Effect of Temperature on the Dispersion of Graphene in Graphene Reinforced Aluminum Matrix Composite

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Abstract. The influence of hot pressing temperature on the dispersion of graphene (GR) in GR reinforced aluminum matrix composites was investigated. The microstructures of the sample were observed by optical microscope, scanning electron microscopy and energy dispersion spectrum, respectively. The temperature is hold at 640-750 °C, and the interval is 10 °C. The results show that GR is mainly distributed at the grain boundary at 640 ℃. And GR is dispersed in the aluminum matrix, without obvious agglomeration at the temperature from 670 ℃ to 680 ℃. However, GR is agglomerated in the aluminum matrix and has obvious regional differentiation at 690-750 ℃, in which the concentrated area of GR is in the middle of the sample, and the dilution area in the rest.

1. Introduction
Graphene (GR) has a unique single atomic layer structure and a large specific surface area. The mechanical properties of the composite can be significantly improved by adding a small amount of GR to the metal matrix. In recent years, GR reinforced metal matrix composites have become a research hotspot [1-4]. Song et al. [5] used molecular dynamics simulation (MD) to simulate the unidirectional tensile strength of single GR reinforced aluminum matrix. It was found that the tensile strength and Young's modulus of the composite were increased by 32.32% and 52.27% respectively by adding GR. Mokhalingam et al. [6] simulated the mechanical properties of single-layer GR reinforced aluminum matrix composite (AMC) with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software, and calculated that the theoretical Young’s modulus of GR reinforced AMC can reach 143.8 GPa. However, the mixed model (ROM) and the half empirical H-T model [7] are used to calculate the strength of composite materials and the result is 137.2 MPa and 107.2 MPa respectively. The related properties of the GR reinforced AMC are far from the theoretical strengthening effect of GR on aluminum matrix, which shows that there is a great space for improving the mechanical properties of GR AMCS. However, the poor wettability and self aggregation between GR and metal matrix lead to poor dispersion in aluminum matrix, and the uneven dispersion leads to two areas in the composite: enrichment area and dilution area [8]. The GR in the enrichment area gathers excessively, resulting in defects and in the process of dilution area, there may be pore defects due to the diffusion of GR. The dispersion behavior of GR in metal matrix is the key problem of reinforced composites. Optimization of preparation methods and parameters is an effective way to improve the dispersion behavior of GR in the matrix. Zhang et al. [9] mixed GR with aluminum powder by high-energy ball milling, and found that GR flake layer after high-energy ball milling can adhere to the surface of aluminum powder, achieving better dispersion, and breaking the strong intermolecular force between GR flakes in the process of ball milling, avoiding agglomeration; but with the increase of ball milling time, the
diameter of GR flake layer will become smaller. Bustamante et al. [10] put 1 wt% of GR and aluminum powder into small bottles made of hardened steel tools and grinding media made of hardened stainless steel, and used methanol and argon as process control agents to grind on high-energy ball mill. With the grinding time, the morphology of aluminum powder changed significantly, and the dispersion of GR in the matrix also improved effectively, indicating the addition of process control agents and the extension ball milling time is helpful to improve the dispersion of GR in matrix. Chu et al. [11] found that when the volume fraction of GR reached 12%, the presence of GR agglomerates was observed in the process of preparing GR copper matrix composite by high energy ball milling. After hot pressing and sintering, GR agglomerates seriously affected the dispersion of GR in the composite. Li et al. [12] prepared GR reinforced aluminum matrix composite under the action of current. GR can be effectively dispersed in the matrix by electrochemical deposition. Some of the preparation processes can effectively realize the uniform dispersion of GR. However, the research on the dispersion of GR in metal matrix is not systematic. In this paper, the diffusion phenomenon of GR in the hot pressing process of GR reinforced aluminum matrix composite prepared by powder metallurgy is studied. The best temperature condition in the preparation process is to be found by controlling the temperature condition, so as to realize the good dispersion of GR in the matrix.

2. Preparation Methods
The inner surface of the graphite mould used in the experiment was brushed with a layer of boron nitride alcohol solution as an isolation layer to prevent the reaction between graphite and aluminum matrix during the preparation process. To remove the alcohol and moisture inside the mold, the mold and related accessories need to keep 70 ℃ for 2 h. The ball milling method was used to mix GR and aluminum powder. The ball material ratio was 10:1, the ball milling process was at 10 Hz for 3h, and the mass fraction of GR was 0.4%. After drying, transfer the composite powder to the inside of the mold cavity for pre pressing, the pressure is 10 MPa, and the holding time is 1 min. Raise the furnace to the preset temperature according to the heating rate of 20 ℃/min, then hold for 1 h. After sintering, the sample is cooled to 400 ℃ with the furnace when the sample is solidified. Finally the temperature is raised to 550 ℃ and pressure treatment is carried out to improve the density of the material.

3. Results and Discussion
Figure 1 is result of the flaky substance in the sample prepared at the temperature of 640 ℃. Through the analysis of energy dispersion spectrum results, the main element in the sheet material is carbon, and the carbon source in the material preparation process is GR, so the sheet material in the sample prepared at 640 ℃ is GR.

Figure 2 is the microstructure of the composite at the holding temperature of 640-680 ℃. It can be seen from figure 2a that there is no obvious agglomeration area of GR in the microstructure at 640 ℃, and GR is distributed at the grain boundary and does not diffuse to the interior of the grain. At 640 ℃, the sintering neck will be formed between the aluminum powder and the adjacent powder, and the GR attached to the surface of the aluminum powder will not enter the grain. Small agglomerates are formed after contacting with the edge of aluminum grain, so there is no obvious GR enrichment area or dilution area. The agglomeration of GR occurs in the sample with the temperature of 650-670 ℃, In this temperature range, the phase transformation occurs in the aluminum matrix, and the movement degree of GR in the matrix increases due to the distribution of GR more uniform than that of 640 ℃.

