Journal of King Saud University – Engineering Sciences (2015) 27, 49–56

King Saud University

Journal of King Saud University – Engineering Sciences

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ORIGINAL ARTICLE

Effects of eggshell on the microstructures and properties of Al–Cu–Mg/eggshell particulate composites

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Received 13 January 2013; accepted 11 March 2013
Available online 20 March 2013

KEYWORDS

Eggshell;
Metal matrix composite;
Mechanical and physical properties

Abstract The effects of eggshell particles (ES) on the microstructures and properties of Al–Cu–Mg/ES particulate composites have been studied. A total of 2–12 wt.% ES particles were added. The microstructures of the Al–Cu–Mg/eggshell particulate composites produced were examined by a scanning electron microscope with energy dispersive spectrometer (SEM/EDS). The physical and mechanical properties measured included: density, tensile strength, hardness values and impact energy. The results revealed that the tensile strength increased by 8.16% at 12 wt.% uncarbonized ES and 14.28% at 12 wt.% carbonized ES, the hardness values increased by 10.01% at 12 wt.% uncarbonized ES and 25.4% at 12 wt.% carbonized ES with decrease in the density by 6.50% at 12 wt.% uncarbonized ES and 7.4% at 12 wt.% carbonized ES. The impact energy decreased by 23.5% at 12 wt.% uncarbonized ES and 24.67% at 12 wt.% carbonized ES particles, respectively. These increases in strength and hardness values are attributed to the distribution of hard phases of the ES particles in the ductile Al–Cu–Mg alloy matrix. These results showed that using the carbonized eggshell as reinforcement in the Al–Cu–Mg alloy gives better physical and mechanical properties as compared to uncarbonized ES particles. Hence addition of ES particles upto 12 wt.% can be used as a low cost reinforcement for the production of metal matrix composites for engineering applications.

1. Introduction

Metal-matrix composites (MMCs) have emerged as a class of materials capable of advanced structural, aerospace, automotive, electronic, thermal management and wear applications. The performance advantage of metal matrix composites is their tailored mechanical, physical and thermal properties that include low density, high specific strength, high specific

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jksues.2013.03.001

modulus, high thermal conductivity, high abrasion and wear resistance (Aigbodion and Hassan, 2007; Naresh, 2006; Kin et al., 1995).

The ever-increasing demand for low cost reinforcement stimulated the interest towards production and utilization of using by-products from industry as reinforcement since they are readily available or are naturally renewable at affordable cost. (Aigbodion, 2007) have used Kankara clay(alumino-silicate) in reinforcing Al–Si alloy, (Bienia et al., 2003) used fly ash in the reinforcement of aluminium matrix, (Naresh, 2006), worked on the development and characterization of metal matrix composite using red mud an industrial waste for wear resistant applications, they all reported good dispersion and recovery of the particles in the composites castings.

Previous studies have proved that Chicken eggshell (ES) is an aviculture byproduct that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the U.S. alone, about 150,000 tons of this material is disposed in landfills (Shuhadah et al., 2008). ES contains about 95% calcium carbonate in the form of calcite and 5% organic materials such as type X collagen, sulfated polysaccharides, and other proteins (Shuhadah et al., 2008; Patricio et al., 2007; Hussein et al., 2011). Although there have been several attempts to use eggshell components for different applications, its chemical composition and availability makes eggshell a potential source of filler in polymer composites (Shuhadah et al., 2008; Patricio et al., 2007; Hussein et al., 2011). Report has shown, among other characteristics that ES has a relatively lower density compared to the mineral calcium carbonate. Egg shell is a biomaterial containing 95% by weight of calcium carbonate in the form of calcite and 5% by weight of organic materials, such as (Al2O3, SiO2, S, Cl, P, and Cr2O3, MnO) (Hussein et al., 2011).

The generalized egg shell structure, which varies widely among species, is a protein lined with mineral crystals, usually of a calcium compound such as calcium carbonate These characteristics qualify ES as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories.

(Patricio et al., 2007), studied ES, a new bio-filler for polypropylene composites. The work proved that ES composites showed lower modulus of elasticity (E) values than talc composites, talc filler could be replaced by upto 75% with ES while maintaining a similar stiffness and E compared to the talc composites.

(Hussein et al., 2011) studied the water absorption and mechanical properties of high – density polyethylene/ ES composite, It was found that the addition of egg shell powder to the polymer leads to decrease in the tensile strength, modulus of elasticity and shore-D hardness. On other hand it increases the % elongation at break and impact strength. Water absorption of the composites behaviour as function of days was also investigated, and it increases by increasing exposure time for the same filler content, while the absorbed amount of water increases, by increasing the wt.% of ES constant exposure time. The potential of using eggshell particles as a reinforcer in metal matrix has not been explored. It is in the light of the foregoing researches that investigation into the possibility of using eggshell in metal matrix particulate composite for engineering applications was motivated.

