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Effect of Granite, Kaolin Clay, Borosilicate Glass and Silicon Carbide in the Production of Graphite Crucibles

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Abstract— **This work investigates the effects of addition of granite, borosilicate glass, silicon carbide and kaolin clay on graphite crucibles. This was borne out of the need to reduce the high reactivity of graphite crucibles and to improve the durability of locally made crucibles for use in high temperature applications. The experimental design was created using design expert software in such a way that the materials to be investigated were varied up to 58%. Beneficiated graphite was sourced from Sama-Borkono (SB) in Warji local Government Area, Bauchi State. While processed granite and kaolin were procured from Akamkpa local Government Area Cross River State and Ogbanzu in Ohiya, Umuahia Abia State respectively. Borosilicate glass was obtained from the local market as PYREX glasses. Determination of Chemical compositions of the materials were carried out using the Shimadzu EDX-720 X-ray Fluorescence Analyzer, whereas the graphite was characterized using the Scanning Electron Microscope and X-ray Diffraction. The prepared samples were mixed into different batch compositions, molded and fired to 1100°C for 3hours 34mins as in the design of experiment. After production, the refractoriness, hardness test, compressive strength and density were investigated. The density ranges from 2.31g/cm^3 to 2.48g/cm^3, refractoriness values from 1300 to 1400°C, hardness values from 62.7 HB to 116.4 HB and the compressive strength from 2.06 N/mm^2 to 4.04 N/mm^2 for sample A and F respectively. Sample F displayed better results for compressive, hardness, refractoriness and density. This could be attributed to the amount of kaolin and granite present in the sample. Hence, the crucible produced has favorable properties in line with graphite crucibles and it can be said that granite, kaolin, borosilicate glass and silicon carbide could serve as a partial replacement for graphite in the production of crucibles.**

Keywords—Composite; graphite crucible composite (GCC), graphite crucible.

I. INTRODUCTION

. Many kinds of materials have been developed and used in production of crucibles. The different type of crucibles is based on the materials composition that was used to form the crucibles. There are graphite crucibles, silicon oxide crucibles and clay crucibles. Crucibles formed of graphite or of other clay materials mixed with graphite, with or without the admixture of sand are the most prevalent. Silicate sand is added during molding of crucibles to prevent shrinkage while drying. According to [1] patent, adding little number of chemical elements in metallic state during production would ensure high adherent glaze which would not spall off during usage.

Graphite crucibles are containers used to hold metals for melting in furnaces. They are free standing vessels that are used for high temperature operations [2]. They are also described as a vessel that has high refractivity and can withstand high heat. They are most often used for melting iron and steel, glasses, various metals and alloys [3] A graphite crucible is essentially composed of graphite or black lead ground to fine scale which are rigidly held in their position by partially melted clay ground up with powdered graphite and little sand. Their use was predominantly in Europe and America and currently gaining ground in other parts of the world. Although from history, crucibles are usually produced using granite and clay, it can still be made from other material that withstands temperature high enough to melt material it contains. Graphite crucibles are ideal for melting aluminum, copper and other metals. Materials required for the production of crucibles include binder and clay material.

However, crucibles can also be produced from composite materials. This involves variation in the percentage that constitute the clay and graphite portion of the production process. For a material to be applied in crucible production, it must possess certain thermal, mechanical and chemical properties. The material must have higher melting point than that of the metal being melted and it must have a good strength even when the metal is white hot. Graphite crucible must also be able to withstand chemical corrosion and thermal shock. Although, graphite and glassy carbon are commonly used as crucible material, when evaporating a carbon reactive material from such crucible, a carbide layer is formed [4].

Granite is another mineral resource that is readily available and utilized mainly in building materials and also in other applications that require high strength. These properties of kaolin and granite make them very suitable to be used for partial replacement of graphite in the production of graphite clay crucibles.

