EFFECT OF FRACTIONAL PRECIPITATION ON QUALITY OF NANOSTRUCTURED ALUMINA PRODUCED FROM ALUMINIUM METAL WASTES

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ABSTRACT

Black aluminium dross produced from a local aluminium smelting plant was used in this study. Solvothermal method was used to produce nanostructured alumina from this waste. Initial product obtained is of low quality with 86.9% Al2O3 content and mixed crystalline phases of 71% α-alumina and 29% calcium dodeca aluminate ($CaO(Al_2O_3)_6$). The introduction of the fractional precipitation stage into the process helps in improving the purity of the alumina product to 96.5% and also produces 100% α-alumina crystalline phase. The study also shows that the crystallite size of the α-alumina products produced from this process is less than 100nm.

Keywords: aluminium dross, α-alumina, fractional precipitation, solvothermal, nanostructured

INTRODUCTION

Nanostructured materials are classified as material that having one of its dimension less than 100 nm [1]. Large surface area and quantum effect are among the major properties that differentiate nanostructured alumina with its bulk counterpart. Nano alumina (Al_2O_3) exists in many crystalline phases but commercially there are only two phases available in the market, the α-alumina and γ-alumina. Of the different crystalline phases or polymorphs of alumina, α-alumina is the only stable crystalline phase. Its properties of high temperature, chemical resistant, high insulating properties as well as the second hardest material after diamond make it suitable for refractory, structural, abrasive and electrical applications. The used of advanced ceramics in the electronic sector accounts for 64.7% of the total advanced ceramics applications in year 2000. A majority of this is in the form of alumina capacitors, insulator and also packaging materials. A major requirement for this alumina product is that the starting material should be of very high purity with minimum content of sodium and iron impurities. High purity alumina produced for this application requires a sodium content of not exceeding 0.1% by weight and iron content not exceeding 0.04% by weight [2].

Conventional method of producing alumina is from the mineral bauxite using Bayer process. This process involves the digestion of the aluminium content in the mineral by sodium hydroxide in autoclaves at elevated temperature of $130^o – 250^oC$ [3]. During the process, most of the aluminium in the mineral will be converted into sodium aluminate. The sodium aluminate will then be precipitated as aluminium hydroxide and later transform into alumina by heat treatment and calcination. Basically there are two types of alumina, the smelter grade alumina is of low purity and produced as a starting material for making aluminium metal. Another alumina grade is known as the technical alumina that is basically a high purity ceramic alumina and used for high technology applications. Presently only about 9% or 4 million tons per year of the total alumina produced is in the form of technical alumina. The chemical, physical and electrical properties of alumina are interdependent. As the purity of alumina is increases the physical and electrical properties tend to improve. Thus for critical applications high purity alumina are used.

In this study we are using black aluminium dross (BAD) waste to produce the high purity nanostructured α-alumina. Aluminium dross is a waste produced during the aluminium smelting process and it is in the form of a solid material floating on the aluminium melt [3]. Worldwide aluminium industry produces nearly five million tonnes of this waste each year. There are two types of aluminium dross waste and this can be differentiating by their white and black colours. White aluminium dross is a salt comprises mainly of aluminum trihydroxide or gibbsite with high purity of about 97.5% Al_2O_3 content. Black aluminium dross on the other hand is in a metallic form with lower aluminium purity of about 50%. In Malaysia, both these aluminium dross waste is classified as a schedule waste and its storage, transportation and disposal activities must be carried out by licensed contractors. Recycling this schedule waste into a value-added material will be a welcoming move to the industrialists as well as safeguarding the environment. As this waste contain considerable amount of impurities, the quality of the final product may not be similar to the commercial nanostructured alumina products. Inclusion of the fractional precipitation stage will tend to improve the quality of this alumina by removal of the unwanted impurities.

MATERIALS AND METHODS

Locally produced BAD obtained from aluminium smelter a plant in Penang was used in this study. A solvothermal synthesis method was used for the production of nanostructured α alumina from this waste [4]. The process involved washing of aluminium metal wastes with water, cutting the metal into smaller pieces, roating followed by leaching with 4M sulphuric acid and precipitation with propanol. After separating the white precipitate from the liquid using a vacuum filter, it is dried overnight in an oven at 70^{o}C. The hydrated alumina powder produced after the drying stage is then calcined at 1300^{o}C for 3 hours in a furnace. Finally X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Flourescence (EDXRF) and Transmission Electron Microscope (TEM) characteristic tests were performed on these samples. The phase and crystallite size analysis was done using Panalytical X'pert XRD system with reference crystal structure data from Inorganic Crystal Structure Data (ICSD), particle morphology by FEI Quanta 400 SEM, elemental content by Thermo Fisher Quant X EDXRF spectrometer and crystal size and morphology by Jeol jem 2100 TEM.