2. Experimental procedure

2.1. Materials/equipment

The ES used in this work was brown ES, obtained from a local tea seller around the Samaru area of Zaria in Kaduna-State, Nigeria, High purity aluminium electrical wires obtained from Northern Cable Company NOCACO (Kaduna), Nigeria, copper, magnesium, Moulding box silica sand, and Bentonite were purchased from a chemical shop in Kaduna, Nigeria. The ES was washed with water and sun dried to remove the membranes (see Fig. 1).

The equipment used in this study included: Pyrometer, Ball milling machine, mechanical stirrer, crucible, electrical resistance furnace, Frank Well test Rockwell Hardness Tester, model 38506, Avery Denison Charpy impact machine, Tinus Olsen tensile machine, JEOL JSM 5900LV Scanning electron microscope (SEM) with e n e r g y dispersive X-ray spectroscopy (EDS).

Figure 1 Photograph of eggshell.

Figure 2 Photograph of eggshell particles uncarbonized.

Figure 3 Photograph of eggshell particles carbonized.

2.2. Method

The dried ES was ball milled at 250 rpm into ES powder (uncarbonized particles)(see Fig. 2), the powder particles were packed in a graphite crucible and fired in an electric resistance furnace at a temperature of 1200 °C to form ES ash(carbonized particles)(see Fig. 3). The particle size analysis of the ES particles was carried out in accordance with BS1377:1990 (Shuhadah et al., 2008). The ES particles were placed onto a set of sieves arranged in descending order of fineness and shaken for 15 min which is the recommended time to achieve complete classification, the particle that was retained in the BS. 100 μm was used in this study.

The composite used in this study was Al-Cu-Mg/ES particles composite containing 2–12 wt.% ES particles (Uncarbonized and Carbonized) at an interval of 2 wt.%. The samples were produced using the double stir-casting method (Aigbodion and Hassan, 2007; Aigbodion, 2010) by keeping the percentage of copper and magnesium constant (3.7% Cu and 1.4% Mg) according to the recommended standard to produce an alloy of type A2009. A control sample without the ES particles was also produced. A preheated sand mould was used to produce cast bars. After casting, the samples were machined into tensile, impact and hardness test samples for the purpose of determining the mechanical properties.

The microstructure and the chemical compositions of the phases present in the eggshell particles and composite test samples were studied using a JEOL JSM 5900LV Scanning Electron Microscope equipped with an Oxford INCA™ Energy Dispersive Spectroscopy (EDS) system. The basic method of determining the density of a sample by measuring the mass and volume of the sample was used.

The hardness values of the samples were determined (ASTM E18-79) (Rajan et al., 2007) using the Rockwell hardness tester on "*F*" scale (Frank Well test Rockwell Hardness Tester, model 38506) with a 1.56 mm steel ball indenter, minor load of 10 kg, and major load of 100 kg and a hardness value of 101.2HRF as the standard block (Rajan et al., 2007; Siva Prasad and Rama Krishna, 2011).

The tensile properties of the as-cast composites sample were conducted on a Tinus–Olsen tensile testing machine with a strain rate of $2 \times 10{-}3\ S{-}1$. The test pieces were machined to the standard shape and dimensions as specified by the American Society for testing and materials.

The impact test of the as-cast composites sample was conducted using a fully instrumented Avery Denison test machine. Charpy impact tests were conducted on notched samples. Standard square impact test sample measuring 75 × 10 × 10 mm with notch depth of 2 mm and a notch tip radius of 0. 02 mm at an angle of 45° was used (Aigbodion and Hassan, 2007; Aigbodion, 2010).

3. Results and discussion

The microstructure of the ES particle (Uncarbonized and Carbonized) reveals that the size and shape of the particles vary; however, they consist of porous irregular shaped particles.

