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Effect of thermal exposure on the microstructure of the interface in a Gr_f/Al composite

Abstract: The microstructure of the interface in a Gr_f/Al composite after exposure at high temperature was investigated. The graphite fiber reinforced aluminum matrix composite was prepared by the pressure infiltration method. After being heat treated at 550°C, 600°C and 640°C for different times, the microstructure of the interface in the composite was studied by using transmission electron microscopy (TEM). Furthermore, the content of Al₄C₃ in the interface was examined using X-ray diffraction (XRD). The results showed that not only the micro morphology but also the content of Al₄C₃ in the interface varied with the increase in temperature. When the composite was heat treated at 550°C and 600°C, Al₄C₃ with a big length-to-diameter ratio was observed in the interface, while Al₄C₃ with a small length-to-diameter ratio was found when the heat treatment temperature was 640°C. With the increase in the time, the content of Al₄C₃ in the interface increased rapidly when the composite was heat treated at 640°C. Based on the dynamic calculation, the interface reaction diffusion rate constant of the Gr_f/Al composite increases rapidly when the temperature is higher than 600°C.

Keywords: Al matrix composite; Al₄C₃; graphite fiber; interface.

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1 Introduction

Al₄C₃ as the main interfacial reaction product has a wide distribution in C/Al composites fabricated by the liquid infiltration method [1–4]. Most of Al₄C₃ in the interface of C_f/Al composites was lath-like [5]. On the one hand, interfacial reaction would damage the surface of carbon fiber and

reduce its strength and toughness [6]; on the other hand, the brittle Al₄C₃ provides a crack source for the failure of fiber, which leads to the lower stress destruction of the composites [7, 8]. Li [9] and Yang [10] reported that the elongation and strength of the composites decrease significantly with the increase of Al₄C₃. Naybe-Hashemi [11] further noted that the increase of Al₄C₃ would lead to the reduction of the fatigue strength of the composites. Hihara [12] found that the aluminum carbide hydrolyzed at a rate of ~1%/h indicated that the degradation resistance of G/Al composites would be severely compromised by the presence of Al₄C₃. The reason is that Al₄C₃ has an unstable chemical property, absorbing water in the surrounding medium and reacting to produce CH₄ and Al(OH)₃. Moreover, the expansion of these products in the interface leads to the peeling of reinforcements from the matrix. It results in the decrease in the corrosion resistance of the composites. Therefore, the study of the interfacial reaction condition of C-Al is significant to the properties and application of Gr_f/Al composites.

Until now, many research works about the techniques to reduce the interfacial reaction have been reported. The techniques such as matrix alloying [13], fiber surface treatment [14] and optimizing preparation process parameters (casting temperature, preheating temperature and time) [15] were attempted. Besides, a high-temperature exposure experiment was performed to investigate the interfacial reaction between C and Al. Khan [8] prepared a C-Al diffusion couple by sputtering aluminum to graphite flake and found that the interfacial reaction of C-Al took place when the temperature was higher than 500°C. The content of aluminum carbide in the interface was measured by Wu [16]. Due to the different graphitization degree, lamellar orientation and lamellar size, the interfacial reactions between different types of carbon fiber and Al have some differences [17]. However, few quantitative research works about the effect of high-temperature exposure on the interfacial reaction in the Gr_f/Al composite were reported.

In this study, the M40 graphite fiber reinforced 6061 aluminum composite was heat treated at high temperature. The influences of temperature and time on the interfacial reaction in the Gr_f/Al composite were studied. Moreover, the quantitative knowledge about the interfacial reaction evolution and its controlling factors in Gr_f/Al composites was investigated.

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2 Materials and methods

The M40 (PAN-based) graphite fiber purchased from TORAY (Tokyo, Japan) was used as reinforcement in the present experiment. 6061 aluminum was obtained from Northeast Light Alloy Co., Ltd., Harbin, Heilongjiang, China. The Gr_f/Al composite with 55% volume fraction of the M40 fiber was fabricated by the pressure infiltration process. In order to accelerate the interfacial reaction between the graphite fiber and the Al matrix, the as-prepared composites were treated with high-temperature exposure at 550°C, 600°C and 640°C for 0.5 h, 1 h, 2 h and 4 h, respectively. Before high-temperature exposure, the specimens were put into quartz tubes for a vacuum condition to avoid oxidation. When the temperature in the air furnace was stable for 0.5 h, the quartz tubes with specimens were put into it. After high-temperature exposure, the quartz tubes were taken out and cooled in the air.

