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Microscopic mechanical properties of titanium composites containing multi-layer graphene nanofillers

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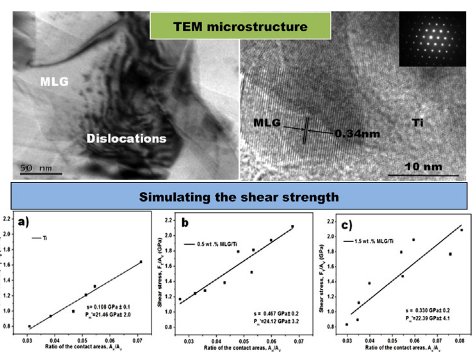
HIGHLIGHTS

- Graphenes promote significantly the indentation yield strength of the composites.
- Graphene reinforced titanium composite exhibits an improved scratch resistance.
- Graphene agglomeration leads to a decrease in mechanical properties.
- Critical length of the added graphenes in the composites was analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, instrumented spherical micro-indentation/scratch tests were conducted to investigate microscopic mechanical properties of multilayer graphene (MLG) reinforced titanium based metal matrix composites (TiMMCs) synthesized using spark plasma sintering (SPS). Raman spectra and microstructure observation illustrated that MLGs survive the harsh SPS processing conditions and homogeneously distribute in Ti matrix. Instrumented indentation and scratch tests showed that mechanical properties in microscopic scale of MLG reinforced TiMMCs such as indentation yield strength and scratch resistance are significantly improved. The computed results corroborated that the critical length of most of the added MLGs satisfies the criterion of critical length of the reinforcement, and the strengthening mechanisms including enhanced dislocation density and Orowan mechanism play significant roles in the improved mechanical properties. This research is expected to facilitate a better understanding of mechanical behavior in microscopic scale of MLG reinforced metal matrix composites.

1. Introduction

Titanium (Ti) and Ti alloys, with combination of light weight, high strength and good chemical resistance, have been widely used as structural materials in aerospace applications [1,2]. However, poor wear resistance significantly limits their further applications [1]. It is well known that metal matrix composites (MMCs) reinforced with ceramic fibers and/or particulates are expected to combine and tailor the best properties of their constituents such as ductility an toughness of the matrix and high modulus and strength associated with the reinforcements, and they usually possess high specific strength and specific elastic modulus over their monolithic alloys [3,4]. Therefore, considerable efforts have been devoted to develop titanium based metal matrix composite (TiMMCs) reinforced with various ceramic particles or fibers such as TiB [5], TiC [6], (TiB + TiC) [7], SiC [8], ZrO_2 [9], Al_2O_3 [10], Y_2O_3 [11]. It is well known that the most important selection concept of an ideal reinforcement in TiMMCs should exhibit not only significant reinforcing

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effect but also relatively lower density. However, it is noted that the densities of abovementioned reinforcements in conventional TiMMCs are usually higher than those of Ti and Ti alloys, and these TiMMCs reinforced with various ceramic particles and/or fibers exhibit improved mechanical properties with the sacrifice of their light weight to some extent.

In recent years, carbonaceous nanomaterials including carbon nanotubes (CNTs) and graphene have emerged as an important class of reinforcing nanofillers in polymers, metals and ceramics owing to their excellent mechanical properties, good self-lubrication and low density [3], and therefore many efforts have been focused on fabrication of CNT reinforced TiMMCs to achieve desired strengthening effect [1,2, 12–14]. Nevertheless, the main challenges for novel TiMMCs reinforced with carbonaceous nanofillers are the homogenous dispersion of reinforcing nanofillers in the metal matrix, good stress transfer efficiency at the interface and retention of structural stability of nanofillers.

Graphene, a single atomic layer of sp^2-hybridized carbon atoms packing densely in a honeycomb lattice and the basic building block of all graphitic forms of carbon, has drawn much attention in the composite field as an promising reinforcement for structural composites due to its excellent mechanical properties (e.g. tensile strength 130 GPa and Young's modulus 0.5–1 TPa) and very high specific surface area (up to 2630 $m^2 g^{-1}$) [15–17]. As compared with CNTs, graphene with higher specific surface area is expected to provide stronger interfacial bonding with metal matrix, and therefore to improve stress transfer efficiency at the interface. In the family of graphene, multilayer graphenes (MLGs) exhibit a thickness of about 1–10 nm and usually consist of a few graphene layers, and they display compatible properties similar to those of monolayer graphene. Moreover, MLGs are much easier to produce and handle. Hence, MLG reinforced metal matrix composites such as MLG/Al [18,19], MLG/Cu [20], MLG/Mg [21], MLG/TiAl [22], MLG/Ni_3Al [23] have been recently developed to achieve improved mechanical properties and tribological properties, in which a decrease in friction coefficient and an enhanced wear resistance could be attributed to the fact that MLGs easily shear and form a protective layer on the sliding contact interfaces [20,21]. However, there is little information available on MLG reinforced TiMMCs. Also, previous research mainly focused on the macroscopic mechanical properties of MLG reinforced metal matrix composites. It is well known that crystalline materials usually exhibit size-independent behavior when a representative volume element of the material is tested, but the microscopic mechanical behavior of a crystalline material become depth and location dependent due to local variation in the microstructure and the inhomogeneous deformation-strain, leading to the fact that the microscopic mechanical behavior of a tested crystalline material is significantly different from the macroscopic one. To the best of our knowledge, few investigations have been made into the comprehensive microscopic mechanical properties of a free-standing graphene reinforced TiMMCs.

