Full Paper

PURIFICATION OF NIGERIAN ANTANG CORUNDUM FOR ADVANCED CERAMIC PRODUCTION

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ABSTRACT

The study deals with purification of *Antang* corundum from Zanga LGA, Kaduna State of Nigeria for ceramic production. The experimental work was on the laboratory-scale beneficiation of *Antang* corundum for possible alumina production in advanced ceramic development. Froth floatation procedure was employed in beneficiating the corundum to get a high-grade alumina while depressing the other minerals by using laboratory-floatation equipment. The results from the experiments presented more than 32 % improvement in the alumina content of the corundum. The alumina content achieved was 86.6 %, which makes the corundum surpasses the 85 % alumina grade in the CoorsTek ceramic properties standard, commonly used for armour ceramic production. The *Antang* corundum can then be used as a substitute for bauxite and alum that are the major sources of alumina through Bayer process and calcination method respectively.

Keywords: Alumina, armour, corundum ceramic, and froth floatation

1. INTRODUCTION

Armour can be generally defined as shielding material provided for ballistic defeat of projectiles or fragments when integral shielding is inadequate within its area of coverage (NIJ, 2014; Mukasey *et al.*, 2008). Armour is commonly divided into hard and soft armours. Hard armour consists of rigid panels (plates) of ballistic-resistant materials. It is designed to offer greater protection against higher threats by breaking and eroding the projectiles. Hard armour plates are used for vehicular and personnel (tactical) armour. Hard armour plates are made from metallic plates, ceramics, compressed laminate sheets or composites that incorporate two or more of these materials. Conventionally, vehicular ballistic protection are primarily made of high hardness steel (Rojek, 2013; Staggs, 2009; Fawaz*et al.*, 2004; Guild *et al.*, 2007) due to its maintenance of structural rigidity and strength (Atapek and Karagoz, 2011; Atapek, 2012). In addition, availability of material, equipment and technical-know-how (personnel) makes steel armour components popular in the fabrication of both commercial and military operational vehicles (Cegla*et al.*, 2015; Dwight, 2008; Unaler, 2005). However, its main disadvantage lies in weight (Zaera and Sanchez-Galvez, 1997) and it is quite simple to design weapons to defeat even the strongest steels (Denzel, 2010).

Weight is critical in armour designing (Staggs, 2009) as majority of systems requiring protection against all kind of projectiles are mobile: military vehicle, tank, airplane and even the military and other security personnel. These necessitated a continued search for high performance, lightweight and cost effective protection for personnel and vehicles to improve survivability and reduce injury when subject to a range of potential threats including blast (Iannucci, 2011; Jovicic, 2003).

Non-metallic materials (such as ceramics and polymers) are therefore been recently integrated into more efficient lightweight armours. Specifically, low density, high hardness, high rigidity and compression strength of ceramics make it popular and suitable for armour systems; including aircraft structures and military vehicles (Silva *et al.*, 2014; Liaghat *et al*, 2013; Medvedovski, 2006; Zhang *et al.*, 2006; Fawaz *et al.*, 2004; Tolochko, 2011).

Composite materials used for protection from high-energy bullets (that is threat projectile that contains a steel core rather than only lead) are mostly combined with a ceramic strike face (Cooper and Gotts, 2003).

The leading ceramic materials used commercially in the development of ballistic armours are alumina (Al_2O_3), boron carbide (B_4C) and silicon carbide (SiC) (Dateraksa *et al.*, 2012). The most important raw material for the production of aluminum oxide is bauxite, which is a mixture of the minerals boehmite (α-AlO(OH)), diaspor (β-AlO(OH)), and gibbsite ($Al(OH)_3$), with a high content of various impurities such as Na_2O, SiO_2, TiO_2, and Fe_2O_3.

Bauxite is refined using the Bayer process while very pure commercial powders are prepared via the calcination of alum, $NH_4Al(SO_4)_2$-$12H_2O$ (Abdullahi *et al.*, 2014; Riedel, 2010; Karen, 2010); these are purely thermal processes (Souto *et al.*, 2000).

However, alumina occurs naturally as corundum (Riedel, 2010) and is a common constituent in many igneous and metamorphic rocks (Karen, 2010; Smith *et al.*, 1987). Corundum will serve as a good substitute to other sources of alumina for advanced ceramics in two folds. First, there is abundant deposit of *Antang corundum* at Antangin Sanga LGA, Kaduna-Nigeria (Abdullahi *et al.*, 2014); locally called "*Shago-shago*". Second, corundum does not require thermal processing for conversion to alumina (Karen, 2010; Smith and Liewellyn., 1987).

It is on this note that the research attempted to produce the alumina indigenously for possible development of ceramic armour in Nigeria. In this research, CoorsTek Ceramics (AD-series) is selected as the control alumina ceramic being the global leading ceramic material manufacturer reported in literature for ceramic armour applications (Serjouei *et al.*, 2014; Bourne *et al.*, 2007; Sarva *et al.*, 2007; Fawaz *et al.*, 2004; Shih *et al.*, 1998; Bless *et al.*, 1996). CoorsTek AD-85 alumina was specifically referred as the material has alumina content (Al_2O_3-85%) close to the developed ceramic.

