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The preparation of Ni/GO composite foils and the enhancement effects of GO in mechanical properties

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ABSTRACT

Graphene oxide (GO) was prepared by an improved Hummers method, and nanocrystalline (NC) Ni and Ni/GO foils were prepared by pulsed electrodeposition. This paper mainly investigated the effects of GO in Ni/GO composites. The surface of the prepared GO has many oxygen-containing functional groups and a high aspect ratio. The addition of GO in Ni/GO foils not only effectively lowers the matrix grain size but also contributes to the growth of Ni toward the (111) direction. Furthermore GO covers the surface of the matrix grains and passes through the grain boundary. Compared to NC Ni, the mechanical properties, such as hardness, elastic modulus, elongation and fracture strength showed significant improvements for the Ni/GO composite foil. The use of GO can effectively inhibit the growth of matrix grain boundaries at high temperatures.

1. Introduction

In the field of the micro-electro-mechanical systems (MEMS), micro- and millimeter-sized components are of great use [1,2]. Nano materials have comparatively small grain sizes and high mechanical performances; thus, they are wildely used as micro- and millimeter-sized components. In certain conditions, a single-phase material may not satisfy the requirements for the practical use. Therefore, reinforcements, such as oxides, carbides and other inorganic nanoparticle, are added to improve their mechanical properties [3–5].

The morphology of the reinforcement material has a great influence on mechanical behavior and matrix grain growth [6]. Materials with a two-dimensional sheet structure with a high aspect ratio are considered great materials for use as reinforcements. The newly discovered graphene (Gr) consists of a small number of layers of covalently bonded sp^2 carbon atoms, hexagonally packed in a honeycomb crystal lattice. Gr exhibits a Young's modulus of 1 TPa and a tensile strength of 130 GPa [7], and graphene oxide (GO) has similar mechanical properties to Gr. Some researchers found that the addition of a small amount of Gr or GO in metal matrices greatly increased the mechanical properties of the composites [8–10]. Recently, Jingyue Wang et al. [11] chose GO and processed Al as precursor materials to successfully prepared a GNS/Al composite using flake powder metallurgy. The composite with only a 0.3 wt% GNS addition exhibited a tensile strength improvement of 62% over the non-unreinforced matrix as well as a uniform elongation well beyond the 5% standard for engineering applications. Zengrong Hu et al. prepared GO- reinforced titanium nanocomposites using laser sintering technology. The average modulus of nanocomposites improved significantly, and the hardness value improved more than three times compared to laser sintered titanium [12].

Electrodeposition is a low-temperature process that can protect composites from degradation or oxidation [13]. This process is different from traditional sintering processes because the planar sp^2 carbon structure of GO can be destroyed at high temperatures [14]. In addition, pulsed electrodeposition is an easy, low cost and effective liquid-phase synthesis method, which can incorporate enhanced nanomaterials homogeneously throughout the matrix. Unlike Gr, GO has many oxygen-containing functional groups, which contribute to the association of GO and metal ions in the matrix during electrodeposition.

In this paper, the preparation of Ni/GO composite foils by pulsed electrodeposition was reported, and we detected the distribution of GO in the Ni matrix. The influences of the GO content on the hardness and elastic modulus of the material as well as the enhancement mechanism were investigated in detail, and the

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inhibitory effect of GO on grain growth at high temperatures was also discussed.

2. Experimental details

The GO was prepared from expanded graphite through an improved Hummers method [15,16]. Ultrasonication was applied at the moderate and high temperature stages during the preparation of GO. GO did not need further functional treatment to disperse in the electrolyte. The composite was prepared via a pulsed composite electrodeposition method. $Ni(NH_2SO_3)_2{\bullet}4H_2O$(300 g/L), $NiCl_2{\cdot}6H_2O$(15 g/L), $Co(NH_2SO_3)_2{\cdot}4H_2O$(5 g/L), H_3BO_3(30 g/L), $C_7H_5NO_3S$(1 g/L), $C_{12}H_{25}NaSO_4S$(0.1 g/L) and GO (0–0.1 g/L) were mixed uniformly, and then the mixed solution was stirred and passed into the pulsed current. The temperature of the plating bath was held at 50 °C, and the pulsed current density was 2 A/dm^2. The 'pulse on' time (T_{on}) was 30 ms, while the 'pulse off' time (T_{off}) was 20 ms. The Ni-based composites were deposited on the cathode with magnetic stirring and a pulsed current. The cathode material was a non-magnetic stainless-steel plate, and the anode material was electrolytic plum nickel blocks (with 99.6% purity) packed in a titanium basket. The two electrodes were connected by an insulating resin sheet. The width of the resin sheet and the distance between the two electrodes were both controlled at 50 mm.