In this work, the aim is to investigate the effect of using granite, borosilicate glass, silicon carbide and kaolin clay as partial replacement for graphite in the production of graphite crucibles. However, the design expert software 11.0 trial version will be utilized to run optimization on the variables using the response surface methodology (RSM), and thereafter, production of graphite crucibles using different proportions of granite, silicon carbide, borosilicate glass and kaolin clay, will be done in the course of this study.

II. LITERATURE REVIEW

A. *Graphite crucible composite (GCC)*

Graphite is a crystalline form of carbon with a hardness of 1 – 2 on Mohr's scale [4]. It is an excellent conductor of heat and electricity and melts at about3, 500ºC. It is very stable up to temperature above 6200ºC above which it is combustible in the presence of oxygen. Crucibles are open mouthed vessels used for melting various metal and alloys. Industries dealing with treatment of ores and other materials for the manufacture of metallurgical, chemical and ceramic products need high temperature, hence, to treat such materials, materials that can withstand such operating temperature and other working conditions such as corrosiveness, erosiveness and load conditions, are needed. Crucibles are class of materials that can withstand high temperature (say 1000^0C), resist the action of corrosive liquids and dust-laden currents of hot gas etc. Refractories are manufactured from naturally occurring substances in the earth's crust – clay, quartzite, magnesite, chromite, bauxite, graphite etc. All these materials do not occur in their pure form hence needs some treatment before manufacturing. Initial processing may include an extensive survey of the deposit, selective mining, stock piling by grade, and beneficiation techniques such as weathering, grinding, washing, heavy media separation, froth flotation etc. are employed. Though some can be used without pre-processing, but many must be subjected to heat treatment.

B. *Reviews on graphite crucible*

[5] Studied 'The relationship between micro fabric and the engineering properties of weathered granite. Their work is aimed at relating the changes in engineering properties of granite caused by weathering to a simple micro fabric model based on electron microscope studies. A model is developed, involving the micro fabric of the clay weathering – product and the extent of decomposition, to explain the typically high angles of friction shown by such material. The study successfully related known engineering properties to observed micro fabrics and in doing so has examined the fundamental relationship between these two aspects of granite weathering.

[6] patent presented invention on graphite article. The invention tried to improve binder for graphite. The work highlighted the methods that the improved binder can be prepared so that the properties of the graphite paste are improved as well. The binder consist of liquid coal tar and act as hardening agent as the binder is heated together with graphite. The preferred ratio of binder to graphite is of about 25% tar by weight and 75% graphite.

[7] Studied Influence of thermal damage on physical properties of a granite rock: porosity, permeability and ultrasonic wave evolutions. Parameters for characterization of connected porosity and over all damage in the thermally cracked rocks of granite, in order to access respectively is transport properties and its mechanical strength are identified and quantified. Samples were heated to a range of peak temperature up to 600˚C at ambient pressure. Characterization was made by measurement of porosity, gas permeability, velocity and attenuation of ultra-sonic waves. The results confirm the strong influence of thermal damage on physical properties and shows clearly the potential of this technique.

[1] invented a new and useful Improvement in Methods of Making Graphite Crucibles. The object of the invention is to provide a graphite or clay crucible or pot which has a lasting and adherent glaze on its surface, and which is of superior quality and has a longer life than such crucibles or pots as heretofore made. The work discovered that if certain non-ferrous metals in a finely divided metallic state, be incorporated in the clay or mixture of clay and graphite from which the crucible or pot is formed, it causes the formation of a glaze which is very adherent, which does not readily spall off, and which, therefore, protects the body of the crucible or pot and increases its life. `

III. METHODOLOGY

A. *Material*

The material and equipment utilized in course of this work are listed as follows: Silicon Carbide (SiC), Granite, Kaolin, Graphite, Borosilicate Glass, Kyanite, and Water. Then, the material descriptions used to obtain the characteristics which are close to the requirement are explained below