To observe the adhesion state of the composite, an evaluation was performed by SEM (Quanta 200FEG, FEI, Hillsboro, Oregon, USA). The TEM observations were conducted under a Tecnai G2F30 electron microscope (FEI, Hillsboro, Oregon, USA) equipped with an energy dispersive spectrometer (EDS) system operating at 300 kV. The TEM foils were sliced from the composite parallel to the long axis of the M40 fiber. In order to evaluate the content of aluminum carbide in the composite after high-temperature exposure, the composite was ground into powder and mixed with corundum (α -Al₂O₃, Shanghai Yue Jiang Titanium White Product Co., Ltd., Shanghai, China) according to the quality ratio of 4:1. Finally, the powder was analyzed and imaged by a Philips X'Pert X-ray diffractometer (XRD, Philips, Netherlands). Software X'Pert graphics & identify (Philips, Netherlands) was used to acquire integral areas of the strongest diffraction peak of aluminum carbide and corundum. Based on the K value in the powder diffraction

PDF card of Al₄C₃, the content of Al₄C₃ in the composite can be calculated according to the following equation:

$$\frac{I_{\text{Al}_4\text{C}_3}}{I_{\alpha\text{-Al}_2\text{O}_3}} = K \frac{\omega_{\text{Al}_4\text{C}_3}}{\omega_{\alpha\text{-Al}_2\text{O}_3}} \quad (1)$$

where I_j is the integral areas of the strongest diffraction peak of the j phase in the sample, ω_j is the mass fraction of the j phase in the sample and K is the ratio of the strongest diffraction peaks of Al₄C₃ and corundum when mixed with equal quantity, respectively.

3 Results and discussion

3.1 Microstructure of the interface in the Gr_f/Al composite

The typical cross-sectional views of the as-fabricated Gr_f/Al composite are shown in Figure 1. The M40 fibers embedded in the Al matrix were shown in good macro-scale homogeneity, and little flaw such as shrinkage cavity and shrinkage porosity was found in the composite.

The microstructure of the interface in the Gr_f/Al composite is shown in Figure 2. Before high-temperature exposure, the interface of the composite was clean and a little amount of Al₄C₃ was observed in the interface. After heat treated at 550°C for 4 h or 600°C for 1 h, a small amount of lath Al₄C₃ with 300–600 nm length and a length-to-diameter ratio over 20 was found between the M40 fiber and the Al matrix. When the heat treatment temperature was increased to 640°C, more Al₄C₃ was observed. With the increase in temperature, the amount of lath Al₄C₃ increases and the length-to-diameter ratio decreases (<8). Especially, the size of some carbide could reach 1 μ m. The

Figure 1: Morphology of Gr_f/Al composites in (A) transverse and (B) longitudinal sections.

Figure 2: Representative interface between graphite fibers and Al matrix in Gr_f/Al composites: (A) no treatment, (B) 550°C/4 h, (D) 600°C/1 h, (E) 640°C/1 h and (C, F) diffraction pattern of areas A and B.

microscope variation of small Al₄C₃ crystals at the interface was also observed by Carotenuto in the Al-SiC composite after heat treatments [18]. In addition, when the composite was heat treated at 640°C for 2 h, a small amount

of trapezoidal flake interfacial reaction products were observed in the interface as shown in Figure 3A. Different from the lath-like morphology in previous research, Al₄C₃ with rhombohedral structure was confirmed according

Figure 3: Interface production in Gr_f/Al composites after 640°C/2 h: (A) morphology, (B, C) series of the rotated diffraction pattern of area A, (D, E) series of the rotated diffraction pattern of area B.

to the series of rotated diffraction patterns as shown in Figure 3B. The Al_4C_3 was space group $R3m$ with lattice parameters $a=0.8520$ nm, $\alpha=22.540^\circ$.