2. MATERIALS AND METHODS

2.1. Materials

The major raw materials required for the experimentation are: *Antang* Corundum, petroleum sulphonate (corundum collector), sulphuric acid (pH regulator), hydrochloric acid (corundum activator), pine oil (frother).

2.2. Methods

2.2.1. Collection of Corundum

Corundum deposit was excavated using the simple tools (digger, shovel, bucket and bowls) shown in Figure 1. In other to have a true fraction representation within the study area, different points using the random sampling techniques were excavated. The mined product was packed in sack (that permitted water percolation) and tied. This was then soaked in water body, Figure 2, for 72 hours in order to dissolve clay and other minerals. The sack was then vigorously shaken to wash off clay material and the remaining content poured on the floor for natural drying. thereafter, manual sorting of the precious stones were done by hand picking; these included topaz, acquamarine (blue sapharine), tourmaline, corundum and gemstone (zaicho) in order of value as depicted in the same order presented in Figure 3. By handpicking, other undesirable visible minerals were carefully selected and discarded. This process was repeated till 53 kg of *Antang corundum* was obtained from the field of *Antang* in Sanga Local Government Area of Kaduna State, Nigeria for this study; Figure 4. The size of the corundum, determined by measuring the average diameters of the samples using vernier calipers, ranges from 4mm to 20mm.

2.2.2. Pulverization

From about 53kg of corundum mined from Antang Kaduna-Nigeria, 5kg was separated for purification process which was achieved via the following processes: crushing, pulverization, sieve analysis and froth floatation. The sample was crushed using jaw crusher and later pulverized to particulate size using ball milling procedure.

2.2.3. Sieve analysis

Pulverized sample was then subjected to sieve analysis by using sieve sizes arranged in a stack of descending order from 250 µm to 25 µm. A cover was placed on top of the coarsest sieve (top) to prevent escape of the sample; while a collecting pan was placed below the 25 µm sieve of the assembly to receive the final undersize. For this corundum, the particulate size of 400 mesh sieve number; 37µm was confirmed to be the liberation size in froth flotation process (Smith and Liewellyn, 1987; Yechezkel, 2003).

2.2.4. Froth Floatation Process

Indirect froth floatation was adopted in the purification of the corundum as carbonate minerals were first floated to ensure a reduced amount of sulfuric acid needed for pH regulation and better yield of corundum (Smith and Liewellyn, 1987). Laboratory floatation machine (serial no. BEA 15867), manufactured by Denver Equipment, England, found at NMDC, Jos, was used. A sample consisting of 800 g of the pulverized *Antang* corundum was measured into the floatation cell (this is the maximum quantity that the cell can contain at a time). Then, 1200 cm^3 of water was added below the cell tip. Agitation of the solution without air followed by starting up the impeller that operates at 2000 rpm with 1cm clearance from the bottom of the cell (Ettu *et al.*, 2014). The floatation set up is shown in Figure 5. This was done for 5 min. Then the pH of the solution was raised to 10 using sodium carbonate. Sodium oleate (collector) at 0.02 kg/ton rate and oleic acid (dispersant and collector) at 0.03 kg/ton was added to the solution and agitated for 3 minutes.

A drop of dextrin (0.0015 kg/ton) was added which served as corundum depressant followed by 0.0015 kg/ton of pine oil, a frother that is responsible for the foaming. The carbonates were thereafter floated while corundum depressed. The depressed corundum was then floated as presented below.

A 5 ml syringe was used to add sulfuric acid at the rate of 0.020 kg/ton in order to lower the pH value to about 2.5 and 3.0 (Smith and Liewellyn, 1987). Then petroleum sulfonate (corundum collector) at a rate of 0.0015 kg/ton and hydrofluoric acid (a corundum activator) at a rate of 0.001kg/ton of feed were added to the solution. Conditioning time was 5 minutes (Ettu *et al.*, 2014). The pH value was continuously monitored and maintained between 2.5 and 3.0 during the process; Figure 6. Then the air was introduced into the floatation cell to create bubbles and the floating of the sample then followed using spatula after a skimmer was used to skim off the bubbles. After floating, the air jet was shut and the impeller was washed with water.

After the above process, the collected froth and the depressed (tailings) samples were allowed to settle for 24 hours before they were decanted. These were later dried in the furnace at the heating rate of 25°C /min in a CARBOLITE Electric Furnace (serial number 8/01/1953, model number RHF 16/15 and maximum temperature capacity of 1600 °C; England) available at NMDC, Jos-Nigeria, at 200 °C. Then the samples were weighed and chemical composition was determined. The floatation of the sample was run twice before optimal alumina concentration was attained.