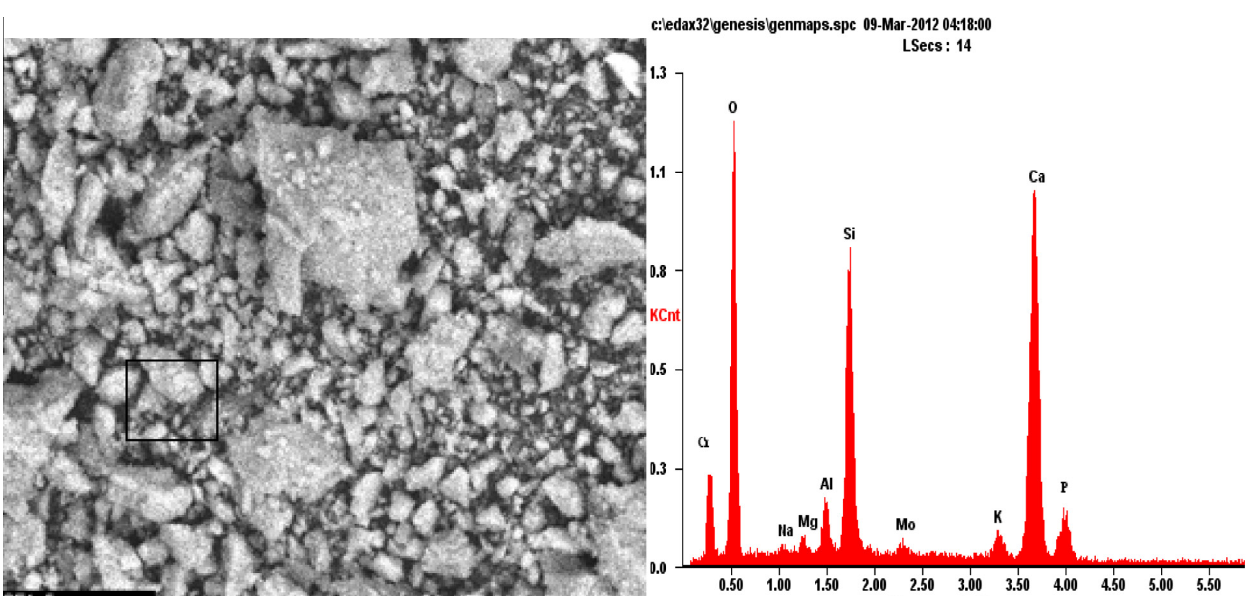

Figure 4 SEM/EDS microstructure of the uncarbonized eggshell particles.

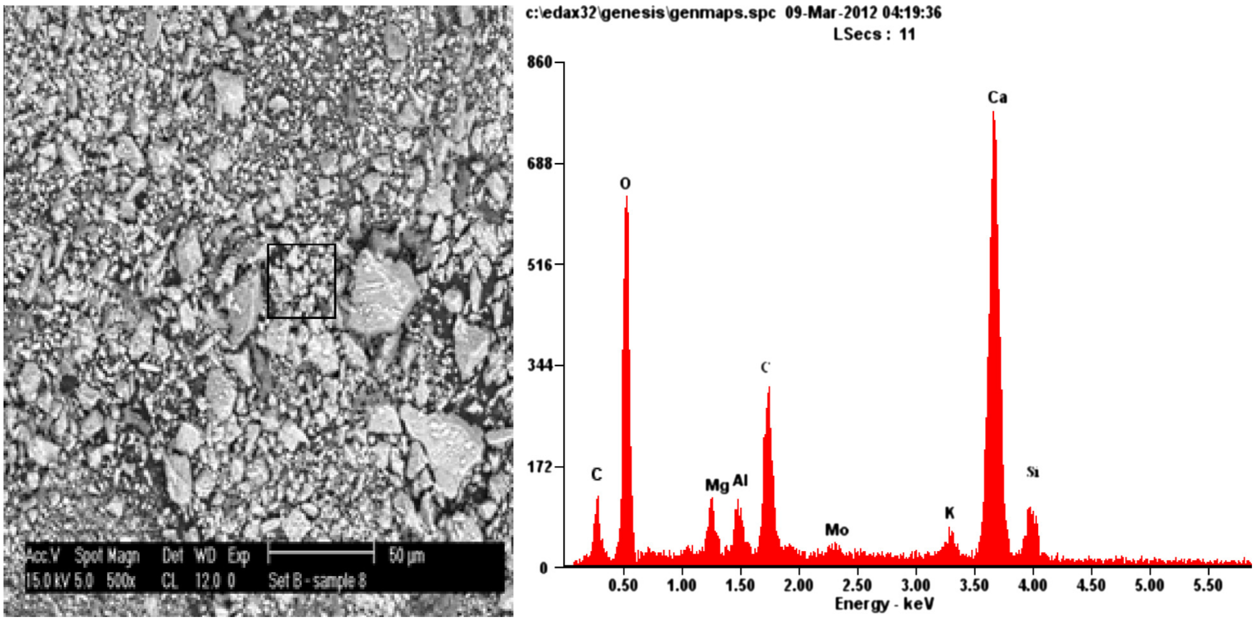

Figure 5 SEM/EDS microstructure of the carbonized eggshell particles.

The EDS of the ES particles reveals that the particles contain Ca, Si, O, C, Mg, p with the presence of C in the carbonized eggshell particles. The carbon presence is due to the carbonization process (see Figs. 4 and 5). These elements confirm that, the ES particles consists of calcium carbonate in the form of calcite ($CaCO_3$), the carbonized ES have carbon in graphite form etc. These analyses are in par with others analysis of reinforcement used by other authors (Kin et al., 1995; Shuhadah et al., 2008; Patricio et al., 2007; Hussein et al., 2011).

The microstructure of the unreinforced Al–Cu–Mg alloy is shown in Fig. 6. The structure reveals the eutectic phase containing Cu_3Al_2, Al_6CuMg_4 in α-aluminium matrix (Aigbodion, 2010). In the Al–Cu–Mg alloy, Cu and Mg are present both in solid solution as well as in precipitated form as Cu_3Al_2, and Al_6CuMg_4 phases both in the grain and along the grain boundaries (see Fig. 6).

