DEVELOPMENT OF GRAPHENE NANOPLATELETS REINFORCED ALUMINIUM MATRIX NANOCOMPOSITES BY A COMBINATION OF SEMI-SOLID STIRRING AND ULTRASONIC TREATMENT

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Abstract
Graphene Nanoplatelets (GNPs) consisting of graphene layers with a thickness less than 100 nm have recently emerged as a promising reinforcement type owing to their excellent physical and mechanical properties to improve mechanical properties of alloys beyond ceramic nanoparticles. Although there are numerous studies on GNPs reinforced polymer matrix composites in the literature, the number of studies related to the incorporation of GNPs in metal matrices is limited. It is a challenging task to incorporate and uniformly distribute GNPs into liquid metals due to their poor wettability and large surface-to-volume ratio. The purpose of this study is to effectively disperse GNPs into liquid aluminium. 0.5 wt.% GNPs with an average thickness of 50-100 nm and size of 5 μm were first incorporated into A360 aluminium alloy under semi-solid stirring, and then the composite was ultrasonically treated in fully liquid state. The microstructural investigation of the nanocomposites by optical and scanning electron microscopy may suggest that relatively uniform distribution and effective deagglomeration of GNPs in the matrix were achieved. The hardness of the GNPs reinforced nanocomposites increased in comparison with that of semi-solid stirred and ultrasonically processed A360 alloy without reinforcement, indicating the potential of GNPs for strengthening metals.

1. Introduction

Metal matrix nanocomposites which are typically strengthened with nano-sized ceramic particles are extensively studied to create new generation materials with lightweight and high specific strength for the automotive and aerospace industries. Graphene, a recently developed 2D material comprising of a single layer of carbon atoms, are attractive for numerous research activities due to its excellent mechanical and physical properties [1]. Industrially produced Graphene Nanoplatelets (GNPs) which consist of graphene layers with a thickness less than 100 nm have emerged as a potential reinforcement type in composite technology for improving mechanical properties significantly [2, 3]. It is considered that the introduction of GNPs into metal matrices could further develop the mechanical properties compared to ceramic nanoparticles. Although there are numerous studies indicating the contribution of GNPs to the properties of polymer matrices, the number of studies on the incorporation of GNPs into metal matrices is limited. The reason behind this situation is most likely to be due to the challenges in the incorporation and uniform distribution of GNPs into metals like ceramic nanoparticles.

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To date, GNPs have been utilized in the strengthening of some metal matrices including Cu [4, 5], Mg [6] and Al [7, 8]. Among these, GNPs reinforced Cu and Al composites were fabricated with only solid state routes including powder metallurgy. There is an increasing demand to fabricate such materials via liquid state routes as economical and versatile routes for the production of engineering components with complex shape. Particularly, the strengthening of aluminium alloys is important since they are widely used in the industry. However, the incorporation of GNPs into molten aluminium complicates achieving uniform dispersion of GNPs due to their poor wettability and large surface-to-volume ratio. Poor wettability of GNPs can be also an obstacle for obtaining good matrix-reinforcement interfacial bonding, deteriorating mechanical properties. The application of high intensity ultrasonic waves into molten metals, namely ultrasonic treatment, has been shown to be effective in terms of uniform dispersion of ceramic nanoparticles through aluminium matrices [9]. It is envisioned that GNPs could be incorporated and effectively dispersed into liquid aluminium alloys with ultrasonic treatment.

The objective of the present work is to determine the feasibility of GNPs reinforced aluminium nanocomposite fabrication by the combination of ultrasonic treatment and semi-solid stirring which could allow GNPs to be incorporated into the semi-solid matrix without floating on the surface. It is also aimed to obtain convincing images showing that GNPs are embedded and effectively distributed into the matrix.

