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Uniform dispersion of multi-layer graphene reinforced pure titanium matrix composites via flake powder metallurgy

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ABSTRACT

In this study, a micro-laminated structure of titanium matrix composite with uniformly dowel-like and aligned multi-layer graphene (MLG) was fabricated by flake powder metallurgy. Flake ball milling method was applied to efficiently obtain flaky Ti powder with embedded MLGs flakes. Spark plasma sintering (SPS) was applied to consolidate mixed powders, in order to obtain the laminated billet which can enable the MLGs to preserve its original structure. Subsequent hot-rolling (HR) was applied to form the tight interface and reduce the internal defection of composites. Results showed that the composites interface owns in-situ formed TiC layer between MLGs and matrix. Also, the composites with micro-laminated structure showed significant improvement of strength. Consequently, a uniform disperse of MLG enabled the as-designed composites to exhibit 280% increase in yield strength (~2 GPa), 96% increase in nano-hardness and 16% increase in elastic modulus as compared to monolithic flake pure Ti (HR normal direction (ND)). The micro-laminated structure and well-dispersed MLGs were believed to be beneficial to harden and strengthen Ti matrix, and the relevant strengthening mechanisms of the composites were carefully discussed.

1. Introduction

MLG is a two-dimensional nano-material which has been considered to be one potential new carbon material in the field of material science and engineering due to its remarkable electrical, thermal and mechanical properties [1–3]. In the past decade, attentions have been increasingly paid to MLG reinforced metal matrix composites (MLG-MMCs), which are wildly used as structural materials in aerospace, automotive, and construction industries [4]. An increasing number of researchers have focused on the fields like aluminum [5–8], magnesium [9], and copper [10,11] matrix materials. A lot of researches have been found that the MLG offer significant improvement in the mechanical properties, such as tensile strength and wear resistance.

Titanium and titanium alloys have many unique features such as high specific strength and light weight which enhance the potential for the use of Ti as matrix material [12–14]. Titanium matrix composites (TiMCs) can be used in various industries , such as automotive, and airplane industries, to meet the increasing demand of energy saving and weight-reduction. Because of the high corrosion resistance, their chemical and petrochemical applications are also excellent. Many researches begin to focus on fabricating MLG reinforced TiMCs (MLG-TiMCs) due to its potential superior mechanical property compared to conventional TiMCs (e.g TiC/Ti, TiB/Ti and SiC/Ti). Shin et al. [15] synthesized 0.7 vol% graphene reinforced pure Ti (compressive yield strength ~1.5 GPa) by using powder metallurgy (consolidated by hot-pressing at 570 °C for 1 h under 140 MPa). Zhen et al. [16] fabricated 0.5 wt% MLG/Ti6Al4V (by applying hot isostatic pressing) under 150 MPa at 700 °C followed by isothermal forging with a subsequent forging process at 970 °C, specially, the composites exhibit significantly improved strength without losing ductility. Zhang et al. [17] fabricated TiMCs by adding low MLG content (0.025 wt%, 0.05 wt% and 0.1 wt%) by applying SPS technique and HR process, and MLG in matrix exhibit excellent load bearing

capacity. From these as-reported MLG-TiMCs, it demonstrates that the interface between MLG and Ti matrix owns effective load-transfer ability because of the strong Ti-C ionic bond and TiC reaction products effect. MLG as one graphenic nanostructure material is believed to retain the desirable properties of single layer graphene such as high surface area and excellent mechanical properties [4]. However, MLG is not easy to be uniformly dispersed in matrix attributed to graphenic nano-characters and strong Vander Waals forces between MLG [18–20], especially when the composite owns high MLG content. The

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agglomeration of MLG in composites could act as defects and stress concentration to worsen the strength. As a result, the distribution of MLG in matrix is a key issue for affecting the MLG-TiMCs strengthening efficiency.

Flake powder metallurgy (Flake PM) is a favorable method in MMCs due to its low cost, flexibility and ease of control. In general, flake Ti powder has a much higher apparent volume than spherical powders, which is beneficial for the uniform distribution of MLG although the large density difference between MLG and metal matrix. In this paper, Flake PM was employed to improve the uniformity of MLG distribution. In Flake PM, the MLG powder was ball milled in agate jar with low speed and then blended with spherical Ti powder with high speed. In this ball milling process, MLG powders attached on the surface of agate milling balls first, then the spherical Ti powder was transformed into flake Ti powder under the compression and shearing force by agate milling balls, meanwhile, small MLG platelets were uniformly distributed in the flake Ti powder. Flake Ti / MLG mixed powders were then consolidated by SPS and strengthened by subsequent HR to obtain novel micro-laminated structure. This architecture enabled the composite display outstanding mechanical properties.

2. Experimental

2.1. Raw materials

Ti powder (CPTi, purity > 99%) with a mean particle diameter of ~45 μm are used as the starting raw material. Table 1 shows characteristics of the Ti powder used in this study. MLG are synthesized from graphene oxide that is prepared by improved Hummers method. Fig. 1(a) shows the scanning electron microscopy (SEM) image of Ti powder. The image shows that the Ti powder with a regular spherical morphology have no aggregation. Fig. 1(b) is the transmission electron microscopy (TEM) image of MLG which shows high aspect ratio and dozens of two-dimensional stacking layers.

