Formation of Al₃Ti/Mg composite by powder metallurgy of Mg–Al–Ti system

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Abstract
An in situ titanium trialuminide (Al₃Ti)-particle-reinforced magnesium matrix composite has been successfully fabricated by the powder metallurgy of a Mg–Al–Ti system. The reaction processes and formation mechanism for synthesizing the composite were studied by differential scanning calorimetry (DSC), x-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). Al₃Ti particles are found to be synthesized in situ in the Mg alloy matrix. During the reaction sintering of the Mg–Al–Ti system, Al₃Ti particles are formed through the reaction of liquid Al with as-dissolved Ti around the Ti particles. The formed intermetallic particles accumulate at the original sites of the Ti particles. As sintering time increases, the accumulated intermetallic particles disperse and reach a relatively homogeneous distribution in the matrix. It is found that the reaction process of the Mg–Al–Ti system is almost the same as that of the Al–Ti system. Mg also acts as a catalytic agent and a diluent in the reactions and shifts the reactions of Al and Ti to lower temperatures. An additional amount of Al is required for eliminating residual Ti and solid-solution strengthening of the Mg matrix.

Keywords: metal-matrix composites (MMCs), Mg–Al–Ti system, powder metallurgy, intermetallics

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, a great deal of interest has been focused on developing lightweight structural materials for aerospace and land transportation. Magnesium matrix composites with ceramic phases such as Al₂O₃, TiC, SiC and B₄C as reinforcement have been intensively developed in the past few years because of their high specific strength and stiffness, good wear resistance and low thermal expansion [1–4].

The possibility of adding intermetallics as reinforcements in metal matrix composites (MMCs) has been considered in recent studies [5–9]. This appears to be a highly promising option in view of their high hardness and compatibility with the metal matrix. Intermetallics, similarly to ceramics, are considered to be excellent candidates as reinforcements in composites since they also have a low density, high strength and a high elastic modulus even at high temperatures. In addition, their thermal expansion coefficients are much closer to those of metals than those of ceramic reinforcements. Thus, the residual stresses generated at the matrix/reinforcement interfaces during high-temperature exposure are much reduced. Furthermore, some of these composites should exhibit better ductility and wear properties than the equivalent materials reinforced with ceramic phases [6].

Among the families of intermetallics, Al₃Ti is one of the most important materials with many attractive...
properties: high melting point (1610 K), low density (3.4 g cm$^{-3}$) and high Young’s modulus (216 GPa). In particular, it is suitable for use as a reinforced phase in nonferrous metal matrix composites [10]. Some studies on Al$_3$Ti-intermetallic-reinforced Al matrix composites have been reported [10–12]. The composites in these studies exhibited attractive combinations of low density, high Young’s modulus, high strength at elevated temperatures, thermal stability and corrosion resistance. The results also suggested that intermetallics are feasible reinforcements for MMCs. However, less work has been carried out for Mg matrix composites with intermetallic compounds as reinforcement. It is supposed that the combination of a Mg matrix and Al$_3$Ti can result in a composite suitable for applications at higher temperatures. Consequently, this motivated us to use Al$_3$Ti as a reinforcement to fabricate an Al$_3$Ti-reinforced magnesium matrix composite.

The present study has been carried out to explore a novel magnesium matrix composite with Al$_3$Ti intermetallic particles as reinforcement. In this study, an Al$_3$Ti/Mg composite was fabricated by the powder metallurgy of a Mg–Al–Ti system. The reaction process and formation mechanism were studied. The resulting new type of composite has properties that are worthy of being explored further in our subsequent work.

2. Experimental procedure

The starting materials used to prepare the preforms were commercially available powders of Mg (99.99 wt.% purity, 200 mesh), Al (99.0 wt.% purity, 200 mesh) and Ti (99.5 wt.% purity, 300 mesh). Powder mixtures were prepared with the composition corresponding to 70 vol.% Mg and 30 vol.% Al$_3$Ti with a molar ratio of Al : Ti = 3 : 1. On the above basis, the function of additional Al of 6–10 wt.% relative to the Mg content was investigated. Powders were blended in a ball-milling machine with a ball-feed ratio of 3 : 1 at a rotation speed of 100 rpm for 24 h. 0.05 mol g$^{-1}$ polyvinyl alcohol was added to the powder mixtures. Then cuboid pellets (30 × 20 × 10 mm$^3$) were uniaxially pressed at a pressure of 30 MPa. The green preforms were dried at 120°C for 6 h in a vacuum oven.

