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Influence of rolling temperature on the interfaces and mechanical performance of graphene-reinforced aluminum-matrix composites

*Chen-yang Huang*1), *Shui-ping Hu*1), *and Kai Chen*2)

1) Institute of Engineering Technology, University of Science and Technology Beijing, Beijing 100083, China
2) School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: To study the influence of rolling on the interfaces and mechanical performance of graphene-reinforced Al-matrix composites, a rolling method was used to process them. Using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and tensile testing, this study analyzed the micromorphology, interfaces, and mechanical performance of the composites before and after rolling. The experimental results demonstrates that the composites after hot rolling has uniform structures with strong interfacial bonding. With an increase in rolling temperature, the tensile strength and elastic modulus of the composites gradually increase. However, when the rolling temperature is higher than 500°C, granular and rod-like Al_4C_3 phases are observed at the interfaces and the mechanical performance of the composites is degraded. When the rolling temperature is 480°C, the composites show the optimal comprehensive mechanical performance, with a tensile strength and elastic modulus of 403.3 MPa and 77.6 GPa, respectively, which represent increases of 31.6% and 36.9%, respectively, compared with the corresponding values prior to rolling.

Keywords: rolling; graphene; composite; interface; mechanical performance

1. Introduction

Al-matrix composites have high specific strength and specific modulus, with excellent high-temperature performance and resistance to fatigue and wear [1]. Additionally, they show good heat-treatment performance and are easily prepared. These properties, which result from the combination of the matrix with reinforced particles, have made them attractive materials and widely used in aerospace and some high-tech industries [1–3].

It has been found that the property of composites is closely related to the reinforcement material and the selection of the reinforcement material is therefore important [4]. Similar to fullerenes and carbon nanotubes (CNTs), graphenes exhibit excellent electrical, thermal, and mechanical properties. Their carrier mobility is 15000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ because of strong sp^2 C–C bonds [5]. Moreover, their thermal conductivity reaches 5000 $W \cdot m^{-1} \cdot K^{-1}$ [6–7], which is about two times as big as that of natural diamond single crystals. The strength, elastic modulus, and specific surface area of graphenes are typically 125 GPa, 1100 GPa and 2630 m^2/g, respectively [8–10]. Therefore, graphenes can greatly improve the mechanical properties of the Al matrix when used as reinforcing agents in metal-matrix composites [11–14]. Shin *et al.* [15] prepared graphene/Al composites using graphene sheets as reinforcement phases. When the graphene content was 0.7vol%, the tensile strength increased by 71.8% compared with that of pure Al. Tian *et al.* [16] prepared graphene/Al composites by spark plasma sintering. A clean, strong interface was formed between the metal matrix and graphene via metallurgical bonding at the atomic scale. However, the interface between the reinforcement phase and the matrix was difficult to regulate, which substantially impeded the development of metal-matrix composites [17–18] and needed further research.

Corresponding author: Shui-ping Hu E-mail: husp@nercar.ustb.edu.cn

Rolling is a conventional processing method and can effectively enhance the mechanical properties of alloys, which is essential for the large-scale application of graphene/Al composites. Recent studies on graphene/Al composites have mainly focused on preparation methods and relevant performance characteristics, however, the effects of processing on the performance of graphene/Al composites and micro-interface bonding are rarely investigated. Lin *et al.* [19] used the hot extrusion process to prepare graphene/Al composites and observed through transmission electron microscopy that a clean and solid interface was formed between graphene and Al matrix. When the graphene content was approximately 1wt%, the tensile strength increased by 66% in comparison with that of pure Al.

In this study, the hot rolling method was used to process graphene-reinforced Al-matrix composites, and the changes in the microstructure, interface morphology, and mechanical performance of the composites were investigated. The results provide a guidance in the optimization of industrial applications of graphene-reinforced Al-matrix composites.