Figs. 7–10 shows the microstructure of the reinforced alloy with ES particle additions. The microstructure reveals that there are reasonably uniform distributions of ES particles in the metal matrix. The ceramic phase is shown as a dark phase, while the metal phase is white (see Figs. 7–10). The distribution of ES particles is influenced by good wettability of the ES particles by the molten metal and good interfacial bonding between particles and matrix material. Good retention of the eggshell particles was clearly seen in the microstructures of the composites. The eggshell particles are well distributed along the grain boundaries of the microstructures of the composites.

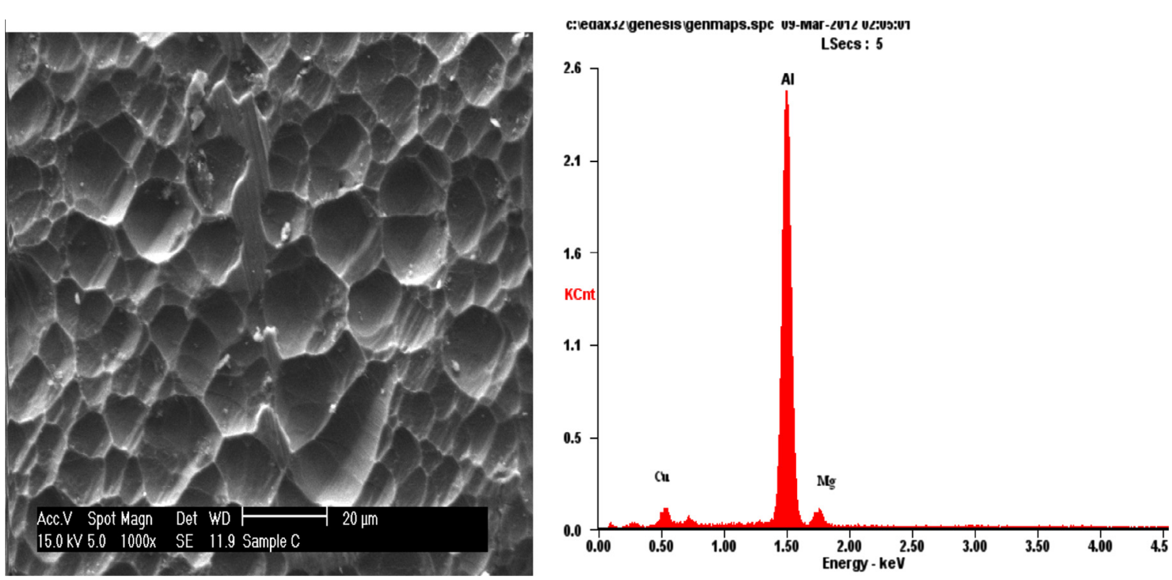

Figure 6 SEM/EDS Microstructure of Al–Cu–Mg alloy.

