Study of microstructure and wear properties of novel aluminium-modified fly ash composite

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Abstract. Aluminium matrix composites (AMCs) were prepared by compocasting route by melting AA 1200 aluminium alloy in a stir casting furnace and adding 2, 4, 6 and 8 wt. % (weight percentage) of modified fly ash (FA). Modified FA was synthesized by treating FA with graphite and magnesium powder in the ratio of 1:1:2.5 at 650°C in nitrogen atmosphere. X-ray diffraction (XRD) analysis of modified FA showed peaks of MgO, MgO₂Si, Mg₃Si and SiC in addition to the peaks of SiO₂, Al₂O₃Si and AlPO₄ present in FA. Tapped density of the modified FA was found to be 0.69 g/cm³. Optical microscopy studies on the cast composites showed segregation of modified FA particles at the grain boundaries. Hardness measurement showed that the hardness of the composite increased with increase in the amount of modified FA. Pin-on-disc wear studies revealed that the wear rate of the composite increased with the increase in the amount modified FA. At 8 wt. % modified FA, the wear rate was found to decrease drastically. The increase in wear rate was correlated to the improper bonding between the particles and the matrix phase due to segregation of particles as confirmed by optical microscopy. The wear process was slowed down with increasing amount of reinforcement due to the prevalent abrasive wear mechanism as the particles dislodged during wear process.

1. Introduction

Aluminium has high strength to weight ratio due to which it is widely used in various applications. However, the tribological properties of aluminium alloys are poor. Therefore, hard ceramic particles are often used as reinforcement in aluminium to improve its wear resistance. Aluminium matrix composites (AMCs) are light weight and have high strength, wear resistance and hardness. They are finding widespread usage in aerospace and automotive industries to improve fuel efficiency and reduce emissions by reducing the weight of the vehicle [1-5].

Research activities on AMCs are focussed on incorporating different type of ceramic particles to improve the mechanical properties of the composites [6-8]. More recent research is on utilizing industrial and agricultural waste as reinforcement in AMCs. The advantage of using these waste products is lowering the cost and addressing ecological concerns at the same time.

In the past few decades several researchers have used fly ash (FA) as reinforcement in AMCs [9-10]. This is because fly ash is available abundantly as a by-product in thermal power plants [1]. The major constituents in fly ash are SiO₂, Al₂O₃ and Fe₂O₃ [1,11]. However, compared to oxides, carbides are known to have higher hardness and therefore produce superior wear resistance properties [3]. Knowing the advantage of using carbides as reinforcement, in the present work, the authors have made a novel attempt to synthesize SiC from SiO₂ present in FA. Many authors have reported the advantage of hybrid composites where a combination of agro-waste/industrial waste and carbides like B₃C [12] SiC [4, 13-14] is used as reinforcement. In the present work, it was anticipated that the beneficial effect of hybrid reinforcement would be obtained.
The conventional methods of SiC production require very high temperature [15-18]. On the other hand, metallothermic reaction is exothermic in nature and therefore can be carried out at much lower temperatures [15]. Therefore, in the present work, the reduction of SiO₂ present in FA was carried out by magnesiothermic reaction which is a metallothermic reaction with Mg as the reducing agent. In this way, the authors intended to obtain the beneficial effects of both SiO₂ and SiC.

Stir-casting is a widely accepted casting route for production of AMC due to its lower production cost, large scale production and simple process [5, 19-20]. The production cost of the AMC can be brought down further if this method is used along with the use of FA as reinforcement. Since the light weight FA particles have a high probability of rejection from the melt, compo-casting route seems to a suitable method where the particles are added to the melt in semi-solid state for homogeneous distribution [19-21]. Therefore, the production of AMC in the present research was carried out using stir-casting and compo-casting route. A detailed microstructural characterization, hardness and wear studies of the cast composites were carried out.

