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ARTICLE

In-situ Reaction Dynamics of Mg_2Si/Al Composites Fabricated by Laser Deposition

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Abstract: In-situ magnesium silicide/aluminum (Mg_2Si/Al) composites were fabricated by laser deposition. A dynamic model of in-situ Mg_2Si/Al composites was established. The laser power (system temperature), Mg-rich layer thickness, Si particle size, and Al content were identified as the main factors affecting the reaction rate and degree. Results show that increasing the laser power (system temperature) and reducing the Mg-rich layer thickness, Si particle size, and Al content accelerate the reaction rate and degree.

Key words: laser deposition; in-situ synthesis; Mg_2Si; aluminum matrix composites; dynamic mechanism

Aluminum (Al) matrix composites have wide application prospects in the field of light rail transportation, due to their high specific strength, stiffness, modulus, wear resistance and thermal resistance[1-3]. Over the last decade, in-situ composites have been studied extensively. These composites are produced via reactions among the composite constituents, ultimately resulting in a strong and reinforced matrix structure with clean interfaces, compared with the composites fabricated by conventional methods[4-6]. Because the in-situ synthesized reinforcements are thermally stable, the composite matrix has sufficient strength to transfer stress.

Compared with conventional fabrication methods for in-situ composites, such as mechanical alloying[7], self-propagating high-temperature synthesis[8], powder metallurgy[9], and exothermic dispersion[10], laser deposition attracts many interests due to its rapid solidification rate[11-13]. Recent literatures on laser deposition of in-situ composites mainly focused on the microstructure and mechanical properties[14] of the composites. There is little information on the dynamic mechanism of in-situ synthesis of composites prepared by laser deposition. The study on dynamics of in-situ reaction can provide effective guidance for controlling the reaction process to prepare uniformly dispersed in-situ reinforced particles.

In this study, a dynamic model of in-situ Mg_2Si/Al aluminum matrix composites was established, and the effects of laser power (P) on the microstructure of in-situ Mg_2Si/Al composite were investigated.

1 Experiment

Pure Al, Mg, and Si powders were used with the average size of ~74 μm. The Mg-to-Si powder ratio corresponded to the stoichiometric ratio of Mg_2Si. The powders were mixed in a high-energy ball mill filled with Ar gas for 2 h. Fig.1 shows the morphology of powder mixtures after milling. During milling, the mass ratio of the ball-to-powder mixtures was 2:1. The targets included 10wt% and 15wt% Mg_2Si separately in the Al matrix after laser melting in-situ synthesis, namely 10wt% Mg_2Si/Al and 15wt% Mg_2Si/Al. The substrate 6061 Al plate was machined to 100 mm×100 mm×10 mm. The substrates were polished to remove the oxide layer and then sandblasted to roughen the surface. Laser processing was conducted by the Laserline LDM2500-60 semiconductor laser. The laser output power was 800, 900, 1000 and 1200 W; the laser beam scanning velocity was 200 mm/min; the diameter of the laser beam spot was fixed at 1.5 mm by defocusing. To prevent the melted pool from heavy oxidation, high-purity Ar gas at 10 L/min was used as protective gas through the coaxial nozzle.

The laser deposited samples with dimension of 70 mm×10 mm×10 mm were obtained. Metallographic samples were obtained by cutting transversely from the middle of the deposited samples and then polished and etched with 0.5vol% HF solution for scanning electron microscopy (SEM) observation with the Tesan VEGAII Lmh system. The phase constitution was determined by SEM with energy dispersive spectroscopy

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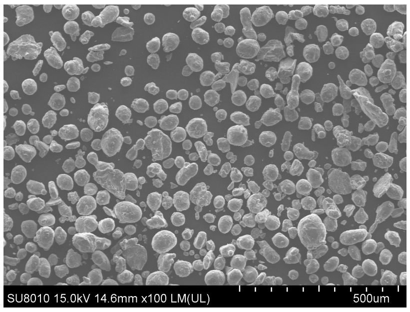

Fig.1 Morphology of powder mixtures after milling

(EDS). The phases were analyzed by X-ray diffraction (XRD) at 40 kV and 40 mA using Cu-Kα radiation (Max-2000X) at 1873 K for 1 h in argon atmosphere.

