

Short Communication

Effect of Coating Parameters on Coating Morphology of Basalt Short Fiber for Reinforcement Preparation of Al/Basalt Metal Matrix Composites

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The interface between the matrix and reinforcement plays a crucial role in determining the properties of metal matrix composites (MMC). Coating of the reinforcement is an important technique by which the interfacial properties can be improved. In this work, weight deposition of copper coating on short basalt fibers was carried out by electroless method. The electroless process used to deposit the copper coating onto the basalt fiber relies on a sequence of sensitization time, activation time and metallization time and these parameters need to be optimized to know the amount of coating thickness. These parameters considered for optimization process are evaluated for different time intervals. An electroless method of coating on basalt fiber with copper deposition is described. The effects of time of sensitization on coating thickness, effects of time of activation on coating thickness and effect of time of metallization on coating thickness on basalt fiber are studied. Using this method it is possible to deposit up to about 25 wt% copper on the basalt fiber with an average coating thickness about 0.1050 to 0.115 μm . We conclude that the role of electroless copper coatings applied on short basalt fibers on the interaction between an aluminium alloy and coated fibers have to be studied to get useful information for the fabrication of basalt fiber reinforced aluminium matrix composites by liquid or semi-liquid processing. The resultant composite fiber was characterized by scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) during and after the coating process.

Keywords: Metal matrix composite (MMCs), Basalt fibers, Coating, Electroless technique.

1. INTRODUCTION

The need for new engineering materials with the advancement of modern technology in the areas of aerospace and automotive industries had led to a rapid development of metal matrix

composites (MMCs). They can be tailored to have superior properties such as high specific strength and stiffness, increased wear resistance, enhanced high-temperature performance and better thermal and mechanical fatigue and creep resistance than those of monolithic materials. Among the various matrix material available, aluminium and its alloys are widely used in the fabrication of MMCs. This is because of the fact that they are light in weight, economically viable, amenable for production by various processing techniques and possess high strength and good corrosion resistance [1].

The interface between the matrix and the reinforcement is the critical region that is affected during the fabrication. If this interface is not tailored properly, it can lead to the degradation of the properties of the composites. The problem associated with the interfaces are the interfacial chemical reaction, degradation of the reinforcement, lack of wettability with the matrix. These interfacial problems are system-specific. Hence, it is difficult exercise to design optimized interfaces common and suitable for all systems. Some of the methods to obtain desired interfaces with better properties are the modification of the matrix composition, coating of reinforcement, specific treatments of the reinforcement and of control of process parameters. Among these, the most important technique to improve interfacial properties is that of coating of the reinforcement [2].

Coating technique has been studied by many researchers in the fabrication of metal matrix composites (MMC) [3-6]. Coating of a reinforcement is one of the successful techniques adopted to prevent interfacial reaction and enhance the wetting of reinforcement. Coating also prevents the diffusion of liquid metal into the reinforcements. Different types of coating given to reinforcements are metallic, ceramic, bilayer and multilayer coatings containing metals and/ or ceramics and are system specific. The various coating techniques adopted aim at attaining a better, uniform and thin layer coating with degradation of the reinforcement properties. Some of important coating techniques are chemical vapour deposition (CVD), Physical vapor deposition (PVD), thermal spraying, sol gel process, electrolytic, electroless and cementation methods. The need for copper coated fibers in the area of composites materials has recently been recognized. Electroless deposition is a process of depositing the coating with an aid of chemical reducing agent in solution and without the application of external electrical power.

Brenner and Riddell are credited with developing the first successful electroless deposition process in the 1940's. Electroless coating technology has been the subject of research interest in the past two decades, emphasis is shifted to the studies of its property and application. By the controlled chemical reduction reaction, the electroless coating chemistry has emerged as one of the leading growth areas in the surface engineering, metal finishing etc. and it is estimated to grow at the rate beyond 15% per annum. Certainly no other chemistry is growing at this rate. Electroless coating has unique physio chemical and mechanical properties for which they are been used increasingly [7].