2. Experimental procedure
2.1. Synthesis of modified FA and its characterization
The FA powder was obtained from Kanakpura power plant in Bengaluru, Karnataka as shown in figure 1(a). It was mixed with graphite and magnesium (in the ratio of 1:1:2.5) and made into pellets using ethanol (as shown in figure 1(b)). The graphite powder used was synthetic graphite, sigma-aldrich make of <20 μm size and the magnesium metal powder (Rolex make) was of 50-150 mesh size. The pellets were dried at 120°C for 3 hours in an electric oven. After drying, weight of the pellets was determined. Meanwhile, the tubular furnace was evacuated of air for 30 minutes using nitrogen gas. The pellets placed in alumina trays were inserted inside the furnace tube and the furnace was sealed. The furnace was heated to 650°C at a heating rate of 150°C/hour and held at that temperature for 1 hour followed by cooling to room temperature. The entire process was carried out in nitrogen atmosphere. The weight of the modified FA, thus obtained, was determined.

Phase identification of FA and modified FA was carried out using a Bruker D2 PHASER X-Ray diffractometer. The X-Ray Diffraction (XRD) measurements were performed in the 2θ range of 10-90° by powder diffraction method using Cu Kα target (1.54 Å) at a scan rate of 0.03°/s. The morphology, particle size and elemental composition of FA were determined using Scanning Electron Microscope (SEM) attached with energy dispersive spectroscopy (EDS) (Tescan make, Vega 3). Tapped density of FA was determined by tapping a graduated cylinder containing the powder until no further volume change took place. The tapped density was calculated as mass divided by the final volume of the powder.

2.2. Casting of aluminium-modified FA composites
The composites were prepared by stir-casting process. Ingots of AA 1200 aluminium procured from Hindalco Industries Limited were used as matrix material for the composites. The stir casting furnace was initially heated to 750±50°C. Simultaneously, modified FA powder was preheated in a furnace to 600°C. The purpose of preheating the reinforcement is to improve the wettability of the particles in the melt by removing surface contaminants and increasing surface energy [19]. The aluminium metal pieces were charged to the furnace in a graphite crucible and allowed to melt. 0.05 wt. % (weight percentage) of hexachloroethane (C₂Cl₆) was added as degasser to the melt and the slag formed was removed while continuous stirring. The temperature was then reduced to around 600°C to bring the melt to semi solid state. The preheated modified FA powder was added to the semi-solid melt along with 1 wt. % of magnesium while continuous stirring. Magnesium was added to ensure good wettability between the reinforcement and the melt [1, 3, 22-23]. The addition of modified FA was carried out over a period of 30 minutes with stirring. Followed by this, the temperature of the melt was raised to 850°C and then stirred for around 15 minutes. Casting was done in sand moulds of 50 X 40 X 20 mm³ dimensions as shown in figure 1(c). The casting was allowed to cool to room temperature. Following the above process, aluminium metal matrix composites containing 2, 4, 6 and 8 wt. % of modified FA were cast. To compare the density, wear properties and hardness, aluminum without reinforcement was also cast into sand moulds of same dimensions.
Figure 1 Photograph showing (a) Fly ash (FA), (b) pellets of FA mixed with graphite and magnesium and (c) sand casting of aluminium matrix composites.

2.3. Characterization of aluminium matrix composite (AMC)

Experimental density of the casting was determined using Archimedes principle with water as the immersion medium. The theoretical density of the casting was determined according to the rule of mixtures [24].

The percentage porosity in the composite was estimated from the theoretical and experimental densities as follows [25].

\[
\% \text{ porosity} = \frac{\text{Theoretical density} - \text{Experimental density}}{\text{Theoretical density}} \times 100 \%
\]

For microstructural characterization, the cross-section of the composite were polished using emery sheets of grades 200, 400, 600, 800, 1000 and 1200 and on a disc polisher using diamond paste. The polished samples were observed under the optical microscope (Carl Zeiss Axiovert A1). For dry sliding pin-on-disc wear test, cylindrical pins of dimensions 8 mm diameter and 30 mm height were machined from the castings. The surface to be exposed to the wear test was polished to a surface finish of 1000 grit emery paper. The tests were conducted on a computerized pin-on-disc (Magnum make) wear testing machine under ambient temperature. The counter disc material was EN 31 steel. The wear tests were conducted at a normal force of 10 N and sliding distance (S) of 3000 m and speed of 500 rpm, track radius 70 mm. The variation of coefficient of friction with respect to the test duration and the loss of height (in micrometres) were measured by the equipment. The volumetric wear loss (\(\Delta V\)) was determined by multiplying the cross-sectional area of the test (pin) specimen with the loss of height. \(\Delta V\) per unit sliding distance (S) gives the wear rate. Hardness of the castings were determined by Brinell hardness machine using a load of 250 kgf and a 10 mm steel ball indenter at room temperature.