Table 1: List of equipment for the research and their uses

S/N	Equipment	Function/Test to be carried out
1.	Temperature Programmable Electric Resistance Furnace	Drying, firing, curing and heat treating
2.	Eisenkraft Gas fired furnace with thermocouple	Firing
3.	Optical Metallurgical Microscope Amscope ME-300T-3M	Microstructural Analysis
4.	Shimadzu XRF analyzer model Ray-NY EDX-720	Chemical composition analyses
5.	Teren Hardness tester	Hardness, Wear resistance
6.	TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer	Thermal behavior
7.	Ametek EZ – 250 digital tension/compression tester	Compression test
8.	Sartorius BP – 410 electronic balance scale	Weighing
9.	Laboratory Ball Mill	Grinding and Mixing
10.	Density bottles	Density measurement

B. Response *surface methodology (RSM) statistical tool.*

To develop an ideal mix for the sample, a mixture design which is a specialized form of the surface response method (RSM) was employed. For the purpose of this design, an; graphite crucible composite (GCC) was reformulated to fine tune four product attribute which are measured as responses from a design experiment.

- Response 1: The Hardness (BHN)
- Response 2: compressive Strength (N/mm)
- Response 3: Refractoriness (^{0}C)
- Response 4: Density (Kg/m^3)

Three primary components vary as shown:

- $7\% \leq A$ (Furnace Slag) $\leq 8\%$
- $2\% \leq B$ (Granite) $\leq 10\%$
- $40\% \leq C$ (Kaolin Clay) $\leq 48\%$

These components represent a total of fifty-eight (58) weight-percent of the total formulation, that is:

$A + B + C = 58\%$

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Other materials (held constant) will make up the difference: 42 weight-percent of the Graphite Crucible composite. These includes; 30 weight-percent Graphite and 12 weight-percent Silicon Carbide (SiC). For purposes of this experiment, they are ignored.

This experiment was conducted with the DESIGN EXPERT SOFTWARE 11.0. The design employs a standard mixture design called a simplex lattice. The design was augmented with axial blend check and the overall centroid. The vertices and overall centroid were replicated, however increasing the experiment size to 15 blends total.

After the design of experiment formulation for the A. Graphite crucible composite (GCC), the data generated was now utilized to for the development of the Table for the various samples. Table 2 shows the various sample description and the weight-percent that they constitute.

Table 2: Various sample description and their weight-percent

S/N	Sample ID	SiC (%wt.)	Graphite (%wt.)	Borosilicate Glass (%wt.)	Granite (%wt.)	Kaolin Clay (%wt.)
1.	A	12	30	7.5	8	42
2.	B	12	30	7.5	8	46
3.	C	12	30	7.5	10	40
4.	D	12	30	7	2	48
5.	E	12	30	7.5	4	44
6.	F	12	30	7.5	8	48
7.	G	12	30	7.5	8	46
8.	H	12	30	7.5	10	42
9.	I	12	30	8	6	46
10.	J	12	30	7.51	6	40
11.	K	12	30	7	4	46
12.	L	12	30	7	6	44
13.	M	12	30	8	2	42
14.	N	12	30	8	4	46
15.	O	12	30	7.505	6	48

B. Sample Preparation Procedures

For the purpose of this work, a total of fifteen (15) samples designated with the sample ID as shown in Table 2 were prepared. The procedures for preparing these compositions are as follows;

Beneficiated graphite was sourced from Sama-Borkono (SB) in Warji local Government Area, Bauchi State. While processed granite and kaolin were procured from Akamkpa local Government Area Cross River State and Ogbanzu in Ohiya, Umuahia Abia State respectively. Borosilicate glass was obtained from the local market as PYREX glasses. Furthermore, samples were objected chemical analysis using Shimadzu X-ray fluorescence Spectrometer EDX 720 and thermal analysis using TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer, respectively, in order to check the stability of the test samples. Thereafter, grinding of the stable test samples to <500microns was carried out using 5kg Laboratory ball mill (Ugwuegbu et al, 2017). The samples were sieved through 500micron sieves to obtain materials containing distribution of particles with maximum particle size of 500microns. The mixing was done in conformation with the design parameters established in Table 2, The blended mix samples were prepared in conformity with ASTM standards 1989 for tests by mixing with water (3 – 4%), molding and pressing with hydraulic press to 300KN. The molded samples were air dried for 24 hours and later fired to 1100°C using the Eisenkraft Gas fired furnace with thermocouple for 3hours 40minutes. And the final finishing would be done using the finishing tools to achieve dimensional accuracy. This procedure was repeated for all the samples.

