Effect of particle size of rice husk ash on aluminium/graphene composites

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Abstract

Aluminium/graphene (Al/G) composite has gained wider engineering applications because of its unique properties such as lightweight, excellent corrosion resistant, improved strength and enhanced thermal conductivity. However, difficulty in dispersing graphene in molten aluminium remains one of the major optimization challenges. This study developed, by stir casting technique, composites of aluminium alloy from recycled aluminium can, 0.4 wt. % graphene (G) and 1.6 wt.% rice husk ash (RHA) with particle sizes of 150, 300 and 600 µm. The tensile, hardness, impact and fatigue properties were analyzed using Instron Extensometer, Vickers hardness tester, Charpy Impact machine and rotating fatigue machine respectively. Furthermore, the cast samples were characterized using scanning electron microscope (SEM) and X-ray diffractometer (XRD). The morphology of the microstructure of all composites showed the retention and uniform distribution of G and RHA particles in the Al matrix devoid of presence of harmful aluminium carbide with improved mechanical properties. The study established a new approach of dispersing graphene in molten aluminium through a stir cast method with 150 µm particle size of RHA given the best mechanical and morphological properties.

1. Introduction

Aluminium is the most commonly used matrix for the metal matrix composites (MMCs) as a result of several beneficial physical and mechanical properties [1-4]. The alloys are quite appealing due to their low density, their capability to be strengthened by precipitation, high thermal and electrical conductivity, their good corrosion resistance and their high damping
capacity. However, defects such as low temperature capability, high thermal expansion coefficient and inadequate mechanical and tribological characteristics limit the use of monolithic aluminium alloy in automobile and aerospace industries.

Reinforcement increases strength, stiffness, temperature resistance capability, but generally lowers the density of metal matrix composites. The prime role of reinforcement is to carry the load that of the matrix to transfer the load to the fibres with maximum efficiency. Sometimes, the reinforcement surface can be coated to prevent a chemical reaction with the matrix. Common reinforcements are silicon carbide (SiC), alumina (Al₂O₃), titanium carbide (TiC), barium carbide (B₄C), barium (B), graphite, graphene, rice husk ash among others. Reinforcement are generally tailored to have superior properties such as high specific strength and stiffness, increased wear resistance, corrosion resistance, improved thermal shock resistance, increase in Young’s modulus and enhanced high temperature performance, better mechanical fatigue and creep resistance than those of monolithic alloys [5].

It has been affirmed that graphene is the strongest material ever measured to have the highest stiffness, the crystal most elastic and most thermally conductive material [6, 7]. Production of Al composite from graphene despite its influence on mechanical and thermal properties is confronted with many challenges especially where increase in tensile property of the composite is required.

A serious challenge is that, carbon nanomaterials like graphene are initially entangled or agglomerated via Van der Waal bonds, and hence they are not easily dispersed in the melt of the Al matrix. The use of solid-state techniques therefore has been considered as more promising routes, thus enabling mechanical dispersion of such nano-materials into metals via severe plastic deformation of the metal matrix [8-14]. Choi et al. [14] emphasized that without solving the critical problem in dispersion, the Giga-Pascal-level strength of the graphene would not be of importance value for automotive, aerospace and other industrial/structural composite applications.

From the foregoing, this work is aimed at solving dispersion problems in the production of aluminium/graphene composites using rice husk ash as carrier and produce Al/RHA/G composites with improved mechanical properties, devoid of harmful intermetallic compounds.
2 Materials and Methods

2.1 Preparation of casting

About 18 kg of waste aluminium cans were melted in a diesel-fired crucible furnace using 30 kg crucible pot following the procedure adopted by earlier workers [15, 16]. The rice husk ash was produced by calcinating the rice husk in a muffle furnace at about 700 °C for about 2 h. The husk was well lagged with cotton wool to prevent excessive oxidation. The ash was sieved and graded into three particle sizes (150, 300 and 600 µm) (Figure 1). Graphene powder (NanoCarbon platelets) was purchased from Graphitene Ltd., Manchester United Kingdom. The powder has thickness less than 5 µm and lateral size ranging between 0.5-5 µm [15].

Two blends of composites namely: Al/RHA and Al/RHA/G were produced according to literature [15,16] from recycled aluminium alloy, rice husk ash particulate between 150-600 µm at 1.6 wt.% and 0.4 wt.% graphene of less than 5 µm particle size. Each blend of composites was mixed in accordance with the design of experiment in a fuel fired crucible furnace melted to 750 ± 2 °C. The particulates were preheated to 600 °C for three hours before dispersing into the molten bath of Al and stirred for homogeneity using a developed and improvised motorized mobile stirrer at 140 rpm for 2 min. The molten bath was poured into a pre-heated mould coated permanent die cavity steel mould and allowed to cool to room temperature before knockout. The cast samples produced were characterized using scanning electron microscope (SEM) and X-ray diffractometer (XRD). Furthermore, the cast were machined in accordance with ASTM standards into appropriate coupon for density measurement and analyses of tensile, impact, fatigue and hardness properties.

