

# **Mg Magnesium Technology 2013**

## **Microstructure**

## EFFECTS OF ALLOYING ELEMENTS AND COOLING RATE ON MORPHOLOGY OF PHASES IN CaO ADDED Mg-Al-Si ALLOYS

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### Abstract

Mg<sub>2</sub>Si formed by the addition of Si in Mg-Al alloys is the very useful intermetallic compound. However, Mg<sub>2</sub>Si phases in the Mg-Al-Si alloys are prone to forming undesirable, coarse Chinese script shape, which will deteriorate the mechanical properties of Mg alloys. Therefore, in order to modify the Chinese script shaped Mg<sub>2</sub>Si phases in the Mg-Al-Si alloys, many methods have been studied such as alloying addition of Ca or P. This study was aimed at improving the mechanical properties of CaO added Mg-Al-Si alloys by the addition of alloying elements and varying cooling rate to change of morphology of Mg<sub>2</sub>Si and CaMgSi phases. The microstructures of specimens were observed by OM and SEM, and the phase analysis was performed by XRD, TEM and EDS. To evaluate the mechanical properties of tested alloys, tensile tests were carried out at room and high temperatures.

### Introduction

Mg is the lightest metal among all structural metals. Its density is only 1.74g/cm<sup>3</sup>, which is less than one-quarter of iron and is about two-thirds of aluminum. Furthermore, Mg alloy has high specific strength, excellent casting ability, good machining ability, high damping capacity, good weld ability, shields against electromagnetic interference, and can be easily recycled [1-3]. These features make Mg alloy an ideal material for use in wide variety of applications, such as automobile, aviation, train, and aerospace as well as electronic application. Mg-Al based alloys such as AZ91 and AM60 are the most commonly used magnesium alloys in automobiles because of a good combination of mechanical properties, corrosion resistance, and die-castability. Despite these advantages, poor mechanical properties, especially creep resistance at high temperature are the most important barriers on the way of expansion of usage of magnesium alloy [4,5]. Therefore, the use of Mg-Al based alloys in automobiles has been restricted to components where creep resistance is of less concern, such as seat frames, steering wheels, instrument panels, valve covers, etc. Magnesium alloys are more and more widely used as structural materials in recent years due to their low density, among which Mg-Al-Si alloys (e.g. AS41 and AS21) have been used as die-casting alloys for elevated temperature applications since a long time ago [6,7]. It can be concluded from the equilibrium phase diagrams of the ternary Al-Mg-Si and binary Mg-Si systems that Si can hardly dissolve into solid magnesium. The maximum solid solubility of Al and Si in Mg is 11.5 and 0.003 at.%, respectively. The main intermetallic compounds in the Mg-Al-Si alloys are Mg<sub>17</sub>Al<sub>12</sub> and Mg<sub>2</sub>Si. Mg<sub>2</sub>Si exhibits high melting point, low density, high hardness and low thermal expansion coefficient. Therefore, Mg<sub>2</sub>Si can act as an

excellent heat-resistant strengthening phase in light metals. The potential of Mg<sub>2</sub>Si to be employed as strengthening particles in the in situ Mg had also been investigated [8-11]. However, molten Mg-Al-Si alloys are easily ignited and oxidized without melt protective gases during melting and casting processes due to their high reactivity.

Furthermore, Mg<sub>2</sub>Si phases in the Mg-Al-Si alloys are prone to forming undesirable, coarse Chinese script shape, which will deteriorate the mechanical properties of Mg alloys. Therefore, in order to modify the Chinese script shaped Mg<sub>2</sub>Si phases in the Mg-Al-Si alloys, many methods have been studied such as alloying addition of Ca or P [12-14]. However, there are some problems like fluidity decrease, die soldering, and hot tearing in magnesium alloys with alkaline earth metals such as Ca. On the other hand, the advantage has been reported to reduce hot tearing susceptibility, and reduce die soldering tendency with low-cost, non-SF<sub>6</sub> process, improvement of oxidation and ignition resistances and mechanical properties improved by addition of relatively inexpensive CaO in Mg-based alloys [15-18].

Based on these result, the ignition resistance and mechanical properties were supposed to be improved by the addition of CaO in Mg-Al-Si alloy. However, while melt cleanliness of CaO added Mg-Al-Si alloys have been increased, Mg<sub>2</sub>Si particle is little modified by adding CaO in Mg-Al-Si alloys. Also, mechanical properties are decreased due to continuously growth of needle type CaMgSi by increasing CaO content. Therefore, the objectives of this work are to investigate the effects of alloying elements (Sr, Ti, Y) on morphology of needle type CaMgSi phases. Because strontium, titanium and Yttrium have negative enthalpy with Si element compared with other elements in CaO added Mg-Al-Si alloy. At the same time, effect of cooling rate is evaluated for the application of Die-Casting process in the future.