2. Material and methods

2.1. Materials

Graphene-reinforced Al-matrix composites produced by Qingdao Haiyuan New Alloy Material Co., Ltd. were used in the experiments. The raw materials were AA 6061 Al-alloy powder (with a particle diameter of 30–50 μm) and multilayer graphene powders. Fig. 1 shows the original scanning electron microscopy (SEM) images of the AA 6061 Al-alloy and multilayer graphene powders. The Al-alloy particles are nearly spherical and exhibited a large difference in particle diameters, as shown in Fig. 1(a). Fig. 1(b) displays SEM images of the graphene used as reinforcing material in sheets. After the two powders were mixed, a dispersant and stearic acid were added and the resultant mixture was ball-milled for 48 h under a liquid N_2 atmosphere. A number of processes such as coating, degreasing, hot isostatic processing, and surface milling were performed in a vacuum environment to prepare the composite Al plates. The chemical composition of the plates is shown in Table 1.

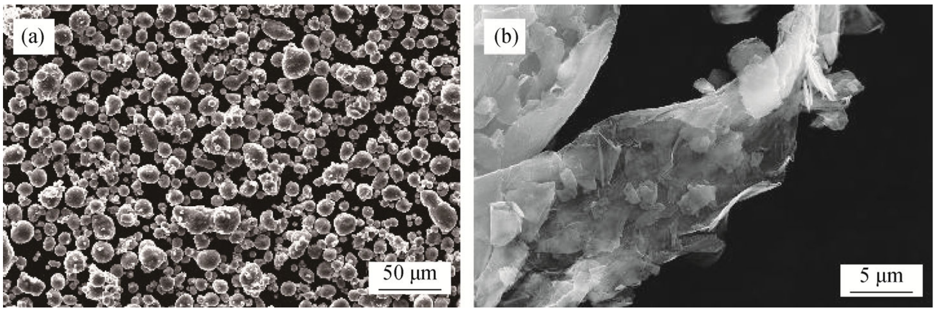

Fig. 1. SEM images of AA 6061 Al-alloy powder (a) and multilayer graphene powder (b).

Table 1. Chemical composition of the graphene-reinforced Al-matrix composite wt%

Graphene powders	Mg	Si	Cu	Al
1.87	1.30	0.42	0.15	Bal.

2.2. Methods

Three small plates with dimensions of 150 mm × 150 mm × 18 mm were cut from a composite Al plate, and a 350 two-high reversing mill was used for rolling and forming the composite Al plates. First, the three small composite plates were placed in environments with temperatures of 450, 480, and 510°C for 2 h for heat preservation; they were then rolled with 10%–15% rolling reduction with each pass. After the rolling reduction reached 50%, the small plates were annealed for 2.5 h at the same temperature and then cooled in air. Finally, the plates were rolled into 2-mm-thick sheets. Fig. 2(a) shows the macromorphology before rolling and Fig. 2(b) presents the macromorphology of the Al plates rolled at different temperatures.

The micromorphology of composites was studied using a QUANTAFEG-450 scanning electron microscope (SEM), and the chemical compositions of the precipitated phases of the composites were measured by energy-dispersive spectroscopy (EDS). A D8 ADVANCEX X-ray diffractometer (XRD) was used for phase analysis of the composites. The microstructural characteristics of the composite interfaces were observed with an FEI Tecnai F20 high-resolution transmission electron microscope (TEM). Also, a Lab HR Evolution Raman spectrometer (RAM) was used to study the generation of interface phases and changes in the graphene structures. Finally, a CMT5105 microcomputer-controlled electronic universal testing machine produced by MTS System Corp. (USA) was used for tensile testing of the graphene/Al composites at a tensile rate of 2 mm/min before and after the samples had been rolled. The tests were conducted at room temperature. The length and gage length of the tensile samples were 90 mm and 25 mm, respectively. Tensile samples were collected from the rolling direction, and the average value of five tests was recorded. The fracture surfaces of the tensile samples were observed by SEM.

