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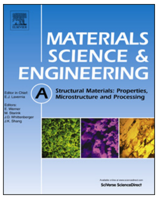

Microstructure and tensile properties of bulk nanostructured aluminum/graphene composites prepared via cryomilling

J.L. Li*, Y.C. Xiong, X.D. Wang, S.J. Yan, C. Yang, W.W. He, J.Z. Chen, S.Q. Wang, X.Y. Zhang, S.L. Dai

Beijing Institute of Aeronautical Materials, Beijing 100095, China

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ABSTRACT

In order to develop high strength metal–matrix composites with acceptable ductility, bulk nanostructured aluminum–matrix composites reinforced with graphene nanoflakes were fabricated by cryomilling and hot extrusion processes. Microstructure and mechanical properties were characterized and determined using transmission electron microscopy, electron dispersion spectroscopy, as well as static tensile tests. The results show that, with an addition of only 0.5 wt% graphene nanoflakes, the bulk nanostructured aluminum/graphene composite exhibited increased strength and unsubdued ductility over pure aluminum. Besides, the mechanical properties of the composites with higher content of graphene nanoflakes were also measured and investigated. Above 1.0 wt% of graphene nanoflakes, however, this strengthening effect sharply dropped due to the clustering of graphene nanoflakes. Furthermore, the optimal addition of graphene nanoflakes into the nanocrystalline aluminum matrix was calculated and discussed.

1. Introduction

Because of its outstanding comprehensive performance such as high specific strength, good formability and excellent corrosion resistance, aluminum alloys have been widely used in aerospace industries [1]. Nowadays, in order to meet the ever increasing service requirements of aeroplanes and spacecrafts, there has been a strong demand for aluminum alloys with a much higher strength. However, the further strengthening of aluminum alloys seems to be hardly achieved by conventional fabrication and strengthening technologies. Thus, some novel approaches in strengthening aluminum alloys are required to be developed.

Over the last two decades, two methods of nanocrystallization and being fabricated as composite were demonstrated to be effective to improve the strength of aluminum alloys. As defined by the well-known Hall–Petch relationship [2,3], the bulk nanocrystalline aluminum alloys (BNAs) exhibite a significant strength increase over conventional aluminum [4,5]. For example, a bulk nanocrystalline Al prepared via cryomilling, hot isostatic pressing (HIP) and hot extrusion processes exhibited a high tensile strength [4]. Aluminum–matrix composites (AMCs), especially the particulate-reinforced AMCs, are also of particular interest due to their attractive physical and mechanical properties such as low thermal expansion, high specific modulus and superior specific stiffness [6,7].

Recently, in order to incorporate the advantages of BNAs and AMCs, nanostructured AMCs have been extensively fabricated and investigated [8–14]. Numerous studies have verified that combining these two advanced materials together by using BNAs as matrices in AMCs represents an effective approach to improve the strength of aluminum alloys [8–14]. Take Tang's research [8] for example, the nanostructured composite (Al 5083/6.5Vol% SiC_p) synthesized by cryomilling, hot isostatic pressing (HIPping) and hot rolling processes showed a ultra-high tensile strength of 813 MPa. However, these efforts have met with only limited success, because such a high strength of the nanostructured AMCs is usually achieved at the expense of ductility. For instance, the nanostructured AMC mentioned above exhibited a significantly low tensile elongation of 0.5% [8].

In effort to improve the poor ductility of nanostructured AMC while retaining a moderate strength level, various strategies such as involving the introduction of a bimodal grain size distribution (also referred to as a tri-modal composite) [9,10] and decreasing the size of the reinforcement to nanoscale [12], have been implemented and verified. However, even in these composites moderate ductility was only obtained for samples tested under compression or at high strain rates. As a matter of fact, for these samples even after annealing tested in tensile tests, the elongation was reported to be less than 3.0% [9,10,12]. It is generally accepted that the inferior ductility of the structural material will lead to a

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* Corresponding author. Tel.: +86 10 6249 7165; fax: +86 10 6249 6407.
E-mail address: ljlhpu123@163.com (J.L. Li).

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decrease both in reliability and difficulty in the following plastic working. In most cases, the tensile elongation of the structural material is required to be 7–8% at least to satisfy the needs of engineering applications [15]. Above all, it is the poor combination of strength and ductility that mostly limits the engineering applications of the nanostructured AMCs.

More recently, it is reported that graphene nanoflakes have a great potential as an ideal reinforcement for AMCs [16]. Thanks to the ultra-high strength [17,18] and multiply wrinkled structure [16] of the graphene nanoflakes, the aluminum/graphene composites exhibited increased strength and unsubdued ductility compared with monolithic aluminum [16]. Compared to monolayer graphene, graphene nanoflakes also referred as graphene platelets (GPLs), graphene nanosheets (GNSs), or graphene nanoplates (GNPs), are structured by several layers of graphene in thickness. In addition, it has also demonstrated that a decrease in the particle size of the reinforcement resulted in an improved ductility of AMCs [12]. In other words, the composite reinforced with nanometric particles exhibits an enhanced ductility relative to the same material reinforced with micrometric ones. On the basis of these results, it is reasonable to believe that the nano-scale characteristic in thickness of graphene nanoflakes will benefit the maintaining of ductility in the nanostructured AMCs.