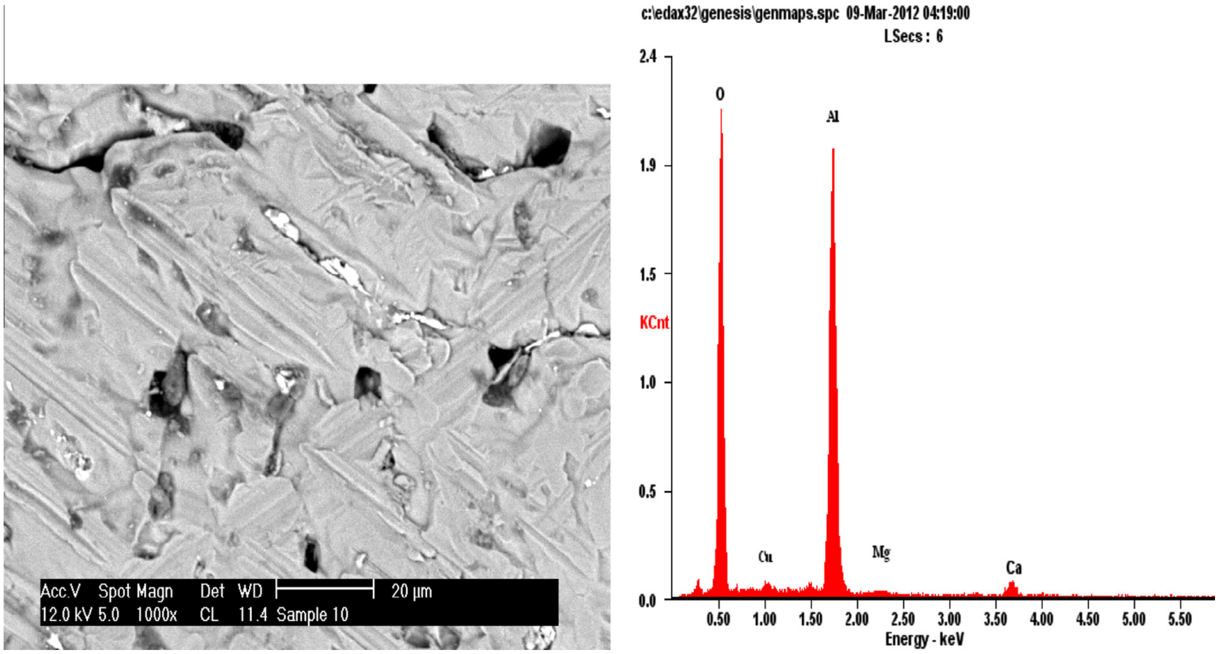

Figure 7 SEM/EDS microstructure of 2 wt.% uncarbonized eggshell particles reinforced Al–Cu–Mg alloy.

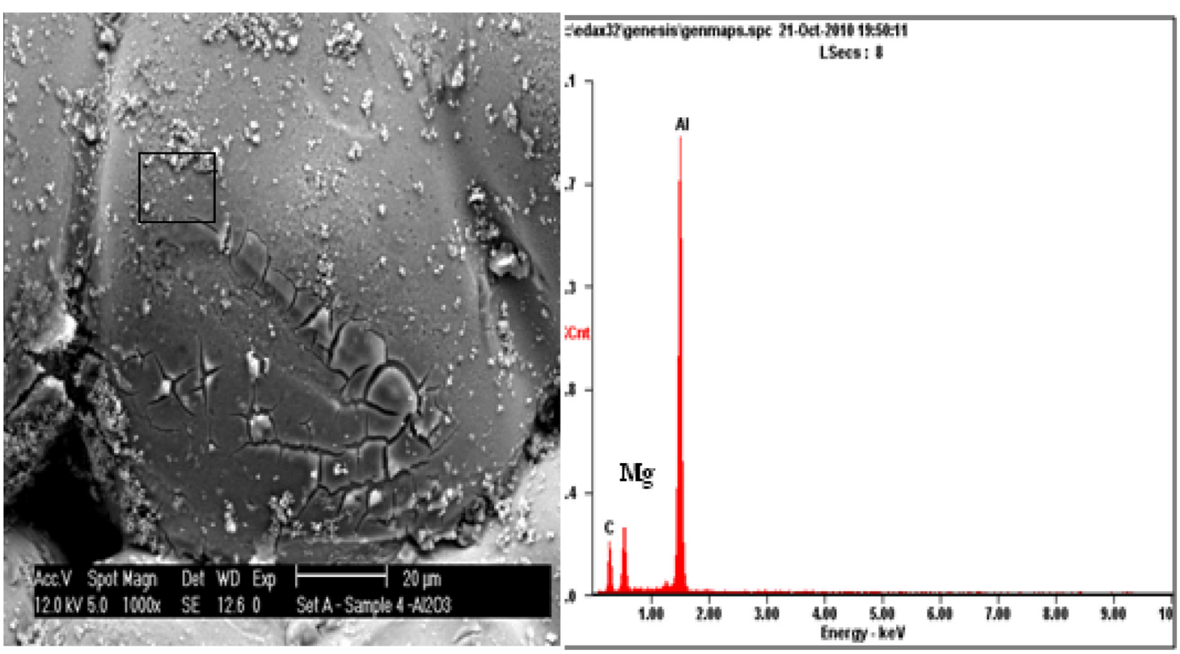

Figure 8 SEM/EDS microstructure of 2 wt.% carbonized eggshell particles reinforced Al–Cu–Mg alloy.

It should be noteworthy, that the grain size of the matrix alloy is somewhat larger than that of the composites. Figs. 7–10, clearly reveal minimal micro porosities in the casting. No clustering of reinforcements was observed in the matrix, and the dispersion of eggshell particles was seen to be almost uniform. No gap is observed between the particle and matrix and reinforcing materials are seen well bonded with the matrix.

The Al–Cu–Mg alloy reveals the presence of α – A l, Cu and Mg as evident from the EDS spectra (see Fig. 6). From the EDS analysis of the composites material (see Figs. 7–10) there is indication of some possible chemical reaction between aluminium melt and ES particles which led to the release of Si, Na, O, C and Ca etc., in the composites(see Figs. 4 and 5). These constituents react with Al and Cu present in the molten matrix alloy depending on the kinetics of reactions. It should be noted that the presence of the carbonized ES particles results in a much smaller grain size in the cast composites compared to uncarbonized ES cast composites. This could be