2. Experimental Procedures

2.1. Materials

A360 commercial aluminium casting alloy was used as the matrix to fabricate the composite since the presence of 10 wt.% silicon could suppress the chemical reaction between liquid aluminium and carbon. The chemical composition of the alloy is shown in Table 1. Commercially available GNPs used in this study have a thickness of 50-100 nm with an average *x*,*y* dimension of 5 μm. The Scanning Electron Microscope (SEM) images of these GNPs are given in Fig. 1.

Table 1. Composition of A360 alloy (wt.%).

Al	Si	Fe	Cu	Mn	Mg	Zn	Ti
Bal.	10.0	0.5	0.10	0.50	0.35	0.10	0.15

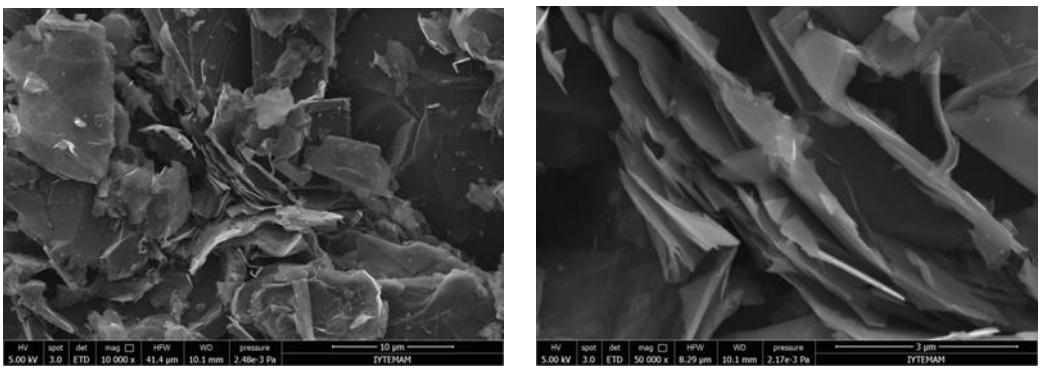

Figure 1. Low and high magnification SEM images of the GNPs used in this study.

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Aluminium and magnesium powders with an average size of ≤ 75 μm and purity of 99% were utilized for the deagglomeration of GNPs by means of ball milling prior to the feeding of GNPs into the melt.

2.2. Preparation of Tablets

It is known that direct introduction of nano-sized reinforcements into liquid metals could lead to severe particle agglomeration and flotation. One of the widely accepted methods to overcome these issues is to fabricate master alloys containing reinforcements, which is to be fed into molten metals [10]. For the preparation of tablets (master alloy) in this work, 6 g aluminium and 6 g magnesium powders were first mixed with 1 g GNPs in a planetary ball mill (Retsch PM 200) for 2 h at 350 rpm. The alumina balls-to-total powder weight ratio was 4:1, and the diameter of the balls was approximately 9.5 mm. The mixture of powders and GNPs (about 6 g for each operation) was then pressed at 250 MPa into tablets 30 mm in diameter. The content of GNPs in the tablet was calculated to be approximately 7.7 wt.%. Aluminium and magnesium powders are likely to encapsulate GNPs and prevent their immediate flotation during feeding. In addition, the reason for using magnesium powders in the table is to reduce the surface tension of aluminium alloy [11, 12], and hence improving the wettability of GNPs.

2.3. Fabrication of Nanocomposites

The schematic experimental setup for the fabrication of GNPs reinforced aluminium nanocomposites is shown in Fig. 2. The A360 aluminium alloy was melted in a graphite crucible with a total melt volume of 200 g at 650 °C. At this temperature, the melt was mechanically stirred with a graphite stirrer at 1000 rpm. During the mechanical stirring, two tablets containing the GNPs, aluminium and magnesium powders were introduced into the molten alloy, one by one (Fig. 2a). While the tablets were being melted, the alloy cooled down to semi-solid temperature (580-590 °C). In order to incorporate the GNPs into the alloy, the semi-solid alloy was stirred with a total processing time of 15 min. The stirrer was then removed and the alloy was reheated to 670 °C. The titanium alloy made ultrasonic probe which is a part of an ultrasonic treatment device (Q700 sonicator manufactured by Qsonica, LLC) generating a 20 kHz ultrasonic wave with a maximum 700 W power output was dipped about 13 mm into the melt (Fig. 2b).