In an attempt to develop the high performance AMCs with a good combination of high strength and acceptable ductility, bulk nanostructured aluminum/graphene composites were successfully prepared via cryomilling followed by hot vacuum degassing and hot extrusion processes in the present work. Hereafter, aluminum/graphene composite and graphene nanoflakes are referred to as Al/Gr composite and GNFs, respectively. After preparation, the microstructures of the composites, the dispersion of GNFs in aluminum matrix and the Al/Gr interfaces were characterized and investigated. Furthermore, the tensile properties and strengthening mechanisms of the bulk nanostructured Al/Gr composites were also measured and discussed.

2. Experimental

2.1. Materials

Gas-atomized aluminum powder with a mesh size of ~70 μm was supplied as the starting matrix material. Table 1 shows the chemical compositions of the aluminum powder. Fig. 1 contains the optical microscopy and SEM images of the aluminum powder. It can be seen that the aluminum powder has an average grain size of ~15–20 μm and a spheric/spherical morphology. GNFs applied in this investigation were chemically synthesized from graphene oxides which were prepared by Hummer's method [19]. Fig. 2 shows the representative morphology of GNFs. GNFs have a large specific surface area and two-dimensional high aspect ratio sheet geometry, as depicted in Fig. 2(a). In addition, transmission electron microscopy of GNFs presents a highly wrinkled structure, as shown in Fig. 2(b).

Table1
Chemical compositions (wt%) of the as-atomized aluminum powders.

Type	Si	Fe	Ca	O	Al
as-atomized	0.50	< 0.01	< 0.01	0.062	Bal

2.2. Experimental procedures

The combination of several processing routes: blending, cryomilling, degassing and hot extrusion was employed in the current study for preparing the bulk nanostructured Al/Gr composite reinforced with zero, 0.5, 1.0, 1.5 and 2.0 wt% GNFs, respectively. Take Al/0.5 wt% Gr composite for example, the detailed fabrication processes are as follows. At the first step, aluminum powder (995 g) and GNFs (5 g) were mechanically mixed with stearic acid (2 g) using a modified V-blender at a speed of 17 rpm for 24 h. Then, the blended powder was cryomilled in a attritor with a stainless steel vial and balls (8 mm in diameter, ball-to-powder weight ratio of 40:1) at a rate of 180 rpm for 2 h. Details of the cryomilling process were reported elsewhere [20,21]. After 2 h of cryomilling, the milled powder was removed from the attritor and packed into an Al-6061 can in an inert atmosphere to prevent oxidation and contamination of the powder prior to consolidation. In order to eliminate any trapped gases (N_2, O_2, H_2, etc.), moisture (H_2O), stearic acid ($CH_3(CH_2)_{16}COOH$) as well as the residual functional groups (–OH, –COOH, etc.) in GNFs, the composite powder was evacuated at 300 °C in a vacuum (2×10^{-3} Pa) for 4 h. At the conclusion of the degassing operation, the evacuation tube of the Al package was sealed by crimping and then welding. Afterwards, the canned composite powder was extruded at 300 °C to form a bar of 15 mm in diameter with an area reduction ratio of 17.6:1. Finally, all specimens were subjected to an anneal heat treatment at 300 °C for 2 h. Additional details of this procedure can be found in the literature [22].

2.3. Characterization

The microstructures of the bulk nanostructured Al/Gr composites were investigated by transmission electron microscopy (TEM) which was performed with JEOL JEM-2100 microscope operated at an accelerating voltage of 200 kV. The interfaces between aluminum and graphene were also investigated under JEOL JEM-2100 microscope by high resolution transmission electron microscopy (HRTEM). The distribution of GNFs in aluminum matrix was characterized by electron dispersion spectroscopy (EDS) equipped within the same JEOL JEM-2100 microscope. The TEM specimens were prepared from the extruded material perpendicular (transverse) to the extrusion. The tensile properties of the extruded samples were determined by a testing machine (Instron 5887) at ambient temperature using a displacement rate of 1 mm/min. For minimizing the experimental error, three tensile specimens for each sample were machined parallel to the extrusion direction with a gauge length of 25 mm and a diameter of 5 mm.

3. Results and discussion

3.1. Microstructure

Fig. 3 contains the TEM image and SAED patterns of the bulk nanostructured Al/Gr composite reinforced with 0.5 wt% GNFs. Microstructural investigation shows that the average dimension of Al grains is ~100–200 nm (determined by measuring 200 individual grains). However, some individual grains larger than 300 nm also can be occasionally observed, as shown in Fig. 3(a). In addition, the polycrystalline rings in SAED pattern, as depicted in Fig. 3(b), also indicates that Al grains are fine enough and randomly orientated.

3.2. Al/Gr interfaces

To be a high-performance composite, a clean and strong interface between the matrix and the reinforcement is desired to achieve an effective load transfer from the matrix to the reinforcement [23]. If the interface is not strong enough, interface debonding will occur when the composite is subjected to an applied load,