Modification effect of calcium-magnesia phosphate fertilizer on microstructure and mechanical properties of $\text{Mg}_2\text{Si}/\text{Mg-4Si}$ composite

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Abstract: In order to modify in-situ synthesized Mg_2Si particles in $\text{Mg}_2\text{Si}/\text{Mg-4Si}$ composite, the modification effect of calcium-magnesia phosphate fertilizer on primary Mg_2Si phase in $\text{Mg}_2\text{Si}/\text{Mg-4Si}$ composite was investigated by means of X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis. The results indicate that the morphology of the primary Mg_2Si phase apparently changes from coarse dendrites to fine dispersive polygonal particles, and the mean size is decreased from 277 μm to 17 μm . With the addition of 4.0wt.% calcium-magnesia phosphate fertilizer as a modifier, the ultimate tensile strength and elongation of the $\text{Mg}_2\text{Si}/\text{Mg-4Si}$ composite are increased from 78.7 MPa and 2.1% to 105.2 MPa and 2.6%, as compared to those of the base composite, which is probably attributed to the formation of the phosphorous compound and the cluster of Ca compounds that acted as the heterogeneous nucleation substrates of the primary Mg_2Si particles, resulting in a refined distribution of these precipitates.

Key words: hot crack; composite; calcium-magnesia phosphate fertilizer; modification; Mg_2Si

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Recently, metal matrix composites (MMCs) have attracted extensive attention in automobile industry, in order to meet the demands of weight reduction and fuel economization^[1-3]. The hypereutectic Mg-Si particulate metal matrix composites (PMMCs) have high potential as structural materials because the reinforcing particulate Mg_2Si intermetallic exhibits a low density of $1.99 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$, a high elastic modulus of 120 GPa, a high melting temperature of 1,085 °C, a high hardness of $4.5 \times 10^9 \text{ N}\cdot\text{m}^{-2}$ and a low thermal expansion coefficient of $7.5 \times 10^{-6} \text{ K}^{-1}$ ^[4,5].

However, as in-situ Mg_2Si reinforced PMMCs, hypereutectic Mg-Si alloys do not have satisfactory mechanical properties in general, due to the exhibition of coarse dendritic primary Mg_2Si particles and the brittle Chinese script shape eutectic Mg_2Si phases^[5,6]. It was proposed that a modification process seems to be the

most hopeful route to improve the mechanical properties of in-situ composite prepared by simple casting^[7]. The modification mechanisms of the Mg_2Si particles by adding various elements, such as B^[8], Ba^[9], Ca^[10,11], P^[12,13] and RE^[14-16], have been discussed in previous studies. Generally, there are two major modification mechanisms for primary Mg_2Si grains. One is the poisoning effect: the modification elements gather on the forehead of growth and restrict the crystal growth^[17]. The other is heterogeneous nucleation: the modification elements or their compounds act as the heterogeneous nucleus^[13,18].

Currently, most scholars considered that the modification mechanism of Ca onto primary Mg_2Si belong to poisoning effect^[10,11], and P to heterogeneous nucleation. Usually, the modifier containing P element was added into Al and Mg alloys via two ways: pure element or master alloy^[12,13]. Meanwhile, the constituent nature of the heterogeneous nuclei of primary Mg_2Si is still in dispute. Kim^[19] and Schmid, et al.^[20] reported that the nucleus of primary Mg_2Si is $\text{Mg}_3(\text{PO}_4)_2$. Nevertheless, Zhao^[13] and Liu, et al.^[21] via EPMA analysis showed that AlP particles act as the cores of primary Mg_2Si . Furthermore, Hou^[22] suggested that Mg_3P_2 phases serve as the heterogeneous nucleation substrates of primary

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Mg₂Si.

However, little has been reported on the addition of a modifier containing P element by use of phosphate, and there is no investigation on the modification of Mg₂Si by the combination of P and Ca. In this work, the modification effects of calcium-magnesia phosphate fertilizer as a modifier in in-situ Mg₂Si/Mg-Si composite is investigated and the purpose of this preliminary experimental study is to find an effective and simplified casting process route to produce a relatively fine and dispersive Mg₂Si particle reinforced magnesium metal matrix composite.

1 Experimental procedure

Pure magnesium (> 99.8 wt.%) and Mg-6.29wt.%Si master alloy were used as raw materials to prepare the investigated Mg₂Si/Mg-4Si composites in a graphite crucible heated by an electric resistance furnace. About 700 g of Mg-6.29wt.%Si alloys (10% burning loss for Si) preheated to 200 °C were added into 500 g pure Mg melt (20% burning loss for Mg) at 760 °C under Ar flux protection. After about 20 min, the dewatered calcium-magnesia phosphate fertilizer was added into the melt and stirred for about 5 min to obtain the modified composites with the designed fertilizer additions of 3%, 4%, 5% and 6%. After holding for 15 min, each melt was poured into a steel mould to produce columnar bars of $\Phi 15\text{ mm} \times 100\text{ mm}$. The commercial calcium-magnesia phosphate fertilizer is produced under Chinese standard (GB 20412-2006).