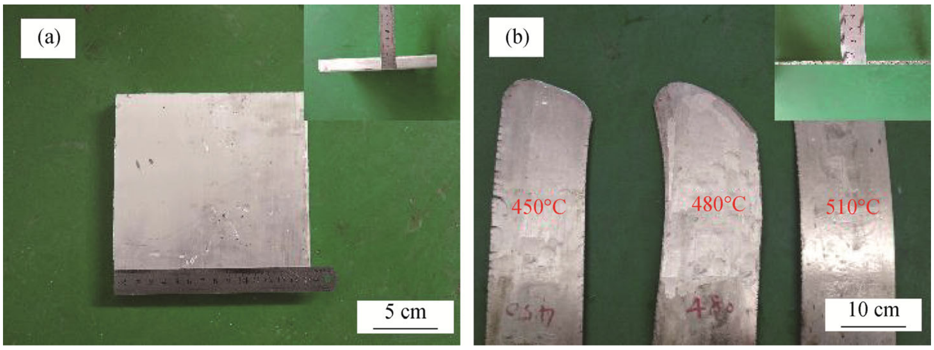

Fig. 2. Macromorphologies of Al plates: (a) before rolling; (b) rolled at different temperatures.

3. Results and discussion

3.1. Microstructure and structure of the graphene/Al composites after rolling

Fig. 3 presents the micromorphologies of the polished graphene/Al composite plates before and after rolling under different processing conditions. Fig. 3(a) shows an SEM image of the composite Al plates before rolling. The composites exhibit uniform structures with no defects. During the preparation, because of mechanical actions such as the impact and shear induced by stainless steel balls on the multilayer graphene powders, the weak van der Waals forces in the interlayer of graphene were damaged, causing further uniform dispersion of the graphene. As shown in Fig. 3(b), after the composites are rolled at 450°C, their microstructures doesn't become loose or show obvious shrinkage of holes distributed uniformly in the structure. The similar phenomenon can also be found in the microstructures of composites rolled at 480°C or 510°C, as shown in Figs. 3(c) and 3(d). Moreover, white granular precipitated phases with dimensions ranging from 0.5 to 1 μm are observed on the surface. Direct observation before and after rolling reveals that the structures of the composites are uniform and free of defects. Therefore, rolling had no major effect on the microstructure of the composites.

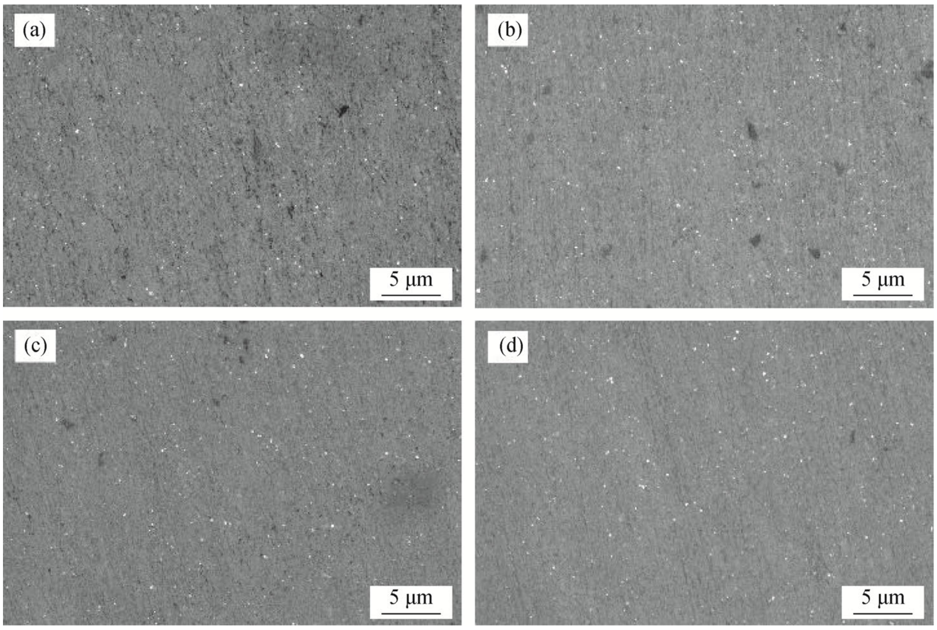

Fig. 3. SEM images of graphene/Al composites: (a) before rolling; (b) rolled at 450°C; (c) rolled at 480°C; (d) rolled at 510°C.

