Study on effects of hot isostatic pressing process on microstructure and properties of CNTs/Al2009 composites

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Abstract. The CNTs/Al2009 composite powders were prepared by cryogenic milling method and then the CNTs/Al2009 matrix composites were fabricated by hot extrusion process or hot isostatic pressing (HIP)/hot extrusion process. The effects of HIP process on microstructure and interface structure of CNTs/Al2009 composites were studied by X-ray diffraction, raman spectroscopy, scanning electron microscopy and transmission electron microscope. Finally, the effects of HIP process on the CNTs/Al2009 composites were characterized by tensile strength at room temperature. The results showed that the cryogenic milling process could disperse 1.0 wt. % of CNTs into the aluminum matrix, and the composites prepared by HIP and hot extrusion process had uniform microstructure and excellent tensile properties at room temperature. The tensile strength, yield strength and elongation of the 1.0 wt.% CNTs/Al2009 composites prepared by HIP and hot extrusion process were 560 MPa, 443.3 MPa and 10.2%, respectively. Hot isostatic pressing process had an important influence on the interfacial bonding strength of CNTs/Al2009 composites. The strength of the composite prepared by HIP and hot extrusion process was 20 MPa higher than that of direct hot extrusion process, and the elongation was basically the same. The main reason was that the high temperature and high pressure conditions of hot isostatic pressing process could promote the reaction of carbon and aluminum at the interface between CNTs and aluminum matrix, so that a few CNTs with severe damage and defects in some CNTs formed Al$_4$C$_3$ phase with aluminum, thereby improving two compatibility, and enhanced interface bonding.

1. Introduction

With high specific modulus and strength, aluminum matrix composites are effective to improve fuel efficiency by weight reduction in aircraft and transportation industries [1–3]. Carbon nanotubes (CNTs) have recently emerged as materials with exceptional properties exceeding those of any conventional material (e.g. Young’s modulus up to 1-1.8 TPa, tensile strength up to 150 GPa, low density of 1.2-1.8 g/cm$^3$, and neglected coefficient of thermal expansion, as well as good ductility and plastic deformation capacity [4-6]). Key requirements to achieve both properties are uniform dispersion of the CNTs in the matrix, and good interfacial bonding between the reinforcement and the matrix. Powder metallurgy techniques have been used extensively due to the ease of incorporating the CNTs in the matrix powder [7-14]. The mechanical dispersion processes (like ball milling, friction stir processing) encounter the problem of CNTs structural damage. The low temperature requirements help minimize possible thermal damage to the CNTs. Some researchers reported manufacturing CNTs reinforced aluminum matrix composites through cryogenic milling [15-17]. The interface acts as a link between...
the reinforcement and the matrix, and has a critical impact on the overall performance of the composites. The interface of CNTs/Al matrix composites is affected by many factors, including the composites preparation process and parameters, the wettability of CNTs and aluminum matrix and the chemical reaction at the interface. These factors together determine the interface state of the interface.

In this paper, the CNTs/2009Al composite powders were prepared by cryogenic milling method and then the CNTs/2009Al matrix composites were fabricated by hot extrusion process. In order to improve the interface bonding between CNTs and aluminum matrix, the preparation process of CNTs/2009Al matrix composites was improved and hot isostatic pressing (HIP) process was added before hot extrusion process. The effects of HIP process on microstructure and interface structure of CNTs/Al2009 composites were studied by X-ray diffraction, Raman spectroscopy, Scanning electron microscopy and Transmission electron microscope. Finally, the effects of HIP process on the CNTs/2009Al composites were characterized by tensile strength at room temperature.

2. Experimental details

2.1. Materials
Multiwalled carbon nanotubes with nominal diameter of 40-60 nm, length of 5-15 μm, and purity more than 97 wt.% were purchased from Shenzhen Nanotech Port Co. The Al2009 alloy powders were produced by Beijing Institute of Aeronautical Materials. CNTs/2009Al composite powders were prepared by cryogenic milling process for 2h milling time and the CNTs content was 1.0 wt.% and then the CNTs/2009Al composites were fabricated by hot extrusion process by HIP/hot extrusion process.

