An innovative process for dispersion of graphene nanoparticles and nickel spheres in A356 alloy using pressure infiltration technique

Sourav Das1 | Amir Kordijazi2 | Omid Akbarzadeh3 | Pradeep K. Rohatgi4

1Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin
2Department of Industrial and Manufacturing Engineering, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin
3Nanotechnology and Catalysis Research Center, University of Malaya, Kuala Lumpur
4Department of Material Science and Engineering, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin

Correspondence
Sourav Das, Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, WI 53211.
Email: sourav328@live.com

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Abstract
In this paper, a unique, innovative liquid metal infiltration process for the dispersion of graphene in the aluminum (Al) matrix in the presence of nickel spheres is introduced. The nickel spheres impart a reaction that induces wettability with molten Al, hence facilitating the infiltration of Al encapsulating graphene. Raman spectroscopy shows the two-dimensional bands, thereby confirming the presence of graphene in the infiltrated composite. The microstructure of the infiltrated composite shows the dispersion of graphene, Al-silicon eutectic, and a reaction product between nickel and Al around nickel spheres. The sample of composite tested in this study exhibits a high contact angle and hydrophobicity, possibly due to the dispersion of graphene particles on the surface of the samples. This presence of graphene on the surface causes a reduction of wetting by water and a decrease in corrosion rate which is demonstrated by polarization testing results.

KEYWORDS
aluminum alloy, corrosion, graphene, hydrophobicity, pressure infiltration, Raman spectroscopy

1 | INTRODUCTION

Melt infiltration has been established as a viable process for producing metal-ceramic composites. In this process, liquid metal is forced through the pores between reinforcements by applying pressure above a threshold value. The infiltrated liquid metal replacing the gas phase within the spaces between the pores and solidifies in the interparticle region resulting in a composite. Recently, there has been considerable interest in developing graphene dispersed aluminum (Al) composites to achieve enhanced properties. It was reported that after the addition of 0.54 wt.% graphene nanoplatelets, the yield and tensile strength enhanced by 116% and 45%, respectively. In the melt route, the dispersion of graphene in liquid metal presents difficulties because of the tendency of agglomeration of graphene and problems with the infiltration of graphene preforms by molten Al due to lack of wettability with graphene. It has been reported that metal coating on...
ceramic dispersoid promotes wettability between liquid metal and ceramic phase by enhancing the surface energy of the solid phase. The nickel (Ni)-coated silicon carbide (SiC) performs have been successfully infiltrated with Al alloys by pressureless and pressure infiltration techniques. Coated samples have shown a higher length of infiltration than that of uncoated ones. Preheating temperature has a great influence on the infiltration of liquid metal. It has been reported that low preheating temperature (500°C) of Ni-coated SiC has less influence in liquid metal infiltration than high preheating temperature (650°C).

Ultrasonic cavitations have been found as an effective process to incorporate nano-sized particles in liquid metal and alloys to synthesize composites. The sonotrode used in the ultrasonic vibration process has assisted the particle disintegration and avoids agglomeration of the second phase. This technique promotes uniform dispersion of second phase particles.

In the present study, the Al melt is pressure-infiltrated through a pre-mix mass of graphene and Ni spheres. The presence of wettable Ni spheres is expected to promote wetting and infiltration of Al alloy melts through the aggregate. The objective of this work is to manufacture Al 356 alloy with graphene dispersed between metal spheres with a unique microstructure via an innovative infiltration process. This microstructure leads to a surface with low wettability and high corrosion resistance.