To determine the compositions of the precipitated phases, EDS analysis was conducted on the precipitated phases and the matrix. Fig. 4(a) displays an SEM image of the composites rolled at 480°C. The matrix area (Area 1) and precipitated phases (Spot 2) were selected for analysis. As shown in Fig. 4(b), characteristic peaks of Al, C, and Cu appear in the spectrum corresponding to the matrix area. As demonstrated in Fig. 4(c), in the white precipitates that appeared after rolling, with the exception of the characteristic peaks of Al and C, the characteristic peak of Cu increased substantially. The precipitated phase can also be found in the composites rolled at 450°C and 500°C. And then XRD analysis was used to determine the phases of the composites. As shown in the Fig. 5, diffraction peaks of Al and Al_2Cu are both observed in the composites before and after rolling. EDS and XRD analysis indicate that the white granular precipitated phase in the composites after rolling is Al_2Cu. It is worth noting that the Al_2Cu phase is also be observed in the composite before rolling. Pérez-Bustamante *et al.* [20] reported that Al and Cu could not form compound in the as-milling condition, but when CNT/Al powders were sintered at 500°C, formation of an Al_2Cu phase was observed through XRD. In this study, the graphene/AA 6061 Al-alloy powders were treated by hot isostatic process, which is also promote Al and Cu to forming compounds.