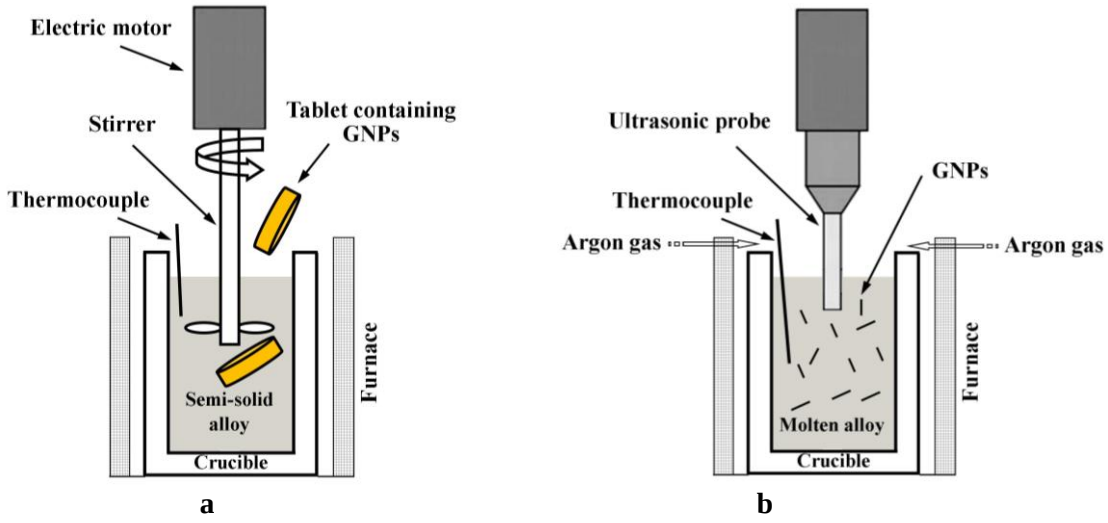

Figure 2. Schematic of experimental setup for the fabrication of GNPs reinforced aluminium nanocomposites; (*a*) semi-solid mechanical stirring of alloy with the introduction of tablets, and (*b*) ultrasonic dispersion of GNPs into the melt.

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The ultrasonic treatment was performed with a working power of 80 W for 15 min. at 650 °C. The probe was removed and the liquid composite was left to solidify in the crucible in ambient conditions to room temperature. The GNPs content in the composite was calculated to be about 0.5 wt.%. A A360 reference alloy was cast employing the similar processing parameters without the addition of tablets and GNPs.

2.4. Microstructural Characterisation and Mechanical Testing

The samples cut from different locations in the composite cast were conventionally ground and polished to a 1 μm finish for the microstructural studies. An optical microscope (Leica DM2500 M) and a Scanning Electron Microscope (SEM, FEI Quanta FEG 250) equipped with an Energy Dispersive X-ray Spectroscopy (EDX) system were employed to observe microstructural changes and possible GNPs embedded into the matrix. For mechanical testing, the Vickers hardness tests were conducted with a load of 5kgf for 10 s. At least five measurements were taken from each sample and the average value was presented.

3. Results and Discussion

First of all, the tablets which contain the ball milled GNPs, aluminium and magnesium powders were characterised. Fig. 3 shows a SEM micrograph of tablets along with the EDX mapping, in which Al, Mg and C maps correspond the powders and GNPs, respectively. The C elemental map potentially indicates that the GNPs were reasonably deagglomerated and distributed between the powders with ball milling. However, it is seen that there are still some GNP clusters remained in the microstructure.