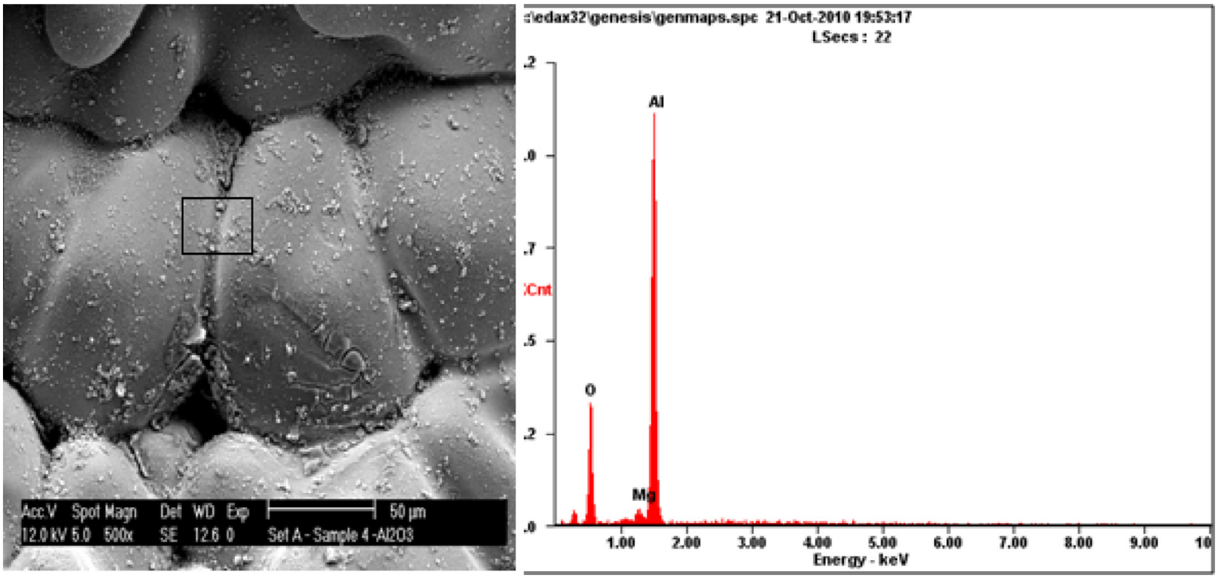

Figure 9 SEM/EDS microstructure of 8 wt.% uncarbonized eggshell particles reinforced Al–Cu–Mg alloy.

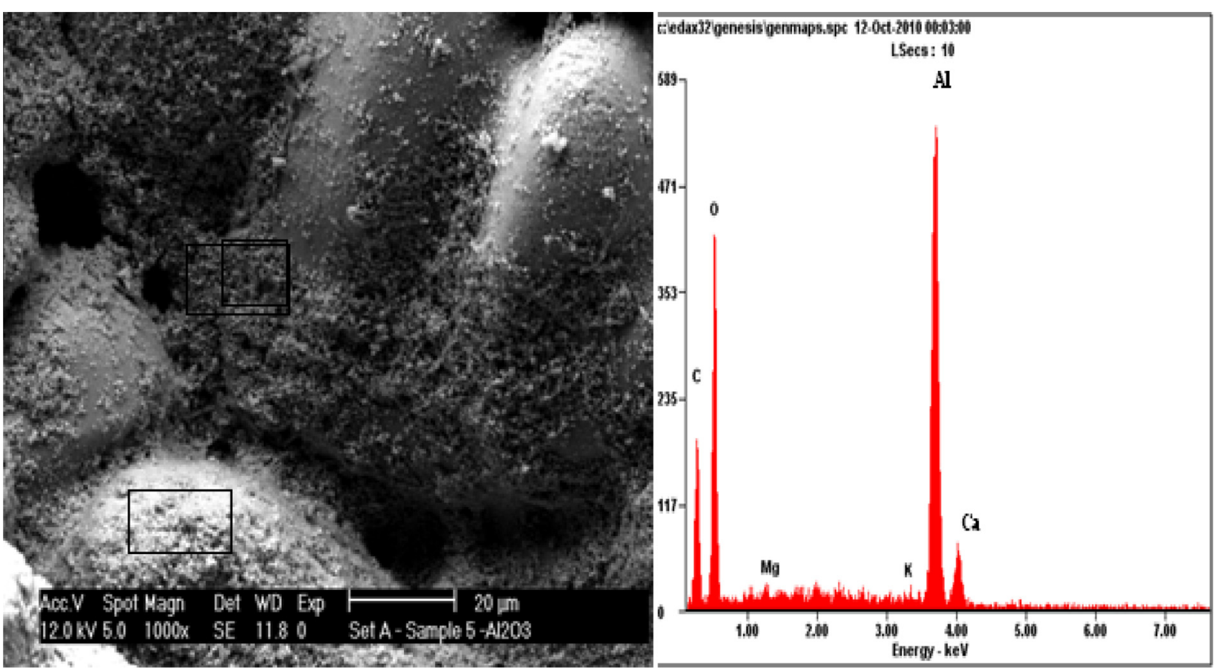

Figure 10 SEM/EDS microstructure of 8 wt.% carbonized eggshell particles reinforced Al–Cu–Mg alloy.