In view of the present scenario, the aim of this research was to explore the potential of using MLGs as reinforcement to titanium for aerospace applications. Moreover, to facilitate a better understanding of mechanical behavior in microscopic scale of MLG reinforced metal matrix composites, the mechanical properties of the sintered composites were evaluated using instrumented indentation and scratch, the role of the MLGs and their contributions towards the mechanical response of the sintered composite was also analyzed.

2. Experimental

2.1. Material preparation

Titanium (purity: 99.8%) with a particle size of ~60 nm from Nanjing Emperor Nano Material Company (China) and MLGs with a thickness of ~5–25 nm and a length of 1–5 μm from Nanjing XianFeng Nano Material Company (China) were employed as the precursor materials. Fig. 1a shows the scanning electron microscopy (SEM; Hitachi S-4700, Japan) image of these as-received MLGs with multilayers. MLG agglomerates were firstly ultrosonicated for 30 min in water with a concentration of about 0.1 mg/ml, in which sodium dodecyl-benzene sulphonate (SDBS) was used as dispersant, and titanium powders were added into the MLG suspension followed by another 30 min. The composite powders were allowed to settle and the excess solvent was drained, and then mixed in ethanol using Si_3N_4 milling balls with a rotation rate of 300 rpm until 12 h. After fully dried in an oven at 80 °C, the resulting powders (Fig. 1b) were loaded into a graphite die with an inner diameter of 20 mm, in which graphite papers were placed between the powders and die/punches for easy specimen removal. The mixed powders were sintered in SPS apparatus (Dr. Sinter 1050, Sumitomo Coal Co. Ltd., Japan) with a hold temperature of 1100°Cand a hold pressure of 40 MPa. Heating rate of 150 °C/min was employed, the maximum temperature was kept for 6 min. The samples were then cooled down to ambient temperature with a cooling rate of furnace. The composites designed here were Ti, 0.5 wt% MLG/Ti and 1.5 wt% MLG/Ti.

2.2. Microstructure observation of the composites

Sintered specimens were polished to remove the graphitic contamination on their surfaces. X-ray diffraction (XRD, X'Pert-Pro MPD, The Netherlands) using Cu Ka radiation with a scanning rate of 2°/min was used to analysis the phase constituents of the sintered samples. Micro-Raman spectroscopy (JR HR800, France) with an Argon ion laser of wavelength 632.8 nm and an acquisition time of 20 s was employed to confirm the existence of MLGs in the TiMMCs. Microstructure of the composites was analyzed using SEM. Dislocation generation within the Ti grain in the sintered composites was identified using transmission electron microscopy (TEM, FEI Tecnai G2 20, The Netherlands).

2.3. Evaluation of microscopic mechanical properties of TiMMCs

Instrumented microindentation experiments were conducted using MCT tester (CSM, Switzerland) with a spherical indenter (radius: 20 μm) to obtain the elastic modulus and hardness at a maximum load 2000 mN (4000 mN/min for load-uploading rate and a dwell time of 10 s). Ten tests were performed at different locations of each sample where the distance between the adjacent indentation marks was at least 500 μm. Moreover, to achieve the indentation stress-strain curves of these sintered samples, spherical instrumented micro-indentation tests with multiple partial unloading were also conducted using Continuous Multi-Cycle (CMC) technique, in which the radius of the spherical indenter was 20 μm. The CMC method consisted of 15 cycles of load/partial unloading indentation performed on the same spot, the applied load was increased quadratically from 200 mN to 2000 mN (20 s loading/unloading time, 15 s holding time at maximum load). At each cycle, the indenter was loaded up to a maximum value and then unloaded to 50% of such load. In this research, 10 individual indentations were performed at 10 separate locations where the distance between the adjacent indentation marks was at least 500 μm.

Scratch behaviors on microscopic scale of the sintered samples were also investigated using MCT tester with a spherical indenter (radius: 20 μm). Scratch tests were performed on the tangential surfaces of

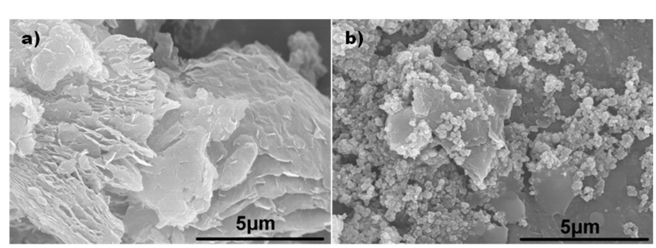

Fig. 1. SEM images of (a) the as-received MLGs and (b)1.5 wt% MLG/Ti powders.