Microstructure and tensile properties of magnesium alloy modified by Si/ Ca based refiner [①]

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Abstract: Microstructure and mechanical properties of pure magnesium and AZ31 alloy with Ca/ Si based refiner addition were investigated. The results indicate that addition of Ca/ Si based refiners to pure magnesium and AZ31 alloy results in remarkable microstructure refinement. With proper amount of refiner addition, the grain size in as cast ingots can be one order of magnitude lower than that without refiner addition. Small amount of refiner addition to AZ31 alloy increases both ultimate strength and yield strength significantly, while the ductility of the alloy with refiner addition is similar to that without refiner addition. Addition of refiner improves the deformability of AZ31 alloy and extruded or hot rolled specimens (rods or sheets) with refiner addition exhibit higher surface quality and mechanical properties than those without refiner addition.

Key words: magnesium alloy; AZ31 alloy; refinement; extrusion; rolling

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1 INTRODUCTION

The use of magnesium in commercial applications has increased dramatically in recent years and the growth of magnesium products for structural applications has been projected to be around 12% per year for the next decade[1]. The increased demand, especially in household electric appliance and automobile parts, can be contributed to its low density, high specific strength and good castability[2].

The main methods in the industrial manufacturing of magnesium alloy products are the die casting and the semi-solid process, and the other methods, such as extrusion, forging and rolling, are rarely used[3]. One reason for this is its relatively poor formability and limited ductility in comparison with aluminum, copper and iron based alloys owing to its hexagonal close packed (HCP) structure. The traditional strengthening principles, such as solid solution strengthening, precipitation hardening and work hardening, are not very effective on improving mechanical properties of magnesium based alloys since the techniques related with the above principles are deleterious to the ductility of metallic materials. Therefore, grain size seems to be more important for magnesium-based alloys. High strength and ductility as well as good deformation formability can be attained from fine grained magnesium based alloy. In the present paper, Si/ Ca based refiner was added to pure magnesium and AZ31 alloy. The grain sizes in the ingots with and without refiner addition were measured and as-cast microstructure of AZ31 alloy was also studied. Some AZ31 ingots were extruded and hot rolled, respectively, and the microstructure and mechanical properties of these extruded and rolled specimens under different conditions were investigated.

2 EXPERIMENTAL

The refiner containing Si, Ca and Al used in the present investigation was prepared in a crucible furnace as a master alloy. The mass ratio of Si to Ca in the refiner is 1.5∶ 1. Melting of magnesium and AZ31 alloy was conducted in a mild steel crucible under the protection of a mixed gas atmosphere of SF_6(1%, volume fraction) and CO_2(Bal.). The refiner was added when the temperature of the melt reached 720 ℃. After the refiner was dissolved, the melt was held at that temperature for several minutes then poured into permanent molds made of cast steel. As-cast specimens were directly cut from the ingots. Some AZ31 ingots were hot extruded into rods with diameter of 15 mm, and the others were hot rolled to sheets with thickness of 2 mm. Tensile tests were performed on specimens with and without refiner addition and microstructure observations of the alloys were conducted

using optical microscopy(OM) and scanning elec-
tron microscopy (SEM), respectively. Micro-
analysis and determination of crystal structure of
precipitates were carried out by X-ray energy dis-
persive spectroscopy(XEDS) and X-ray diffractom-
etry(XRD), respectively.

3   RESULTS

3. 1   Microstructure

Fig. 1 shows the grain structure of magnesium
ingots with and without refiner addition. It can be
clearly seen that the ingot without refiner addition
has very coarse grain structure with columnar
grains in the area near the edge and equiaxed grains
in the central area. The average grain size in the
central area is about 5 - 6 mm, as shown in Fig. 1
(a). With 0. 5% (mass fraction) of refiner addi-
tion, the grain structure of ingot is significantly re-
fined and the average grain size in the equiaxed
grain area decreases to 0. 6 - 0. 8 mm.