### Experimental procedure

Four alloys, of nominal chemical compositions listed in Table 1 were prepared in a mild steel crucible under the protection of a mixed gas atmosphere of SF<sub>6</sub> and CO<sub>2</sub>. High purity Mg, Al, Al-25Si, Mg-3.0CaO, Al-10Sr, Al-10Ti master alloys were prepared by adding the following alloying materials. The melt was held at 690 °C for several minutes and then poured into permanent mold (40 mm), step mold (3, 6, 9, 12 mm) as shown Fig. 1, which were preheated to 200 °C.

The microstructural analysis was carried out using an Optical microscopy (OM) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) after etching with a solution of 2 vol.% nitric acid + ethyl alcohol. Aspect ratio was measured by using image analyzing program.

Also, the tensile tests were performed at room and high temperatures and conditions of tensile test were listed in Table 2.

## Results and discussion

### Microstructure

The typical microstructure of permanent mold cast AS51 (Mg-5Al-0.7Si) alloy were illustrated in Fig. 2. The as-cast microstructure consisted of Chinese script type  $Mg_2Si$  particles with interdendritic  $\beta-Mg_{17}Al_{12}$  phases in matrix ( $\alpha-Mg$ ). On the other hand, the deformation of needle type CaMgSi phases had been observed with addition of CaO in AS51. In fact, it has the same characteristics as the one recently observed in Mg-Si-Ca alloys [19]. When the addition of Sr, Ti, Y elements was added in ASO5105 alloy the modified CaMgSi phases have been observed as shown in Fig. 3.

Because heat of mixing, Sr ( $\Delta h_{mix} = -32$  kJ/mol), Ti ( $\Delta h_{mix} = -56$  kJ/mol), Y ( $\Delta h_{mix} = -49$  kJ/mol) elements have more negative enthalpy with Si element compared with other elements in ASO5105 alloy.

$$\Delta h_{mix} = h_m - x_1 h_1 - x_2 h_2 = Q/m$$

Among Sr, Ti, Y added ASO5105 alloys, the modification effect of Sr added ASO5105 alloy was more effective than Ti, Y added ASO5105 alloys as shown in Fig. 3. Also, the modification effect of needle type CaMgSi phases have been confirmed by increasing cooling rate in accordance with the difference of mould thickness as shown in Fig. 5. Especially, in the result of aspect ratio, even if the cooling rate is decreased, the modification effect of Sr added ASO5105 alloy is more than Ti, Y added ASO 5105 alloys as shown in Fig. 5. Also, Sr, Ti, Y included CaMgSi phase is observed by SEM(EDS) as shown in Fig. 4 and chemical compositions listed in Table 3.

Table 1. Nominal chemical compositions of experimental alloys (wt.%)

Alloy ID	Mg	Al	Si	Ca	Sr	Ti	Y
ASO5105	Bal.	5.0	0.7	0.5	-	-	-
ASO5105+0.3Sr	Bal.	5.0	0.7	0.5	0.3	-	-
ASO5105+0.3Ti	Bal.	5.0	0.7	0.5	-	0.3	-
ASO5105+0.3Y	Bal.	5.0	0.7	0.5	-	-	0.3

Table 2. Condition of tensile test

	Type	Gauge length (mm)	Thickness (mm)	Strain rate (mm/min)
Room temp.	Plate	2.5	3.0	1.0
High temp. (150°C)	Plate	2.5	3.0	0.4