The pellets were placed into a tubular resistance furnace and underwent pressureless sintering in an argon atmosphere. They were heated at a rate of 50°C min$^{-1}$ to 400°C for 30 min to volatilize the adhesive adequately. Subsequently, the samples were heated to 800°C for 1 h and cooled in the furnace by turning off the power. To study the formation process of the composite, the samples were heated at 800°C for different durations (15, 30 and 45 min and 1 h) and rapidly cooled in an argon atmosphere.

The reactions of the mixed powder were analyzed using a NETZSC-STA449C differential scanning calorimeter (DSC). To further clarify the function of Mg in the Mg–Al–Ti system, a series of thermal explosion experiments were performed for Mg–Al–Ti compound powders with 0, 7.5, 15, 30 and 45 wt.% Mg. The samples were heated in a tubular resistance furnace at a rate of 15°C min$^{-1}$ up to 800°C. In the heating process, the starting temperatures of the thermal explosion were recorded for the various Mg–Al–Ti compound powders.

Metallographic samples were prepared in accordance with standard procedures used for metallographic preparation. The samples were ground using abrasive papers then polished with diamond paste and cleaned with alcohol. Four vol.% nitrate alcohol was used as an etching reagent for all the samples. The microstructures, compositions and phases of the composite were investigated using a TXA-840A scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectroscopy (EDS) analyzer and a Rigaku D/Max-2500/pc x-ray diffractometry (XRD) system.

3. Results and discussion

3.1. Analysis of phases and microstructures

The composite was made by sintering preforms comprising 70 vol.% Mg–(3Al–Ti) system in an argon atmosphere at 800°C for 1h. Figure 1 shows the XRD pattern of the composite. Al$_3$Ti and Mg are found to correspond to the reinforcement and the matrix in the composite, respectively.

The Al$_3$Ti particles are almost spherical with a diameter range of 0.5–6 μm, as shown in figure 2(a). It is clear that they closely bind with the matrix and relatively homogeneously distribute in the matrix. From the microstructural features observed in all the specimens, we are able to confirm that the Al$_3$Ti/Mg composite in our study is characterized by fine and homogeneously distributed intermetallic particles and good cohesion at the matrix-reinforcement interface.

It must be pointed out that the above microstructure was attained through the addition of extra 6 wt.% Al to the 70 vol.% Mg–(3Al–Ti) system. If there is no addition of extra 6 wt.% Al, there is a small amount of residual Ti (figure 2(b)), which is verified by EDS line scanning analysis (figure 3). However, the amount of Ti is too small to be detected by the XRD. This means that in the 70 vol.% Mg–(3Al–Ti) system, the addition of extra 6 wt.% Al does not change the XRD pattern of the composite.

The requirement for extra Al may be explained by the fact that Al is diluted by Mg. Consequently, additional Al is
required to complete the reactions of Ti with Al. It is found that an additional 6–10 wt.% Al relative to the Mg content can ensure the full reaction of Ti. In other words, additional Al is necessary for eliminating residual Ti. In addition, the extra Al can dissolve in Mg to achieve solid-solution strengthening of the Mg matrix [13].

3.2. Function of Mg in the Al–Ti–Mg system

DSC analyses of the 3Al–Ti and Mg–3Al–Ti systems were performed to fully clarify the function of Mg in the Al–Ti–Mg system. The mixed powders of the 70 vol.% Mg–(3Al–Ti) system and 3Al–Ti system were heated at 10 °C min⁻¹ to 900 °C in an argon atmosphere.

Figure 4 shows the DSC curve and XRD pattern of the final product in the 3Al–Ti system. It is clear that the endothermic peak at 659 °C corresponds to the melting of Al. Subsequently, two exothermic peaks appear at 705 and 752 °C (figure 4(a)). The exothermic intensity of the former peak is larger than that of the latter. The final product of the Al–Ti system is confirmed to be Al₃Ti (figure 4(b)). It is pointed out in the literature [14] that Al₃Ti is formed by multistep reactions in the Al–Ti system with a transitional product of AlTi(s). Thus, it can be deduced that the former exothermic peak is mainly generated by the instantaneously completed reaction 3Al(l) + [Ti] → Al₃Ti(s), which is an intensely exothermic reaction. The latter peak is generated by the reactions Al₃Ti(s) + 2Ti(s) → 3AlTi(s) and AlTi(s) + 2Al(l) → Al₃Ti(s), which are slow exothermic processes controlled by the diffusion [14].
Figure 5. Analysis of the mixed powder of the 70 vol.% Mg–(3Al–Ti) system: (a) DSC curve and (b) XRD pattern of the final product.