Discontinuously reinforced metal matrix composites [MMC's], although still relatively expensive to manufacture, are important structural materials in the aerospace, automotive and leisure industries because of their improved specific strength, stiffness and wear resistance, as compared to monolithic alloys [8]. The interface plays a most vital role in the overall performance of composite material. Improper wetting and chemical reaction occurring between the dispersoid surface and the matrix at the interface during the synthesis or under service conditions, can degrade the mechanical properties of the composites [9]. Special alloying additions to the matrix and the refractory material

coatings on the dispersoid can effectively reduce the chemical reaction between the matrix and the dispersoid surface [10]. Copper and nickel coatings on carbon fibers prior to dispersion enhance the wettability of the carbon fiber with molten aluminium. In both the cases, the coating materials, i.e. copper and nickel were dissolved in the matrix aluminium to give brittle intermetallics and at the same time, the density of the possible interfacial reaction between molten aluminium and the carbon fiber were also reduced [11].

Carbon fibers are used as a reinforcement of aluminium alloys because they increase the strength and the stiffness of the alloys, improving their electrical and thermal conductivities while reducing their density. Carbon fibers also reduce the friction coefficient of aluminium alloys composites and increase their wear resistance. However, manufacturing problems have limited the industrial applications of these materials [12].

Carbon wettability by molten aluminium is limited at the typical temperatures used for casting aluminium composites (700°C - 800°C), even for a long time exposures. Because of their low reactivity, the reinforcement segregates from the matrix and gives place to highly heterogeneous composites. This behaviour is even more critical in high modulus carbon fibers which have a thin skin in which the carbon planes of the graphite structure are predominantly parallel to the surface, with the most reactive carbon atoms located at the edge of the carbon planes and at the defect sites of those planes [13].

One of the solutions given to these problems is the deposition of coatings around fiber reinforcements, either short or continuous fiber. Metal coatings of refractory materials have been used because of their inertness with both, molten metal and fiber reinforcement, but this type of coating is very expensive and does not solve the wettability problems [14].

As per authors knowledge although many researchers worked on coating techniques of copper/nickel coatings on short fibers and particulates but very few /no research works are focused on the effect of coating basalt short fiber for reinforced MMCs. The objective of the work, investigate the effect of coating parameters on coating morphology of basalt short fiber for reinforcement of Al/Basalt metal matrix composites.

2. EXPERIMENTAL PART

2.1 Materials and methods

Mukhtha Giri industrial corporation, Mumbai supplied the basalt fibres used in this study in the form of continuous basalt fibres(CBF). In the present investigation the deposition of copper coating on short basalt fibers by an electroless route has been optimized.

2.2 Pre-procedure

Continuous basalt fibers in the chopped form were used in the present investigation. The continuous basalt fibers of average diameter 6µm were cut down to short fiber of length about 1mm to 2mm. The complete process of coating starts with the treatment of fibers in a muffle furnace for 10 min at 500°C to eliminate the pyrolytic coatings around as – received fibers.

2.3 Electroless coating

The electroless process is used to deposit the copper coatings onto the basalt fiber relies on a sequence of preheating, sensitizing, activation and metallization, with important cleaning, rinsing, and drying stages also being included. The conditions used are detailed in Table 1.

2.4 Test procedure

Basalt fibers in the chopped form were used in the present investigation. The sizing and finished treatment from the surface of the fibers, prior to coating, were removed by heating them to about 970 K for 10 min in air. Subsequently they have an average diameter of 6 μ m, an elastic modulus of 90 GPa, and a yield stress of 4500 MPa. The continuous fibers were cut down to about 0.5mm to 1mm. The coating procedure consist of three well defined stages namely sensitization, activation and metallization. Table 1 summarizes the best working procedure used, which is based on improving different solutions used by some authors [14-18].