The effect of refiner addition on the micro-
structure of AZ31 alloy is similar to that in pure
magnesium. The as-cast microstructure of AZ31

alloy without refiner addition is also coarse (Fig. 2
(a)) and the β phase network distributes at gain
boundaries. Fig. 2(b) shows the as-cast micro-
structure of AZ31 with refiner addition. In com-
parison with Fig. 2(a), the effect of grain refine-
ment caused by the refiner is also apparent. SEM
observations reveal some tiny particles in the as ex-
truded alloy with refiner addition, as shown in
Fig. 3. Microanalysis performed on these particles
indicates that the compositions of these particles
are approximately Mg-45%Si(mass fraction). Fig.
4 shows the XRD pattern taken from AZ31 alloy
with refiner addition, in which all peaks are in-
dexed as arising from two phases, α-Mg and
Mg_2Si, which has a cubic structure C1 (S. G.
Fm3m). Thus, the particles shown in Fig. 3 can be
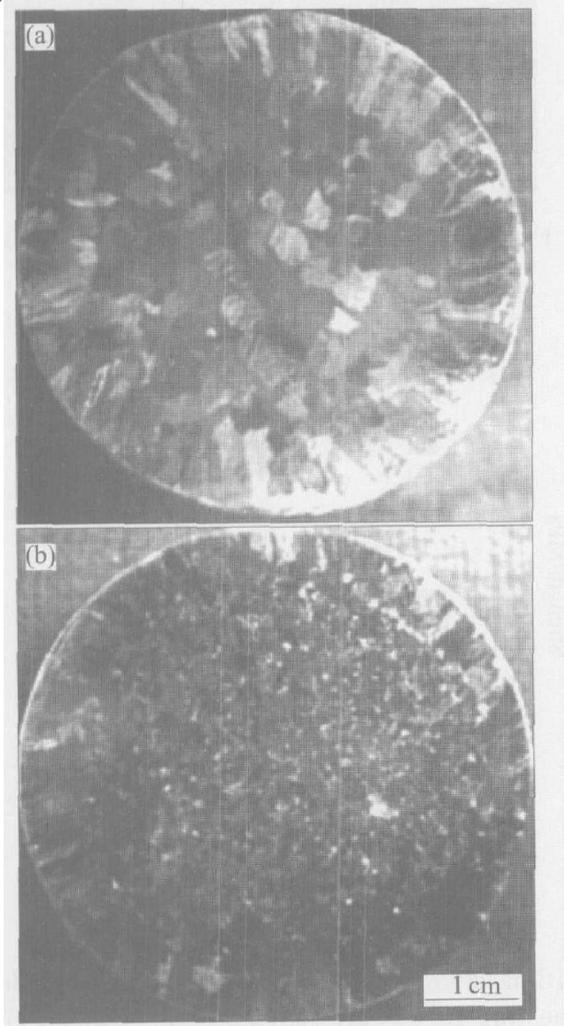identified as Mg_2Si.

Fig. 1   Grain structures of
as cast magnesium ingots
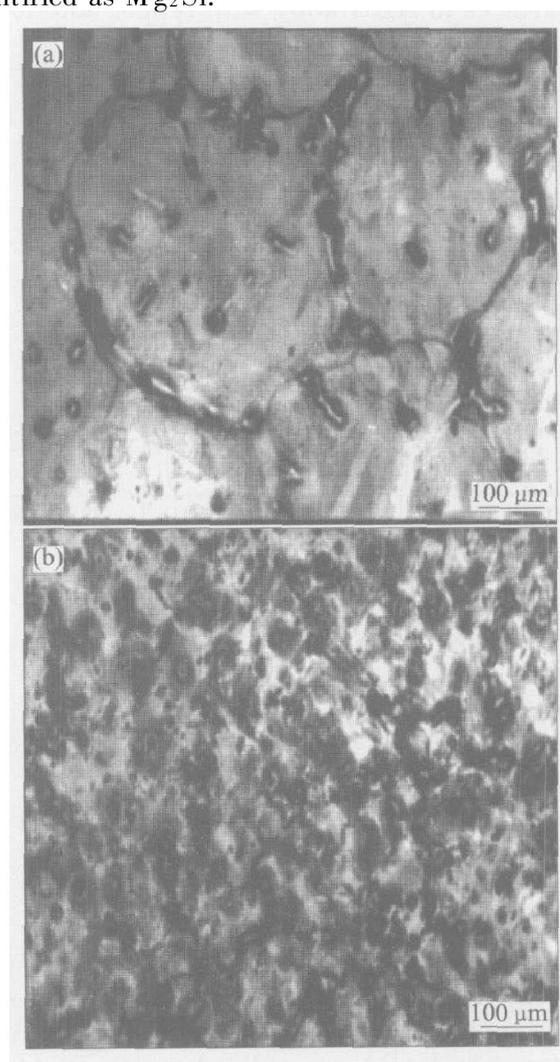(a) —Without refiner addition; (b) —With refiner addition

Fig. 2   OM micrographs of as cast AZ31 ingots
(a) —Without refiner addition;
(b) —With refiner addition