RESULTS AND DISCUSSION

The initial work was done in characterizing the BAD samples used in this study. This was done by analyzing the crystal morphology by the digital microscope, purity of the sample by EDXRF and also determining the crystalline phase by XRD. Figure 1 (a and b) below show the crystalline phase analysis and morphology of the BAD sample by the XRD and digital microscopy techniques.

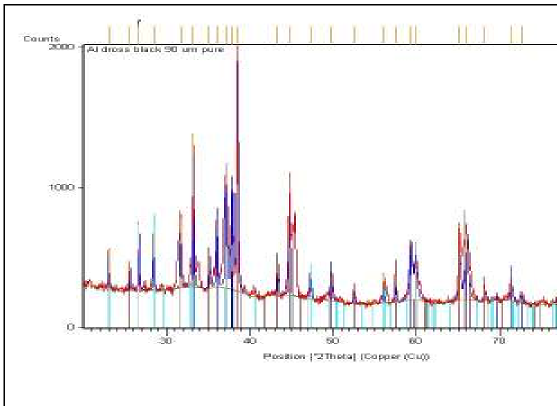

Fig1(a): XRD diffractogram of BAD sample

Fig1(b): Digital microscope micrograph of BAD sample (10x magnification)

The diffractogram produced from this sample has very sharp peaks indicating that the sample is a crystalline. Crystalline phase was identified and the sample is identified to comprise of aluminium metal, corundum, spinel and kesterite phases. The crystalline phases identified by the XRD for the BAD samples were also similar to the earlier publications [5, 6, 7]. EDXRF analysis was also performed on the samples and the result shows that the BAD has a purity of 49.3% with Ca, Mg, Fe, Sn, Zn and Pb impurities. The purity of the BAD sample increases to 81.3% after separating and collecting the sample that is less than 180 μm particle size from the sieving process.

The solvothermal method used for the synthesis of α-alumina from this aluminium dross waste involved H_2SO_4 leaching to dissolve the aluminium into its sulphate solution and followed by precipitation of the aluminium hydroxide using propanol and finally calcined it into the α alumina. Roasting stage was added to enhance the aluminium dissolution. Mixing of aluminium sulphate and propanol involves a sol-gel reaction where the changes of the solution from sol to gel can be observed during the synthesis. Fig. 3 (a and b) below show the XRD diffractogram and SEM micrograph of alumina products after calcinations of 1300^{o}C produced from the BAD sample. Analysis of this alumina product shows that it consists of mixed 71% α-alumina and 29% calcium dodeca aluminate ($CaO(Al_2O_3)_6$) phases. The quantitative phase analysis was done by using the Reitveld's method with the crystal structure data available from Inorganic Crystal Structure Data (ICSD).

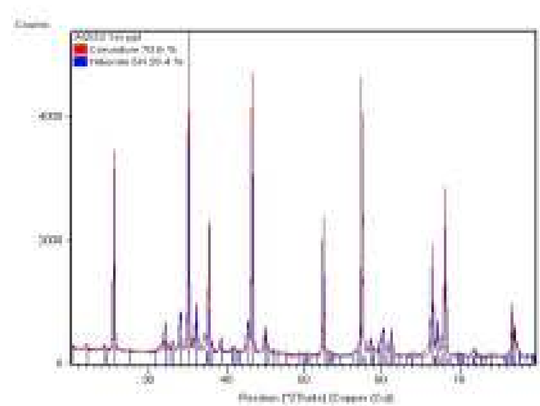

Figure 2a: XRD diffractogram of WAD after calcination at 1300^{o}C

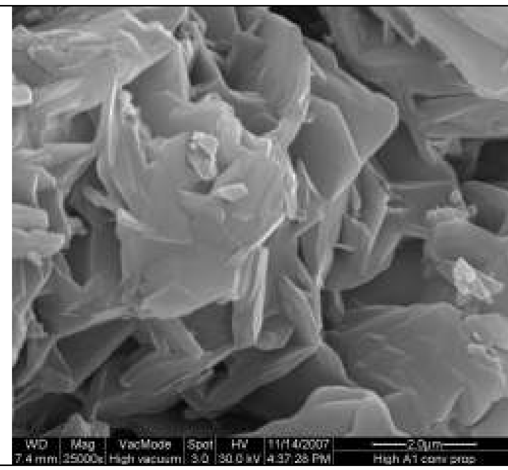

Figure 2b: XRD diffractogram of BAD after calcination at 1300^{o}C

SEM micrograph of the sample shows that plate type of morphology obtained from this alumina sample. The size of the crystal is large of about 4 – 5 µm. We also determined the crystallite size of the both alumina product by the Sherrer's method on the most intense α alumina XRD peak (104) and the result we obtained is 91.6nm.

