Effects of graphene addition on the microstructure of 7075Al

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Keywords: 7075 aluminum alloy, graphene, As-cast microstructure, grain refinement

Abstract

In this paper, the effect of the addition of graphene on the as-cast and homogenized annealing microstructure of 7075 aluminum alloy (AlZnMgCu) was studied. The analytical model devised in this study has demonstrated the significant grain refinement of graphene-7075 aluminium matrix composites (G-7075) due to large surface area of graphene. The results showed that the as-cast microstructure of graphene-7075 aluminum matrix composite was refined significantly, which the average grain size of the composite decreased from 78 μm to 45 μm and lattice distortion is more significant. The effect of the dissolution of the non-equilibrium eutectic structure and the secondary phase distribution of the graphene-7075 aluminum matrix composite is better after annealing at 470 °C for 16 hours.

1. Introduction

Al–Zn–Mg–Cu alloys are a kind of crucial structural materials with high specific strength, superior machinability and mechanical properties [1], which makes them widely used in lightweight aerospace and automobile industry [2–6]. In the industrial production of Al–Zn–Mg–Cu alloy, casting is the most commonly used manufacturing technology [7]. Therefore, it is necessary to study the as-cast microstructure since they have a genetic effect on the subsequent treatment [8, 9].

As-cast Al–Zn–Mg–Cu alloys have serious chemical segregation and coarse secondary phase near the grain boundary, which affect the mechanical properties and stress corrosion resistance of the alloy [10, 11]. Different types of intermetallic phases of η (MgZn2), η′ (AlZnMgCu), S (Al1CuMg), Q (Al1Cu) and Al1CuMg1Fe were included of the casting process of Al–Zn–Mg–Cu alloy [12–14]. Therefore, further addition of alloy elements may cause the change of the composition of intermetallic phases. A large number of coarse intermetallic phases increase the fracture tendency of the crack at the grain boundary and thus deteriorate the properties [15–21].

In recent years, Al–Zn–Mg–Cu alloys are mainly studied by adding other alloy elements, such as scandium zirconium, or by adding reinforcing phases to improve their comprehensive properties [22–25]. For example, the transition element of Zr is usually added in the aluminum alloy, which effectively refines the grain size to improve the mechanical properties of the alloy [26]. However it is difficult to eliminate the Zr segregation in the solid solution, so the formation of Al1Zr dispersion is usually unevenly distributed in a single grain, resulting in the Zr segregation to the dendrite center during the casting process. Nowadays, composite materials based on Al–Zn–Mg–Cu system have been widely researched [27, 28]. Ma et al prepared 7055 Al C–1N–1T–1 composite by adding carbon nanotubes (CNTs) with high tensile modulus and ultimate tensile strength. However, the tensile elongation is obviously reduced, which is mainly due to the entangling of carbon nanotubes which become the source of local cracks during deformation [29]. Graphene is one of the most promising reinforcements because of its excellent mechanical properties. Venkatesana et al [30] successfully prepared AA7050 graphene composite by stirring and squeeze casting. When the content of graphene is 0.3 wt%, the best mechanical properties are obtained and the defects such as pores and holes are eliminated.

In the present work, the effect of the addition of graphene on the as cast and homogenized annealing structure of 7075 Aluminum alloy is studied and discussed in detail.
2. Experimental

Two different 7075 aluminum alloy and graphene-7075 aluminum matrix composite were studied which mainly differentiated by graphene, via. 7075 and G-7075. The exact chemical composition of 7075 and G-7075 is given in table 1. In this study, the Al ingots (99.7%), Mg ingots, Zn ingots, Al–50Cu master alloys, Al-4Ti master alloys, Al-5Cr master alloys as raw materials were melting at a resistance furnace with clay/graphite crucible. Blowing the mixed powder of graphene and aluminum powder into the melt by inert gas and then stirring the melt evenly. Finally, the melt was cast into cylinder samples with diameters of 90 mm and length of 300 mm.

For analysis of the as cast structure of 7075 and G-7075, the specimens for microstructure observation and performance characterization were cut at a distance of \( D/4 \) from the center of the section. According to the previous research work, 470 °C heat preservation for 16 h was selected as the homogenization process.

Samples were prepared by conventional mechanical polishing method, and then corroded by keller reagent (1%HF + 1.5%HCl + 2.5%HNO3 + 95%H2O). The microstructure of 7075 and G-7075 were observed by optical micrograph. In order to characterize the as-cast and homogenized structure more accurately, the microstructure of 7075 and G-7075 were analyzed by scanning electron microscope (SEM), and the chemical composition of the samples was analyzed by energy dispersive spectrometer. The as-cast microstructures of 7075 and G-7075 were studied by means of X-ray diffraction measurement (XRD) (scanning from \( 2\theta = 20^\circ \) to \( 2\theta = 90^\circ \), step size of 0.02°, counting time of 0.3 s per step). Differential scanning calorimetry (DSC) was used to measure the thermal properties of 7075 and G-7075 with a constant heating rate of 10 °C min\(^{-1}\) from 25 °C to 700 °C under argon gas flow.