Hot extrusion of the alloys with and without
refiner addition causes partially dynamic recrystal-
lization as shown in Fig. 5(a), however, it does
not occur during hot rolling and finer grain struc-
ture is observed in as-rolled specimens as shown in
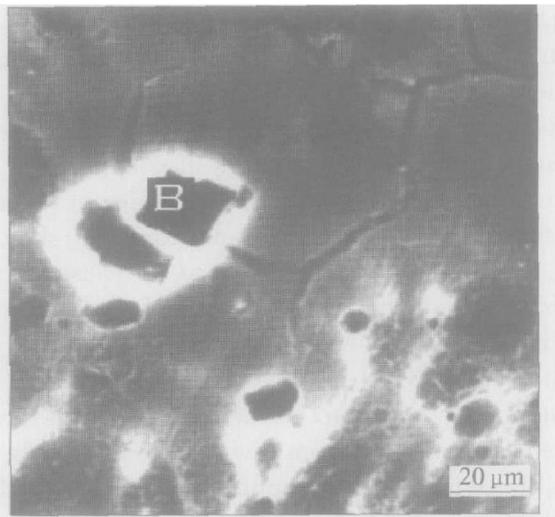Fig. 5(b). The as-extruded and as-rolled struc-

Fig. 3 SEM micrograph showing Mg₂Si particles in AZ31 alloy with refiner addition
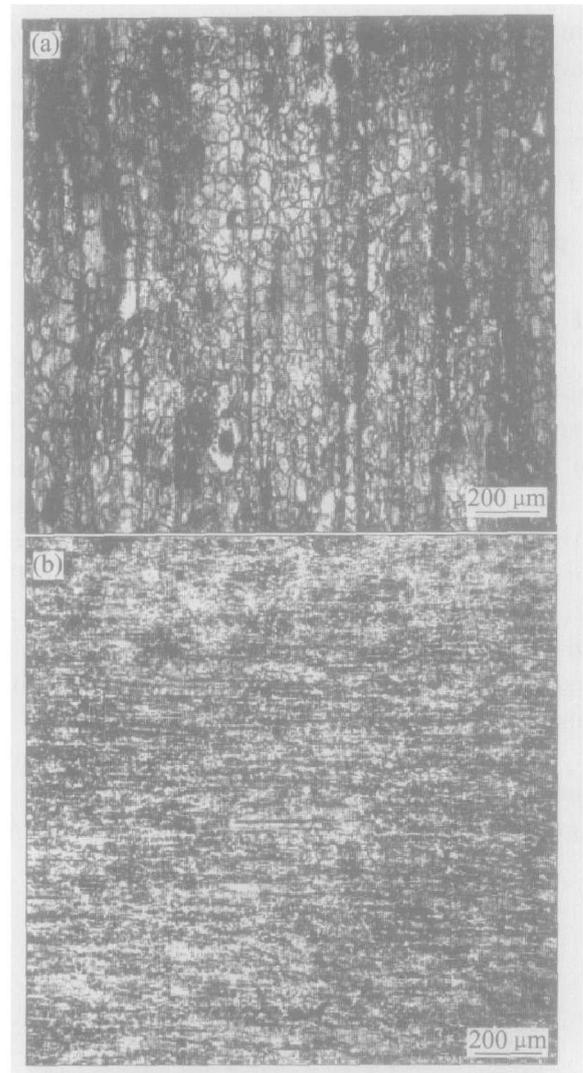

Fig. 4 XRD pattern taken from AZ31 alloy with refiner addition

Fig. 5 Microstructures of AZ31 alloy with refiner addition
(a) —As-extruded; (b) —As-rolled

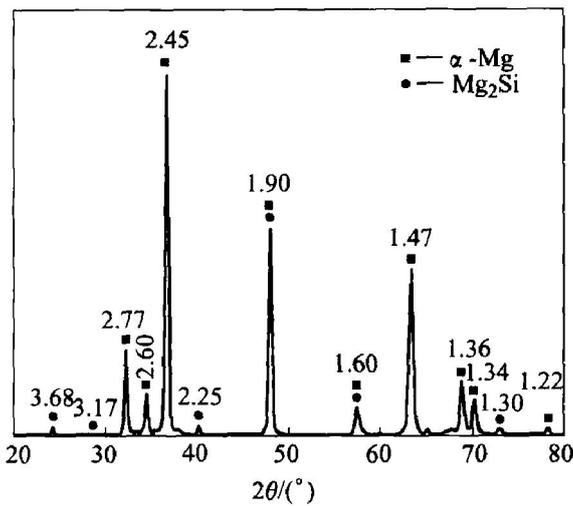tures of the alloys with and without refiner addition are similar; however, the deformability of the ingots with refiner addition is much better. The extruded rods and hot rolled sheets are crack free and show high smoothness on surface.