EDXRF analysis of initial alumina product produced from BAD is 86.9% Al_2O_3. Improvement on the purity of the alumina product produced from BAD was done by fractional precipitation method. Fig.3 below also shows the increase in α-alumina phase content for the different number of precipitation stages where a single phase α-alumina was registered after the 4th precipitation.

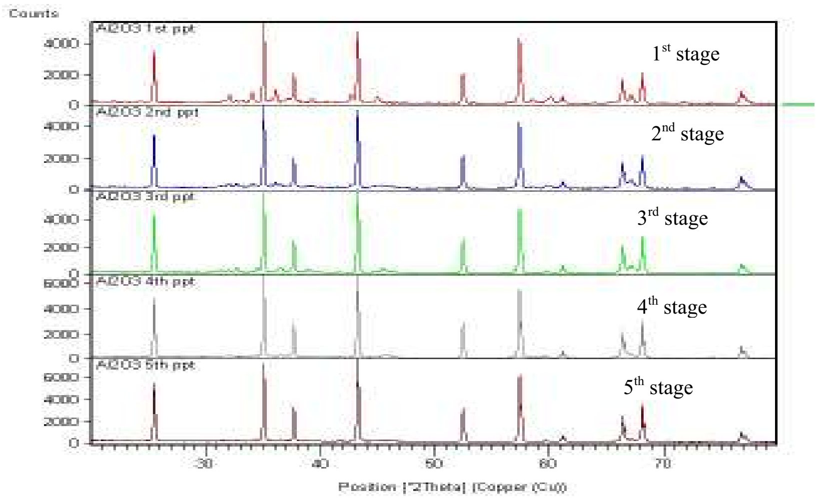

Fig.3: XRD diffractograms for different precipitation stages of the fractional precipitation process for BAD

The reason for the formation of a single α-alumina phase by the 4th stage may be attributed to the increase in the purity of the sample as the number of fractional precipitation stages is increase. This can be related in the Table 1 below. Purity of α-alumina produced the first stage is 86.9% and this tends to increase to 94.2% in the 4th stage of the fractional precipitation process. Finally by the fifth stage a purity of 96.5% was achieved. However the crystallite size for the α-alumina does not follow a down-ward trend where it is smaller to 82.1 nm by the second stage and there after it increases as the fractional precipitation stage is increase. By the fifth stage the crystallite size of α-alumina is 91.4 nm.

Table 1: Purity and crystallite size of α-alumina produced from fractional precipitation

Number of precipation stage	Al_2O_3 (%)	Crystallite size (nm)
1	86.9	91.6
2	92.0	82.1
3	93.4	87.8
4	94.2	89.7
5	96.5	91.4

The morphology of the α-alumina product produced by adding the fractional precipitation stage was also determined by SEM as shown in Fig. 4 below. Unlike the large plate crystal structure that was obtained in our initial product, the morphology of the crystals are almost spherical polycrystalline similar to that of the commercial nanostructured α-alumina product (8).

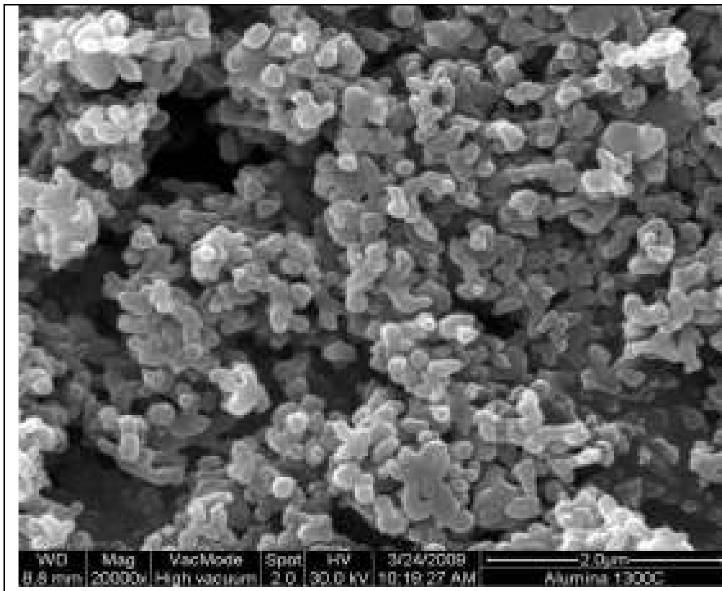

Figure 4: SEM micrograph of alumina produced from BAD (20,000x magnification)

CONCLUSION

The addition of fractional precipitation stage in the solvothermal processing of BAD resulted in a better α-alumina product. Purity of the product increases from 86.9% to 96.5% and it also produced a 100% α-alumina crystalline form. The study also shows that the produced is nanostructured α-alumina with crystallite size of less than 100nm. The addition of fractional precipitation also changes the morphology from plate to almost spherical polycrystalline.

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