Figure 3 is the microstructure of the samples prepared at 680-750 ℃. Obvious GR agglomeration has appeared in the samples at the holding temperature of 680 ℃. With the increase of the holding temperature, the agglomeration of GR is more and more severe, and the regional differentiation of the GR enrichment area and the dilution area is formed in the sample. With the increase of holding temperature, the viscosity of aluminum matrix decreases, and the resistance of GR lamellar movement decreases. At the same time, the molecular thermal movement becomes violent with the increase of temperature, so the phenomenon of GR agglomeration become more and more severely. With the
increase of agglomeration, the GR in the aluminum solution gradually gathered to the GR aggregate, forming the GR enrichment area.

**Figure 1.** Energy spectrum scanning results of flaky substance in 640 °C sample: (a) Flaky morphology in 640 °C sample by SEM, (b) distribution of element C in (a), and (c) Element content in selected area.

**Figure 2.** Microstructure of sample by optical microscope: (a) 640 °C, (b) 650 °C, (c) 660 °C and (d) 670 °C.
Figure 3. Microstructure of sample by optical microscope: (a) 680 °C, (b) 690 °C, (c) 700 °C, (d) 710 °C, (e) 720 °C, (f) 730 °C, (g) 740 °C and (h) 750 °C.

Figure 4 shows the microstructure of the sample prepared at 750 °C. Figure 4a shows the poor area of GR. It can be seen that the metallographic structure in this area is typical aluminum alloy microstructure. Figure 4b shows the rich area of GR in the sample. It can be seen that the GR in this area shows obvious agglomeration and enrichment. It can be seen from figure 4c that the boundary between the rich area and the poor area is clearly. At 750 °C, the aluminum matrix is transformed into liquid phase and the GR flakes attached to the aluminum powder particles fall off and are suspended in the aluminum liquid after ball milling. Due to the action of molecular thermal movement, the GR
sheets gradually approach each other, and some GR forms aggregates. During the solidification process, the samples solidify gradually from the edge to the internal area, and the GR move to the non-solidification area under the driving force of solid/liquid solidification interface. Finally, the aggregates occur in the center of the sample, forming the obvious differentiation of GR dilution area and enrichment area.

Figure 4. Microstructure of sample prepared at 750 °C: (a) GR dilution area, (b) GR enrich area and (c) Junction of enrichment area and dilution area.

4. Conclusion
In this paper, the microstructure of the prepared samples was observed and analyzed by controlling the holding temperature, and the following conclusions can be obtained.

(1) When the holding temperature is 640 °C, GR is mainly distributed at the grain boundary, which can not be effectively dispersed.

(2) The dispersion of GR in aluminum matrix is relatively uniform when the holding temperature reach 650-670 °C.

(3) GR agglomerates severely and differentiates obviously in the aluminum matrix at the temperature during 680-750 °C.

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References
[1] Stephen F B, Joseph P, Mohammad A R, et al. 2017 Graphene-aluminum nanocomposites Materials Science and Engineering A 528 (27) 7933-7937
[2] Wang J, Li Z, Fan G, et al. 2012 Reinforcement with graphene nanosheets in aluminum matrix composites Scripta Materialia 66 (8) 594-597
[3] Wang T, Zhang Y T, Li G D, et al. 2018 Enhanced Mechanical Properties of Al 7075 Alloy with Graphene Nanoplates Prepared by Ball Milling and Hot Extrusion. Springer Nature Singapore Pte Ltd 827-834
[4] Kumar S J N, Keshavamurthy R and Haseebuddin M R 2017 Mechanical properties of aluminium-graphene composite synthesized by powder metallurgy and hot extrusion Transactions of the Indian Institute of Metals 70 (3) 605-613
[5] Song H Y, Zha X W 2010 Mechanical properties of Ni-coated single graphene sheet and their embedded aluminum matrix composites *Communications in Theoretical Physics* **54** (1) 143-147

[6] Mokhalingama A, Kumara D, Srivastava A, et al. 2017 Mechanical behaviour of graphene reinforced aluminum nano composites. *Materials Today: Proceedings* **4** (2) 3952-3958

[7] Liang J, Huang Y, Zhang L, et al. 2009 Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites *Advanced Functional Materials* **19** (14) 2297-2302

[8] Yu W 2013 *Microstructure and Properties of 2024 Aluminum Matrix Composite Reinforced by CNTs/SiCw Hybrid* Master Thesis: Harbin University of Technology pp 38-39

[9] Zhang H P, Xu C, Xiao W L, et al. 2016 Enhanced mechanical properties of Al5083 alloy with graphene nanoplates prepared by ball milling and hot extrusion *Materials Science and Engineering A* **658** 8-15

[10] Bustamante R P, Morales D B, Martínez J B, et al. 2014 Microstructural and hardness behavior of graphene-nanoplatelets/aluminum composites synthesized by mechanical alloying *Journal of Alloys and Compounds* **615** (1) S578-S582

[11] Chu K and Jia C C 2014 Enhanced strength in bulk graphene-copper composites *Physica Status Solidi A* **211** (1) 184-190

[12] Li N, Zhang L and Xu M T 2016 Preparation and mechanical property of electrodeposited Al-graphene composite coating *Materials and Design* **111** 522-527