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Reinforcement with graphene nanoflakes in titanium matrix composites

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ABSTRACT

Graphene reinforced bulk titanium matrix composites (TMCs) were successfully fabricated via powder metallurgy approach. 0.5 wt% graphene nanoflakes (GNFs) and Ti6Al4V mixture powders were prepared by a wet process. The composites were then consolidated using hot isostatic pressing (HIP) with a pressure of 150 MPa at 700 °C followed by isothermal forging with a forging ratio of 3 at 970 °C. The microstructure and mechanical properties of TMCs had been investigated by optical microscopy, SEM, TEM and static tensile tests. Microstructure observation illustrated a uniform distribution of graphene in the composite and in-situ formed TiC particles at the metallurgical interface between titanium matrix and graphene. Compared with the unreinforced titanium matrix, the 0.5 wt% GNFs reinforced composite exhibits significantly improved strength without losing ductility, which demonstrates that GNFs could actually act as superb reinforcements in TMCs.

1. Introduction

Graphene is a single-atomic-layer material consisting of sp^2-hybridized carbon atoms. It has attracted great scholarly attention recently due to its superior properties, such as excellent mechanical properties, high electrical conductivity and good thermal conductivity [1–3]. Graphene nanoflakes (GNFs) composed of multiple layer graphene could be produced from chemical reduced graphene oxide. They possess properties similar to that of single-layer graphene but are much easier to prepare and handle. To utilize their superior properties, GNFs are generally dispersed into various matrices (e.g. polymers, metals and ceramics). GNFs have recently been reported as reinforcements in metal matrices (e.g. aluminum [4–6], magnesium [7,8] and copper [9,10]) to improve the properties of the matrices. The results indicated that graphene is sufficiently robust to improve mechanical properties of the metal matrix composites. For example, Li et al. [11] have synthesized the aluminum/graphene composites via powder metallurgy process and found that both tensile and yield strengths were remarkably increased by GNFs without loss of ductility performance.

Titanium (Ti) and titanium alloys are extensively used in aeronautical, marine and chemical industries because of their high specific strength, high specific modulus, good oxidation and corrosion resistance [12–15]. Considering energy saving and fuel consumption, the further improvement of mechanical properties of Ti alloys is significantly important when they are applied to those industries. Dispersion strengthening is one of the effective methods to improve the mechanical response of titanium matrix composites (TMCs). In previous works, reinforcement materials such as ceramic particles (SiC [16], TiC [17], TiB [18]), carbon nanotubes [19,20], carbon fibers [21] and SiC fibers [22] were used to improve the strength of Ti and its alloys by powder metallurgy method. However, the above-mentioned reinforced TMCs showed a combination of high strength and low elongation-to-failure. Namely, the incorporation of hard reinforcements increases the tensile strength and stiffness yet decreases their tensile ductility and fracture toughness. It results in a poor reliability of the composite materials [23]. Compared with the above filling materials, GNFs have higher strength, elongation and larger specific surface area. GNFs could cause a good match between strength and ductility in the as-fabricated composites so that they would be a favorable candidate to reinforce TMCs. However, few works present TMCs reinforced with GNFs in current science and practice.

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TMCs reinforced by GNFs have the potential to become a major structural material in the next-generation. In this study, they were prepared through powder metallurgy approach. It is strongly expected that the combination of titanium and GNFs will serve superior mechanical properties to the conventional TMCs. The microstructures and the tensile properties of the composites were investigated and compared with those of the matrix alloy.

2. Experimental

Gas-atomized Ti6Al4V powder with a mean particle diameter of ~35 μm was supplied as the starting matrix material. Table 1 shows chemical composition of the matrix alloy used in this study. Fig. 1a is the scanning electron microscopy (SEM) image of titanium powder which has a spherical morphology. GNFs applied in this investigation were chemically synthesized from graphene oxides which were prepared by Hummer's method [24]. Fig. 1b shows the transmission electron microscopy (TEM) image of GNFs which have a large specific surface area and two-dimensional high aspect ratio sheet geometry.

The GNFs reinforced Ti6Al4V composites were prepared in a number of steps: blending, degassing, hot isostatic pressing (HIP) and isothermal forging. Samples of pure Ti6Al4V powder and Ti6Al4V powder reinforced with 0.5 wt% GNFs were prepared respectively. Dispersion of GNFs in metal matrix is more challenging than other reinforcement materials due to their greater interfacial contact area [3], hence a low weight fraction of graphene was chosen for this study. Take Ti/0.5 wt% GNFs composite for example, the detailed fabrication processes are as follows. At the first step, Ti6Al4V powder (2 kg) and GNFs (10 g) were mechanically mixed with stearic acid (4 g) using a modified V-blender for 24 h. The mixed powder was added into ethyl alcohol (1000 ml) and mechanically stirred at 70 °C in a water bath until it turned into semi-dry state. Then it was fully dried in an oven at 60 °C. Fig. 1c shows the morphology of the mixed powder after blending. It presents that the titanium particles are covered by several well-distributed GNFs. After that, the mixture was sealed in a cylinder-shaped 304 stainless steel can, and pumped to 5×10^{-2} Pa. In order to further remove the moisture, the remaining gas and stearic acid from the mixed powder, the steel can was heated to 480 °C for 6 h. Subsequently, the can was hot isostatic pressed at 700 °C and 150 MPa for 2 h. Then the canned composite powder was isothermal forged at 970 °C with a forging ratio of 3. Finally, the specimen was subjected to an anneal heat treatment at 780 °C for 2 h.