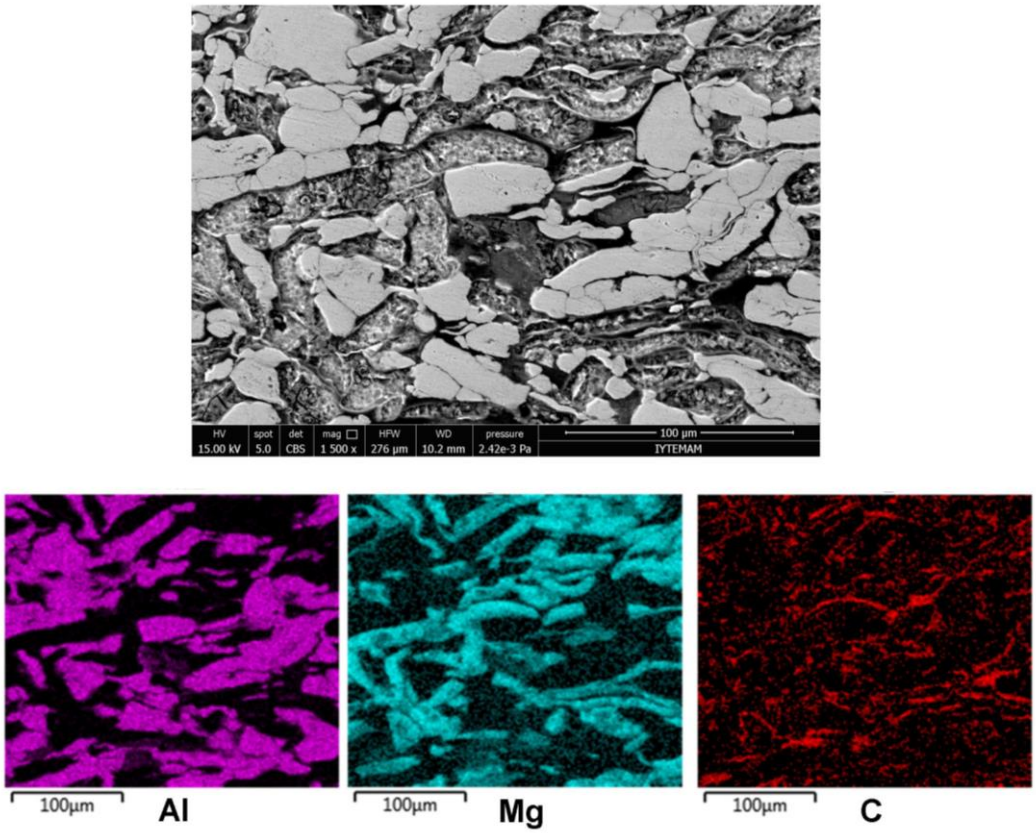

Figure 3. Backscattered electron (BSE) image and EDX mapping of the tablet containing GNPs, aluminium and magnesium powders.

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Regarding the fabrication of nanocomposites, no flotation of GNPs on the melt surface was observed during the tablet feeding or the whole process The optical micrographs of the reference A360 alloy and the fabricated nanocomposite (A360/0.5 wt.% GNPs) are given in Fig. 4. It could be suggested from these micrographs that the addition of GNPs into the matrix did not change the morphology of α-aluminium grains significantly but led to more uniform eutectic microstructure compared to the needle-shaped eutectic as seen in Fig. 4a.