3. 2　Tensile properties

　Tensile properties of as-cast magnesium specimens cut from ingots with and without refiner addition are shown in Fig. 6. It can be seen that not only strength but also ductility has remarkably increased with refiner addition. The improvement of mechanical properties caused by refiner addition has also been obtained in AZ31 alloy. Fig. 7 illustrates the tensile properties of AZ31 alloy with and without refiner addition. For the specimens under all the conditions studied (as-cast, as-extruded and as-rolled), both ultimate strength and yield strength of the alloy have increased with refiner addition and the ductility of the alloy with refiner addition is similar to that without refiner addition.
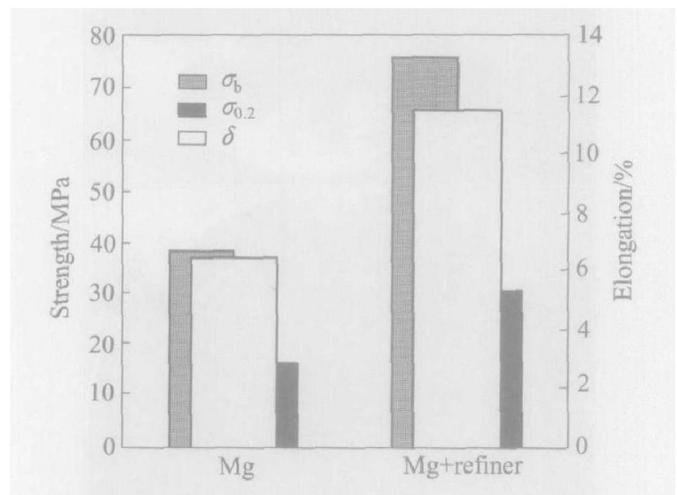

Fig. 6 Tensile properties of as-cast magnesium specimen

Annealing of as-extruded and as-rolled specimens results in the increase of ductility and slight reduction of ultimate strength and yield strength. The data of tensile properties of the specimens annealed
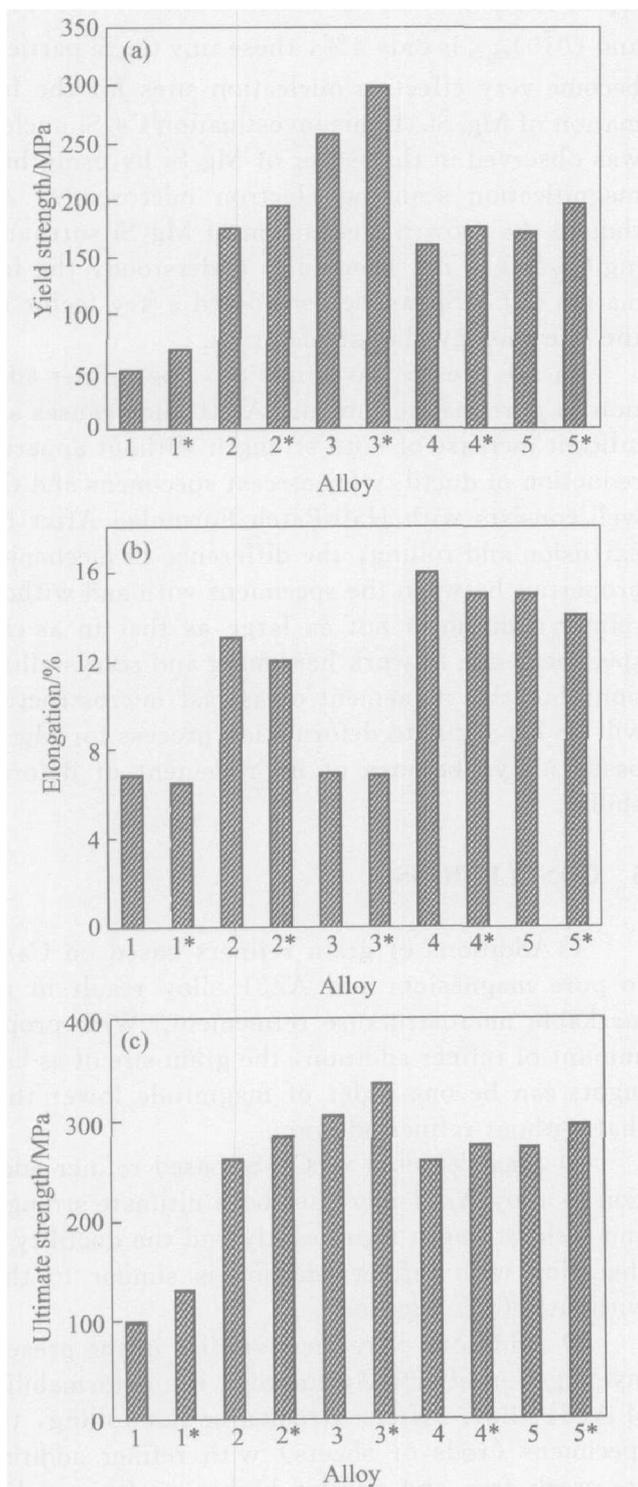
Fig. 7   Tensile properties of AZ31 alloy
with and without refiner addition
(a) —Yield strength; (b) —Elongation;
(c) —Ultimate strength
1 —As cast alloy; 2 —As extruded alloy;
3 —As rolled alloy; 4 —As extruded alloy after annealing;
5 —As rolled alloy after annealing
(* —With refiner)