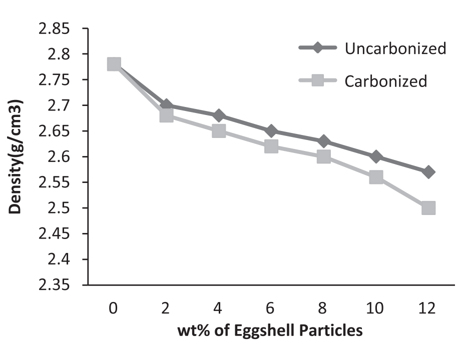

Figure 11 Variation of density with wt.% of eggshell particle.

attributed to the great fineness and smaller particles of carbonized ES than uncarbonized ES particles (see Figs. 4 and 5).

The density decreased with increasing percentage additions of ES particles (see Fig. 11). The densities of uncarbonized and carbonized ES particles were 2.47 and 1.98 g/cm^3, respectively. The overall density of Al–Cu–Mg/ES particulate composites decreased with wt.% additions of ES particles e.g., the density of the composites decreased from 2.78 g/cm^3 at 0 wt.% to 2.57 g/cm^3 and 2.50 g/cm^3 at 12 wt.% for uncarbonized and carbonized ES particles, respectively. This shows that composites with light weight can be made with ES. This is in agree-

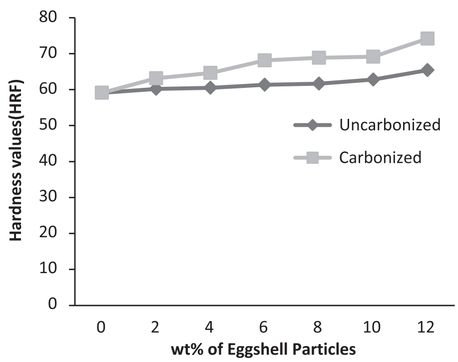

Figure 12 Variation of hardness values with wt.% of eggshell particles.

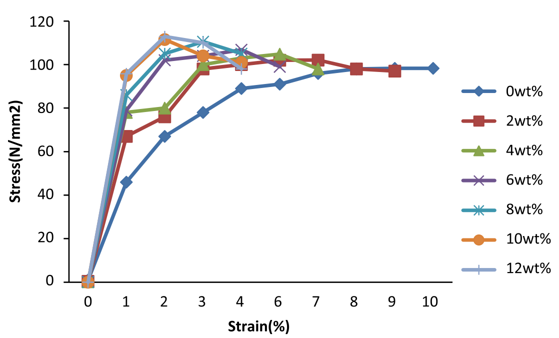

Figure 13 Variation of stress–strain curve for composites with carbonized eggshell.

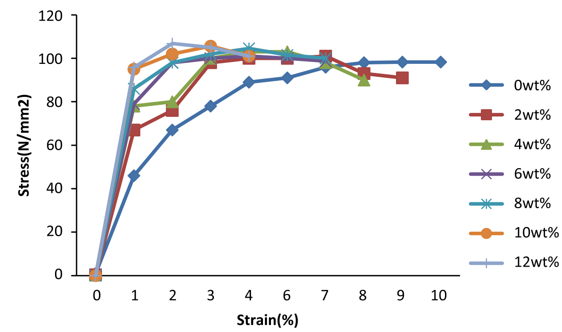

Figure 14 Variation of stress–strain curve for composites with uncarbonized eggshell.

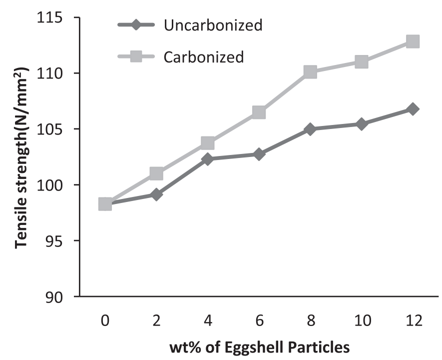

Figure 15 Variation of tensile strength with wt.% of eggshell particles.

ment with the earlier work of (Aigbodion, 2010) and (Rajan et al., 2007).

The hardness values increased as the weight percentage of ES particles addition increased in the Al–Cu–Mg alloy (see Fig. 12). For example the hardness values increased from 59.12HRF at 0 wt.% to 65.41HRF at 12 wt.% for uncarbonized ES particles and 74.17HRF at 12 wt.% for carbonized ES particles respectively. These increments are attributed to an increase of the weight percentage of hard and brittle phases of the ES particles in the Al–Cu–Mg alloy. This hardness of the ES particles is obtained from $CaCO_3$, C and SiO_2 of the chemical made up of the particles (Patricio et al., 2007; Hussein et al., 2011). Also the presence of eggshell particles in the Al-Cu-Mg alloy increases the dislocation density at the particles-matrix interfaces. This is a result of differences in the coefficient of thermal expansion (CTE) between the hard and brittle reinforced particles and soft and ductile metal matrix which results in elastic and plastic incompatibility between the matrix and the reinforcement (Aigbodion and Hassan, 2007; Aigbodion, 2010; Rajan et al., 2007; Siva Prasad and Rama Krishna, 2011). This is in par with the work of Naresh(Naresh, 2006) and Aigbodion(Aigbodion, 2010).