C. Optimization using the D-Optimal Mixture Design

Surface Methodology (RSM) is a collection of statistical and mathematical techniques Response useful for developing, improving, and optimizing processes. RSM is an important branch of experimental design. The objectives of quality improvement, including reduction of variability and improved process and product performance, can often be accomplished directly using RSM. RSM can be of first order and second order equations as shown below:

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots, + \beta_k x_k \text{ ;..................... (1)}$$

$$\eta = \beta_o + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i<} \sum_{j=2}^{k} \beta_{ij} x_i x_j \quad \text{.............. (2)}$$

In the practical application of RSM, it is necessary to develop an approximating model for the true response surface. The approximating model is based on observed data from the process or system and is an empirical model. Multiple regression is a collection of statistical techniques useful for building the types of empirical models required in RSM. Regression Analysis is utilized to identify the relationships between the responses and the variables to establish a mathematical model that satisfies the relationship between a group of test factors and objective functions. This model was used to explore the optimal solution in the experimental area based on its practicability. RSM tends to focus on the relationships between multiple factors x_1, x_2, $x_3 \dots x_k$ of the designed experiment and the response y. Consequently, the functional relationship between the responses and the independent variables should first be determined to produce a proper approximating function, and then the factor setting levels x_1, x_2, $x_3 \dots x_k$ needed to obtain the optimal response was identified. The relationship between the response variables and the independent variables (factors) was presented in the form of an equation below:

$$y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \varepsilon \text{ ;.......................... (3)}$$

$$y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \varepsilon \text{............. (4)}$$

Regression Analysis is utilized to identify the relationships between the responses and the Also, a contour plot and three-dimensional response surface graph for each response were generated by Design-Expert Software Version 11.0 for a better explanation. The results generated from the optimization can be seen in result and discussion section.

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IV. RESULTS AND DISCUSSION

A. Optimization Analysis using Response Surface Methodology (RSM)

An introductory study on graphite crucible composite (GCC) formulation was done by investigating the components that made up the crucible material. Four excipients were chosen for the graphite crucible composite (GCC) formulation based on their function. Three of them and graphite were used as variables in response surface methodology (RSM) as they may have effect on the responses. The ranges of variables were also studied by using RSM in design expert software. Table 3 shows the summary data table of the actual design after experiment.

Table 3: Summary of the Design table for the optimization

Run	Factor 1 A:Borasilicate Gl... wt%	Factor 2 B:Granite wt%	Factor 3 C:Kaolin Clay wt%	Response 1 Hardness BHN	Response 2 Density g/cm3	Response 3 Compressive N/mm2
1	7.5	8	42	62.7	2.33	2.06
2	7.5	8	46	86.2	2.37	2.69
3	7.5	10	40	70.8	2.31	2.56
4	7	2	48	75.1	2.48	2.47
5	7.5	4	44	79.9	2.41	3.18
6	7.5	8	48	116.4	2.48	4.04
7	7.5	8	46	95.4	2.42	2.47
8	7.5	10	42	99.5	2.37	3.63
9	8	6	46	93.8	2.39	3.58
10	7.51	6	40	94.4	2.32	1.79
11	7	4	46	89.1	2.44	3.72
12	7	6	44	76.2	2.4	3.58
13	8	2	42	57.5	2.33	3.25
14	8	4	46	115.5	2.38	3.53
15	7.505	6	48	104.85	2.47	2.29

B. Predicted and Actual Results for the three (3) Responses

For Hardness value;

Utilizing the design expert software, optimization was conducted on experimental design table. The coded equations were generated on each case and utilized to calculate the predicted values of the experiment. Fig. 1 shows the graphical representation of the predicted and actual values of the hardness value. The graph confirms that the predicted value of the hardness value is 94.40BHN while the actual value is 80.96BHN showing high similarities for the predicted and actual values for the Hardness value.