at 250 ℃ are also shown in Fig. 7.

4   DISCUSSION

Efforts have been made to search refiners for magnesium based alloys for several decades and zir-conium has been found very effective on grain refinement for aluminum free magnesium alloys[4], but it can not be used in Mg-Al based alloys because of the reaction between Zr and Al. However, Mg-Al based alloys, such as AZ91, AZ31 and AM60 alloys, are most important magnesium alloys and have being used in approximately 90% of all magnesium products as structural materials. Therefore it is still necessary to develop new refiners suitable for Mg-Al based alloys. Recently, Liu et al[5] reported Al_4C_3-SiC/Al was effective on the Mg-Al-Zn alloys and Jin et al[6], Eiji et al[7] declared that carbon addition was also able to result in grain refinement.

The mechanism of grain refinement can be described as a result of constitutional undercooling generated by the growth of a grain adjacent to a nucleant particles suspended in the melt[8-11]. There are two factors which can enhance the number of successful nucleation events. The first is the solute elements present in the melt and the other is the number and potency of the nucleant particles. The effect of solute elements on the grain refinement can be defined by the alloy's growth restriction factor when the potency of the nucleant is very high. The growth restriction factor (GRF) is defined by[8]

$$ f = \sum m_i c_{0,\ i}(k_i - 1) \tag{1} $$

where m is the slope of the liquidus line, c_0 is the initial composition, and k_i is the equilibrium partition coefficient for element i. A large GRF indicates that the growing crystal generates constitutional undercooling quickly and the liquid around the adjacent nucleants is therefore more quickly undercooled sufficiently to allow a stable nucleus to form on nucleant particles compared with an alloy having a small GRF. Fig. 8 shows the relation-
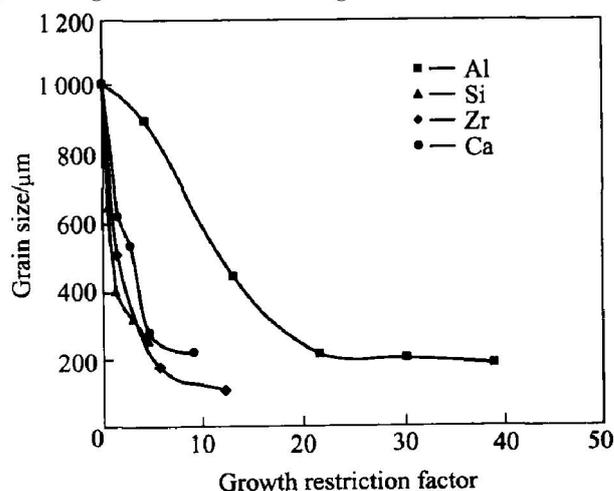

Fig. 8   Relationship between grain size and
growth restriction factor (GRF) of
elements Al, Ca, Si and Zr for
binary magnesium alloys[8]

ship between grain size and GRF of the elements Al, Ca, Si and Zr for binary magnesium alloys. It can be seen that both Ca and Si are much efficient elements on the grain refinement for magnesium alloys. This is well consistent with the results of the present work.