According to the previous studies, it was confirmed by Diwanji and Hall [17] that the formation of Al_4C_3 with rhombohedral structure is a conventional two-step process of nucleation and growth. The nucleation occurs preferentially at graphite edge planes on the carbon surface, while the growth is restricted along matrix planes and directions. Furthermore, Al_4C_3 follows an anisotropic growth mechanism: the side face of Al_4C_3 follows a ledge movement mechanism and restricted by nucleation of a two-dimensional crystal nucleus with a lower growth rate. And the presence of surface steps onto carbide faces was observed by De Sanctis et al. [6]. However, the end face of Al_4C_3 is the rough interface. The growth of Al_4C_3 with a faster rate was controlled by diffusion of carbon atoms. Therefore, it was found that the precipitate carbides should develop as thin platelets.

Based on the microstructure of the interface in the Gr_f/Al composite after high-temperature exposure, it is clear that the length-to-diameter ratio of lath Al_4C_3 in the interface decreases with the increase in temperature. The formation of two-dimensional nuclei along the radial direction is difficult on the side face at low temperature, while the growth of carbide along the axial direction mainly depends on the diffusion of a carbon atom in Al_4C_3 . The results showed that the lath Al_4C_3 with a large length-to-diameter ratio was formed in the interface when the temperature was 550°C and 600°C . With the increase in temperature,

not only the driving force of two-dimensional nucleation on the side face increases, but also the diffusion rate of the carbon atom could be accelerated. The results showed that the carbide could grow along both axial direction and radial direction. Therefore, the length-to-diameter ratio of lath Al_4C_3 decreased with the increase in temperature.

3.2 The content of Al_4C_3 in the interfacial reaction products

Since the graphite fiber was not corroded by hydrochloric acid solution and De Sanctis et al. [6] indicated that lath aluminum carbides could cause formation of deleterious surface notches on the fiber. Therefore, the composites after high-temperature exposure were put into hydrochloric acid solution and graphite fibers were extracted. Figure 4 shows the typical views of the graphite fibers extracted from the composites after heat treated at different temperatures for different time periods. It is clear that the surface of graphite fibers was uneven and rough when the heat treatment temperature was 640°C . Therefore, it can be inferred that the content of Al_4C_3 in the interface increased with the increase in temperature and time.

In order to evaluate the content of aluminum carbide, the composites were ground into powder after heat treatment. Figure 5 shows the XRD of the powders with corundum ($\alpha\text{-Al}_2\text{O}_3$). It is clear that the Al_4C_3 was the only aluminum carbide formed in the composites. As shown in Figure 5A, few diffraction peaks of Al_4C_3 were observed

Figure 4: SEM morphology of fibers extracted from heat-treated Gr_f/Al composites by pickling.

Figure 5: X-ray diffraction patterns of Gr_f/Al composites after heat treated.

when the temperature was 550°C. With the increase in temperature, the diffraction peaks of Al₄C₃ rose. According to the diffraction peaks of Al₄C₃ between 30° and 33°, as shown in Figure 5B, it can be inferred that a little Al₄C₃ was formed after heat treatment at a temperature of 550°C. A similar result was also found by Yang et al. [5] that the interface of C_f/Al composites treated at 540°C for 48 h was fairly stable. While the characteristic peaks of Al₄C₃ were obviously observed when the composite was heat treated at a temperature of 640°C for 2 h.

According to Equation (1), the content of Al₄C₃ in the composites can be calculated. Figure 6 shows the evolution of the mass fraction of Al₄C₃ with time. With the increase of time, the mass fraction of Al₄C₃ in the composite after heat treated at 600°C slowly rose, while it remarkably increased when the temperature was 640°C. It can be inferred that the Al₄C₃ nucleated at high temperature. At a temperature of 640°C, the nucleation position of Al₄C₃ increased. In addition, the diffusion of carbon atoms in the interface was easier than at 600°C. It was found that the content of Al₄C₃ significantly increased after heat

treated at 640°C. However, the diffusion of carbon atoms from the carbon fiber to the reaction front in the interface was difficult at 600°C. As a result, the content of Al₄C₃ slowly increased with the extension of holding time.