Table 1. Chemical compositions

Stage and conditions	Concentration of chemicals
Sensitization 5min, 10min & 15 min at room temperature	12 g/l SnCl ₂ · 2 H ₂ O 40 ml/ HCl 0.2g/l PdCl ₂
Activation 5min, 10min & 15 min at room temperature	2.5 m/l HCl 10g/l CuSO ₄ · 5 H ₂ O 45g/l EDTA
Metallization Multiple conditions tested 40 ^o C and 50 ^o C pH 12 and pH 13 2 min - 20 min	20 g/l NaCOOH 16 ml/l HCHO 36% NaOH for adjusting pH

The complete process of metallization starts with the treatment of fibers in an open oven for 10 min at 500 °C to eliminate the pyrolytic coatings around as – received fibers. The heat cleaned fibers were first treated with glacial acetic acid to activate the surface, and then again activated using stannous chloride (SnCl₂) and they were sensitized for different times (5min, 10min & 15min) under continuous stirring. Afterwards, fibers are filtered and cleaned with distilled water. In order to have catalytic surfaces, the sensitized fibers were exposed to an aqueous solution containing palladium chloride (PdCl₂) and HCl under ultrasonic agitation. This process, called activation, produces the formation of Pd sites on the fiber surface which allow the subsequent metallization with copper.

Metallization is produced by immersion of activated fibers into a solution containing $\text{CuSO}_4 - 5 \text{H}_2\text{O}$ as metal ion sources also held under agitation. Different metallization conditions have been tested, pH (12 & 13), time (2min to 20min) and temperature (40°C & 50°C), and continuous and crystalline coatings with homogeneous thickness have been obtained. The reactive volume used assures that the concentration of the diluted copper can be considered constant during the deposition. The coatings obtained at different metallization temperature, time and pH values were studied by SEM and the thickness of the copper layer was determined in transversal cross section.

2.5 Preparation of moulds for Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS)

The specimen was mounted on a metal stub on top of which double sided carbon tape was used and the sample was stuck on a carbon tape. Later the entire stub was placed in the coating machine for the metal coating process. For an electrically conductive specimen, observation of the specimen without metal coating was the best method, but for a non-conductive specimen, however metal coating was usually applied to give the specimen electrical conductivity. This decreases the specimen's capacity to acquire an electrostatic charge and increases the yield of secondary electrons. The important thing to remember when applying a metal coating was that the coat of metal film must be as thin as possible so that the specimen surface morphology is not completely covered by coating. The resultant images reveal remarkable structural resolution down to a few nanometers with great accuracy, because the film provides a continuous coating over all the sample contours. The mould or stub was kept in the vacuum chamber and SEM imaging and EDS was done through JEOL JSM 6360 - A model with a magnification capacity of X500, X1000, X2000 and accelerating voltage of 20 KV with working distance (WD) 10 mm and a spot size 58. First area of image was chosen and focused then through software EDS analysis was done on the same image by either selecting spot analysis or line analysis or area analysis. In our case area analysis was taken and after the X-ray scan was complete, the EDS result was also obtained both qualitatively and quantitatively.