2.2. Analysis and characterization
The X-ray diffraction was measured using a Bruker D8 Advance diffractometer with a Cu Kα radiation source (50 kV and 30 mA) in the 2θ range from 20° to 90°, the step size and scan rate were 0.02 and 4°/min. Raman spectroscopy (Jobin Yvon HR800) with a laser wavelength of 532 nm was used to evaluate the disorder and structure evolution in CNTs. The microstructure and interface structure of composites were characterized by scanning electron microscope (SEM, Nova Nano SEM 450) and transmission electron microscope (TEM, JEOL 2100). Tensile test of dog-bone cylindrical sample with a diameter of 5 mm and gauge length of 25 mm was carried out using an Instron testing machine at room temperature.

3. Results and discussion

3.1. Effects of hot isostatic pressing process on microstructure of composites
Figure 1 showed XRD pattern of CNTs/Al2009 composites prepared by hot extrusion process and by HIP and hot extrusion process. As shown in Figure 1, no other diffraction peaks were found in the composite except for the α(Al) and S(Al2CuMg) phases, regardless of whether or not HIP process was used. After quenching, the aluminum alloy formed a supersaturated solid solution and was in an unstable state. It spontaneously decomposed to produce a second phase at room temperature. The main strengthening phase of Al-Cu-Mg alloy was θ(Al2Cu) phase and S(Al2CuMg) phase. With the difference of Cu and Mg ratio, the phase composition was also different. The higher the Cu content, the smaller the S phase and the more θ phase. On the contrary, the Mg content increased, and the smaller the θ phase, the more S phase. In general, when Cu/Mg ≤ 2.6, the precipitated phase was almost all S phase, and when Cu/Mg > 2.6, S + θ phase or θ phase was formed. In this paper, the content ratio of Cu and Mg was 2.6, which was at the critical value, and the main strengthening phase was the S phase. Due to the low content of CNTs (1 wt.%) and the carbon atomic number of 6, which was a light element, this may be the reason why CNTs were not detected.
As seen from Figure 2, there were two distinct characteristic peaks on the Raman spectrum curve, the G peak at around 1580 cm\(^{-1}\) and the D peak near 1350 cm\(^{-1}\). Composite powders, composites prepared by hot extrusion process and prepared by HIP/hot extrusion process had ID/IG values of 1.25, 1.33 and 1.17, respectively. And CNTs had the highest defects in composites obtained without HIP process. In addition, the G peak in the composite material moved toward the high frequency direction, indicating that a certain internal stress was generated in the CNTs due to the hot extrusion process. The ID/IG value of the material obtained by HIP process was slightly lower than that of the ball milled powder. The defects of CNTs in the composite would be consistent with the CNT state in the powder, or slightly deteriorated. In the composites by HIP and hot extrusion process, there was a small peak near 850 cm\(^{-1}\), which was Al\(_4\)C\(_3\).

Figure 3 showed grain structure of CNTs/Al2009 composites prepared by hot extrusion process and by HIP and hot extrusion process. It could be found from the figure that the composites maintained a fine grain size regardless of whether it was subjected to HIP process and the grain length was about 1 to 2 \(\mu\)m and the width was about several hundred nanometers. A large number of second phase particles were precipitated in both the crystal and the grain boundaries of the composite. In addition,
regions in which dislocations strongly interacted with the second phase particles were also observed from within the grains of the composites.

3.2. Effects of hot isostatic pressing on interface structure of composites

Figure 4 showed interface structure of CNTs/Al2009 composites prepared by hot extrusion directly. As shown in Figure 4, CNTs basically maintained a layered structure, but some atomic layers were disordered, indicating an increase in defects, because strong mechanical collisions in the high-energy ball milling process caused certain damage to the CNTs structure. The interface between the CNTs and the aluminum matrix was smooth and had no interfacial reactants. Figure 4 (c) showed the interface between the CNTs tip and the aluminum matrix, and aluminum atoms enter between the tube walls of the CNTs. Graphite and aluminum were not wetted. At high temperature, the atom became active, and the diffusion rate of Al was accelerated. During the hot extrusion process, the high temperature and high pressure closely combined the CNTs with aluminum through the interatomic force. As shown in Figure 4 (d), there was also a crystalline transition layer between the CNTs and the aluminum, which had a thickness of about 2 nm and was completely coherent with the aluminum matrix. Although the material type of the transition layer was not clear, it was obvious that its existence would be able to improve interface wettability and improve interface bonding strength.
Figure 4. Interface structure of CNTs/Al2009 composites prepared by hot extrusion process