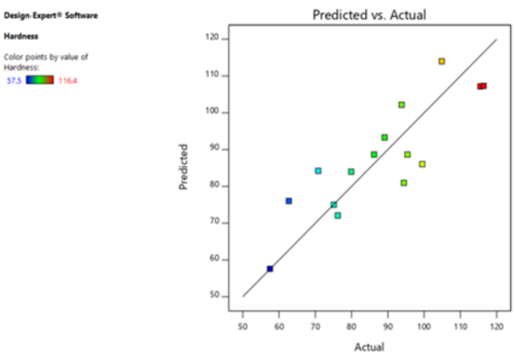

Figure 1: predicted and actual values for hardness value

For Compressive Strength;

Figure 2 shows the graphical representation of the predicted and actual values of the compressive strength experiment. The graph confirms that the predicted value of the compressive strength is 1.79N/mm^2 while the actual value is 1.73N/mm^2 showing high similarities for the predicted and actual values for the Impact strength experiment.

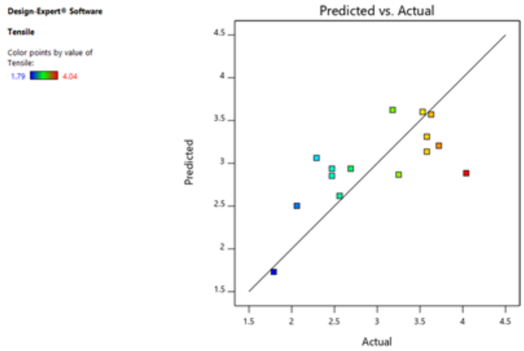

Figure 2: Predicted and actual values for the Compressive Strength

For Density Value;

Fig. 3 shows the graphical representation of the predicted and actual values of the density experiment. The graph confirms that the predicted value of the density is 2.32g/cm^3 while the actual value is 2.31g/cm^3 showing high similarities for the predicted and actual values for the density experiment.

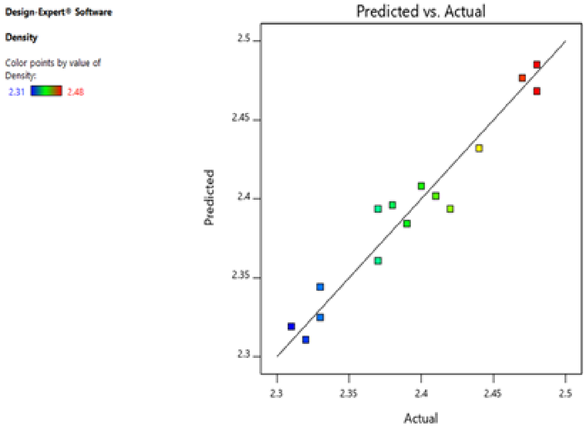

Figure 3: Predicted and actual values for the density value

C. Evaluation interaction results

A critical evaluation was conducted on the experimental results for the interaction of each experiment and the following were observed. Fig.4 shows evaluation analysis for hardness test results. From the result, it was observed that the maximum value was experienced at sample ID F having a hardness value of 116.4BHN While the minimum value was experienced on sample ID M having a value of strength of 57.5BHN. The figure below shows the relationship between the variables (Borosilicate Glass and Granite) and Hardness test.