3. RESULTS AND DISCUSSION

3.1 Characterization of the copper coating

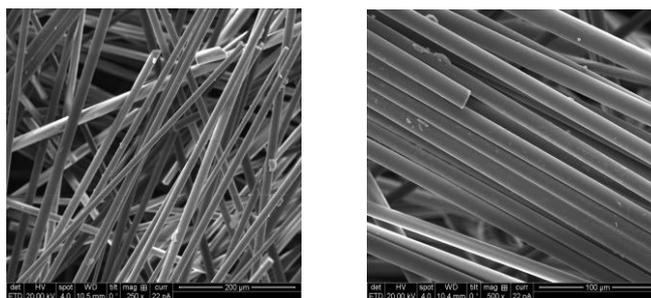


Figure 1. SEM images of uncoated basalt fiber

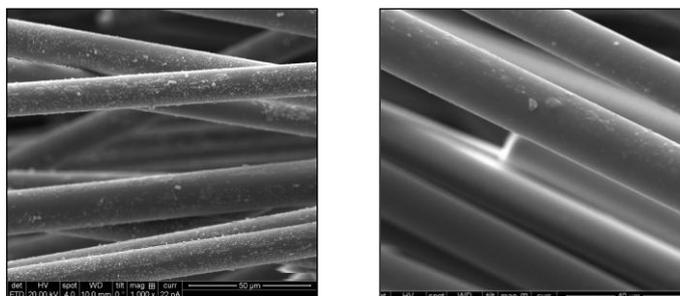


Figure 2a. SEM images of copper coated basalt fiber

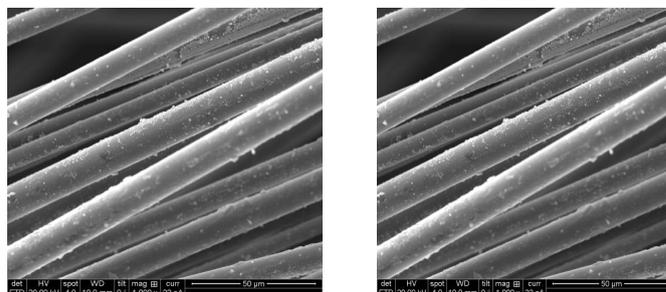


Figure 2b. SEM images of copper coated basalt fiber

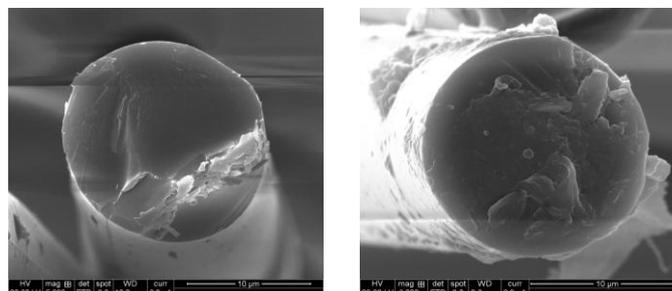


Figure 2c. Transversal section SEM images of copper coated basalt fiber

Fig. 1 shows the surface characteristics of uncoated fibers, of copper coated ones (Fig. 2a and 2b) under different metallization conditions, and Fig. 2c shows the transversal section of copper coated fibres as observed with light microscopy. As it can be seen in the images, the thickness and morphology of the copper layers is highly dependant on the metallization conditions, mainly sentisization time, activation time, metallization time, temperature and pH. Bath temperature must be kept below 45⁰C because higher temperature unstabilizes the metallization solution. At this or higher temperatures dendritic growth of the coating (Fig.1) is promoted. Using lower bath temperatures under the same pH conditions (pH 14) homogeneous thickness can be achieved on the coatings.

To obtain any copper deposition, the pH of the metallization solution must be higher than 13. For pH 13 or higher the deposition rate increases as the pH increases so shorter deposition times are needed to get the same thickness. For pH 13, the minimum time needed to get continuous copper coating is 3 mins. After the first stage, the thin copper coating grows homogeneously in thickness without evidence of dendritic growth (Fig. 2a, Fig .2b & fig.2c) shows the surface characteristics of

uncoated fibers and the copper coated ones (fig 1 & 2a) under different metallization conditions and time.

3.2 Coating Thickness, distribution and mechanism

Typical transverse cross-sections of copper coated basalt fiber by the electroless method, mounted in resin are shown in Fig. 2c, the coating thickness is uniform through out the circumferences of the fibers and more than 95% of the fiber surface was found to have been covered. Fig. 3a and b are typical histograms showing the variation in the coating thickness as a function of number of fibers coated by the electroless method. The numbers inside the histograms indicate the percentage of coated fibers in that thickness. From fig. 3a it is seen that, the coating thickness ranges between 0.1 and 0.8 μm with above 80% of them having coating thickness between 0.2 and 0.6 μm .

The SEM examination of the coated fibers showed that when coating thickness was less than 0.2 μm , isolated patches of copper were formed at the fiber surface, when coating thickness exceeded 0.2 μm , a continuous metal spread was seen as shown in fig.2c. Further increase in coating thickness results a few massive crystal growths at isolated places over smooth and continuously coated copper.