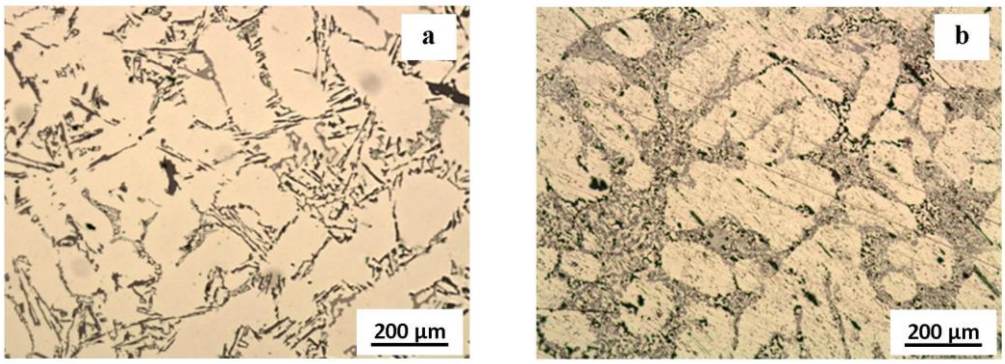

Figure 4. Optical microscopy images of (*a*) the reference A360 alloy, and (*b*) A360/0.5 wt.% GNPs nanocomposite fabricated by a combination of semi-solid stirring and ultrasonic treatment.

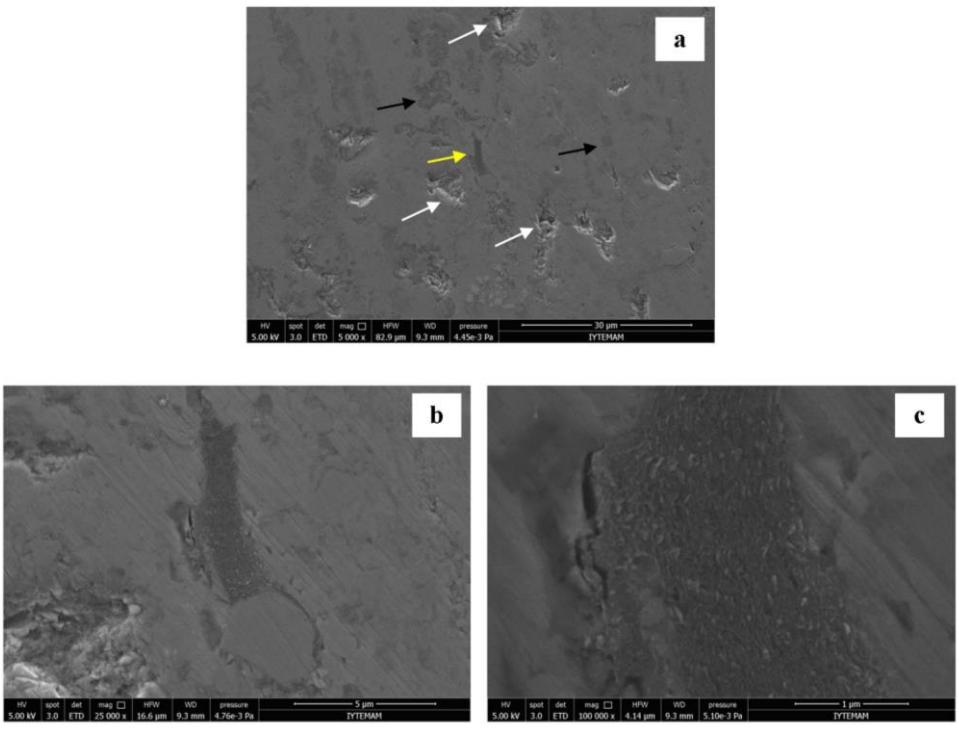

Figure 5. Secondary electron (SE) SEM images of the A360/0.5 wt.% GNPs nanocomposite; (*a*) image at relatively low magnification (The potential GNPs and their clusters are marked with yellow and black arrows, pores are marked with white arrows), (*b*, *c*) high magnification images of a potential cluster of GNPs located with the yellow arrow in *a*.