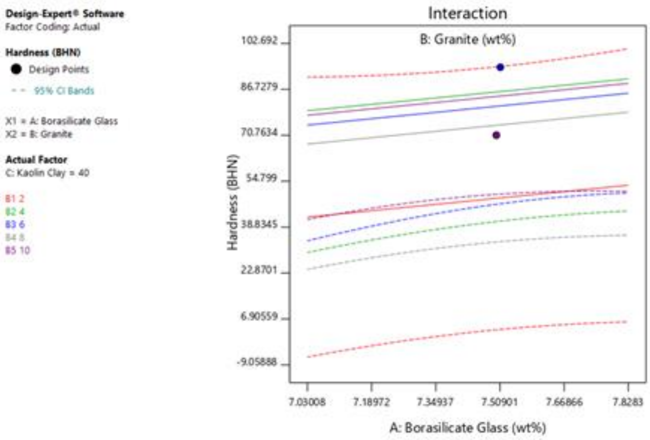

Figure 4: Evaluation for Hardness Test (Interaction)

Again, evaluation analysis for density results, showed that the maximum amount of density was experienced at sample ID D& F having a value of 2.48g/cm^3. While the minimum amount of strength was experienced on sample ID C having a value of 2.31g/cm^3.The figure below shows the relationship between the variables (Borosilicate Glass and Granite) and density.

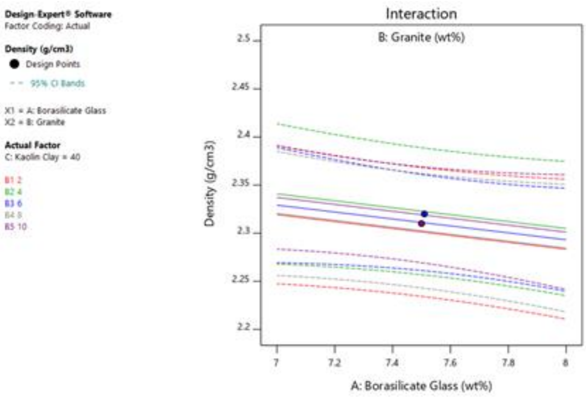

Figure 5: Evaluation for Density (Interaction)

Finally, the evaluation analysis for compressive test results showed that the maximum amount of strength was experienced at sample ID F having a value of strength of 4.04N/mm^2. While the minimum amount of strength was experienced on sample ID J having a value of strength of 1.79N/mm^2.The figure below shows the relationship between the variables (Borosilicate Glass and Granite) and Compressive test.

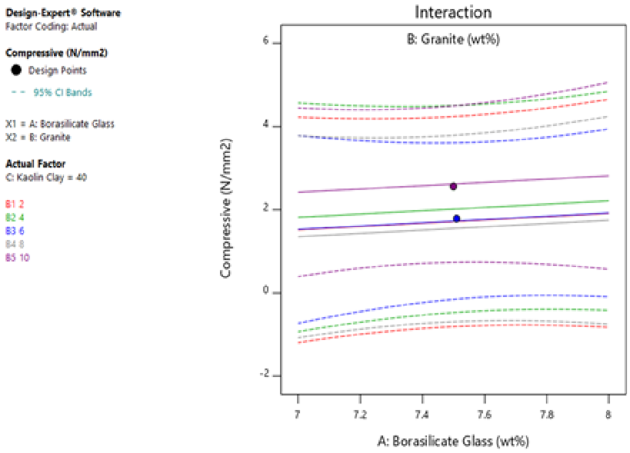

Figure 6: Evaluation for Compressive strength (Interaction)

V. CONCLUSION

From the above results and discussions, the following conclusions are made:

1. Graphite crucibles were successfully produced by the partial replacement of graphite with granite, borosilicate glass, silicon carbide and kaolin at a molding pressure of 300KN and firing temperature of 1100°C for 3hours 34mins.

2. The densities, refractoriness, hardness and compressive strength of the crucibles were in conformation with that of graphite crucibles. However, sample F with composition of 30% graphite, 12% silicon carbide, 48% kaolin, 8% granite, and 7.5% borosilicate glass, had the highest hardness value of 116.4 HB, refractoriness of 1400°C, density of 2.48g/cm^3 and compressive strength of 4.04N/mm^2.

3. Good bonding between the constituents of the graphite crucible resulted in higher values of densification obtained.

4. This work has established that better hardness and compressive values can be obtained from graphite crucibles produced from the partial replacement of graphite with borosilicate glass, granite, kaolin and silicon carbide.

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