2 Results and Discussion

2.1 Microstructure

Fig.2 shows the effects of laser power on the microstructure of 10wt%Mg_2Si/Al. Chinese script particles were observed in the microstructures. As the laser power increases, the size and content of the Chinese script particles decrease gradually. When the laser power is 800, 1000 and 1200 W, the hardness of the composites is 1140, 1310 and 1040 MPa, respectively. Fig. 3 shows the microstructure of 15wt% Mg_2Si/Al, and the polygon and Chinese script particles were observed. XRD pattern and EDS results of the composites are shown in Fig.4 and Table 1, respectively. The results indicate that the polygonal particles and Chinese script particles are Mg_2Si, which is in agreement with the pseudobinary phase diagram of Al-Mg_2Si[15]. The microstructure of in-situ Mg_2Si/Al composites fabricated by laser deposition consists of α-Al phase, Si phase, and Mg_2Si particles.

2.2 Dynamic model of in-situ Mg_2Si/Al composites

In the present research, the setting that Mg-to-Si powder ratio corresponds to the stoichiometric ratio of Mg_2Si should result in no Mg and Si in the microstructure. However, the results in Fig. 4 show the presence of Si without Mg in the microstructure. A dynamic model of in-situ synthesis of Mg_2Si is established for theoretical calculations, as shown in Fig.5.

The following hypotheses are put forward to simplify the calculation: (1) the Si powders are globular and distributed uniformly in the melt; (2) there is a Mg-Al middle layer with the thickness of δ around the Si powder; (3) the diffusion coefficient $D=D_0\exp(-Q/RT)$ of Mg atoms-to-Si atoms is only related to the temperature; (4) the interfacial reaction rate of Mg on the surface of Si particles is much greater than the diffusion rate of Mg in the middle layer because the diffusion coefficient of Mg in liquid Al is only about ~10^{-7} m^2/s[16]. So there is no accumulation of Mg in the middle layer.

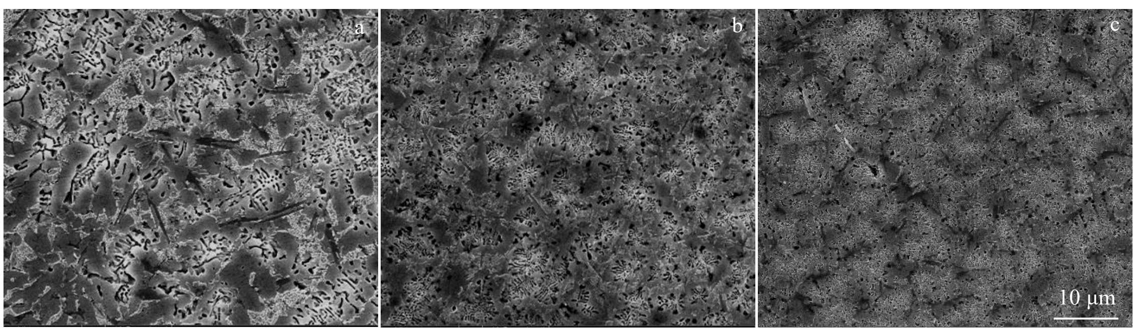

Fig.2 Microstructure of 10wt%Mg_2Si/Al composite with laser power of 800 W (a), 1000 W (b), and 1200 W (c)