3. Result and discussion

Figure 1 shows the as-cast microstructures of 7075 and G-7075. It can be seen that the microstructure of 7075 and G-7075 were composed of gray α-Al matrix and black grain boundary. Moreover, the grain size of graphene-7075 aluminum matrix composite is obviously smaller than that of 7075 aluminum alloy. Figure 2 shows the grain size distribution of 7075 and G-7075 in as-cast state. The average grain size of 7075 is about 78 μm, while the average grain size of G-7075 is about 45 μm. Additionally, the grain size distribution in G-7075 samples is more concentrated. The average grain size of as-cast G-7075 is basically the same as that of the material prepared by Venkatesana [30] but the grain size distribution of the former is more uniform. The average grain size in this work is smaller than that of SiC-7050 prepared by Dasgupta [28].

The grains of G-7075 are even smaller because the two-dimensional graphene provides sufficient nucleation sites, and decreases the surface energy in nucleation process. Thus nucleation process of aluminum is easy to realize, and as a result, the grains are refined.

The free energy of the system during the liquid phase of aluminum changes to solid phase can be expressed as follows:

\[
\Delta G = \Delta G_0 - S \sigma
\]

Where \( \Delta G_0 \) is volume free energy; \( S \) is the surface area of aluminum liquid embryo; \( \sigma \) is surface energy. Assuming that the embryo is spherical which the radius is \( r \), the free energy of embryo during cooling can be calculated as follows:

\[
\Delta G = \frac{4}{3} \pi r^3 \Delta G_0 + 4 \pi r^2 \sigma
\]

The rate of change of free energy of the system can be expressed as:

\[
d\Delta G = 4\pi r^2 \Delta G_0 + 8\pi r \sigma
\]

Only when the free energy of the system decreases, the globular embryo can exist stably, that is, \( d\Delta G \leq 0 \). Therefore, the minimum critical nucleation radius \( r_k \) and the critical nucleation work \( \Delta G_k \) can be expressed as:

\[
r_k = \frac{2\sigma}{\Delta G}
\]

| Table 1. Chemical composition of two materials studied (wt%). |
|-----------------|-----|-----|-----|-----|---|-----|---|
| Zn   | Mg  | Cu  | Fe  | Cr  | Ti | Graphene | Al |
| 7075 | 5.6 | 2.5 | 1.6 | <0.1| 0.2| 0         | Balance |
| G-7075 | 5.6 | 2.5 | 1.6 | <0.1| 0.2| 0.2       | Balance |
Assume that the aluminum liquid forms a spherical crown crystal embryo with an angle of $Q$ on the two-dimensional plane of graphene when graphene is added, surface energy can be expressed as:

$$
\sigma_{\text{tot}} = \sigma_{\text{LG}} + \sigma_{\alpha} \cos \theta
$$

Where $\sigma_{\text{LG}}$ is surface energy between liquid aluminum and graphene; $\sigma_{\alpha}$ is surface energy between aluminum embryo and graphene; $\sigma_{\alpha} \cos \theta$ is surface energy between aluminum embryo and liquid aluminum. The total surface energy can be expressed as:

$$
\Delta G_t = \frac{1}{3} 4\pi r_k^2 \sigma
$$

Where $\sigma_{\text{LG}}$ is surface energy between liquid aluminum and graphene; $\sigma_{\alpha}$ is surface energy between aluminum embryo and graphene; $\sigma_{\alpha} \cos \theta$ is surface energy between aluminum embryo and liquid aluminum. The total surface energy can be expressed as:

$$
\Delta G_t = \sigma_{\alpha} S_1 + \sigma_{\alpha} S_2 - \sigma_{\text{LG}} S_3
$$

Where $S_1$ is the surface area between aluminum embryo and aluminum liquid; $S_2$ is the surface area between aluminum embryo and graphene; $S_3$ is the surface area of graphene and aluminum liquid before the formation of embryo. The total system free energy can be expressed as:
The minimum critical nucleation radius \( r_k \) and the critical nucleation work \( \Delta G'_k \) can be expressed as:

\[
\Delta G'_k = \left( \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \sigma_{SL} \right) \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right)
\]  

The critical nucleation work \( \Delta G'_k \) after adding graphene is always less than that without adding graphene. And a small amount of graphene can play a great effect because graphene has a large specific surface area, about 2630 \( \text{m}^2 \text{g}^{-1} \), which contributes to significant refinement grain.