2 EXPERIMENTAL PROCEDURES

Al alloy (A356) was taken as the base metal with a composition of 7.5 wt.% silicon (Si), 0.5 wt.% Fe, and 92 wt.% Al. 0.72 wt.% M5 graphene and 0.73 wt.% Ni spheres (diameter ~400-600 μm) were used as a premixed mass for infiltration. Initially, the graphene sheets were mixed with 20 mL toluene and 20 mL ethanol and then mixed with 450.23 g of small zirconia balls followed by shearing in an attritor mill for 4 hours. In this process, the graphene sheets were converted into finer particles. The grounded mass was dried for 24 hours at 75°C. This dried powder was put in an ultrasonic vibrator for the separation of zirconia balls from graphene. Ni spheres were washed with ethanol and dried, and then mixed with graphene to form a preform. The preform was then placed in a quartz tube of 18 mm outer diameter and 120 mm length. The quartz tube was coated with zirconia wash and dried in a furnace for 2 hours at 80°C. After drying, the quartz tube was sprayed with graphite. The quartz tube was filled with a Ni-graphene mixture. The A556 Al piece was placed above the Ni graphene mixture preform was then placed inside a furnace. The photograph of the melt infiltration unit is shown in Figure 1A. After placing the quartz tube inside the furnace 356, the temperature of the furnace was slowly increased to 750°C and kept for 30 minutes. Once the Al alloy melted, Argon (Ar) gas with a pressure of 300 psi was applied. By the application of pressure, the Al alloy melt penetrated through the premix mass of graphene and Ni spheres. After the infiltration, the whole setup was left for 8 hours for cooling down to room temperature. The infiltrated mass was taken out after breaking the quartz tube. Figure 1B shows a typical Al composite mass prepared by the melt infiltration technique.
For microstructural examination, the Al composite sample was cut and polished using the normal metallographic techniques, etched with Keller's reagent and observed under an optical microscope. A scanning electron microscope interfaced with EDX was used to find the elements present in the sample. To analyze the distribution of graphene, Raman spectroscopy was done. The contact angle between the composite and water was found out by Rame-Hart Goniometer. A potentiodynamic polarization test was performed to study corrosion resistance of the Al-Ni-Si-graphene composite sample. SP-200 BioLogic potentiostat/galvanostat was used to run the corrosion test. The electrolyte used for the corrosion test is 3.5% NaCl solution. The composite sample and graphite rod were used as the working electrode and counter electrode, respectively. For the reference electrode, standard calomel electrode was used.

3 | RESULTS AND DISCUSSION

3.1 | Surface characterization

Figure 2 shows typical optical micrographs at different magnifications. They show spherical particles of Ni and a thin layer of presumably NiAl₃ intermetallic layer formed on the surface of the Ni spheres, which formed as a result of the reaction between Ni and molten Al; the spaces between Ni spheres are a composite of Al-Si and graphene platelets formed during infiltration. A higher magnification micrograph clearly shows a faceted Si phase (arrow marked) in graphene sheets (black color). The region between Ni spheres formed due to the solidification of Al-Si alloy between graphene particles.

Figure 3 shows a typical SEM (Scanning Electron Microscope) micrograph along with the EDX (Energy Dispersive X-Ray) analysis of a typical region of Al-graphene-Ni composites. It shows different peaks corresponding to Al, Ni, Si, and C. The weight percentage of Al, Ni, Si, C appear to be 22, 64, 3, and 7, respectively.

Figure 4 shows the results of Raman spectroscopy analysis of the infiltrated composite surface. The spectrum shows the presence of graphene in the Al alloy matrix. The D-band (1350/cm) in Raman spectra suggests a disordered structure of graphene. The presence of distortion in the sp2-hybridized is reflected by the D band. G band (1580/cm) arises due to the stretching of the C-C bond in the graphene structure and is common in the SP2 carbon system. Raman spectra also show an interesting 2D band (2650/cm) confirming the presence of graphene in the structure. A sharp and high-intensity
peak suggests single-layer graphene, whereas, a less intense and splitting two-dimensional (2D) bands indicates few layers of graphene sheets. Figure 4 shows a less-intense single 2D peak which signifies the presence of multilayer graphene sheets.\textsuperscript{15}

### 3.2 Wettability (water contact angle measurement)

When water flows over a surface, it acts as an electrolyte which can lead to corrosion of the substrate based on field conditions. Corrosion depends on the area of contact, therefore, reducing contact area can improve corrosion resistance. One way to achieve this is by increasing the contact angle between water and the solid surface. Until now, the focus for corrosion and drag-reduction efforts has been on the development of techniques including application of hydrophobic coatings, addition of polymers to the fluid, addition of bubbles or air layers, and the utilization of compliant walls and riblets, and creation of surface roughness via laser patterning, CVD, lithography, ion beam patterning, and spraying.\textsuperscript{16} All these techniques cannot be applied readily to large complex-shaped components used in the industry. These methods are costly and nondurable.