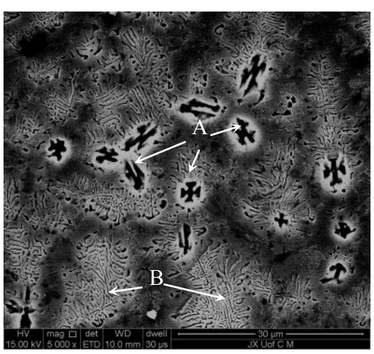

Fig.3 Microstructure of 15wt%Mg_2Si/Al with laser power of 900 W

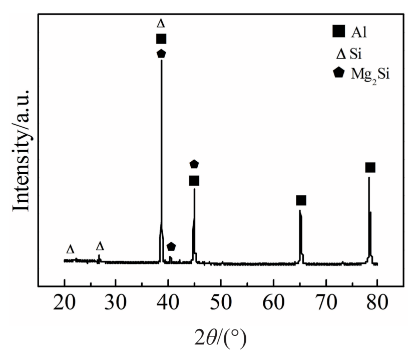

Fig.4 XRD pattern of 15wt%Mg_2Si/Al

Table 1 EDS results of points A and B in Fig.3 (at%)

Point	Mg	Al	Si
A	9	86.5	4.5
B	62.53	6.21	31.26

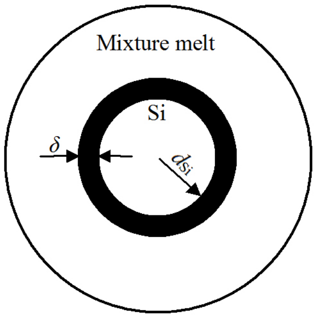

Fig.5 Dynamic model of in-situ synthesis of Mg_2Si

Therefore, the reaction equation in the melt is 2Mg+Si+xAl =Mg_2Si+xAl where x is the mole number of Al.

Accord to the hypothesis (3), the diffusion flux J based on Fick's second law can be expressed as follows:

$$\frac{\partial (JA)}{\partial x} \mathrm{d}r = 0 \tag{1}$$

where A is the spherical surface area of any middle layer (m^2), and r is the distance from the middle layer to the core of the Si particle (m).

The diffusion flux J based on Fick's first law can be defined as follows:

$$J = -D\frac{\mathrm{d}C_{Mg}}{\mathrm{d}r} \tag{2}$$

where D is the diffusion coefficient of Mg in the Al-Mg melt (m^2/s), and C_{Mg} is the concentration of Mg at position r in the middle layer.

According to Eq.(1) and Eq.(2), the distribution of Mg can be obtained as follows:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(Dr^2\frac{\mathrm{d}C_{Mg}}{\mathrm{d}r}\right)=0 \tag{3}$$

Based on the hypothesis (4), the concentration of Mg on the surface of Si particles is 0. Thus, the boundary condition of Eq.(3) can be defined as follows:

$$r = r_{Si},\ C_{Mg-m} = 0 \tag{4}$$

$$r = r_{Si} + \delta,\ C_{Mg} = C_{Mg-m} \tag{5}$$

where r_{Si} is the radius of the Si particle at a certain time (m), δ is the distance showed in Fig.5, and $C_{Mg\text{-}m}$ is the mole concentration of Mg at a certain time.

Therefore, the Mg concentration at the position with radius r can be obtained using Eq.(3)~Eq.(5):

$$C_{Mg}(r) = \frac{C_{Mg-m}d_{Si}(d_{Si}+2\delta)}{4\delta r} + \frac{C_{Mg-m}(d_{Si}+2\delta)}{2\delta} \tag{6}$$

where d_{Si} is the diameter of the Si particle at a certain time (m).

Thus, the diffusion rate of Mg (V_{Mg}) across the middle layer to the surface of Si particle is as follows:

$$V_{Mg} = JS_{Si} = -\pi DC_{Mg-m}\frac{d_{Si}(d_{Si}+2\delta)}{\delta} \tag{7}$$

where $S_{Si}=4\pi r^2$ is the surface area of the Si particle (m^2).

The depletion rate of Si particles during in-situ synthesis can be defined as a volume reduction of Si particles:

$$V_{Si} = -\frac{1}{M_{Si}}\frac{\mathrm{d}}{\mathrm{d}t}\left(\rho_{Si}\pi\frac{d_{Si}^3}{6}\right) \tag{8}$$

where t is the time.

