Fabrication of Titanium Metallic Composites Reinforced with Graphene Nanosheets

Zaiyu Zhang and Yilong Liang

ABSTRACT

Graphene-reinforced titanium matrix powders were successfully synthesized through ball milling and powder metallurgy. The prepared-samples were fabricated for the first time by vacuum arc remelting (VAR). The microstructures were observed by scanning electron microscope (SM) and X-ray diffractometer (XRD). At the same time, the defects and the number of layers of graphene added in titanium alloy were studied by Raman spectroscopy. The results show that this kind of composite material has good physical properties.

INTRODUCTION

Graphene, as the perfect two-dimensional lattice of sp2-bonded carbon atoms [1,2], has recently attracted tremendous attention due to its excellent properties, such as high fracture strength (125GPa)[3], extreme thermal conductivity (5000Wm-1K-1)[4] and super charge-carrier mobility (200,000cm2V-1s-1)[4]. Graphene nanosheets (GNSs) composed of a few graphene layers possess properties similar to that of single-layer graphene but are much easier to produce and handle. It has been supposed that GNSs may significantly outperform carbon nanotubes (CNTs) and have great potential in composite fields as a superior thermal component and ideal reinforcement.

On the other hand, titanium and its alloys are widely used for dental and orthopedic implants due to their excellent stability, good mechanical and

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biocompatibility properties [5-7]. However, low thermal conductivity of titanium alloys greatly imposes restrictions on its applications. One approach to enhance the thermal conductivity of titanium alloys is to use materials with extremely high thermal conductivity as reinforcement. Due to its excellent thermal conductivity, GNS is a good candidate for the reinforcement of titanium matrix to enhance the thermal conductivity.

Fortunately, the flake powder metallurgy route [8-10], which is recently developed to fabricate CNTs/Ti composites, has also proved the possibility for fabrication of GNSs/Ti composites. However, to our knowledge, there have been few reports on the fabrication and actual properties of bulk GNS-based Metal Matrix Composites. In this work, we fabricated GNSs/Ti powders by first flake powder metallurgy, followed by VAR and hot extrusion to obtain prepared samples. The samples’ mechanical properties were tested and the relevant strengthening mechanism of GNSs is discussed based on the primary experimental evidences.

**EXPERIMENTAL PROCEDURE**

In the experimental progress, GNS was used as the raw materials because it can generate many hydroxyl and epoxy groups on the surface of the solution in absolute ethyl alcohol, which makes it easy to disperse in solvents and form more stable solutions. Though there are some residual oxygen and point defects left on the surface of the solution, this method enabled effective and uniform dispersion of graphene in the flake Ti powder and the final GNS/Ti composites. Herein, we fabricated GNS/Ti composites by vacuum arc remelting and hot extrusion.

Two steps are involved in the fabrication of our samples.

**Raw Material Blending**

Firstly, GNSs (99% in purity) were added to absolute ethyl alcohol and the solution was performed by an ultrasonic dispersion. Secondly, the spherical Ti powders (100g, 45 um in diameter, 99% in purity) were transformed into 10 um thick Ti flakes through ball milling in an attritor at 325rpm. Thirdly, the refined Ti flakes were added to the solution containing the graphene to form a powder-slurry. The mixed slurry was mechanically stirred until its color was changed from brown to transparent, before being filtered and rinsed by absolute ethyl alcohol to obtain GNS/Ti composite powders. The GNS/Ti composite powders were heated to 100°C, until finally GNS/Ti composite powders were obtained.

**Compacting and Consolidation of GNS/Ti Composite Powders**

The GNS/Ti composite powders were first compacted into 20mm×10mm billets, which were consolidated by sintering at 1200°C for 2 hours. Many billets formed an electrode. The electrode was smelted in VAR
furnace and became into GNS/Ti ingot. The above three processes all worked under a vacuum condition lower than 1 Pa. The ingot was smelted by VAR furnace again and followed by hot extrusion at 820°C at an extrusion ratio of 10:1.

RESULTS AND DISCUSSION

Hardness Analysis

Micro hardness of samples was randomly measured. The results are shown in Table 1.

As can be seen from Table 1, the micro hardness of the samples was significantly higher than that of the pure titanium matrix composites. This shows that the addition of graphene has a good effect on the mechanical properties of titanium alloys.

<table>
<thead>
<tr>
<th>PREPARED SAMPLE</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITANIUM MATRIX (HV)</td>
<td>145</td>
<td>148</td>
<td>158</td>
<td>149</td>
<td>159</td>
<td>141</td>
<td>150</td>
</tr>
<tr>
<td>0.3%wtGNS/Ti (HV)</td>
<td>188</td>
<td>208</td>
<td>192</td>
<td>195</td>
<td>192</td>
<td>209</td>
<td>197</td>
</tr>
</tbody>
</table>

Figure 1. SEM morphology of (a) original GNPs and (b) GNPs in Ti matrix.

Morphological Observation

As shown in Fig. 1, the surface of the GNS/Ti composite has many wrinkles. As testified by many researchers[11], fine wrinkles such as shown in Figs. 1 and 2 are signs of homogeneous dispersion of graphene oxide nanosheets.
Raman Spectroscopy and XRD Analysis

Fig. 2 shows the Raman spectra and XRD patterns of the titanium-graphene alloy with the content of 0.3wt%GNPs. Both Raman spectra exhibit three main characteristic peaks: the G mode, a doubly degenerate phonon mode (E2g symmetry) at the Brillouin zone center observed at 1570cm⁻¹ originating from in-plane vibration of sp² carbon atoms; the D mode arising from the doubly resonant disorder-induced mode (~1332 cm⁻¹) and the symmetry-allowed 2D overtone mode (~2677 cm⁻¹), which are the typical features of thick graphene stacks. T. As shown in Fig.3, XRD shows the characteristic peaks of the TiC, Ti and C.

![Figure 2. Raman spectra patterns of graphene /Ti.](image)

From the above discussion, it is quite clear that GNS has intactly entered the Ti composite. Its structure can maintain original shape. The thermal conductivity was increased from 15.25 to 20.50Wm⁻¹K⁻¹ by the addition of 0.3wt% GNS, which demonstrates that GNS is very promising as an effective reinforcement in titanium matrix composite and our technical route is a feasible and successful way to fabricate graphene-reinforced metal matrix composites. The relevant strengthening mechanisms involved the GNSs/Ti composites will be discussed in the future.

![Figure 3. XRD patterns of graphene /Ti.](image)
CONCLUSIONS

GNS/Ti composites were successfully fabricated by VAR. In the fabrication process the graphene reinforcement was applied in the form of graphene/alcohol colloid for a safer and simpler manufacturing process. The results of Raman spectroscopy suggest that graphene reinforcements were successfully mixed into the titanium matrix by the intense stirring and mixing of materials during dispersion of GNS.

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