Morphology and property characterization SEM images were obtained with a field emission scanning electron microscope (SEM; JEOL JSM-7001) equipped with an energy-dispersive X-ray spectrometer (EDS). The microstructures of the bulk Ti/GNFs composite were investigated by optical microscopy, SEM and transmission electron microscopy (TEM) which was performed with JEOL JEM-2100 microscope operated at an accelerating voltage of 200 kV. The interfaces between titanium and graphene were also investigated by high resolution transmission electron microscopy (HRTEM) on JEOL JEM-2100 microscope. The TEM specimens were prepared from the forged material parallel to the forging direction. The structure integrity of GNF was examined by Raman spectroscopy (Renishaw inVia) with an Ar^+ laser wavelength of 633 nm. The phase composition was characterized by Rigaku D/Max 2500 v/pc X-ray diffraction (XRD) with Cu K_a radiation. The bulk density of the composite was measured by the Archimedes method. The tensile specimens with a gage length of 25 mm and a diameter of 5 mm were machined perpendicular to the forging direction and pulled to failure on a testing machine (Instron 5887) at ambient temperature. For minimizing the experimental error, three tensile specimens for each sample were tested with stretching rate of 1 mm/min.

Table 1
Chemical composition (wt%) of the as-atomized titanium powders.

Powder	Al	V	Fe	O	N	C	H	Ti
Ti6Al4V	6.24	3.98	0.20	0.087	0.01	<0.01	0.002	Bal

3. Results and discussion

The mechanical properties of TMCs are not only determined by the volume fraction, morphology and type of reinforcements but also affected by the morphology of matrix and the distribution of reinforcements [2,25]. Fig. 2a shows the optical microscopy of the Ti/GNFs composite reinforced with 0.5 wt% GNFs after HIP. XRD scan for the Ti/GNFs composite (Fig. 2b) shows the peaks corresponding to α-Ti phase. It is found the sample consists of equiaxial and elongated α-Ti phase. XRD pattern does not show formation of any new phase (such as TiC), namely that GNFs did not react with titanium matrix at 700 °C during HIP process. Furthermore, the GNFs dispersed in the matrix could not be recognized clearly by optical microscopy (Fig. 2a). Fig. 2c presents SEM image of the Ti/GNFs composite after HIP. The GNFs that dispersed in titanium matrix are confirmed by the Raman spectra in Fig. 2d, which shows the characteristic peaks of D (1351 cm^{-1}), G (1592 cm^{-1}) and 2D (2660 cm^{-1}) band of the GNFs. In the process of HIP, the titanium powders were consolidated effectively. Consequently, the GNFs that covered on the titanium powders (Fig. 1c) appeared to be line-like in the SEM image (Fig. 2c). It can be seen that GNFs are homogeneously distributed in the titanium matrix.

Fig. 3a shows the optical microscopy the Ti/GNFs composite reinforced with 0.5 wt% GNFs after isothermal forging and heat treatment at 780 °C for 2 h. The microstructure of the composite consisted of equiaxed bright α-Ti phase grains and intergranular gray β-Ti phase, which is typical from α+β titanium-base alloys that have been underwent an annealing treatment. To investigate the microstructure characteristics more clearly, SEM observation of the as-forged composite at high magnification is shown in Fig. 3b. It can be seen that the stripped or granular β-Ti phase located at intragranular and grain boundary sites. Additionally, the density of the composite after isothermal forging is 4.40 g/cm^3, which is 99.1% of the theoretical density (4.44 g/cm^3). It can be concluded that the whole process including blending, degassing, HIP and isothermal forging is effective to fabricate compact Ti/GNFs composite.

Fig. 4a and b presents bright-field TEM images of graphene in the fabricated Ti/GNFs composite. The results show that the graphene located around the boundary of titanium grains. According to the EDS spectrum, the ribbon-like region consisted of pure carbon (Fig. 4c) completely, indicating the graphene still remained in the composite. Besides, Fig. 4b exhibits that the interlayer space is about 0.34 nm, which confirms the structure of graphitic layers. In order to characterize the interface microstructure, the HRTEM image of the area “A” in Fig. 4a was carried out (Fig. 4b). It demonstrated that there is a strong interface bond between titanium grain and graphene with formed TiC particles in the Ti/GNFs composite. The existence of TiC layer surrounding the graphene indicates that the titanium matrix reacted with graphene to form titanium carbide during isothermal forging. The results also elucidate that when the temperature is relatively high (970 °C), GNF is reactive to form titanium carbide with titanium matrix. Due to the high stability of its chemical properties, it could still maintain its layered microstructure to some extent.

Table 2 shows the tensile properties of the Ti/GNFs composite containing 0.5 wt% GNFs together with the tensile response of pure