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Fig. 5 shows the SEM images of a sample cut from the bottom of the A360/0.5 wt.% GNPs nanocomposite cast. The partially clustered and embedded GNPs into the matrix are indicated in Fig. 5c. The GNPs were generally encountered in the microstructure as clusters in 1-3 μm in size. It is more likely that individual GNPs were incorporated into the matrix. However, it was not possible to locate these potential GNPs due to spatial resolution limit of SEM. Therefore, Transmission Electron Microscopy (TEM) studies are recommended to observe these GNPs within the matrix and determine whether any chemical reaction took place between the matrix and GNPs for future work. In order to observe how the GNPs were distributed through the matrix, another sample was cut from the top of the nanocomposite cast and examined under the SEM (Fig. 6). Along with Fig. 5, Fig. 6 suggests that the GNPs were reasonably distributed in different locations of the nanocomposite. An EDX analysis was performed on a potential cluster of GNPs shown in Fig. 6b (Fig. 7). This analysis implies that the structure is most likely to be composed of the GNPs fed into the liquid alloy due to the relatively higher carbon content. Overall, it may be suggested that the GNPs were relatively effectively distributed through the matrix, although their clusters (a few microns in size) are present in the microstructure. It is considered that playing the processing parameters such as increasing ultrasonic power and treatment time could further break these clusters and improve the rate of GNPs dispersion.

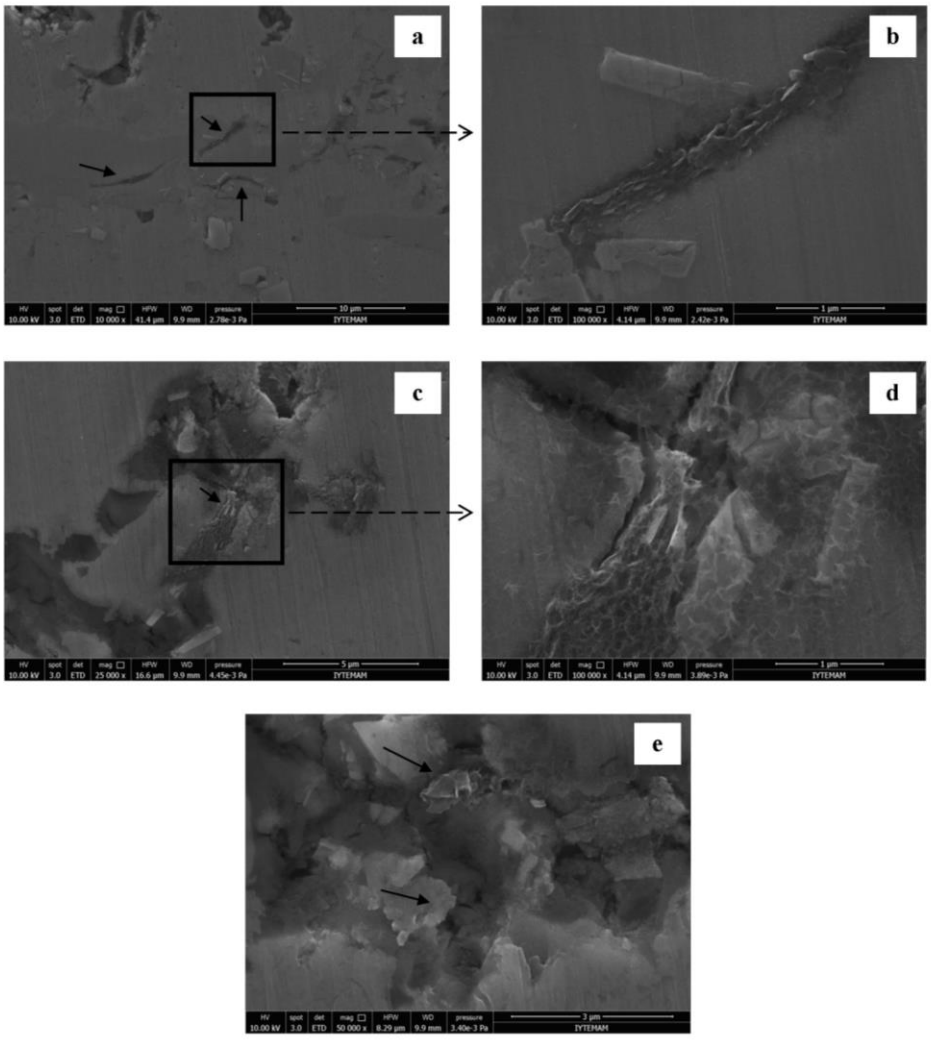

Figure 6. SE images of a sample cut from the top of the A360/0.5 wt.% GNPs nanocomposite cast (The potential GNPs and their clusters are marked with black arrows, *b* and *d* are the magnified images of the areas marked with black squares in *a* and *c*, respectively).