Figure 1: Excavation/Bagging of corundum mine

Figure 2: Soaking of Excavated mine

Figure 3: Sorted precious stones: A-topaz, B-acquamarine, C-tourmaline, D-Antang corundum and E-gemstone (zaicho)

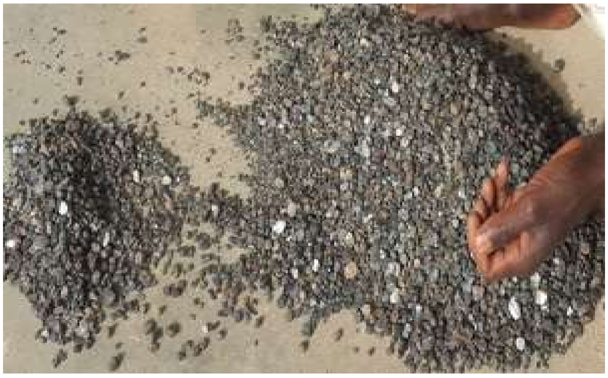

Figure 4: Mass of Antang corundum collected from the field

Figure 5: Laboratory Froth Floatation

Figure 6: pH meter, beakers & measuring jar

3. RESULTS AND DISCUSSION

Table 1 shows result of the chemical composition of the corundum. X-ray fluorescence (XRF) was used to determine the composition in the raw *Antang* corundum, beneficiated corundum and the tailings using Mini Pal4 ED-XRF at Defence Industries Corporation of Nigeria, Kaduna.

It is observed in Table 1 that the targeted alumina (Al_2O_3) in the raw *Antang* Corundum was raised from 65.4 % to 86.6 % in the beneficiated corundum through the froth floatation process. This is a significant improvement that meets a class (AD-85, 85% Al_2O_3) in the ceramic properties standard (CoorsTek, 2008) as well as the various polycrystalline alumina composition presented by Riedel (2010). The result indicated close alumina content in comparing with the work of Smith and Liewellyn (1987) that was able to get a concentrate of 89.7 % alumina. The difference could be traced to different rock formations and consequently corundum variations. Also, the corundum recovery was 77% which is in agreement with the same work.

It is also observed from the work that the alumina did not contain Na_2O that the alumina obtained from the thermal treatment of Gibbsite resulted from Bayer process significantly contains (0.1 - 0.7 Na_2O impurity). This impurity is reported to concentrate at the corundum grain boundaries leading to severe deterioration of the mechanical properties of its finished product (Souto *et al.*, 2001). Also, the iron oxide (Fe_2O_3) in the corundum was significantly reduced from 16.09 % to approximately 3.57 %. However, this value is higher than the value (0.015 - 0.097 Fe_2O_3 impurity) obtained by Souto (2001) through application of calcination process. The only significant oxide aside the alumina in the beneficiated corundum is SiO_2 with 5.9 % concentration. This is a bit higher than the result obtained by Smith (1987) that also utilized froth floatation but achieved 1.8 percent SiO_2 content.

Table 1: Chemical composition of raw, beneficiated Antang corundum and tailings

Compounds	Concentrations (%)		
	Antang Corundum	Beneficiated Corundum	Tailings
Al_2O_3	65.4	86.6	63.3
SiO_2	7.9	5.9	14
P_2O_5	0.02	0.40	0.13
SO_3	0.03	n.d	0.03
K_2O	0.13	0.114	0.184
CaO	0.566	0.323	0.589
TiO_2	2.04	0.949	1.71
V_2O_5	0.11	0.037	0.085
Cr_2O_3	0.161	0.0728	0.150
MnO	0.092	0.033	0.079
Fe_2O_3	16.09	3.575	13.41
NiO	0.080	0.012	0.077
ZnO	0.11	0.011	0.080
CuO	0.095	n.d	0.13
Ga_2O_3	0.27	0.072	0.20
ZrO_2	0.15	0.20	n.d
Ag_2O	0.676	1.11	0.587
BaO	0.35	0.14	0.52
Eu_2O_3	0.22	0.077	0.19
Ta_2O_5	0.61	0.10	0.49
WO_3	0.33	n.d	n.d
Re_2O_7	0.34	0.093	0.30
PbO	4.3	n.d	3.5
Ti_2O_3	n.d	0.19	n.d
SeO_2	n.d	n.d	0.33

NB: n.d is not detecte

However, Ag_2O was found to increase from 0.676 to 1.11 percent. The oxide was not observed in the previous works but could be traced to the chemicals employed in the floatation process or mineralogical content of the *Antang* corundum. Other compounds are in traces and it is in agreement with the reports from Souto *et al.* (2001) and Smith and Liewellyn (1987). The tailings were also analyzed and the result is as well presented in the Table 1.0. It was observed that the alumina content of the tailings is 63.3 % while the SiO_2 was raised to 14 %. Another significant compound observed in the tailings is 13.41 % of Fe_2O_3.

4. CONCLUSION

The research employed froth floatation procedure in raising the alumina content of *Antang* corundum for possible advanced ceramic material development especially for ceramic armour applications. The froth floatation process produced high alumina concentrate that exceeded the minimum 85 % alumina found in the CoorsTek (2008) ceramic properties standard for armour fabrication. The concentrate alumina content of 86.6 % was achieved with a recovery of approximately 77 % of the corundum. This makes the *Antang* corundum suitable for armour ceramic development.

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