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Laser sintered single layer graphene oxide reinforced titanium matrix nanocomposites

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A B S T R A C T

Single layer graphene oxide (SLGO) reinforced titanium (SLGO-Ti) nanocomposites have been achieved by laser sintering. This study focuses on the graphene oxide dispersion and survival in titanium matrix during laser sintering process. Through laser sintering, graphene oxides were dispersed uniformly into titanium matrix to fabricate SLGO-Ti nanocomposites. Microstructures and components of the nanocomposites were studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), Energy-dispersive X-Ray spectroscopy (EDS) and Raman spectroscopy. It was confirmed by XRD patterns, EDS maps and Raman spectrum that graphene oxide survived in SLGO-Ti nanocomposites after laser sintering. Nanoindentation measurements showed the laser sintered SLGO-Ti nanocomposites hardness was improved by more than 3-folds than that of pure titanium counterpart.

1. Introduction

Titanium (Ti) and titanium alloy are widely used in various fields like biomedical, aerospace and automobile industries, due to their outstanding specific strength, toughness and the ability to withstand higher temperature than steel and aluminum alloy. However, utilization of titanium and titanium alloy in many fields requires even higher strength and thermal conductivity, especially in aerospace field. In fact, some applications are also limited for their poor thermal conductivity [1]. It is well known that composites which are made from two or more constituent materials have many attractive properties, and can be much stronger, lighter and with improved thermal and electrical properties when compared with traditional intrinsic materials. Nanocomposites become more and more attracting, especially metal matrix nanocomposites which are considered as infrastructure materials for its outstanding properties, such as high hardness, high specific stiffness, low coefficient of thermal expansion, high yield strength, anti-corrosion property, and creep resistance in high temperature environment etc. [2]. Therefore, plenty of research works have been carried out to study different sorts of metal matrix composites (MMCs) and nanocomposites. Various nanoparticles have been considered as composite filler materials, especially carbon nanotubes (CNTs) and graphene [3–8].

Graphene, with demonstrated high strength and thermal conductivity [9], has the potential to serve as a reinforcement for improving not only mechanical but also thermal properties of titanium and titanium alloy. Graphene is just one layer carbon atom thick sheet, in which carbon atoms form flat honeycomb lattice. The special structure brings exceptional properties, such as high electric property [10], high Young's modulus [11], outstanding tribological property [12,13], and high tensile stress [14], besides the superior thermal conductivity. Thereby, it is expected that graphene-titanium composites would have superior thermomechanical properties. Recently, a few graphene reinforced metal matrix nanocomposites have been studied [15–20]. These research works showed great promise to enhance the properties of metal matrices. However, it is extremely difficult to disperse graphene homogeneously in metal

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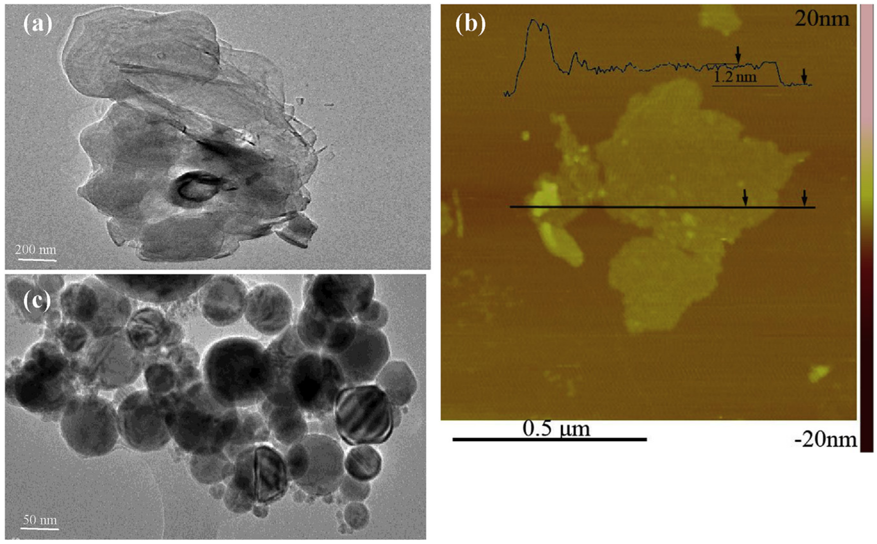

Fig. 1. (a) TEM image of SLGO, (b) AFM image of SLGO, (c) TEM image of Ti-SLGO before laser sintering.

matrix [4]. It is even more difficult to make graphene reinforced titanium nanocomposites, since titanium is an active metal can react with carbon easily.