3. Results and discussion

3.1. Properties and composition of modified FA

The final weight of the modified FA powder obtained after treatment in the inert atmosphere was found to be same as the weight of the initial FA powder. This suggested that there were no volatile particles in FA and there was no mass loss due to the chemical reaction that took place at the reaction temperature. The tapped density of FA was found to be 1.42 g/cm\(^3\) while that of modified FA was found to be 0.69 g/cm\(^3\).

The XRD patterns of FA and modified FA are shown in figure 2. The XRD results show that FA was mainly composed of SiO\(_2\) along with Al\(_2\)O\(_3\)Si and AlPO\(_4\). After treatment of FA with Mg and graphite in inert atmosphere at 650°C, additional peaks of MgO, MgO\(_2\)Si, Mg\(_2\)Si and SiC were observed.
Figure 2 X-Ray diffraction patterns of FA and modified FA showing presence of SiC along with 
MgO, Si, Al₂O₃, MgO, AlPO₄, Mg₂Si after furnace treatment.

It is known that magnesiothermic reaction involves the reduction of SiO₂ by Mg in presence of carbon 
to produce SiC [15]. The reaction of SiO₂ takes place at around 650°C [16, 19, 21]. The following 
reactions have been suggested by several authors [17-18, 26].

\[
\text{SiO}_2 + \text{Mg} \rightarrow \text{Mg}_2\text{Si} + 2\text{MgO} \quad (1)
\]

\[
\text{Mg}_2\text{Si} + \text{SiO}_2 + \text{C} \rightarrow 2\text{SiC} + 2 \text{MgO} \quad (2)
\]

The overall reaction is given as follows:

\[
\text{SiO}_2 + 2\text{Mg} + \text{C} \rightarrow \text{SiC} + 2\text{MgO} \quad (3)
\]

In the present synthesis, the peak obtained at 2θ value of 35.6° correspond to (111) peak of β-SiC [17, 
18]. The high amount of Mg₂Si in the modified FA suggests that the reaction process was probably 
not complete. This could be due to incomplete penetration of gaseous magnesium to the interior to 
react with the remaining SiO₂ [16]. Nonetheless, the advantages of MgO and Mg₂Si as reinforcement 
in aluminium composites are also well known [2, 5]. Therefore, Mg₂Si and MgO formed by the 
magensiothermic reaction was retained and not removed from the modified FA.

Figure 3 shows the SEM micrographs of FA and modified FA particles. The particles were found to 
be spherical in shape in case of FA (16-37 microns) while they were irregular in case of modified FA 
(15-30 microns). Although the particle size was similar, the higher tap density of modified FA was 
probably due to the irregular shape of the modified FA particles. EDS analysis of FA showed the 
presence of Si, Na, Al, K, Ca, Mn and Fe while, as expected, modified FA showed more amount of 
Mg in addition to the above elements.

3.2. Density of AMC
The theoretical and experimental densities of the composites were compared and are shown in table 1. 
The results show that the theoretical as well as experimental densities are lower than the density of Al 
which is 2.71 g/cm³. The porosity level in the composites was found to be very less, in the range of 
0.04-0.22 %. It can be observed from the table that the theoretical density of the composite decreased 
as the amount of reinforcement increased. This is due to the low density of the modified FA. A 
general trend could not be observed in case of experimental density due to the presence of different 
percentages of porosity.

3.3. Results of microstructural studies on composites
Optical microscopy of the microstructural samples containing 2, 4, 6 and 8 wt. % modified FA
showed the presence of agglomeration of particles in all the four samples. Typical optical micrographs are shown for reference in figure 4. The particles showed a tendency towards segregation and clustering probably due to the huge density difference between the matrix and reinforcement particles [19].