2.2 Preparation of test specimens

The microstructures were studied using scanning electron microscope equipped with an Oxford INCA™ energy dispersive spectroscopy system using a polished sample firmly held on the sample holder of a double-sided carbon tape before putting the inside the sample chamber. The SEM operation was carried out at an accelerating voltage of 5 to 20 kV. The operation was carried out at Spectrum Analytical Facility, Department of Physics, University of Johannesburg, South Africa.
XRD analyses with Cu-Kα radiation monochromatic multilayered mirrors were used for the analysis, using a PANalyticalX'Pert PRO. The machine was operated at a voltage of 45 kV and 40 mA current. A Rietveld refinement software, TOPAS™ was used to quantitatively analyze the results.

Specimens of dimensions 50 × 10 × 10 mm were prepared to determine the density. Digital Pioneer weighing balance by Ohaus Corporation, USA was used to determine the mass while the volume was obtained by Archimedes principle using graduated measuring cylinder. The rise in volume of water was recorded and used together with the mass to calculate the densities using equation 1.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$  \hspace{1cm} (1)

The Vickers diamond test was carried out using LECO AT700 micro hardness tester at University of Lagos. A fine-grained emery polishing papers was used to prepare the samples for accurate measurement of microhardness. The specimen was further prepared using phenolic powder, grinded and then polished to produce a hardness specimen with a smooth surface finish. Then, applied load of about 50 Kg was used to indent the specimen with a dwelling time of about 10 seconds at three different positions on the specimen noting the depth of indentation to obtain the microhardness of each specimen.

Tensile test was conducted using Instron Extensometer, (model: Instron 3369), system ID: 3369S3457 at Engineering Materials Development Institute (EMDI) of Akure, Ondo State, Nigeria. The tensile test specimen was prepared in accordance with the American Society for Testing and Materials E8.

The impact energies of the control and produced composites were determined using aids of Avery Denison Universal Impact Testing Machine at Mechanical Engineering Department, University of Lagos. Specimen was prepared in accordance to ASTM A370.

Fatigue test was measured using SM 1090 Rotating Fatigue Machine at Department of Mechanical Engineering, Lagos State Polytechnic, Ikorodu. Specimen was prepared in line with ASTM E466 standard for fatigue measurement.
Figure 1. Graded rice husk ash into (a) 150 (b) 300 and (c) 600 µm

3. Results and Discussion

3.1 Compositional Analysis

The elemental composition of the unreinforced aluminium alloy sample as obtained from the spectrometric analysis shown in Table 1 revealed that the waste aluminium can is very rich in aluminium with reasonable amount of Zn, Cu, Ti and Si. These elements are expected to greatly influence the phase reactions at various particle sizes, including physical and mechanical properties of the developed composites. Table 2 shows the results of X-ray fluorescence (XRF) analyses of the rice husk ash. Oxides like SiO₂, Al₂O₃ and Fe₂O₃ present in the ash could make the matrix harder and more durable and therefore result in improved physical-mechanical properties of the composites. Al₂O₃ and SiO₂ as previously stated [17-18] are well-known reinforcing additives for improving wear resistance and strength for Al composites. CaO could react with alumina and silica to form aluminates and calcium silicates, which have good adhesive properties and improve the load bearing capability of the composites. The presence of MgO which is a refractory material, can improve the high temperature capability with low thermal conductivity [19]. Formation of several intermetallic compound is also expected in the XRD analysis due to chemical reactions between these elements/compounds and Al alloy during casting.
Table 1. The elemental composition (wt.%) of the unreinforced cast aluminium alloy ingot.

|     | Al   | Si   | Fe   | Cu   | Mn   | Mg   | Zn   | P    | Ni   | Ti   |
|-----|------|------|------|------|------|------|------|------|------|------|
|     | 94.0218 | 0.825 | 0.332 | 1.065 | 0.770 | 0.0046 | 2.014 | 0.021 | 0.053 | 0.912 |
| S   | 0.016 | 0.005 | 0.0023 | 0.006 |      |      |      |      |      |      |