All the observed specimens were cut at the same position

of the columnar bars, 10 mm from the bottom, and prepared in accordance with standard procedures as well as etched by 4vol.% nital for 10 s. The microstructures of the investigated composites were observed using optical microscope and scanning electron microscope (SEM, JSM-6610) equipped with an energy-dispersive spectrometer (EDS, Inca X-Max). The average sizes of primary Mg₂Si particles were measured using image-pro plus 6.0 software and each reading was an average of 10 separate measurements at random field. The phase constituent analysis was carried out by X-ray diffraction (XRD, Shimadzu XRD-7000). The tensile tests were conducted on an electronic universal testing machine (WDW3050) at a constant cross-head speed of 1 mm·min⁻¹, and the ultimate tensile strength and elongation of the Mg₂Si/Mg-4Si composites were determined by the mean value of 3 specimens.

2 Results and discussion

2.1 Microstructure of unmodified Mg₂Si/Mg-4Si composite

Figure 1 shows the representative microstructure and XRD pattern of the unmodified Mg₂Si/Mg-4Si composite. The microstructure of the unmodified Mg₂Si/Mg-4Si composite consisted of dendritic primary Mg₂Si particles, lamellar eutectics of Mg+Chinese script type Mg₂Si and α -Mg halos, as marked in Fig. 1a. As shown in Fig. 1b, the XRD result reveals that the phase constituents of the obtained composite are Mg₂Si and Mg phases, which completely fit the predictions^[23].

Fig. 1: (a) OM microstructure and (b) XRD pattern of unmodified Mg₂Si/Mg-4Si composite

2.2 Microstructures of Mg₂Si/Mg-4Si composites modified with calcium-magnesia phosphate fertilizer

Figures 2 and 3 show the XRD patterns and OM micrographs of the tested composites. According to the XRD patterns, as shown in Fig. 2, the phase components of all modified composites are still α -Mg and Mg₂Si phases. No new phase was detected. As shown in Fig. 3, the morphology of primary Mg₂Si changed

from coarse dendrite (Fig. 1a) to fine dispersive polygon particles when calcium-magnesia phosphate fertilizer modifier was added into the composite. The average grain sizes of the primary Mg₂Si and α -Mg halos were decreased initially and then slowly increased with the increase of modifier content of the calcium-magnesia phosphate fertilizer, as shown in Fig. 4. It is obvious from Fig. 4 and Fig. 3(b) that the finest size of primary Mg₂Si particles is 17 μm which was obtained in the condition of

Fig. 2: XRD patterns of modified composites with (a) 4.0 wt.%, (b) 5.0 wt.% and (c) 6.0wt.% calcium-magnesia phosphate fertilizer

Fig. 3: OM micrographs of modified composites with (a) 3.0wt.%, (b) 4.0wt.%, (c) 5.0wt.% and (d) 6.0wt.% calcium-magnesia phosphate fertilizer

Fig. 4: Average size of primary Mg_2Si particles in all investigated composites

4.0wt.% calcium-magnesia phosphate fertilizer addition. This is much smaller than that of 277 μm in the unmodified composite, as shown in Fig. 4 and Fig. 1.

In the highly magnified SEM images of the composite modified with 4.0wt.% calcium-magnesia phosphate fertilizer as shown in Fig. 5(a) and 5(d), it is clear that there are two tiny cores marked by crosses inside primary Mg_2Si particles which may act as a heterogeneous crystallization nucleus for the primary Mg_2Si . In order to verify their compositions and infer the modification mechanism, further EDS analyses were carried out, as shown in Fig. 5(b), 5(c) and 5(e). The results of the EDS analyses on point A indicate that the core is mainly consisted of Mg, Si, P and O elements, and point B is mainly consisted of Mg, Si, Ca, P, O and F elements, as shown in Fig. 5(b) and 5(e). The EDS line scans through point A reveal that the content of O element at the core was changeless. Even so, the exact chemical constituents were unable to be quantified with this technique. Furthermore, there was no Al element in the melt. Hence, AIP can be excluded. Considering the information from previous studies^[12, 13, 19-21] and EDS detections, it is possible that the core of primary Mg_2Si is phosphorous compound.

In the present study, the size and morphology of primary Mg_2Si phase in the $Mg_2Si/Mg-4Si$ composite are controlled by the capability of the substrate for heterogeneous nucleation

Fig. 5: (a) and (d) SEM image of the composite modified by 4.0wt.% calcium-magnesia phosphate fertilizer, (b) EDS results of point A, (c) EDS line scans of M-N and (e) EDS results of point B

after being modified by calcium-magnesia phosphate fertilizer. The stronger the capability of the substrate for heterogeneous nucleation, the lower the undercooling degree is needed for nucleation, the more beneficial to increase the nucleation rate. The ability of heterogeneous nucleation depends on the interfacial energy between the nucleated substrate and crystalline phase^[24].