However, the microstructure was free from macro defects like voids, porosities and cracks which indicate that the semi-solid slurry probably absorbed less air during compo-casting [20]. The less percentage of porosity is also evident from the table 1.

![Figure 3 SEM micrographs of (a) FA and (b) modified FA particles.](image)

#### Table 1 Theoretical and experimental density of AMC containing 2, 4, 6 and 8 wt. % reinforcement.

| Sample            | Theoretical Density (g/cm$^3$) | Experimental Density (g/cm$^3$) | % Porosity |
|-------------------|--------------------------------|--------------------------------|------------|
| Al                | 2.71                           | 2.43                           | 0.10       |
| 2 wt % modified FA| 2.67                           | 2.08                           | 0.22       |
| 4 wt % modified FA| 2.63                           | 2.12                           | 0.19       |
| 6 wt % modified FA| 2.55                           | 2.45                           | 0.04       |
| 8 wt % modified FA| 2.56                           | 2.14                           | 0.16       |

![Figure 4 Optical micrographs of aluminum- 6 wt. % modified FA at (a) 100 X and (b) 200X magnification showing agglomeration of particles at grain boundaries.](image)

### 3.4. Hardness test results

Hardness measurement showed that the hardness of the composites increased with the addition of modified FA particles (see figure 5 (a)). This shows that the hard ceramic particles increased the resistance of the matrix material to plastic deformation during hardness testing.
Figure 5 (b) shows the variation of the wear rate (mm$^3$/m) with duration of the test. It can be observed from the graph that the wear rate increased with increase in reinforcement till 6 wt. % (as evident from the steady part of the individual graphs). However, the wear rate drastically decreased for 8wt. % modified FA composite. It is known that wear rate is inversely proportional to the hardness of alloys which in turn improves wear resistance [27]. However, in the present case, the increase in hardness resulted in increase in wear rate till 6 wt. % of modified FA. The probable reason for the increase in wear rate could be poor bonding between the matrix and reinforcement which could have resulted in easy detachment of the particles during the wear process. This could be due to the tendency of particles to segregate as evident from optical microscopy (refer figure 4). These detached particles could have resulted in increase in the removal of material due to wear.

However, the wear process definitely slowed down with the increase in amount of reinforcement in the composite, as evident from the decrease in slope of the curve before it reaches steady state. This is probably because of increase in abrasive wear mechanism with the increase in amount of reinforcement [25, 28-29].

4. Conclusions
The microstructure, hardness and wear behaviour of aluminum reinforced with 2, 4, 6 and 8 wt. % (weight percentage) modified fly ash (FA) were studied. The modified FA powder was prepared by heating FA with graphite and magnesium in the ratio of 1:1:2.5 at 650°C in nitrogen atmosphere. XRD (X-ray diffraction) analysis showed that the FA powder was mainly composed of SiO$_2$ along with Al$_2$O$_3$Si and AlPO$_4$. After furnace treatment of FA, additional peaks of MgO, MgO$_2$Si, Mg$_2$Si and SiC were observed. Tapped density of the modified FA was found to be 0.69 g/cm$^3$. The composite was prepared by compocasting route by melting AA 1200 aluminium in a stir casting furnace and adding modified fly ash. Optical microscopy showed segregation of particles along grain boundaries in all the samples. Hardness of the composites was found to increase with increase in the amount of modified FA. Pin-on-disc wear studies showed that the wear rate of the composite increased with the increase in the amount modified FA till 6 wt. %, beyond which the wear rate decreased. The increase in wear rate was correlated to the improper bonding between the particles and the matrix phase due to segregation of particles. Interestingly, the wear process was slowed down with increasing amount of reinforcement, probably due to the increase in abrasive wear mechanism as the particles dislodged during the wear test.

Acknowledgements
The authors would like to acknowledge Prof. Chaitanya Lekshmi Indira for helping us with furnace facility, Mr. Rahul Pillai for helping with the furnace treatment and Mr. Muralidhara for helping us in casting and preparing samples for studies.
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