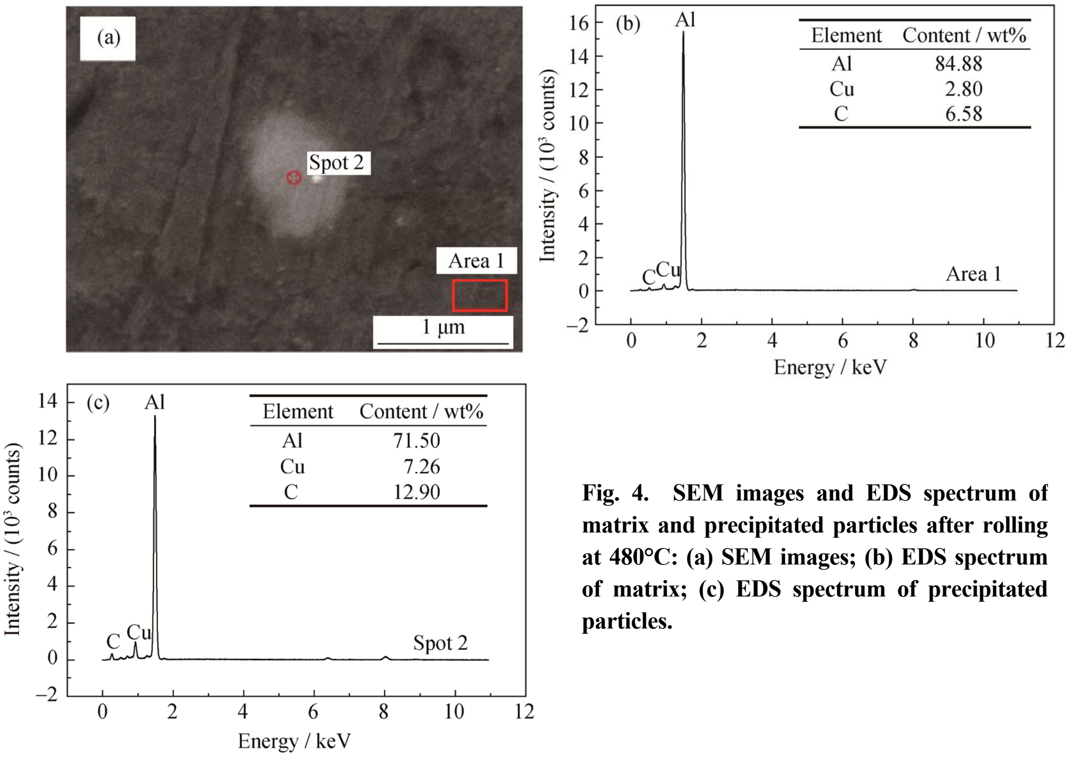

Fig. 4. SEM images and EDS spectrum of matrix and precipitated particles after rolling at 480°C: (a) SEM images; (b) EDS spectrum of matrix; (c) EDS spectrum of precipitated particles.

In additionally, in the Fig. 5, no characteristic peak of graphene appeared at $2\theta = 26.6°$, indicating that the graphene has dispersed and that no agglomeration occurred. Meanwhile, no diffraction peaks of the Al_4C_3 brittle phase are found in the composites either before or after rolling. However, in the general systems of metal-matrix composites, the interface of C/Al composites is more likely to incur reaction. The Al_4C_3 reactant ($4Al_{(s)} + 3C_{(s)} = Al_4C_{3(s)}$) can be formed at the interface of the C/Al composite at 500°C, and on the basis of experimental data from other studies [21–22], it can be speculated that the formation of Al_4C_3 compounds greatly depends on the processing temperature. So the reason Al_4C_3 is not detected in the composite rolled at 510℃ may be that the amount of Al_4C_3 generated by the interfacial reaction is lower than the detection limit of the diffractometer.

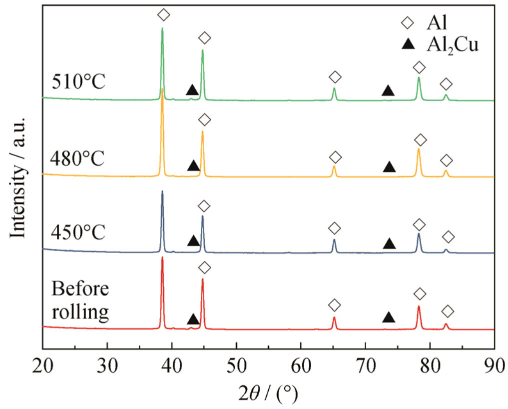

Fig. 5. XRD patterns of graphene/Al composites before and after rolling.

3.2. Interface performance of the graphene/Al composites

As illustrated in Figs. 4 and 5, XRD could not completely characterize the phases in the composites. Raman spectroscopy was therefore used to comprehensively characterize the products at the interface. The Raman spectra of the graphene/Al composites rolled at different temperatures were shown in Fig. 6. A typical D band (resulting from defects and amorphous carbon), G band for graphite, and 2D band (the shape of second-order Raman band) of the graphite carbons are observed at 1359, 1603, and 2705 cm^{-1}, respectively. When the rolling temperature is 510°C, a characteristic peak of Al_4C_3 appears at 830 cm^{-1} in the corresponding spectrum.

As shown in Fig. 6, as the rolling temperature is increased, the 2D characteristic peak of graphenes shifts and weakens, indicating that defects appear in the graphene structure during the rolling process. When the rolling temperature reaches 510°C, a characteristic peak of an Al carbide is observed in the corresponding Raman spectrum. This result demonstrates that the Al_4C_3 brittle phase forms at the interface of graphene and the Al matrix when the rolling temperature exceeds 500°C, thus influencing the performance of the composites.

Fig. 7(a) shows the micromorphology of the graphene/Al composites before rolling. The interface is clean, with some dislocations in the surrounding area. Because of the different thermal expansion coefficients of the graphene and the Al matrix, internal stress is generated during the cooling

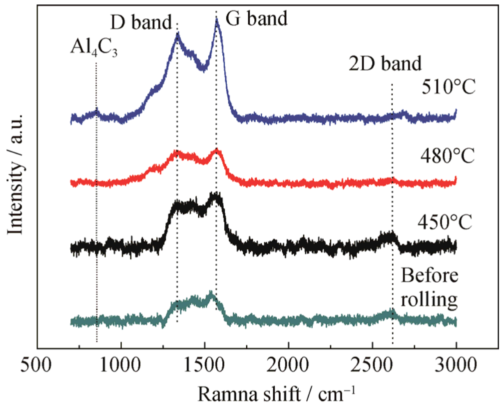

Fig. 6. Raman spectra of the graphene/Al composites before and after rolling at different temperatures.