The mechanism of copper- coating on the basalt fiber shows that during coating, the copper deposits over energetically favored sites followed by bridging of these sites covering the entire surface of the fiber. The observed variation in the coating thickness (Fig. 3) could be mainly due non-uniform activation of the surface of the fibers prior to deposition. When the total amount of metal ions available in the coating bath is much lower than the amount required for coating about 0.6 μm thick layer over all the fibers in the bath, most of the fibers are found to be partially coated but few fibers are completely coated. It also observed when the total metal ion concentration was much higher than the optimal amount for 0.6 μm thickness coating, a small percentage (around 2%- 5%) of fibers were found to be still coated, others fully coated.

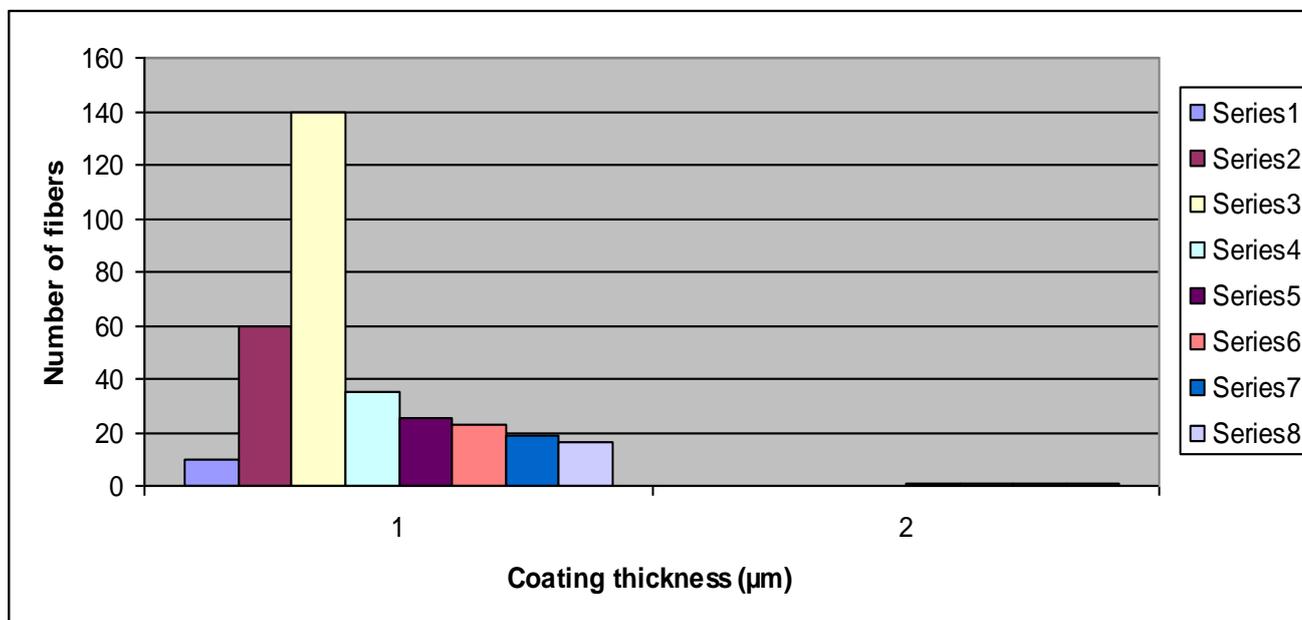


Figure 3. Variations in coating thickness as a function of the number of coated fiber