Table 2. Chemical compound (wt. %) composition of rice husk ash burnt at 700 °C

|     | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₂ | K₂O | Na₂O | Others | LOI |
|-----|------|-------|-------|-----|-----|-----|-----|------|--------|-----|
|     | 97.095 | 1.135 | 0.316 | 0.073 | 0.825 | 0.146 | 0.181 | 0.092 | Balance | 0.965 |

3.2 Scanning Electron Microscopy Analysis

It can be seen from Figures 2a-g that the control sample and all composites at different particle sizes showed reasonably uniform distribution and retention of RHA and G particles due to proper stirring adopted in the use of improvised mobile stirrer. The presence of reinforcements in grain refinement and reduction in porosity can be observed for all composites when compared to the control sample. The effect of particle sizes of RHA is clearly seen in all composite with micrographs of 150 µm having the fineness grain structure and fewer grain boundaries both for Al/RHA and Al/RHA/G composites. However, the effect of graphene in further refining the grain structure of the composites and the greyish colour of the matrix of all Al/RHA/G is also obvious as a result of changes in the intermetallic compounds when compared to the composites of Al/RHA.
3.3 Phase Analysis of the control sample, rice husk ash and composites

It can be seen from the XRD diffractograms (Figure 3a) of the unreinforced Al that the major diffraction peaks occurred at diffracting angles (2θ) of 38.85° and 45.07° with inter-planar distance of 2.32 Å and 2.01 Å and relative X-Ray diffracting intensities of 27756.48 and 11197.12. As a result of chemical reactions formed between aluminium and other major elements in the recycled Al cans during melting and solidification, intermetallic bond formed around Al. X-ray diffractometric profiles of RHA particulate is shown in Figure 3b such that major diffraction peaks occurred at diffracting angles (2θ) of 29.60°, 39.65°, 43.40° and 48.73° with inter-planar distance of 3.02 Å, 2.27 Å, 2.09 Å and 1.91 Å and relative X-Ray diffracting intensities of 1256.10, 355.38, 341.56 and 515.81. The phases present are in agreement with the XRF analysis of RHA.

In all composites, reactions between Al, Ti, Si, Cu, Zn and SiO₂ to form compounds are clearly seen from various intermetallic bond formed within the composites. These intermetallic compounds enhanced the mechanical properties of the composites as revealed in the mechanical test results. However, for all samples, there is a shift in the diffracting angles due to reactions of reinforcements with Al alloy. As a result, major and common diffraction peaks occurred at diffracting angles (2θ) of about 39°, 42°, 43°, 45°, 65°, 78° and 82° with inter-planar distance of about 2.05 Å, 2.15 Å, 2.09 Å, 2.03 Å, 1.43 Å, 1.22 Å and 1.17 Å.
respectively. In the combined XRD of the control sample, Al/RHA and Al/RHA/G at different particle sizes, formation of SiC from RHA was revealed at 1.6 wt. % RHA at all particle sizes with metal-metal, metal-SiC and metal-oxide inter atomic bond for Al/RHA composites. However, reaction of graphene with RHA also revealed breakdown and transformation of graphene flakes to smaller molecules called fullerene of C$_{60}$ type in all particle sizes of RHA. Al/RHA/G composites are characterized with metal-oxide, C$_{60}$-Si, metal-metal and metal-SiC atomic bonds. Phase reactions of this type go a long way to confirm that Al/RHA/G composites possess good mechanical properties when compared to monolithic Al alloy and Al/RHA composites (Figure 4).

**Figure 3.** XRD of (a) Control sample (b) Rice Husk Ash
3.4 Density and Mechanical Properties

Figure 5 shows the variation of density and mechanical properties at different particle sizes. The density of the composites of Al/RHA and Al/RHA/G increased gradually with increase in particle size when compared to the control sample (Figure 5a). However, all composites of Al/RHA/G composites have lower density than composites of Al/RHA. This occurs as a result of replacement of soft high density Al matrix with hard and low density RHA and graphene.

From Figure 5b, it is observed that the hardness increases as the particle size decreases for both Al/RHA and Al/RHA/G composites. The highest hardness obtained at 600 µm, 300 µm and 150 µm mesh sizes are 97.00 HV, 94.20 HV and 115.60 HV respectively for Al/RHA/G composites (Figure 5b).

The ultimate tensile strength according to Figure 5c decreases with increase in particle size of RHA for 150 µm, 300 µm and 600 µm mesh sizes accordingly. Al/RHA/G also showed the same trend but with higher ultimate tensile strength. These results are in agreement with the...
Hall-Petch relationship (equation 2), that the grain size is inversely proportional to tensile strength.

\[ \sigma_y = \sigma_o + KD^{-1/2} \]  

(2)

Where \( \sigma_y \) is the yield stress of the material; \( \sigma_o \) is a materials constant for the starting stress for dislocation movement of the material; \( K \) is a measure of resistance to dislocation and \( D \) is the diameter of the particulate size. As \( D \) decreases, that is decrease in particulate size, the repulsion stress felt by a grain boundary dislocation decreased and the applied stress needed to propagate dislocations through the material increased.

