41	0.16	0.00
Manganese	MnO	0.01	0.00	0.00
Sulphur	SO_4	0.05	0.06	0.00
Strontium Oxide	SrO	0.00	0.00	0.00
Phosphorus	P_2O_5	0.00	0.02	0.00
	L.O.I	-	14.81	14.31

Source; Umar and Hendsman in Garkida (1998); Atta, Ajayi and Adefila (2007); Aigbodion (2014)

Table 2 Properties of Kankara Kaolin

Property Value	Measured
Plasticity	low
Dry shrinkage	6%
Bisque shrinkage	2%
Glaze shrinkage	6.5%
Total shrinkage	14.5%
Adsorption at Biscuit	13.5%
Adsorption at 1300^{o}C	12.5%

Source; Gukas in Okewu, (2014)

The following data on ball clay found at Bomo-Zaria, Kaduna state is given by Aluwong in Okewu, (2014).

Plasticity medium
Shrinkage 11%
Fusibility Vitrifiable

Using the instrumental Neutron Activation Analysis (NAA) 26 elements were reportedly determined in Bomo ball clay by Garkida (1998) as seen in Table 3:

Table 3: Results of NAA reported for Bomo Ball clay

Elements	Conc. (ppm)	Element	Conc. (ppm)	Element	Conc. (ppm)
Na	3499	Sb	0.03	Cr	188
Mg	5059	Cs	0.75	Mn	336
Al	7.47%	Ba	75.4	Fe	0.91
K	1.50%	La	92.0	Co	4.29
Ca	3932	Ce	170	Rb	6.07
Sc	15.5	Sm	15.1	Lu	9.07
Ti	3516	Eu	1.64	Ta	5.33
V	51.4	Dy	5.76	Pa (Th)	21.2
U	10.3	Hf	9.07		

Source; Garkida, (1998)

Table 4: Five different composition of Bomo clay, Kankara Kaolin and Kankara Kaolin Grog

Material	Body 1 (% wt)	Body 2 (% wt)	Body 3 (% wt)	Body 4 (% wt)	Body 5 (% wt)
Bomo clay	50	40	30	40	30
Kankara Kaolin	20	30	40	30	30
Kankara Kaolin Grog	30	30	30	30	40
Total	100	100	100	100	100
Grog Mesh Sizes	30 mesh (600μ)	30 mesh (600μ)	30 mesh (600μ)	30 retained on 50 (300μ) mesh	30 retained on 50 (300μ) mesh
Fraction	All Fractions	All Fractions	All Fractions	coarse Fraction	coarse Fraction

Table 5: Physical Properties of the crucibles

Composition	Dring Shrinkage	Firing Shrinkage (fired to 1300^{0}C)	Water Absoption (fired to 1300^{0}C)
Body 1	9%	6.6%	0.51%
Body 2	8%	5.4%	0.47%
Body 3	8.5%	3.8%	0.51%
Body 4	9%	4.5%	0.41%
Body 5	6%	4.2%	0.37%

Table 6: Thermal Properties of the Crucibles

Body Composition	Thermal Shock (water quenching) at 1300^{0}C	Refractoriness I Fired to 1300^{0}C	Refractoriness II Fired to 1500^{0}C
Body 1	Resisted with no cracks	Vitrified	Vitrified and stable
Body 2	Resisted with no cracks	Vitrified	Vitrified and stable
Body 3	Resisted with no cracks	Vitrified	Vitrified and stable
Body 4	Resisted with no cracks	Partially Vitrified	Vitrified
Body 5	Resisted with no cracks	Dense	Partially Vitrified

Plate 1: Good throwing property of bodies 1 - 3

Plate 2: Good throwing property of bodies 1 - 3

Plate 3: Poor throwing property of body 4 & 5 due to insufficient plasticity

Plate 4: Poor throwing property of body 4 & 5 due to insufficient plasticity

Plate 5: Firing shrinkage bars for bodies 1-5 (A, B, C, D, & E)

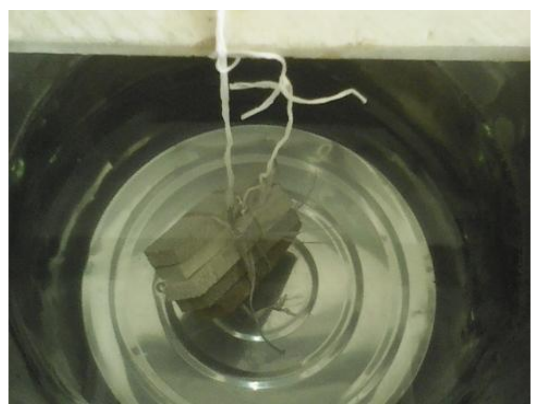

Plate 6: Water absorption test for bodies 1-5 for 2hrs cooled for 4hrs

Plate 7: Water quenching of crucible fired to 1300°C during thermal shock resistance test

Plate 8: Water quenching of crucible fired to 1300°C during thermal shock resistance test

Plates 10: Result of water quenching test of bodies 1-5

Plates 11: Physical differences between naturally cooled and water quenched pieces

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