Graphene oxide (GO), a graphene derivative, is mono-layer of sp^2-hybridized carbon atoms derivatized by a mixture of carboxyl, hydroxyl and epoxy functionalities [21]. It is well known that GO can be easily dispersed in water, because of the oxygen functional groups, attached on the basal planes and edges of GO sheets, which significantly alter the van der Waals interaction between the GO sheets. GO has similar mechanical properties with graphene, which exhibits high tensile strength [22] and less possibility to react with titanium matrix due to the passivation of functional groups. In addition, GO can be mass-produced from graphite oxide with low costs. These virtues make it an ideal reinforcement for nanocomposites. It was reported that addition of 1wt.% GO could simultaneously improve the strength and toughness of GO-chitosan composites [23]. And for GO-cement composites, 0.05% GO sheets improve the compressive strength and flexural strength by 15–33% and 41–58%, respectively [24]. For metal matrix composites, GO-iron composites were reported in 2014, the surface microhardness of laser sintered 2 wt. % GO-iron composite was 600 HV, which has increased 93.5% compared with the base material [7]. To date, to the best of our knowledge, there is still no report of GO reinforced titanium matrix composites.

Herein, a laser sintering technique was used to fabricate graphene oxide reinforced titanium nanocomposites. Laser sintering is a rapid heating and rapid cooling process, which helps to keep graphene oxide in the titanium matrix from reacting with the matrix. At the same time, graphene oxide melting point is over 3000 °C [25], and titanium nanopowders melting point is 1660 °C (even lower melting point of Nano size Ti powder) [26], which also helps graphene oxide survive in the laser sintering process.

Single layer graphene oxide nanoplatelets were mixed with titanium nanopowders in deionized water, ultrasonic dispersing for 1 h. Then the mixed solution was dipped on mechanically polished AISI 4140 substrate surface [27–29], after natural air drying, a thin layer of graphene oxide and titanium mixture was coated. The layer thickness can be controlled by coating times, and the volume ratio of graphene oxide and titanium also can be controlled easily. Finally, laser was used to sinter the coatings, which were put into a transparent chamber filled with argon gas to protect titanium from oxidation or nitridation. Afterwards, SLGO-Ti nanocomposites were successfully deposited. It was expected that the nanocomposites would have excellent mechanical properties.

2. Experiments

Materials: The substrates AISI 4140 plate was cut into small pieces of 10 mm × 8 mm × 2.35 mm. The titanium powders (average diameter 30–50 nm) and single layer graphene oxide (thickness 0.7–1.2 nm, average X&Y dimension 300–800 nm, Cheap Tubes, Inc.) were used for the experiment. Fig. 1a is the TEM image of SLGO, and Fig. 1b is the AFM image of SLGO. It can be seen from Fig. 1b that the thickness of SLGO is 1.2 nm, and its size is about 600 nm.

Laser sintering experiments: Ti nanopowders and SLGO nanoplatelets were used to make two kinds of solution by ultrasonic dispersion. Firstly, mix 1.9 g Ti nanopowders, 0.1 g SLGO nanoplatelets and 23 g deionized water; secondly, 2.0 g Ti nanopowders and 23 g deionized water, respectively, ultrasonic dispersed it for 1 h. Fig. 1c is the TEM image of Ti-SLGO before laser sintering. The AISI 4140 samples were first ultrasonically cleaned and mechanical polished to a surface roughness about 0.05 μm [5–8,30]. Then the samples were coated several times with the previous prepared suspension by using a dropper, until the dried coating layer thickness reached 0.2 mm. Fig. 2a shows the schematic cross-section after coating. An IPG fiber pulse laser (wave length: 1064 nm, pulse duration: 400 ns) system was used to perform the laser sintering process at the frequency of 50 kHz. The selected laser parameters were: laser intensity (80 W), beam size (0.8 mm), scanning speed (2 mm/s) and step size (0.25 mm). The coverage area was the whole sample surface, as shown in Fig. 3. The samples were sintered in a transparent chamber filled with Argon (Ar) gas which protected the samples from oxidation and nitridation during laser sintering process. The chamber was fixed on a numerical controlled (NC) x-y stage. Fig. 2b represents the schematic cross-section after laser sintering. With proper technical parameters, the graphene oxide nanoplatelets survived and were distributed uniformly in the titanium matrix after laser sintering process. The coated layer was melted together with substrate by laser sintering.

Microstructure characterization: A Bruker D8 Focus X-Ray diffractometer was used to characterize the material composite with Cu-Kα source. Laser sintered samples were prepared for XRD