According to Eq. (1), the diffusion rate of Mg atoms towards the surface of Si is half of the depletion rate of Si particles:

$$2\pi DC_{Mg-m}\frac{d_{Si}(d_{Si}+2\delta)}{\delta} = \frac{1}{M_{Si}}\frac{\mathrm{d}}{\mathrm{d}t}\left(\rho_{Si}\pi\frac{d_{Si}^3}{6}\right) \tag{9}$$

The diameter of Si particles is d_0 when t=0, and the melt consists of 1 mol Si+2 mol Mg+x mol Al. When t>0, the mole number of Al, Mg, Si and Mg_2Si is x, $\frac{\pi\rho_{Si}d_{Si}^3}{3M_{Si}}$, $\frac{\pi\rho_{Si}d_{Si}^3}{6M_{Si}}$, and $\frac{\rho_{Si}}{M_{Si}}\pi\left(\frac{d_0^3}{6}-\frac{d_{Si}^3}{6}\right)$, respectively; the molar volume of Al, Mg, Si, and Mg_2Si is $x\frac{M_{Al}}{\rho_{Al}}$, $\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{3}\frac{M_{Mg}}{\rho_{Mg}}$, $\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{6}\frac{M_{Si}}{\rho_{Si}}$, and $\frac{\rho_{Si}}{M_{Si}}\pi\left(\frac{d_0^3}{6}-\frac{d_{Si}^3}{6}\right)\frac{M_{Mg_2Si}}{\rho_{Mg_2Si}}$, respectively. ρ_{Si}, ρ_{Al}, ρ_{Mg}, and ρ_{Mg_2Si} are the density of Si, Al, Mg and Mg_2Si (kg/m^3), respectively; M_{Si}, M_{Al}, M_{Mg}, and M_{Mg_2Si} are the molar mass of Si, Al, Mg and Mg_2Si (g/mol), respectively.

Therefore, the molar concentration of Mg in the melt at a certain time t is as follows:

$$C_{Mg-m} = \frac{\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{3}}{x\frac{M_{Al}}{\rho_{Al}}+\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{3}\frac{M_{Mg}}{\rho_{Mg}}} \tag{10}$$

The forming rate of Mg_2Si (or the depletion rate of Si particles) can be obtained by incorporating Eq.(10) into Eq.(9), as follows:

$$\frac{\mathrm{d}(d_{Si})}{\mathrm{d}t} = -\frac{D\pi d_{Si}^2(d_{Si}+\delta)}{6\delta\left(x\frac{M_{Al}}{\rho_{Al}}+\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{3}\frac{M_{Mg}}{\rho_{Mg}}\right)} \tag{11}$$

It can be seen from Eq.(11) that the forming rate of Mg_2Si is related to the diffusion coefficient of Mg in the melt, the thickness of the middle layer, the diameter of the Si particle, and the Al content, with M_{Si}=28 kg/kmol, M_{Al}=27 kg/kmol, M_{Mg}= 24 kg/kmol, $\rho_{Si}=2.33\times10^3$ kg/m^3, $\rho_{Al}=2.7\times10^3$ kg/m^3, and $\rho_{Mg}=1.74\times10^3$ kg/m^3.

The reaction degree η of the Si particle is defined as follows:

$$\eta = \left(1-\frac{d_{Si}}{d_0}\right)\times 100\% \tag{12}$$

with

$$d_{Si} = \int -\frac{D\pi d_{Si}^2(d_{Si}+\delta)}{6\delta\left(x\frac{M_{Al}}{\rho_{Al}}+\frac{\rho_{Si}}{M_{Si}}\frac{\pi d_{Si}^3}{3}\frac{M_{Mg}}{\rho_{Mg}}\right)}\mathrm{d}t$$

The diffusion coefficient of Mg depends on the temperature. The temperature, which is related to the laser powder and scanning velocity, is as follows:

$$T = 5.1728Pe^{-v} + 828 \quad (13)$$

where *Pe* is the laser power (W) and *v* is the scanning velocity (mm/s). When the scanning velocity is 200 mm/min, the corresponding temperature is 980, 1000, 1019, 1038, and 1057 °C for the laser power of 800, 900, 1000, 1100, and 1200 W, respectively.