However, for both Al/RHA and Al/RHA/G composites, the impact energy increases with particle size. (Figure 5d). This is because the composites with the highest filler particle size showed the highest resistance to impact but with a corresponding low hardness, fatigue, yield and tensile strength values. Hence, it is recommended that for applications where impact energy is of utmost importance, increasing the particle size of the reinforcement within the composite matrix is favourable.

It can also be seen from Figure 5e that the fatigue increases as the particle size decreases. However, with addition of graphene nanoplatelets of high stiffness, the fatigue strength of the Al/RHA.G composites has further improved by about 1.2 \%. 
Solid lines represent Al/RHA

(a)

Solid lines represent Al/RHA
Dash lines represent Al/RHA/0.4G

(b)
Solid lines represent Al/RHA
Dash lines represent Al/RHA/G

Ultimate Tensile Strength in MPa

Particle Size of RHA

Impact Strength in Joules

Particle Size of RHA
3.5 Mechanism of formation of Fullerene from RHA and Graphene

Reactions between graphene, RHA and aluminium alloy after solidification did not reveal retention of graphene in its original form from the XRD results, rather, formation of fullerene of C$_{60}$ was revealed together with other intermetallic compounds. Earlier workers [20, 21] have explained the mechanism behind the formation of fullerene from graphene without addition of RHA to graphene. In this present study, formation of fullerene could be justified from modification of earlier submission [21]. That is, the reactions between amorphous carbon from RHA, graphene and aluminium alloy could have been powered by high melting temperature of about 750 °C and shear stress of mixing/stirring of the mixture in the crucible pot, coupled with high liquid phase-solid phase transformation pressure in the die cavity steel mould during casting. These reactions could have led to the breakdown of graphene to fullerene. There is also possibility of the graphene flakes used for reinforcement to have vacancy at the middle. Such graphene flakes accordingly are energetically unstable [20], and

Figure 5. Variation of density and mechanical properties with particle size of RHA
the probability of return motion back to the middle is negligible. Therefore, this effect of middle vacancy of graphene flakes together with high temperature and pressure of synthesizing RHA and graphene could have instigated the etching of graphene for subsequent transformation to proceed to formation of fullerene in line with the mechanism earlier suggested [21]. It was also asserted that oxidation of porous structure of RHA may occur during synthesis process due to high temperature which makes the mixture to be highly reactive [22]. Thus, confirming the ability of rice husk ash to react very actively with graphene when heat and temperature act as catalyst. The mechanisms for such transformation are described as shown in Figure 6.

That is, **rice husk ash (amorphous carbon) + graphene (carbon nanoplatelets) → fullerene**

Choi *et al.* [14] affirmed that fullerenes with a spherical structure may possibly be considered a more fascinating reinforcing agent when compared to carbon nanotubes or graphene, as a result of their zero-dimensional geometric characteristics. This is because they could easily disperse and difficult to destroy during severe mechanical dispersion processes in the metal matrix. This was further corroborated by earlier workers [23] that improvement of yield strength of aluminium from 150 to 250 MPa by reinforcing fullerenes via severe plastic deformation is possible. Khalid *et al.* [24] also developed aluminium-based composites by liquid metal infiltration technique, where the micrographs of the composites revealed good interfacial bonding between aluminium and fullerenes but with mechanical properties of the composites still below the theoretical expectation when compared to the actual stiffness/strength of fullerenes.
**Figure 6.** Modified mechanisms of formation of fullerene from rice husk ash and graphene [21].
4. Conclusion

Aluminium alloy was successfully cast from recycled waste aluminium cans and reinforced with RHA of different particle sizes and graphene to produce Al/RHA/G composites by stir casting technique. The morphology of the composites showed that the reinforcements were uniformly dispersed to give composite castings with isotropic grain structure. The phase analysis revealed composite castings with inter atomic bond showing no formation of harmful aluminium carbide. The best morphological and mechanical properties of Al/RHA/G composites were obtained from RHA having 150 µm particle sizes, therefore the most suitable to disperse graphene freely in molten aluminium. Modified mechanisms of formation of fullerene from rice husk ash and graphene was developed. The mechanical properties of the Al/RHA/G greatly improved when compared to the control sample and Al/RHA composites.

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