The stress–strain curves are shown in Figs. 13 and 14. The tensile strength increased with increasing percentage of ES particles in the Al–Cu–Mg alloy (see Figs. 13–15). For example the tensile strength increased from 98.28 N/mm^2 at 0 wt.% to 106.79 N/mm^2 and 112.84 N/mm^2 for uncarbonized and carbonized ES particles, respectively. The increases in tensile strength with percent ES particle additions are due to the formation of nearly uniform distribution of ES particles in the Al–Cu–Mg alloy matrix (Aigbodion, 2010). The dispersion of ES particles in a soft ductile Al–Cu–Mg alloy matrix results in improvement in strength (Aigbodion, 2007). Improvement in tensile strength may be due to the matrix strengthening that might have occurred following a reduction in composite grain size and the generation of a high dislocation density in the matrix as a result of the difference in coefficient of thermal expansion between the matrix and reinforcements (Bienia et al., 2003; Siva Prasad and Rama Krishna, 2011). Wettability is one of the dominating factors to ensure good bonding between the matrix and reinforcement (Arun Kumar and Swamy, 2011). A good bonding between reinforcement and soft aluminium matrix favours an enhancement of the ultimate tensile strength of the composite (Arun Kumar and Swamy, 2011).

It is found that the addition of ES particles has a significant effect on the tensile properties. The addition of the ES particles increases strength mainly by the load transfer from matrix to the reinforcement due to the differences in the elastic constants. It is noteworthy, that the composites with carbonized ES particles have a higher tensile strength than the composites with uncarbonized ES particles, this is attributed to the great fineness of the carbonized ES particles which resulted in more uniform distribution in the microstructures of the Al–Cu–Mg/carbonized ES particulate composites. Hence, the more the grain sizes/particles in the microstructures of the composites, the more the obstacles to dislocation movement which resulted in a higher strength of Al–Cu–Mg/ carbonized ES particulate

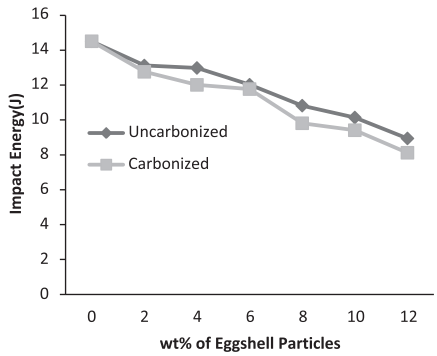

Figure 16 Variation of impact strength with wt.% of Eggshell particles of figures.

composites than that of the Al–Cu–Mg/ uncarbonized ES particulate composites.

The impact energy decreases as the percent eggshell particles addition increases in the composites (see Fig. 16). The brittle nature of the reinforcing materials (ES) plays a significant role in degrading the impact energy of the composites. On the other hand, as can be suggested from the impact test, the elastic behaviour of the matrix proportionately varies with the addition of the ES particles (see Figs. 13 and 14). As the loading of ES particles increases, the ability of the composites to absorb impact energy decreases since there is less ratio of the matrix to particles. However the results obtained remained within the standard level (Aigbodion, 2010).

However, the properties obtained with Al–Cu–Mg/carbonized ES particulate composites showed higher values than Al–Cu–Mg/uncarbonized ES particulate composites, this can also be attributed to the volatile matters and moisture that are given off during carbonization. This may also account for the poor distribution and dispersion of the uncarbonized ES particles in the Al–Cu–Mg alloy matrix resulting in weak-particles-matrix interaction (Rajan et al., 2007). This poor particles dispersion will reduce the particles-matrix interaction and consequently decreases the ability of the uncarbonized ES to restrain gross deformation of the Al–Cu–Mg matrix.

4. Conclusions

From the results and discussion in this work, the following conclusions can be drawn:

ES particles were successfully incorporated in Al–Cu–Mg alloy by using the stir casting technique. The microstructure analysis shows the uniform distribution of ES particles in the aluminium alloy. The microstructure also revealed good retention of carbonized ES particles in the matrix. The uniform distribution of the ES particles in the microstructure of the composites is the major factor responsible for the improvement in the mechanical properties.

The addition of ES particles reinforcement to Al–Cu–Mg alloy increased the tensile strength, the hardness value of the Al–Cu–Mg/ES particulate composites with a slight reduction in impact energy. The increase in strength and hardness was the result of the increase in the amount of the hard ES phase in the ductile metal phase which leads to increase in dislocation density at the matrix-particle interphase.

Incorporation of ES particles in the aluminium matrix can lead to the production of low cost aluminium composites with improved hardness and strength. These composites can find applications in automotive components like pistons, cylinder liners and connecting rods as well as applications where light weight materials are required with good stiffness and strength.

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