The DSC curve and XRD pattern of the final product in the Mg–3Al–Ti system are shown in figure 5. It is found that a small endothermic peak appears at 584 °C. This can be considered to be the melting point of the Mg–Al alloy, which results from the partial diffusion among solid powders of Mg and Al. The two exothermic peaks appear at 659 and 736 °C (figure 5(a)). Similarly to figure 4(a), the exothermic intensity of the former peak is larger than that of the latter.

It was found for the Mg–3Al–Ti system that the combustion reaction is initiated as soon as the Mg–Al alloy starts to melt at a temperature lower than the melting points of Al and Mg. As the temperature reaches approximately 659 °C, Al and Mg start to melt, thus endothermic peaks should appear. However, the endothermic peaks overlap with the exothermic peak generated by the reaction 3Al(l) + [Ti] → Al₃Ti(s). Similarly to the Al–Ti system, the subsequent exothermic peak at 736 °C corresponds to the reactions Al₃Ti(s) + 2Ti(s) → 3AlTi and AlTi(s) + 2Al(l) → Al₃Ti(s).

XRD analysis of the DSC product also indicates only Mg and Al₃Ti in the Mg–Al–Ti system (figure 5(b)). In this system, Mg is believed to act as a solvent during the reactions, because there is no reaction between Mg and Ti at this temperature range.

### Table 1. Effect of Mg on the starting temperatures of thermal explosion in the Mg–Al–Ti system.

| Mg content (wt.%) | 0  | 7.5 | 15 | 30 | 45 |
|-------------------|----|-----|----|----|----|
| Starting temperature (°C) | 702 | 663 | 669 | 675 | 678 |

It is found from figures 4(a) and 5(a) that the exothermic peaks of the Al–Ti reaction in the Mg–Al–Ti system are at lower temperatures than those in the Al–Ti system. Clearly, the existence of Mg makes the reactions of Al–Ti occur at lower temperatures. To further clarify the function of Mg in the Mg–Al–Ti system, a series of thermal explosion experiments were carried out for the Mg–Al–Ti compound preforms with different Mg contents. The starting temperatures of the thermal explosion for various Mg–Al–Ti compounds are shown in table 1.

It is clear that the addition of Mg in the Al–Ti system decreases the starting temperature of the thermal explosion. The starting temperature of the Al–Ti thermal explosion is lowered from 702 to 663 °C with the addition of 7.5 wt% Mg. This fully means that Mg promotes the formation of Al₃Ti in the Mg–Al–Ti system. However, with further increases in Mg content, the starting temperature of the thermal explosion starts to increase slightly for the Al–Ti system, although the starting temperature of the Mg–Al–Ti thermal explosion remains lower than 702 °C. As a consequence, it is suggested that Mg also acts as a catalytic agent and a diluent in the reactions of the Mg–Al–Ti system.

#### 3.3. Formation mechanism of Mg–Al₃Ti composites

It can be deduced from the above analyses that the reaction products of the Mg–Al–Ti system are almost the same as those of the Al–Ti system. Although Mg₁₇Al₁₂ should be formed in the Mg–Al–Ti system, it cannot be distinguished by the XRD, because of the small amount formed. Therefore, the formation of Mg₁₇Al₁₂ is not mentioned hereafter.

Because Al₃Ti is formed by multistep reactions with a transitional product of AlTi in the Al–Ti system [14], the reaction process of the Mg–Al–Ti system can be summarized as follows:

\[
\text{Al(s) } \rightarrow \text{Al(l)}, \\
\text{Mg(s) } \rightarrow \text{Mg(l)}, \\
\text{Ti(s) } \rightarrow [\text{Ti}], \\
3\text{Al(l)} + [\text{Ti}] \rightarrow \text{Al₃Ti(s)}, \\
\text{Al₃Ti} + \text{Ti(s)} \rightarrow \text{AlTi(s)}, \\
\text{AlTi} + 2\text{Al(l)} \rightarrow \text{Al₃Ti(s)}. 
\]

Figure 6 and table 2 show the various products of Al and Ti during the sintering process. Through the results of semi-quantitative EDS analysis, it was found that pure Ti
Figure 6. Al–Ti products of the Mg–Al–Ti system during the sintering process.