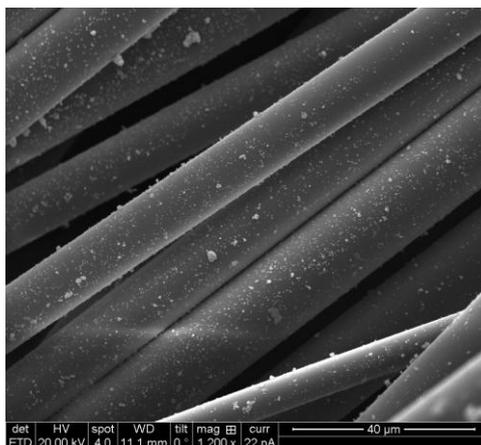


Figure 4. surface of a basalt fiber copper-coated with thickness about 0.2 μm

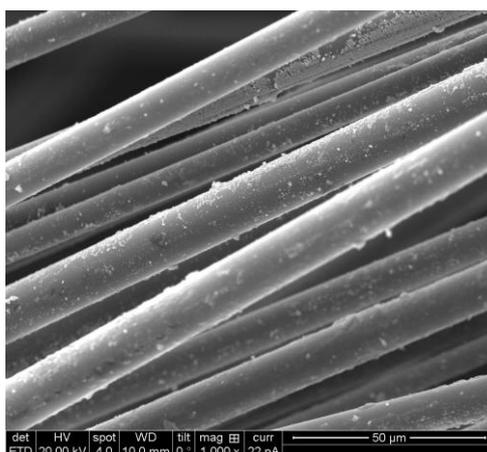


Figure 5. surface of a basalt fiber copper-coated with thickness about 0.8 μm

3.2 SEM& EDS analysis of copper coated fiber

The morphology of original basalt fiber and coated basalt fiber was observed using a field emission scanning electron microscope (SEM) measurements were held with a JEOL JSM 6360 - A model with a magnification capacity of X500, X1000, X2000 and accelerating voltage of 20 KV with working distance (WD) 10 mm and a spot size 58. Microscopes were equipped with analytical facilities (energy dispersive X-ray spectroscopy-EDS).

The aim of the experimental plan is to find the important factors and combinations of Assistance of advanced measurement techniques has been taken to measure coating thickness of fiber at a micro-scale. The experimental results were confirmed by micro - structural studies using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of short basalt fiber obtained from the chemical test. Through the SEM images, the thickness of copper coating on the basalt fiber was measured. EDS scanning results shows the composition of material which was predominantly copper, from the large Si peaks; it also contains alumina and iron as shown in fig 3b.