The wettability with water is one of the important characteristics of a solid surface that influence the corrosion resistance. The contact angle of a water droplet on the surface is used to measure wettability.\textsuperscript{17} Wettability of a multiphase...
solid is determined by phases present on the solid surface and the roughness of the surface. Studying microstructure and wettability of solid surfaces helps in developing surfaces with low wettability. Different water droplet volumes were used for contact angle measurements that include 0.5, 0.8, 1.5, 1.9, 2, 2.5, 2.2, and 2.4 μL. Figure 5 shows the values of contact angles for different drop sizes. In most cases, the contact angle values are larger than 90° indicating hydrophobicity of the Al composite surface.\(^{17,18}\) It should be noted Al, Ni, and Si are hydrophilic materials with contact angles less than 90°.\(^{19}\) The high CA observed for the Al-Si-Ni-graphene composite in this study is probably due to the presence of graphene in the composite structure.

As shown in Figure 5 the contact angle values increase with increasing water droplet size. The reason is that the larger droplets occupy more area and have a greater probability of interaction with graphene particles which results in an increase in the contact angle values between Al-Si-Ni-graphene and water.

### 3.3 Corrosion resistance

To evaluate the corrosion resistance of the Al-Si-Ni-graphene composite samples, a potentiodynamic polarization experiment was performed in a 3.5% NaCl solution. The result was compared with the corrosion result of cast iron as it is shown in Figure 6A,B and Table 1.

The corrosion rate of each sample was calculated using Equation (1).

\[
CR = \frac{K_1 \times W}{n \times \rho} i_{corr}
\]

where CR is corrosion rate (mm/year), \(W\) is atomic weight, \(n\) is the valence of the element, \(\rho\) is density (g/cm\(^3\)), \(i_{corr}\) is corrosion current density (μA/cm\(^2\)) which is obtained from the Tafel plot (Figure 6A) and listed in Table 1 for each sample, and \(K_1\) is equal to 3.27×10\(^{-3}\) (mm g/μA cm year).\(^{20}\)

As shown in the result the composite sample shows high corrosion resistance as compared to cast iron. The high corrosion resistance of Al-Ni-Si-graphene composites is probably due to the hydrophobicity of the composite sample which is a result of its unique microstructure containing graphene and distribution of other phases. It has been shown that there is often a direct relationship between hydrophobicity and corrosion resistance of alloys. The more hydrophobic the alloy is, the more resistant it is against corrosion.\(^{21-24}\) This makes the alloy a suitable choice for the applications where low wettability and high corrosion resistance are required.\(^{25,26}\)
4 | CONCLUSION

A356 Graphene Ni composite was manufactured using a pressure infiltration technique; the technique involved infiltration of a mixture of Ni spheres and graphene platelets by molten Al-Si alloy. The wettability of Ni spheres facilitates the infiltration of Al-Si alloy in Ni-graphene perform. The microstructure showed partly unmelted Ni spheres coated with a layer of Ni-Al intermetallic with Al-Si eutectic and graphene between the spheres. Characterization techniques including optical microscopy, SEM, EDX, and Raman spectroscopy demonstrated that the graphene is present between the Ni spheres; a layer of Ni-Al intermetallic phase was observed around the Ni spheres due to their reaction with Al. This composite’s surface exhibited a high contact angle ($\theta > 90^\circ$) due to the hydrophobic nature of graphene which is present in the matrix. This presence of graphene in the Al-Si-Ni-graphene composite results in higher resistance against corrosion in this composite.

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CONFLICT OF INTEREST

Authors declare no conflict of interest.

AUTHOR CONTRIBUTION

Sourav Das contributed to the conceptualization, data curation, formal analysis, investigation, methodology, project administration, resources, software, writing the original draft. Amir Kordijazi contributed to the conceptualization, data curation, formal analysis, investigation, methodology, project administration, software, visualization, writing the original draft, reviewing and editing. Omid Akbarzadeh contributed investigation, validation, visualization, reviewing, and editing. Pradeep Rohatgi contributed to the conceptualization, funding acquisition, methodology, resources, reviewing and editing.

ORCID

Sourav Das https://orcid.org/0000-0001-7940-5470
Omid Akbarzadeh https://orcid.org/0000-0002-0904-5593

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