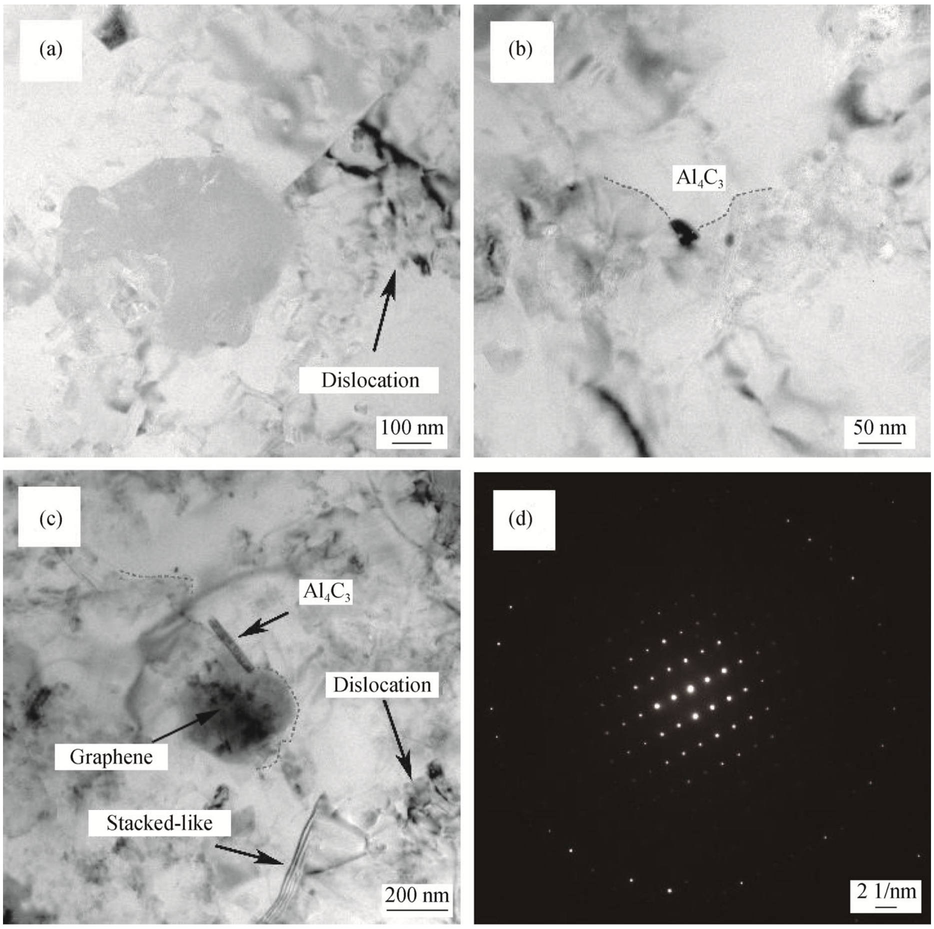

Fig. 7. TEM images of the graphene/Al composites before and after rolling: (a) original material; (b) granular Al_4C_3 phases in composite rolled at 510°C; (c) rod-like Al_4C_3 phases and stacked graphenes in the composite rolled at 510°C; (d) diffraction spots corresponding to the selected area of the graphenes in (c).

process and dislocations occur when the internal stress reaches a certain threshold level. Good dispersion and strong interfacial bonding occur between the Al and the graphene. A strong interface enabled larger loads to be transferred from the matrix to the reinforcement phases of the graphene, effectively reducing deformation and fracture of the Al matrix and thus improving the mechanical performance of the composites. However, the pinning effects of graphene sheets on the grain boundary of the Al matrix reduce the ductility of the composites.