Table 2. EDS analysis results of Al–Ti products during the sintering process.

| Point | Mg (wt.%) | Al (wt.%) | Ti (wt.%) | Al–Ti products |
|-------|-----------|-----------|-----------|---------------|
| 1     | 0.36      | 0.00      | 99.64     | Pure Ti       |
| 2     | 0.36      | 1.90      | 97.74     | α-Ti          |
| 3     | 1.15      | 37.64     | 61.21     | AlTi          |
| 4     | 1.39      | 36.22     | 62.39     | AlTi          |
| 5     | 9.86      | 59.92     | 30.22     | Al$_3$Ti     |
| 6     | 16.60     | 54.12     | 29.28     | Al$_3$Ti     |

*Mg was included in the EDS analysis result for Al–Ti products, which affect molar ratio of Al and Ti.

(bright white, point 1), α-Ti with a solid solution of Al (gray-white, point 2), AlTi (points 3 and 4) and Al$_3$Ti (gray, points 5 and 6) are formed during the sintering process. AlTi exists as a thin layer between Al$_3$Ti and α-Ti. Thus, it can be verified that AlTi is formed as an intermediate phase.

Figure 7 shows the formation process of the Al$_3$Ti/Mg composite. It is clear that Al$_3$Ti particles are first formed by a reaction between liquid Al and as-dissolved Ti around the Ti particles (figure 7(a)). As Al$_3$Ti forms around the Ti particles, Al diffusion through Al$_3$Ti into Ti becomes a predominant stage during the sintering process. In addition, Al in the liquid state can penetrate into the gaps between Al$_3$Ti particles due to capillary action. Thus, the reaction of Al with Ti can be continued and Al$_3$Ti particles are continuously formed (figures 7(b) and (c)). As the sintering time is increased, the number of intermetallic particles is increased by the reaction of Al with Ti through the continuous dissolution of Ti(s) and the diffusion of Al in Ti until the Ti(s) is exhausted. It was found that many intermetallic particles tend to accumulate at the original sites of the Ti particles (figures 7(b)–(e)). As the sintering time increases further, the accumulated intermetallic particles slowly disperse and reach a relatively homogeneous distribution in the matrix (figures 2(a) and 7(f)).

On the basis of the above result and analysis, the formation mechanism of the Al$_3$Ti/Mg composite is suggested, as shown in figure 8. As the temperature approaches the melting point of the Al-Mg alloy, Al and Mg start to melt, and Ti particles start to dissolve in the melt. The as-dissolved Ti reacts with the Al melt to form Al$_3$Ti particles around the Ti particles. Subsequently, AlTi is formed as an intermediate phase. The reactions in this process are thought to be $3\text{Al}(l) + \text{[Ti]} \rightarrow \text{Al}_3\text{Ti}(s)$, $\text{Al}_3\text{Ti}(s) + 2\text{Ti}(s) \rightarrow \text{AlTi}(s)$ and $\text{AlTi}(s) + 2\text{Al}(l) \rightarrow \text{Al}_3\text{Ti}(s)$. Because of the lower Gibbs free energy of Al$_3$Ti, Al$_3$Ti particles stably exist. The accumulated Al$_3$Ti particles in the Mg–Al melt are gradually dispersed by capillary action. After cooling, the Al$_3$Ti/Mg composite is achieved.
4. Conclusion

An Al$_3$Ti/Mg composite is produced by the powder metallurgy of a Mg–Al–Ti system. Al$_3$Ti particles are synthesized in situ in the Mg alloy matrix. During the reaction sintering of the Mg–Al–Ti system, the Al$_3$Ti particles are formed through the reactions of liquid Al with as-dissolved Ti around the Ti particles. The formed intermetallic particles are found to accumulate at the original sites of the Ti particles. As sintering time increases, the accumulated intermetallic particles disperse and reach a relatively homogeneous distribution in the matrix. Mg also acts as a catalytic agent and a diluent in the reactions. In the reactions of the Mg–Al–Ti system, Mg shifts the reactions of Al and Ti to lower temperatures. An additional amount of Al is required for eliminating residual Ti and solid-solution strengthening of the Mg matrix.

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