3.3 Dynamics analysis on interfacial reaction

Since the diffusion of elements in the interface depended on the temperature and time of the heat treatment, it is important to study the dynamics of the interfacial reaction. Wang et al. [19] discussed the thermodynamics of the interfacial reaction between carbon fiber and aluminum. The study indicated that the Gibbs free energy of the interfacial reaction was less than zero and the reaction between carbon and aluminum could occur when the content of Mg was <8.5%. Besides, the reaction rate depended on the dynamics of the interfacial reaction. Combined with the data of the XRD test, the influence of temperature and time on the interfacial reaction in the Gr_f/Al composite was discussed and the rate constant related to the diffusion coefficient was calculated.

It is confirmed that the interfacial reaction between C and Al is determined by the diffusion of an atom [5]. The thickness of the reaction layer Z and time t satisfy the following empirical equation:

$$Z = k\sqrt{t} \quad (2)$$

where k is the rate constant and depends on temperature T and reaction activation energy Q . It can be described by the Arrhenius equation

$$k = k_0 e^{-\frac{Q}{RT}} \quad (3)$$

Assuming that Al₄C₃ as the diffusion layer in the interface was evenly formed on the surface of graphite fiber,

Figure 6: Content of Al₄C₃ in Gr_f/Al composites after heat treated.

Figure 7: Kinetic curve of the interfacial reaction in Gr_f/Al composites: (A) relation of thickness of reaction layer and time; (B) relation of rate constant and temperature.

the thickness of the Al₄C₃ layer could be calculated. After high-temperature exposure, the relationship between the thickness of the diffusion layer Z and $\sqrt{t}$ is obtained, as shown Figure 7A. After linear fitting, Equations (4) and (5) can be obtained:

$$Z_{600^\circ\text{C}} = 0.5398\sqrt{t} + 37.6658 \quad (4)$$

$$Z_{640^\circ\text{C}} = 4.9637\sqrt{t} - 163.87. \quad (5)$$

Then diffusion rate constants can be obtained by comparing Equations (4) and (5) with Equation (2),

$$k_{600^\circ\text{C}} = 0.5398 \text{ nm/s}^{1/2} \quad (6)$$

$$k_{640^\circ\text{C}} = 4.9637 \text{ nm/s}^{1/2}. \quad (7)$$

It is obvious that the diffusion rate constant has an increment of 920% with a 40°C increase in temperature.

By substituting Equations (6) and (7) into Eq. (3), the relationship between the diffusion rate constant and the temperature could be obtained as shown in Figure 7B. Besides, the activation energy of the interfacial reaction $Q = 367.564$ kJ/mol could be calculated. As shown in Figure 7B, it is obvious that the diffusion rate constant is almost zero when the temperature is < 840 K (570°C), while it increases rapidly when the temperature is higher than 870 K (600°C). Combined with the previous results, it is confirmed that the growth of Al₄C₃ in the interface of the Gr_f/Al composite is slow when the temperature is lower than 600°C, while the growth is rapid with the increase in time when the temperature is higher than 600°C. As the increase of Al₄C₃ in the interface has an adverse effect on the mechanical property, the residence time at 600°C should be reduced as much as possible during the period of use for the Gr_f/Al composite,

$$k = 1.41 \times 10^{15} e^{\frac{367564}{RT}}. \quad (8)$$

4 Conclusion

In this study, an aluminum matrix composite reinforced by graphite fiber was fabricated by the pressure infiltration process. The effect of thermal exposure on the microstructure of the interface in the composite was studied. The main conclusions can be summarized as follows:

1. After heat treatment at 550°C and 600°C, Al₄C₃ with a large length-to-diameter ratio was observed, while Al₄C₃ with a small length-to-diameter ratio was formed in the interface when the temperature was 640°C.
2. With the increase of time, there is no obvious increase of interface reaction in Gr_f/Al composites at 550°C and 600°C, while there is a rapid increase at 640°C.
3. The dynamics calculation fits well with the experimental results. For Gr_f/Al composites, the diffusion rate constant of interfacial reaction increases rapidly after 600°C, so the residence time at temperature higher than 600°C should be reduced during utilization.

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