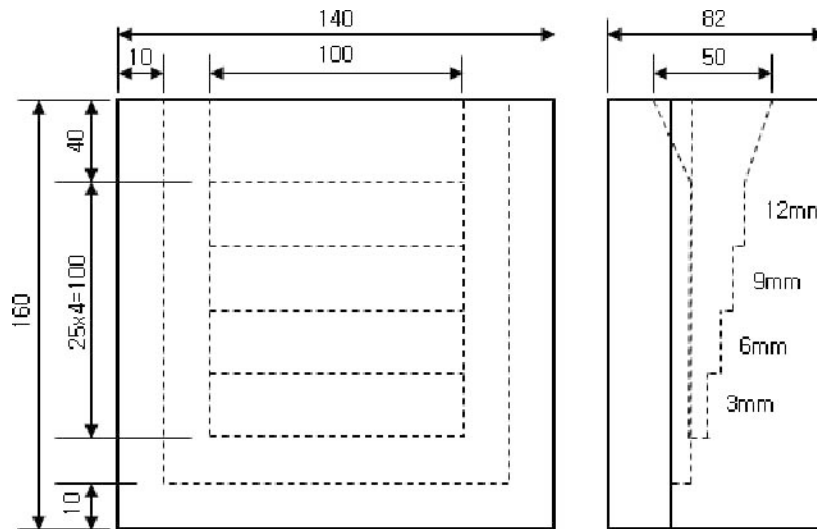


Fig. 1. Schematic drawing of the step mold

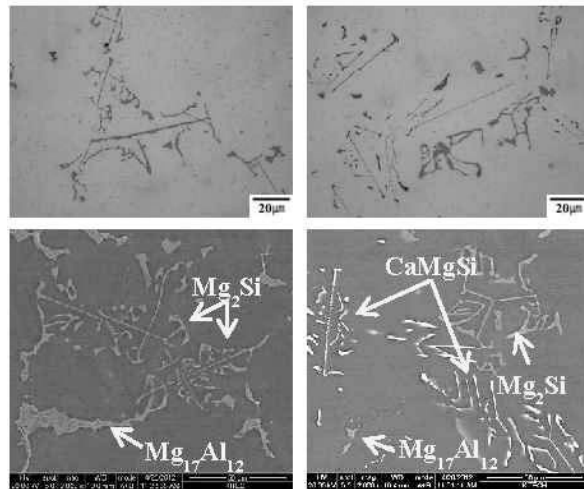


Fig. 2. Microstructures of as-cast (a) AS51, (b) ASO5105

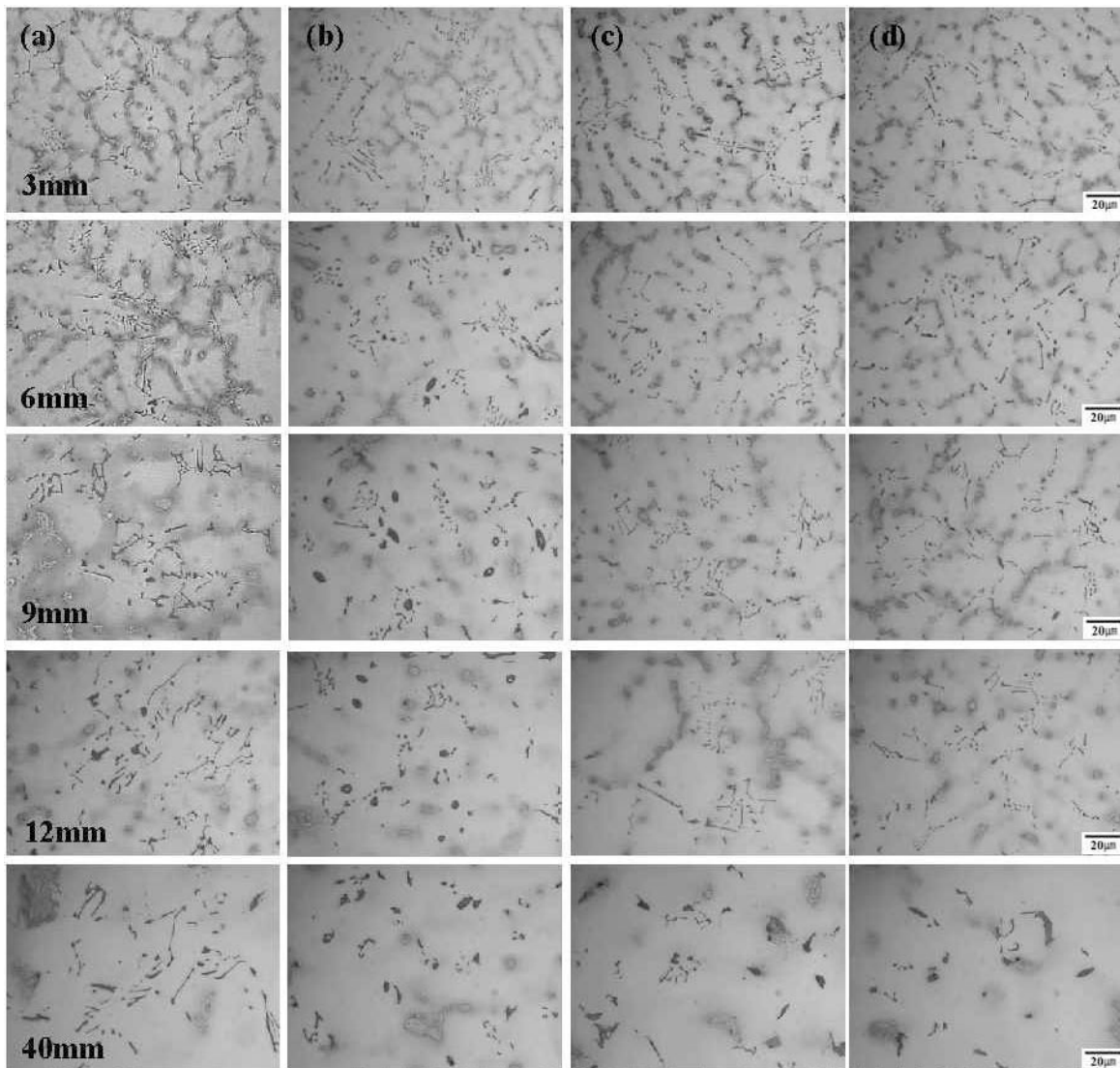


Fig. 3. Microstructures of as-cast (a) ASO5105, (b) ASO5105+0.3Sr, (c) ASO5105+0.3Ti, (d) ASO5105+0.3Y

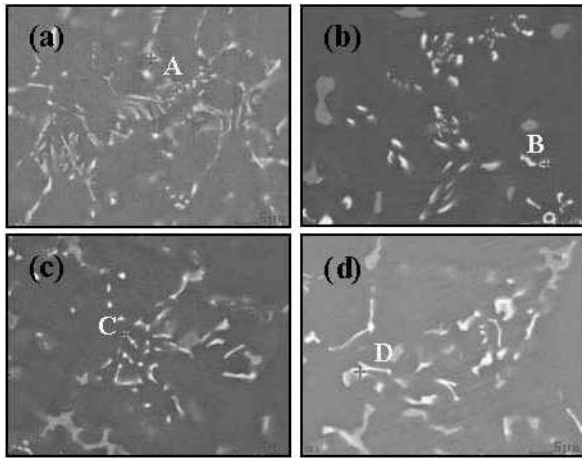


Fig. 4. Scanning electron microscopy (SEM) images of as-cast (a) ASO5105, (b) ASO5105+0.3Sr, (c) ASO5105+0.3Ti, (d) ASO5105+0.3Y

Table 3. Chemical compositions of area A, B, C and D analyzed EDS in Fig. 4 (wt.%)