The effects of laser power on the forming rate of Mg_2Si and the reaction degree of Si particles are shown in Fig. 6. The forming rate of Mg_2Si and the reaction degree of Si particles increase with increasing the laser power.

The effects of middle layer thickness δ on the forming rate of Mg_2Si and the reaction degree of Si particles are shown in Fig. 7. The forming rate and the reaction degree decrease as the thickness of the middle layer increases. This is attributable to the increase in the diffusion distance from Mg atoms to the Si particles.

The effect of the diameter of Si particles d_0 on the forming rate of Mg_2Si and the reaction degree of Si particles is shown in Fig. 8. The forming rate and reaction degree decrease as the diameter of the Si particles increases. The smaller the diame-

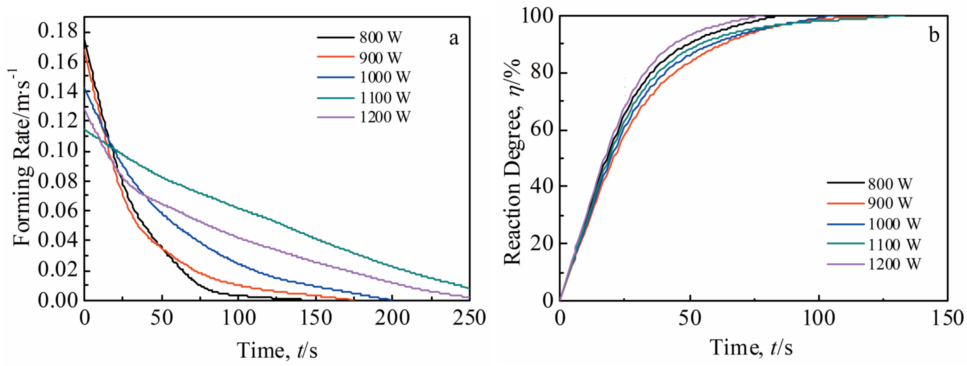

Fig.6 Forming rate of Mg_2Si (a) and reaction degree of Si particles (b) with different laser powers

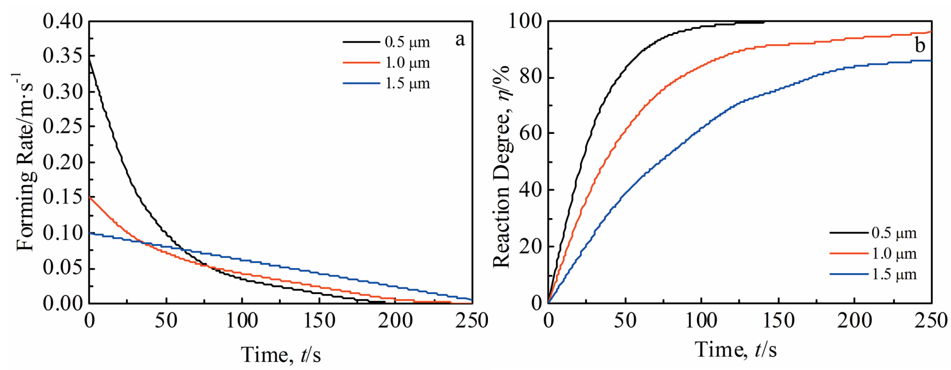

Fig.7 Forming rate of Mg_2Si (a) and reaction degree of Si particles (b) with different middle layer thicknesses