2.2. Fabrication of composites

Fig. 2(a) depicts the schematic of the fabrication of Flake Ti/MLG and details of the preparation process can be found in (I-IV). The fabrication process of Flake Ti/MLG mainly contains four steps.

I) MLG Dispersion. Ball milling (BM) method is a relatively more convenient and effective way to disperse the graphene [21]. MLG powders were ultrasonic dispersed and solely mixed with agate milling balls in agate jar. After low-speed ball milling at 150 rpm for 6 h, the MLG powders were well-dispersed and physical absorbed on the surface of agate milling balls (ball to powder weight ratio was 1000:1). The 0.8 wt%MLG/Milling balls were dried in vacuum oven, and prepared to mix with spherical Ti powder.

II) Flake Ball milling (Flake BM). 30 g Ti powder compound with alcoholic solution was mechanical stirred to form the Ti slurries for 20 min. The Ti slurries mixed with 0.8 wt%MLG/Milling balls and then sealed into agate jar. The BM time is 2.5 h with 400 rpm speed. Spherical Ti powder was ball milled into Ti flakes attributed the ‘micro-rolling’ by MLG/Milling balls [22]. Meanwhile, MLG platelets were uniformly distributed on the flake Ti powder. Fig. 1(c) shows the morphology of mixed powders. It presents that the MLG embedded in Ti platelets (100–150 μm).

III) Preforming. In this step, we expected to form high-density blocks in which MLG have nearly no reduction product with Ti matrix. It relied on SPS technique which could offer much more rapid heating and cooling rate (> 500 °C/min) and low sintering temperature [23,24]. The dried powders were loaded into steel die with internal diameter 25 mm and external diameter 55 mm. SPS system (Sojitz Machinery Corporation, Tokyo, Japan) was used to consolidate the mixed powders. The vacuum, applied holding compressive pressure and sintering temperature were adjusted to 1 Pa, 300 MPa and 826 K, respectively. The size of cylinder billet was Ø25 × 12.

IV) Forming. Deformation processing was an effective way to disperse carbon nano-materials in metal matrix and eliminate defects [25]. Moreover, during the hot-working process, the MLG/metal interface bonding regime may transformed from mechanical bonding to chemical bonding due to the growth of reaction products [26,27]. In this study, HR (three pass, 60% reduction) temperature was 1223 K to finally form the composites. Composites were reheated in furnace during each rolling pass, thus the heat loss can be neglected in this paper.

Table 1
Characteristics of the Ti matrix powder.

Powder	Impurity content (mass%)					True density (g/cm^3)	Bulk density (g/cm^3)	Particle size (μm)
CPTi	O	Fe	N	C	H			
	0.15	0.07	0.01	0.01	0.003	4.51	1.25	~45

2.3. Characterization of flake Ti/MLG

The microstructure and fracture morphology of the composites were observed by a field emission scanning electron microscope (FESEM, HITACHI S-4800N, Japan) coupled with energy dispersive X-ray spectrometry (EDX) and high resolution TEM (HRTEM, Tecnai 20 G2, FEI, Netherlands). The Raman spectroscopy (Renishaw inVia, excitation laser 514 nm at a laser power of 5.63 mW) was used to investigate the structure of MLG. The nano hardness and elastic modulus of the composites were investigated using a MTS nano Indenter XP with a Berkovich diamond tip at 45 mN. The composites were mirror polished before the nano-indentation tests. For each composite at least 9 indentations were performed in the form of 3 × 3 array at 3 different positions. The nano hardness (H) and elastic modulus (E_0) of the sintered compacts were calculated according to the Oliver and Pharr method [28]. The Ø4 × 4 cylindrical specimen was cut along with the rolling (*R*), normal (N) and transverse (T) directions of the sample for compression test. The compression tests were conducted at room temperature to investigate the compressive properties of the composites using Instron 5848 Microtester at a constant strain rate of 1.0×10^{-3} s^{-1}. For each composite, at least three compressive samples were performed to acquire the average value.

3. Results and discussion

3.1. Microstructure of flake Ti/MLG

The 3D-SEM microstructure of the hot rolled Flake Ti/ MLG is shown in Fig. 2(b) which reveals the novel micro-laminated structure. It is worth noting that lots of dowel-like (0.5–3 μm) and aligned (almost parallel (0–30°) to RD and TD, 0.5–10 μm) MLGs distributed on the boundary of deformed flaky Ti grains. Thus the quasi-continuous and compressed network will be generated under the synergistic effect by Ti matrix evolution and MLG distribution during sintering and HR. In order to explain the formation of the micro-laminated structure, the microstructure and morphology of MLG in each fabrication process should be further investigated. Fig. 3 shows the SEM microstructure of the rolled composites and pure Ti (transverse cross-section). The pure Ti flake powders were sintered and hot rolled under the same processing conditions. Fig. 3(a) shows the strong elongated α-Ti grains generated along the RD. Fig. 3(b) shows the SEM microstructure of Flake Ti/ MLG billet. It can be observed that Ti and MLG flakes compactly accumulate with each other to form a laminated structure due to the high pressure of SPS. Moreover, some MLG cluster (indicated by white circles) still