Preparation of graphene coated aluminum composite powders by high-energy ball milling

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Abstract: The preparation of composite powders has an important impact on the properties of the synthesized bulk materials. In this work, graphene coated aluminum composite powders were successfully prepared by high-energy ball milling. The microstructure of graphene/aluminum mixed powders was characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD). The effects of the micro-morphology of the composite powders and the ratio of the ball to the particle size of the graphene-coated aluminum composite powders were analyzed in detail. The results show that graphene can be uniformly dispersed in aluminum powder without significant agglomeration in the case of ball milling parameters with a ball-to-powder ratio of 5:1. When the ratio of ball to material is 6:1, the dispersion effect was not so obvious. However, the level of agglomeration in the composite powders at ratios 7:1 and 8:1 differed respectively; some particles were deformed and the dispersion effect was reduced. The particle size of the graphene coated aluminum composite powder increased with the increase of ball to material ratio. Thermodynamic analysis of the interface reaction between graphene and aluminum composite powders shows that the maximum content of graphene microflakes on the surface of aluminum powder is 0.3wt%.

1. Introduction
Graphene is composed of one or several layers of carbon atoms, which is tightly packed into a honeycomb network. It has some unique properties, such as mechanics, heat, electricity, magnetism, optics, acoustics, corrosion resistance and so on[1,2]. This makes many scientists to carry out in-depth research on it. Up to now, graphene is considered to be the most ideal reinforcement material for metal matrix composites[3,4].

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With the development of automotive and aerospace fields, higher requirements have been put forward for aluminum matrix composites, such as specific strength, specific modulus, conductivity and thermal conductivity. Traditional ceramic fibers and particle reinforced materials cannot meet the requirements of high performance materials. Now there are many reports that silicon carbide and carbon nanotubes are added to aluminum alloy as reinforcements, but the reinforcement effect cannot meet the requirements of industrial and daily use. In view of the above analysis, graphene can be used as reinforcement of aluminum matrix composites because of its various characteristics, which makes it possible to improve the properties of aluminum matrix composites\cite{5-9}. Therefore, it has attracted wide attention from researchers.

When graphene is added to aluminum powder particles as reinforcement, the primary problem is to make graphene disperse evenly in aluminum matrix. At present, the commonly used dispersing methods are liquid and ball milling. However, ball milling has the advantages of low reaction temperature, high yield and uniform particle size distribution, which makes it play an important role in the grinding and mixing of powders. The microstructure and particle size distribution of graphene/aluminium composite powders prepared by high-energy ball milling were studied in this work, and its thermodynamic properties were analyzed.

2. Experiment

This experiment used the YXQM planetary ball mill machine for ball milling. Mixed powders containing 0.5% of graphene and 99.8% of aluminum powder were ball milled using four different ball to powder weight ratios of 5:1, 6:1, 7:1, and 8:1 respectively. Ball milling parameters were as follows: speed was 300r/min, ball milling time was 1h. In order to obtain the best ball milling effect, the proportion of stainless steel balls with a diameter of 3mm, 5mm, and 8mm was 3:5:2, respectively. The ball milling process was performed under argon atmosphere to prevent oxidation.

3. Results and Discussion

3.1 Microstructure analysis of graphene/aluminum composite powders

The SEM micrographs at different magnifications of the graphene/aluminum composite powders after milling using the different ball to powder weight ratios are shown in Figure1. As can be seen from the Figure 1, at the 5:1 ball to powder weight ratio, the vast majority of particles are approximately spherical or approximately ellipsoidal, there are a small number of particles with a large particle size distributed in them. There is no obvious agglomeration phenomenon and the dispersion is good. At a 6:1 ball to powder weight ratio, the low magnification electron micrograph is similar to the 5:1 case, but a small amount of particles are found to be deformed. Some irregularly shaped particles appear and there is a slight agglomeration and the dispersion is slightly worse. At a 7:1 ball to powder weight ratio, it can be seen that partially spherical or nearly spherical particles become irregular shapes, and some particles become rod-like particles after ball milling, and agglomeration occurs. At the 8:1 ball to powder weight ratio, most of the particles are deformed and become flat, especially in electron micrograph at high magnification. The phenomenon of agglomeration is more serious and many particles are stuck together irregularly. The dispersion is uneven and poor.
3.2 XRD pattern data analysis of graphene/aluminum composite powder

Figure 1  SEM image of graphene/aluminum composite powder with different ball material ratio after ball milling
(a) 5:1 low magnification; (b) 5:1 high magnification; (c) 6:1 low magnification; (d) 6:1 high magnification;
(e) 7:1 low magnification; (f) 7:1 high magnification; (g) 8:1 low magnification; (h) 8:1 high magnification

Figure 2 X-ray diffraction patterns of graphene/aluminum composite powder with different ball material ratio
after ball milling
The XRD pattern of different ball to powder weight ratios is shown in Figure 2. The four types of patterns are basically similar, only the diffraction peaks of aluminum, and no characteristic peak of graphite appearing at 2θ=26.6°. A peak with a small peak intensity appears around 20°, indicating that there is no graphite in the composite powder, and no serious agglomeration of graphene occurs. It is shown again that graphene can be uniformly dispersed in aluminum powder by high-energy ball milling[10,11]. While the above-mentioned 7:1 and 8:1 ball to powder weight ratios have agglomeration phenomenon, there is no graphite peak in the XRD pattern. It shows that the agglomeration phenomenon of graphene is not so severe; hence the signal of graphite was not detected.

3.3 Thermodynamic analysis of interfacial reaction of graphene/aluminum composite powders

![Fig 3 Al-C binary phase diagram](image)

According to the Al-C binary phase diagram shown in Figure 3, it is possible to generate the interface product Al₄C₃, and its reaction equation is as follows:

$$4[\text{Al}]+3[\text{C}(s)] = [\text{Al}_4\text{C}_3](s) \quad (1)$$

In the formula, Al is aluminum powder during the ball milling process, C is graphene, and Al₄C₃ is an interface product that may be generated. During the ball milling process, the grinding ball strongly impacts, grinds and agitates the aluminum powder and graphene, causing a large impact force and shearing force. The instant of collision produces a great deal of energy at the collision site, which transfers more energy to the powder, resulting in an increase in temperature at the interface between aluminum powder and graphene. Therefore, this interface reaction is a spontaneous reaction, and it can generate Al₄C₃ hard and brittle phase.

4 Conclusions

In this paper, graphene coated aluminum composite powders were successfully prepared by mixing graphene with aluminum powder by high energy ball milling. It is shown that the particle size of graphene coated aluminum composite powder increases with the increase of the ratio of ball to material. The particle size of 5:1 ball material ratio is uniform and has no obvious agglomeration, and the particle size is the smallest. Therefore, the ball ratio is the best parameter in the four ball milling parameters. The XRD analysis showed that graphite, Al₂O₃ was not found in the graphene/aluminum composite powders, indicating that graphene/aluminum composite powders with 7:1 and 8:1 were not
particularly serious and graphite was not formed. Thermodynamic analysis shows that during high energy ball milling, the interface of graphene/aluminium composite powders will react spontaneously to form hard-brittle Al₄C₃ interface products.

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