Fig. 7(c) shows some obvious characteristics of the graphenes. To determine whether graphenes were present, the selected area was analyzed by electron diffraction, as shown in Fig. 7(d). The results demonstrate that graphenes are stacked and not damaged, as well as maintain its original state. Some Al_4C_3 phases are found, as shown in Figs. 7(b) and 7(c), with granular and rod-like Al_4C_3 phases produced at the interface. Most of the Al_4C_3 phases are granular, while the rod-like Al_4C_3 phases are approximately 120 nm long. On the C/Al composite, only Al_4C_3 could form on the interface at temperatures greater than 500°C. The phases with granular and rod-like morphology in the present study are quite similar to those reported previously [21–22]. Because aluminum carbide are the brittle phase, when stress is transferred to the interface, the presence of Al_4C_3 adversely affects the mechanical performance.

3.3. Mechanical performance of the graphene/Al composites

Table 2 summarizes the elastic modulus, tensile strength, and ductility of the composites at different rolling temperatures. Compared with the mechanical performance of the original materials, that of the rolled materials are substantially improved. When the rolling temperature is 450°C, the tensile strength reaches 398.6 MPa. At a rolling temperature of 480°C, the tensile strength and elastic modulus of the composites are 403.3 MPa and 77.6 GPa—an increase of 31.6% and 36.9% compared with that of the original material. However, when the rolling temperature reaches 510°C, the tensile strength is 391.4 MPa. A possible explanation for this diminished performance is that, when the rolling temperature exceeds 500°C, the Al_4C_3 brittle phases appeared in the cross section of the composites, adversely affecting their mechanical performance. In our experiments, the tensile strength of graphene/AA 6061 composites could reach to maximum value of 403.3 MPa after rolling with a little decrease of ductility, and this value is higher than that of some other's experimental studies. For example, Wang *et al.* [23] prepared an Al-matrix composite reinforced with graphene nanosheets (GNSs) and a tensile strength of 249 MPa could be achieved; Radha *et al.* [24] also prepared graphene/AA 6061 composites, however, the tensile strength of the composite was only 230 MPa.

Table 2. Mechanical performances of the composites before and after rolling

Material status	Elastic modulus / GPa	Tensile strength / MPa	Ductility / %
Before rolling	56.7	306.5	7.3
Rolled at 450°C	72.8	398.6	5.6
Rolled at 480°C	77.6	403.3	6.2
Rolled at 510°C	72.3	391.4	5.2

Enhancement mechanisms of the mechanical performance of composites after hot rolling can be mainly explained from two perspectives: stress transfer and dislocation strengthening. Under the effects of external loads, dislocation movements in the composites to bypass the 2D nanostructure of graphene, which is with a unique and super-large surface area that acts as a dislocation wall, are more difficult than to bypass or cut particulate reinforcement materials because the dislocation movements to bypass graphene warrant greater energy. Dislocation initiation and slippage are hindered, which effectively prevents plastic deformation of the matrix and greatly improves the strength of the composites. In addition, after rolling, the density of dislocations increases in the composites, resulting in dislocation strengthening and accounting for the increase of material strengthen and modulus (as shown in Table 2). However, the enhanced mechanical strengthen after hot rolling is often at the cost of ductility. Besides, the pinning effects of graphenes on the grain boundary is also responsible for the reduced ductility of the composites.

On the basis of the experimental mechanical performance data, the rolling temperature should be controlled in the range 450–480°C and the optimal rolling temperature is determined to be 480°C.