According to Mg-Ca and Mg-Si binary phase diagrams, the solubility of Ca and Si in the α matrix of magnesium is very low. Small amount of Si addition to magnesium results in the formation of Mg_2Si interphase, which has a cubic C1 structure. Min[12] has calculated that the mismatch between the α-Mg and Mg_2Si on some crystallographic planes with low indices and the results are listed in Table 1. It can be seen that the mismatches between $(11\bar{2}2)_{Mg}$ and $(0\bar{1}1)_{Mg_2Si}$, $(10\bar{1}0)_{Mg}$ and $(0\bar{1}1)_{Mg_2Si}$ are 9.7% and 6.5%, respectively, lower than 12%. According to the theory proposed by Bramfitt[13] that the particles are very effective nucleation sites for heterogeneous nucleation during solidification if the mismatch between the matrix and particle is lower than 12%. In the present investigation, some tiny Mg_2Si particles are found in SEM image (Fig. 3), verifying that the nucleation sites in the melt of AZ31 alloy with Si/Ca based refiner addition are Mg_2Si particles. On the other hand, Ca plays a role of modifying the morphology of Mg_2Si particles. In the Mg-Al-Si based alloys, Mg_2Si particles have a unique morphology, which is described as Chinese Script Type[14]. Small amount of Ca addition modifies the morphology of Mg_2Si so that the mechanical properties of the alloy are improved[14, 15]. Min proposed that the modification of Mg_2Si morphology is due to the formation of Ca_2Si, which has a complex cubic C23 structure. When the temperature of melt containing Si and Ca decreases, Ca_2Si nuclei form in the

liquid first. As the mismatch between $(0\bar{1}0)_{Mg_2Si}$ and $(0\bar{1}0)_{Ca_2Si}$ is only 4%, these tiny Ca_2Si particles become very effective nucleation sites for the formation of Mg_2Si. In his investigation Ca_2Si nucleus was observed in the center of Mg_2Si by using high magnification scanning electron microscopy. Although the growth mechanism of Mg_2Si surrounding Ca_2Si has not been fully understood, the formation of Ca_2Si can be considered a key factor for the morphology change of Mg_2Si.

In the present investigation, the refiner addition to pure magnesium and AZ31 alloy causes significant increase of both strength without apparent reduction of ductility for as-cast specimens and this well consists with Hall-Patch Formula. After hot extrusion and rolling, the difference of mechanical properties between the specimens with and without refiner addition is not as large as that in as-cast specimens due to work hardening and recrystallization, but the refinement of as-cast microstructure will be beneficial to deformation process for Mg-Al based alloys because of improvement of deformability.

5   CONCLUSIONS

1) Additions of grain refiners based on Ca/Si to pure magnesium and AZ31 alloy result in remarkable microstructure refinement. With proper amount of refiner addition, the grain size of as-cast ingots can be one order of magnitude lower than that without refiner addition.

2) Small amount of Ca/Si based refiner addition to alloy AZ31 increases both ultimate strength and yield strength significantly and the ductility of the alloy with refiner addition is similar to that without refiner addition.

3) Additions of refiners studied in the present investigation effectively improve the deformability of AZ31 alloy. After extrusion or hot rolling, the specimens (rods or sheets) with refiner addition are crack free and exhibit higher surface quality and mechanical properties than those without refiner addition.

Table 1   Match factor of α-Mg matrix and Mg_2Si phase in plane with low crystal factor[12]

Orientation relationship	$[hkl]_{Mg}$	$[hkl]_{Mg_2Si}$	$\theta/(°)$	δ	$\delta^{[hkl]_{Mg_2Si}}_{[hkl]_{Mg}}/\%$
$(11\bar{2}2)_{Mg} \parallel$ $(0\bar{1}1)_{Mg_2Si}$	$[\bar{1}\bar{1}121]$	$[100]$	0	4.4	
	$[2\bar{4}21]$	$[211]$	7	6.0	9.7
	$[1\bar{1}00]$	$[011]$	0	18.7	
$(10\bar{1}0)_{Mg} \parallel$ $(0\bar{1}1)_{Mg_2Si}$	$[\bar{1}2\bar{1}1]$	$[100]$	0	0.5	
	$[\bar{1}2\bar{1}1]$	$[211]$	3.8	5.6	6.5
	$[0001]$	$[011]$	0	13.3	
$(0001)_{Mg} \parallel$ $(1\bar{1}1)_{Mg_2Si}$	$[\bar{1}2\bar{1}0]$	$[110]$	0	40.7	
	$[\bar{1}100]$	$[121]$	0	40.7	40.7
	$[\bar{2}110]$	$[011]$	0	40.7	

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