Previous investigation results show that Ca atoms on the growth front of the primary Mg_2Si caused a poisoning effect^[10, 11]. Since the atomic radius of Ca (2.23×10^{-10} m) is much larger than that of Mg (1.72×10^{-10} m) or Si (1.46×10^{-10} m), the surface energy of Mg_2Si crystals is reduced when the Ca atoms in the melt adsorb onto the growing planes of Mg_2Si crystals, causing the lattice distortion change of the growing habit planes and the suppression of Mg_2Si growth^[10, 11]. Furthermore, M. E. Moussa's^[11] study shows that the Ca addition cannot reduce the critical nucleus

radius and increase the number of potential nucleus of Mg_2Si . Currently, the compounds containing Ca elements act as the core in primary Mg_2Si [in Fig. 5(d) and 5(e)]. However, the exact chemical constituent and modification mechanism of this phenomenon requires further investigation. One possibility is that, the cluster of Ca compounds in the melt act as an inoculant for the nucleation process. Thus, it would increase the nucleation rate of the primary Mg_2Si particles. As a result, numerous primary Mg_2Si nuclei cannot grow and develop to dendrite during solidification.

2.3 Mechanical properties

The mechanical properties of the investigated composites are determined by tensile test and the results are listed in Table 1. It can be seen that the ultimate tensile strength and elongation of the composites modified by the calcium-magnesia phosphate

Table 1: Mechanical properties of investigated composites

	Composite with different contents of modifier (wt.%)				
	0	3	4	5	6
UTS (MPa)	78.7	91.2	105.2	101.4	95.0
EL (%)	2.1	2.3	2.6	2.5	2.4

fertilizer are much superior to that of the unmodified $Mg_2Si/Mg-4Si$ composite. With the addition of 4.0wt.% calcium-magnesia phosphate fertilizer, the ultimate tensile strength and elongation of the $Mg_2Si/Mg-4Si$ composite is increased from 78.7 MPa and 2.1% to 105.2 MPa and 2.6%, respectively. Obviously, the improvement of mechanical properties can be mainly attributed to the change of morphology and the refinement of primary Mg_2Si particles, since micro-cracks can easily nucleate along the

boundary between the Mg_2Si phases and the Mg-matrix under a lower stress^[25,26].

2.4 Fracture characteristics

Fracture surfaces of the unmodified and modified with 4.0wt.% modifier $Mg_2Si/Mg-4Si$ composites are shown in Fig. 6. Basically, damage in particulate metal matrix composite (PMMCs) generally occurs at two types, particle decohesion and particle fracture^[3]. When stress is applied, the matrix deforms plastically, gradually transferring stress to the particles. The behavior of the particles depends on the relative strength of the matrix/particle interface. When the matrix/particle interface is strong enough, the load is transferred to particles, with particle fracture normally occurring when the critical stress is reached. However, if the matrix/particle interface bonding is weakened, the load will not reach the critical stress, and particle decohesion arise.

When load is applied on the unmodified composite, the microcrack is easily initiated from the coarse dendritic primary Mg_2Si particles by debonding Mg_2Si particles from matrix or self-cracking, which results in particle decohesion or particle fracture. Figure 6(a) demonstrates the coarse dendritic primary Mg_2Si particles detached from matrix and both detached and cracked particles are present simultaneously in Fig. 6(b), as previously expected.

Fig. 6: Typical micrographs of fracture surfaces in different sample: (a) and (b) unmodified, (c) and (f) with 4.0wt.% modifier, (d) and (e) higher magnification of (c)

Another effective factor on the fracture behavior is particle size. Previous results^[3, 27] indicate an increase in strength and ductility by decreasing particle size. Figure 6(c), 6(d) and 6(e), clearly depicts the particle decohesion and particle fracture marked by red arrows in the Mg₂Si/Mg-4Si composite modified with 4.0wt.% modifier. As contrast to the base composite [Fig. 6(a) and 6(b)] the cleavage characteristic becomes smaller. Furthermore, Fig. 6(f) shows the crack growth trajectory that impeded by an octahedral primary Mg₂Si particles. This confirmed the functions of the Mg₂Si particles in PMMCs and the effect of size, morphology and distribution of the Mg₂Si particles on mechanical properties.

3 Conclusions

(1) The primary Mg₂Si particles in the Mg₂Si/Mg-4Si composite can be significantly modified by the addition of calcium-magnesia phosphate fertilizer with 3wt.% to 6wt.%. The morphology of the primary Mg₂Si particles is changed from coarse dendrite to fine dispersive polygon, and the mean size is significantly decreased from 277 μm to 17 μm.

(2) The refinement mechanism may be attributed to the appearance of phosphorous compound and the cluster of Ca compounds during solidification which acts as heterogeneous nucleation cores for the primary Mg₂Si particles and results in the modification of primary Mg₂Si particles.

(3) With 4.0wt.% calcium-magnesia phosphate fertilizer modifier introduced, ultimate tensile strength and elongation of the Mg₂Si/Mg-4Si composite is increased from 78.7 MPa and 2.1% to 105.2 MPa and 2.6%, as compared to that of the base composite.

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