In the present study, nanoindentation was carried out to investigate the effects of Ni and Ni/GO on the hardness and elastic modulus. These mechanical properties were obtained by nanoindentation (Nano indenter G200) techniques by applying a maximum load of 70 mN. The peak hold time was 10 s and the strain rate was $5 \times 10^{-2}\ s^{-1}$. The thermal drift during nanoindentation was lower than 1 nm/s. The nanoindentation results presented in this work are the statistical average of a set of 20 indentations to determine the hardness or elastic modulus for each sample performed under similar conditions. The tensile specimens, shown in Fig. 1, were made to size using wire electrical discharge machining, and tensile tests were performed on an Instron-3343 universal testing machine at a strain rate of $6.67 \times 10^{-4}\ s^{-1}$. For the uniaxial tensile test at high temperature, the composite was placed in a furnace at 500 °C for 1.5 h, and the composite was subsequently cracked under external force.

The surface morphology, crystallographic orientation, grain size and distribution of GO and the composite foils were examined by scanning electron microscopy (SEM, powered by Helios NanoLab 600i), transmission electron microscopy (TEM, powered by Tecnai G2 F30) and X-ray diffraction (XRD, Rigaku incorporation). The functional groups of GO were observed by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet Avatar 360). The layer thickness and horizontal distance of GO were obtained by atomic force microscopy (AFM, Dimension FastScan).

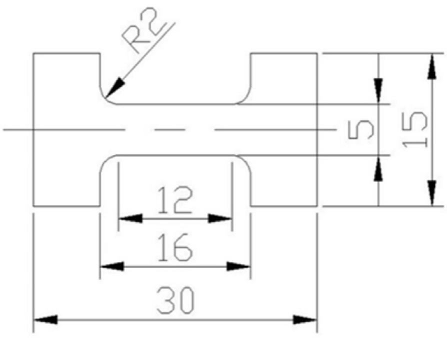

Fig. 1. Picture of tensile sample.

3. Results

3.1. The analysis of surface morphology and structure of GO

Fig. 2 shows some basic properties of GO. The XRD spectrum (Fig. 2a) of GO shows a peak near $2\theta = 12°$, which is the characteristic peak of GO. This indicates the prepared material is GO. According to Bragg's law, the crystal plane spacing is approximately 0.88 nm, and this indicates that the GO was well stripped. The functional groups of GO were characterized by FT-IR (Fig. 2b). There were five adsorption peaks in the FT-IR spectra. The broad peak at 3410 cm^{-1} was caused by the -OH stretching vibration of water. -OH may enhance the hydrophilic nature of GO, which would facilitate the preparation process of the composite in aqueous solutions. The peaks at 1736 cm^{-1}, 1624 cm^{-1}, 1400 cm^{-1}, 1092 cm^{-1} are caused by the vibration of the aldehyde groups (C=O), and ketone groups (C=O, C=C and C-*O*-C), respectively. The existence of oxygen-containing functional groups not only indicates that graphite was oxidized completely but also promotes the combination between of GO and the metal matrix during the electrodeposition process.

The TEM image of GO shows many wrinkles in the material. The thickness of single-layer GO is approximately 0.6–1.2 nm [17,18], and the thickness of the wrinkle is 5 nm (the red mark in Fig. 2c), which indicates the layer number of the prepared GO was less than five. The diffraction spot indicates a hexagonal crystal structure of GO. Moreover, there are crimps and wrinkles on the GO. These are caused by the thinness of the GO layer and its relatively large free energy [19,20]. Fig. 2d shows the AFM image and height profile of GO. A height difference of 3 nm is shown in the height profile indicating that the layer number of GO is less than five, which is in accordance with the TEM test result. At the same time, the two measurements in the line are two endpoints of the GO layer, and the measured horizontal distance is 3 μm.

3.2. The analysis of surface morphology and structure of Ni and Ni/GO

Fig. 3 shows the surface morphology of Ni and Ni/GO. The TEM image indicates that the grain size of pure nanocrystalline (NC) Ni is approximately 50–70 nm (Fig. 3a), while the grain size of the Ni/GO composite is approximately 30–50 nm (Fig. 3b). The addition of GO can make the grain size of the matrix decrease by 10–20 nm. The grain size of the electrodeposited NC material can be controlled by the nucleation number and crystal nucleus growth, and the smaller sized material can be obtained with a large nucleation rate and slow nucleus growth rate. When the second phase of the GO and matrix Ni are deposited in the aqueous solution at the same time, GO works as the core for the matrix nucleation, which improves the nucleation rate of the matrix Ni grain and increases the grain number. Furthermore, the core GO does not have secondary growth, and the growth of the matrix Ni grain can be inhibited. Compared to traditional electrodeposition of a single metal, the grain size of the composite is smaller by using this process.

Fig. 3c clearly shows that GO exists in the composite, and it covers and links to the matrix metals (at the red box position). The SEM image (Fig. 3d) of the surface of the Ni/GO foil shows that GO covering the surface of Ni matrix passes through the grain boundary of Ni.

Three main conditions for the electrodeposition mechanism of the composite exist [21,22] as follows. The reinforcement phase and the surface of the cathode are adsorbed by van der Waals forces to achieve the composite deposition. When the reinforcement phase moves to the surface of cathode under the effect of stirring, it can be captured by the growing matrix metal. Under the effect of electric