Fig. 8 shows the tensile fractures of the composites. As demonstrated in Fig. 8(a), before rolling, the original fracture of composites is dense and contained some number of micropores. Also, some dimples are observed and the fracture has a large macrostrain associated with typical ductile fracture. These observations, showing in the Figs. 8(b), 8(c), and 8(d), reflect bonding effects between the matrix and the reinforcement phases after rolling. With increasing rolling temperature, dimples in the fracture of the composites are smaller and shallower and torn ridges became thin and small. Moreover, the number of micropores decrease, whereas the microstructures became denser. It can be found that dimples and torn ridges are observed in the fracture of these alloys, characteristic of ductile fracture and corresponding to the similar ductility (shown in Table 2).

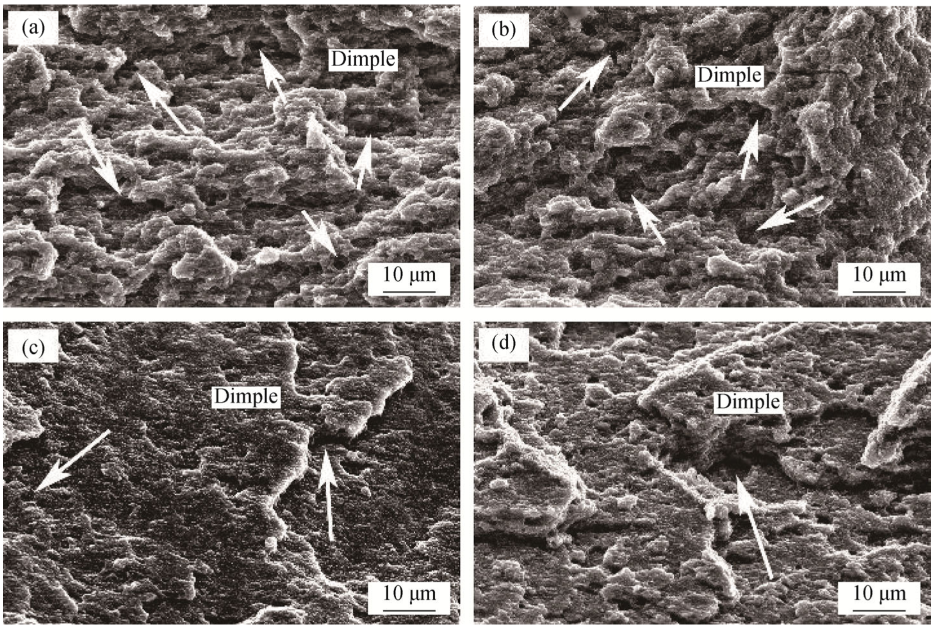

Fig. 8. SEM images of fractures of the graphene/Al composites: (a) before rolling; (b) as-rolled at 450°C; (c) as-rolled at 480°C; (d) as-rolled at 510°C.

4. Conclusions

The graphene-reinforced Al-matrix composites were successfully processed by rolling. The effects of rolling temperature (450°C, 480°C, or 510°C) on the interfaces and mechanical performance of the composites were investigated. From this research, the following conclusions are drew.

(1) After rolling, the graphene/Al composites are dense and the graphenes are distributed uniformly without a change in morphology; thus, the mechanical performance are improved substantially.

(2) When the graphene/Al composites prepared by hot isostatic pressing treated, Al_2Cu phase was observed through XRD.

(3) For the specimen rolled at 510°C, a characteristic peak of Al_4C_3 appeared in its Raman spectra. TEM images reveal that granular and short rod-like Al_4C_3 phases with 120 nm length formed at the interface. The Al_4C_3 is a brittle phase that could diminish the mechanical performance of the composites. After rolling, more dislocations are observed; these dislocations play a role in dislocation strengthening.

(4) In comparison with the composites before rolling, the elastic modulus and tensile strengths of the rolled graphene/Al composites show an obvious increase, whereas their ductility decreased slightly. When the rolling temperature is 480°C, the mechanical performance of the composites is optimal. Furthermore, the tensile strength and elastic modulus are 403.3 MPa and 77.6 GPa, respectively, which represent 31.61% and 36.9% increases compared with those before rolling. The fracture surface of composites before and after rolling showed the characteristics of ductile fracture.

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