Figure 5 showed interface structure of CNTs/Al2009 composites prepared by HIP and hot extrusion process. The tubular CNTs could be clearly seen in Figure 5 and it was indicated that the CNTs structure was intact and the tube end was closed. As shown in previous research work [15], the presence of CNTs (on the side of the rod phase), but they were gathered together. Part of the rod-like phase was amorphous, which could be presumed to be amorphous carbon, and the crystalline region was Al₄C₃ phase formed by a partial reaction of CNTs with aluminium, which was in the presence of Al₄C₃ phase as described in Figure 2.
3.3. Effects of hot isostatic pressing process on properties of composites

Table 1 showed the tensile properties of CNTs/Al2009 composites at room temperature. As seen from Table 1, the tensile strength and yield strength of the composites prepared by HIP and hot extrusion process were higher than those prepared by hot extrusion process, which were increased by about 20 MPa. The elongation of the two materials was basically the same. The main reason of the increase in tensile strength was also the increase in interfacial bonding strength. Combined with XRD, TEM and Raman spectroscopy, it was indicated that a small amount of Al₄C₃ appeared in the CNTs/Al2009 composites obtained by HIP and hot extrusion process. During the HIP process, the composite powders were in a high temperature and high pressure state for a long time, which provided conditions for the reaction of carbon and aluminum at the interface between the CNTs and the aluminum matrix. The stability of the CNTs was very high, but many openings were formed by the chopping of the CNTs in the ball milling, or some defects occured in the tube walls, and the reactivity in these places was increased, thereby forming an intermetallic compound with aluminum matrix. The severely damaged CNTs reacted with aluminum to form carbides and the number of high-defective CNTs decreased, so the relative amount of low-defective CNTs increased, and the Raman scattering intensity also increased. Therefore, the ID/IG value of the material obtained by HIP process was decreased. Among composites without HIP process, some of the CNTs with higher defects were still retained, and the influence of plastic deformation during the extrusion process was affected, so the ID/IG value of the composite showed a slight increase.

CNTs and aluminum matrix were generally non-wetting (wetting angle was about 127°), while Al₄C₃ formation could significantly reduce the wetting angle, thereby increasing the wettability between the two. A very small amount of nano-scale reaction product generated by the interface between CNTs and aluminum matrix could improve the interfacial bonding force between the two, so that the load acting on the matrix could be effectively transmitted to the reinforcement and improved the performance of the composites. Obviously, the positive effect of the HIP process was twofold, which converts the severely damaged CNTs and aluminum matrix reaction into Al₄C₃, which not only improved the interfacial bonding strength, but also reduced the defects in the CNTs.

Table 1. Tensile properties of CNTs/Al2009 composites at room temperature.

| Process               | Tensile strength/MPa | Yield Strength/MPa | Elongation/% |
|-----------------------|-----------------------|--------------------|--------------|
| Hot extrusion         | 540                   | 423.3              | 10.0         |
| HIP and hot extrusion | 560                   | 443.3              | 10.2         |

4. Conclusions

Following conclusions were drawn from this work:

1. The cryogenic milling process could disperse 1.0 wt. % of CNTs into the aluminum matrix, and the composites prepared by HIP and hot extrusion process had uniform microstructure and excellent tensile properties at room temperature. The tensile strength, yield strength and elongation of the 1.0 wt.% CNT/Al2009 composites prepared by HIP and hot extrusion process were 560 MPa, 443.3 MPa and 10.2%, respectively.

2. Hot isostatic pressing process had an important influence on the interfacial bonding strength of CNTs/Al2009 composites. The strength of the composite prepared by HIP and hot extrusion process was 20 MPa higher than that of direct hot extrusion process, and the elongation was basically the same. The main reason was that the high temperature and high pressure conditions of HIP process could promote the reaction of carbon and aluminum at the interface between CNTs and aluminum matrix, so that a few CNTs with severe damage and defects in some CNTs formed Al₄C₃ phase with aluminum, thereby improving two compatibility, and enhanced interface bonding.

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