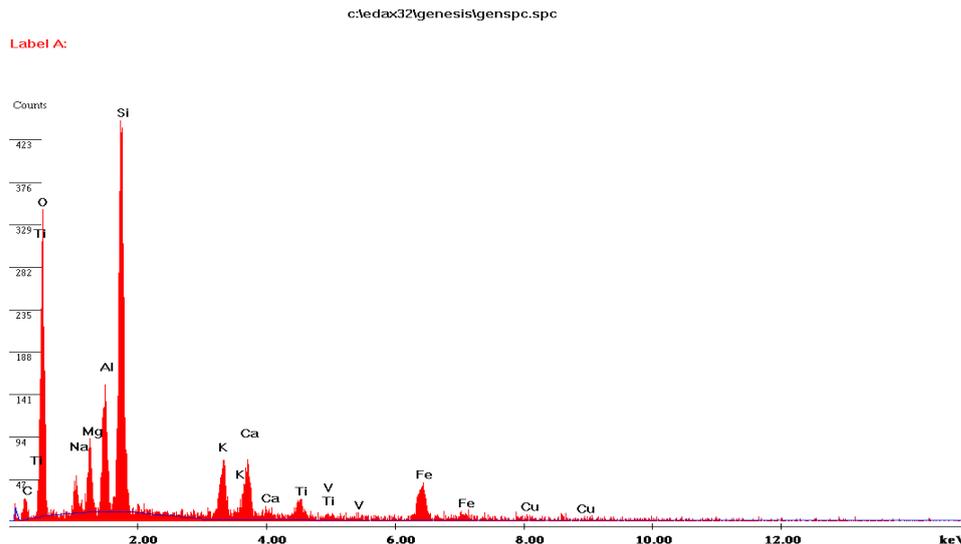


Figure 7a. EDS image of uncoated basalt fiber

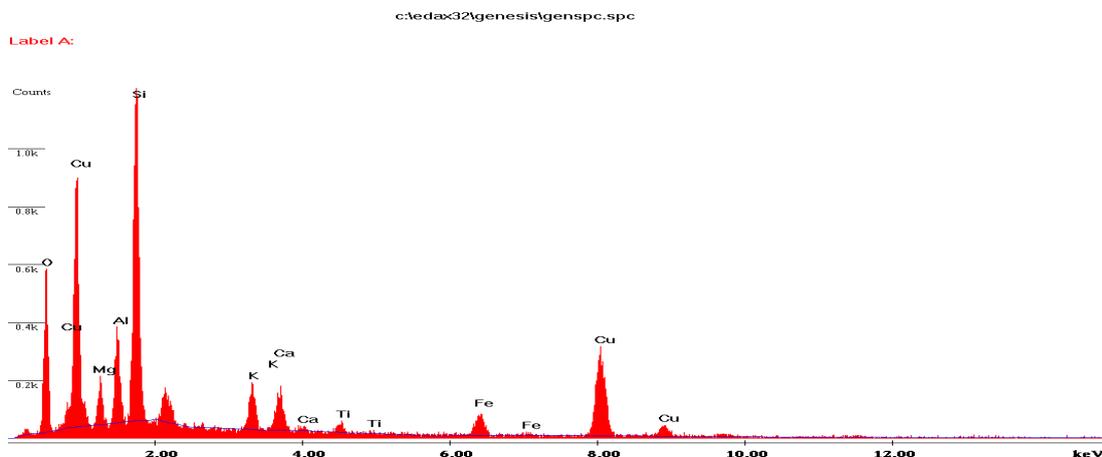


Figure 7 b. EDS image of copper coated basalt fiber

Fig. 2 (a) shows the SEM micrographs of as-received basalt fiber and Fig. 2 (b) and 2 (c) shows electroless copper coated basalt fibers with low and higher magnification. As shown in Fig. 2 (a) basalt fibers have smooth surface striations along the fiber axis. In spite of the different surface morphology, the electroless copper films have been deposited on the fiber surface with good adhesion as indicated in Fig. 2(b) and 2(c). From Fig. 2 (c) we observe that there is deposition of copper layer on the surface of basalt fiber and the thickness of coating was measured using SEM. Fig. 7 (a) and (b) shows the EDS pattern of uncoated and copper coated basalt fiber respectively. The serious aggregations among the basalt fiber were observed due to the high chemical activity of copper atoms. The original basalt fiber exhibit a glossy surface. After sensitization and activation, the surface becomes dim. The EDS results confirmed the presence of Cu indicating a successful sensitization and activation process.

4. CONCLUSION

In the present work, short basalt fiber is coated with copper deposition by electroless method. The effects of time of sensitization on coating thickness, effects of time of activation on coating thickness and effect of time of metallization on coating thickness on basalt fiber were studied. Based on the experimental observations, the following conclusions are drawn.

- The thickness of copper coating deposited on the basalt fiber by electroless method depends on sensitization time, activation time and metallization time, bath temperature and pH value, hence these parameters need to be optimized.
- Uniform and continuous coating of copper was given to basalt fibers using electroless deposition techniques. From the experimental results, it was observed that maximum coating thickness was observed at 15 min of sensitization time, 15min of activation time, 3mins of metallization time, 45^oC bath temperature and pH value of 13.
- After optimizing the sensitization time, activation time and metallization time, the basalt fiber was coated up to 25 % of copper using a copper sulphate solution by electroless method.
- The coating thickness ranged between 0.02 μ m to 0.1112 μ m, maximum coating thickness of 0.1112 μ m was observed at 15 mins of sensitization time, 15 mins of activation time and 3min of metallization time.
- The coating carried out above this optimized value had no improvement on the deposition of copper on the basalt fiber.
- The SEM & EDS analyses showed that that there was a relatively dense, uniformly distributed copper deposition on the basalt fiber. With help of SEM images the surface characteristics of uncoated fibers & copper coated ones were studied under different metallization conditions and coating thickness were measured from SEM & EDS data also show distinct peak of silica followed by oxygen, copper aluminum and iron respectively. By observing the EDS data, it was observed that there is an increase copper in peak of coated fiber as compared to uncoated fiber, clearly indicating the deposition of copper on basalt fiber.

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