Both as-cast 7075 and G-7075 are equiaxed in grains and dendritic in grain boundary, which are lamellar non-equilibrium eutectic structures due to large cooling rate in the casting process. With the decrease of the temperature of aluminum liquid, \( \alpha \)-Al solid solution crystallizes below the liquidus, and then grow up gradually to the equiaxed crystal shape. At the same time, \( \text{Zn}, \text{Mg}, \text{Cu} \) and other solutes diffuse to the liquid phase, which increases the solute concentration in the liquid phase region. The eutectic reaction will occur, resulting in the formation of non-equilibrium eutectic structure when the temperature continues to drop to the eutectic composition area. EDS analysis was performed for grain boundary and the matrix respectively, and the results are shown in figure 3. Among them, point 1 refers to the grain boundary and point 2 refers to the matrix component. It can be considered that the non-equilibrium eutectic structure at the grain boundary is \( \text{Mg}(\text{Zn}, \text{Al}, \text{Cu})_2 \).

The diffraction pattern of the as-cast 7075 and G-7075 is shown in figure 4. It can be seen that there are obvious Al peaks and weak MgZn\(_2\) diffraction peaks without C diffraction peaks, which shows that there is no obvious aggregation of graphene. According to Bragg formula and calculation formula of crystal surface spacing:

\[
2d \sin \theta = n \lambda
\]
The lattice constants and lattice distortion of Al and MgZn\textsubscript{2} is calculated according to the strongest diffraction peaks of Al and MgZn\textsubscript{2} and the results are shown in table 2. The results show that the lattice distortion of G-7075 is more serious than 7075.

Figure 4 shows the XRD patterns of 7075 and G-7075 in as-cast stage.

Table 2. Lattice distortion of 7075 and G-7075 in Al and MgZn\textsubscript{2}

|                | Al-G-7075 | Al-7075 | MgZn\textsubscript{2}-G-7075 | MgZn\textsubscript{2}-7075 |
|----------------|-----------|---------|-----------------------------|---------------------------|
| Lattice distortion | 0.44%     | 0.19%   | 0.69%                       | 0.40%                     |

Figure 5 shows the DSC curves recorded on constant-rate heating for as-cast 7075 and G-7075 in the temperature range from 25 to 700 °C. The endothermic peak A is caused by the reverse peritectic transformation of a small amount of S (Al\textsubscript{2}CuMg)-phase or T (AlZnMgCu)-phase and endothermic peak B corresponds to the

\[
d_1 = \frac{a_1}{\sqrt{h^2 + k^2 + l^2}} \quad (12)
\]

\[
d_2 = \frac{a_2}{\sqrt{\frac{4}{3}(h^2 + kh + k^2) + \left(\frac{a_1}{a_2}\right)^2}} \quad (13)
\]

The lattice constants and lattice distortion of Al and MgZn\textsubscript{2} is calculated according to the strongest diffraction peaks of Al and MgZn\textsubscript{2} and the results are shown in table 2. The results show that the lattice distortion of G-7075 is more serious than 7075.

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dissolution of MgZn$_2$. The results show that the addition of graphene has little effect on the thermal properties of as-cast 7075.

Figure 6 shows the scanning microstructure of 7075 and G-7075 after homogenization annealing at 470 °C for 16 h. It can be observed that the non-equilibrium eutectic structure at the grain boundary is discontinuous and a large amount of white second phases are formed in the Al matrix. For G-7075, the dissolution of the non-equilibrium eutectic structure is better and the second phase is more uniform formed in the grain. Figure 7 schematically illustrates the proposed mechanism of the non-equilibrium eutectic structure at the grain boundary during homogenization heat treatment based on the experimental observations from figures 3 and 6. In the first step, Al, Zn, Mg, Cu atoms in the grain boundary began to diffuse into the matrix, which led to the narrowing of the grain boundary. In the second step, the solid solution atoms continue to diffuse into the grain, and the grain boundary continues to be thin until it become discontinuous. In the third step, the solute atoms begin to nucleate and grow in the matrix, forming a large number of dispersed fine MgZn$_2$ phases.
4. Conclusion

(1) The graphene addition refined the grain size of 7075Al alloys from 78 μm to 45 μm because graphene can promote heterogeneous nucleation. Moreover, the addition of graphene has little effect on the thermal properties of as-cast 7075.

(2) The homogeneous annealing of graphene-7075 aluminum matrix composite at 470 °C for 16 h, is more effective, indicating that addition of graphene also has a good effect on subsequent heat treatment.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (Nos. 51871111), the Shandong Provincial Natural Science Foundation of China (ZR2018LE001), and the Key Research and Development Program of Shandong Province (Grant No.2019RKB01018).

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