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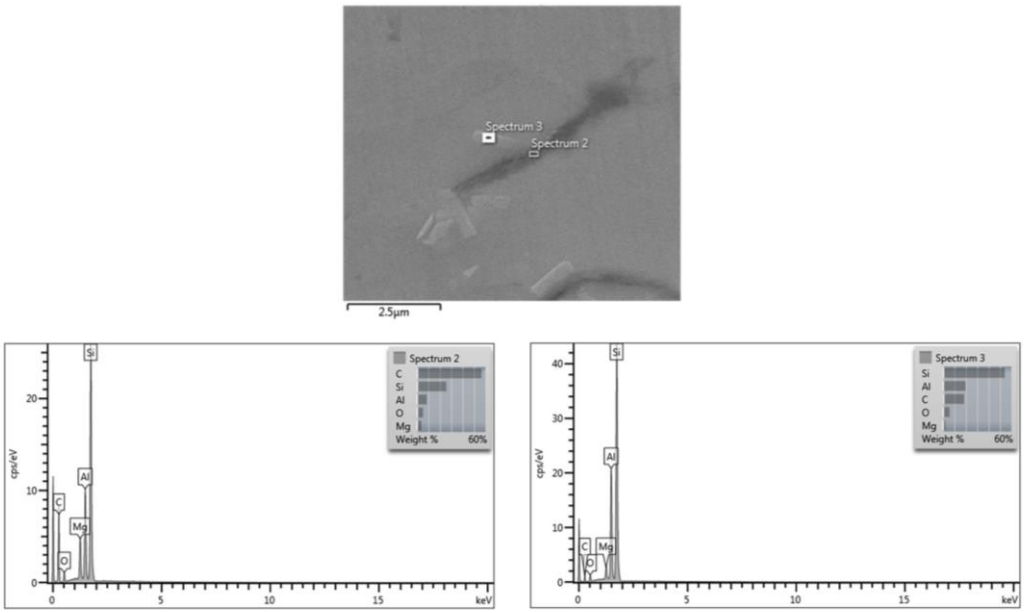

Figure 7. EDX analysis of a cluster of GNPs (Spectrum 2) embedded into the A360/0.5 wt.% GNPs nanocomposite.

The average Vickers hardness value of the A360 reference alloy increased from 58±5.9 to 62±5.2 with the addition of GNPs. Although the increment in the hardness is limited, this result indicates potential strengthening effect of GNPs as reinforcements in metal matrix composites. The limited increase in the hardness could be attributed to the presence of GNP clusters/agglomerates in the microstructures. Also, it is the fact that the addition of aluminium and magnesium powders in the tablet was likely to modify the microstructure forming different phases or intermetallics between α-aluminium grains in A360 alloy. In order to discuss this effect on the hardness increase, further detailed investigation by means of SEM and EDX analysis is required.

4. Conclusions

A360 alloy/0.5 wt.% GNPs (an average thickness of 50-100 nm and size of 5 μm) nanocomposite was fabricated by a combination of semi-solid stirring and ultrasonic treatment. This combined method involved the introduction of the prepared tablets, in which GNPs, aluminium and magnesium powders are ball milled and pressed together, into the semi-solid alloy under mechanical stirring followed by ultrasonic treatment of liquid nanocomposite for uniform dispersion of GNPs. The microstructural investigation of the nanocomposites by optical and scanning electron microscopy may suggest that relatively uniform distribution and effective deagglomeration of GNPs in the matrix were achieved. Therefore, this combined method was found to be promising for dispersion of GNPs. The hardness of the GNPs reinforced nanocomposites increased in comparison with that of the reference alloy without reinforcement.

Acknowledgments

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