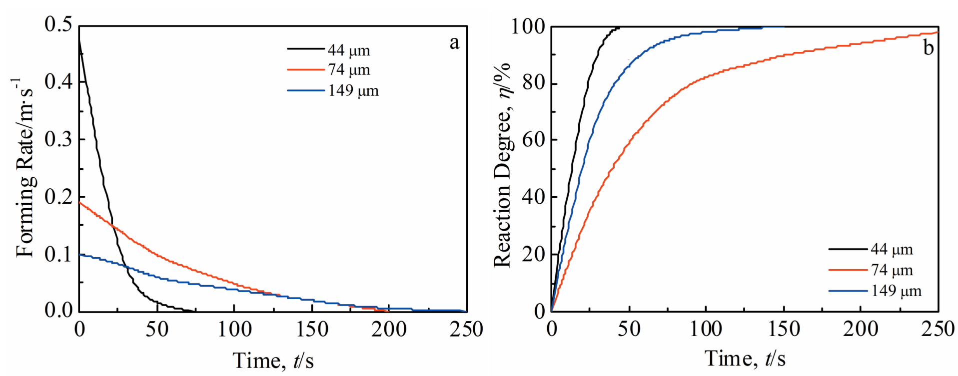

Fig.8 Forming rate of Mg_2Si (a) and reaction degree of Si particles (b) with different diameters of the Si particles

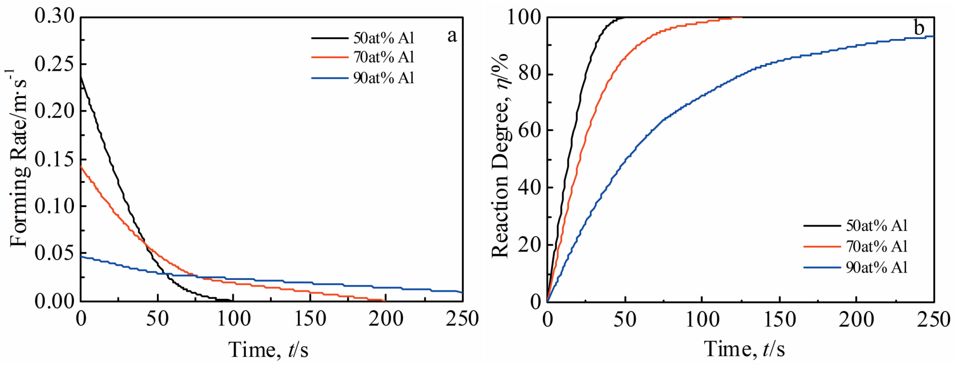

Fig.9 Forming rate of Mg_2Si (a) and reaction degree of Si particles (b) with different Al contents

ter of the Si particles, the quicker the formation of Mg_2Si. However, the flow of the powder is disrupted, resulting in a discontinuous powder feed. In this study, the optimum diameter of Si particles is 74 μm.

Fig.9 shows the effect of Al content on the forming rate of Mg_2Si and the reaction degree of Si particles. The forming rate and the reaction degree decrease with increasing the Al content. This is attributed to the low Mg content. Thus, the interaction between Mg and Si is less likely.

Fig.6b, 7b, 8b, and 9b all indicate that Si particles have long reaction time. However, the solidification rate is very fast (10^3~10^6 K/s)[17]. Thus, not all of the Si particles have time to react during the laser deposition process. In the present research, the Mg-to-Si powder ratio corresponds to the stoichiometric ratio of Mg_2Si, but there is no evidence of Mg in Fig.4. This may be due to the volatilization of Mg during the laser deposition process as the temperature approaches the boiling point of Mg.

3 Conclusions

1) The microstructure of in-situ Mg_2Si/Al composites fabricated by laser deposition consists of α-Al phase, Si phase, and Mg_2Si particles.

2) The forming rate of Mg_2Si and the reaction degree of Si particles are related to the laser power (system temperature), Mg-rich layer thickness, Si particle size, and Al content.

3) Increasing the laser power (system temperature) accelerates the reaction rate and reaction degree. With increasing the Mg-rich layer thickness, Si particle size, and Al content, the reaction rate and the reaction degree reduce.

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激光沉积Mg_2Si/Al的原位反应动力学

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摘　要：通过激光沉积制备了原位Mg_2Si/Al复合材料，建立了其动力学模型。结果表明，激光功率（温度）、富Mg层厚度、Si颗粒大小及Al含量是影响原位生成Mg_2Si/Al复合材料的速率及程度的主要因素。增加激光功率（温度）、降低富Mg层厚度、缩小Si颗粒大小及减少Al含量使原位反应的速率及程度提高。

关键词：激光沉积；原位自生；Mg_2Si；铝基复合材料；动力学机制

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