Area	Mg	Al	Si	Ca	Sr	Ti	Y
A	69.78	7.16	14.28	8.78	-	-	-
B	63.44	1.83	18.40	9.38	6.96	-	-
C	74.91	1.53	13.39	9.94	-	0.23	-
D	64.55	1.42	17.82	14.84	-	-	1.36

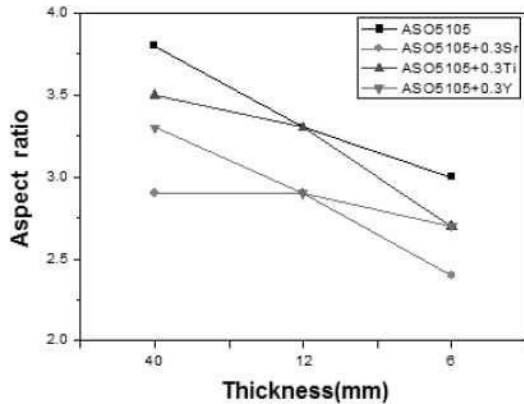


Fig. 5. Aspect ratio of Sr, Ti, Y added ASO5105 alloys

Table 4. Tensile properties of the as-cast ASO5105 and Sr, Ti, Y added ASO5105 at room temperature

Alloy ID	Room temperature					
	6mm			40mm		
	TYS(MPa)	UTS(MPa)	E(%)	TYS(MPa)	UTS(MPa)	E(%)
ASO5105	96.8	174.2	4.0	77.6	153.4	6.6
ASO5105+0.3Sr	97.3	173.2	5.2	80.9	157.6	5.4
ASO5105+0.3Ti	96.9	170.5	5.1	78.9	156.1	6.3
ASO5105+0.3Y	95.8	177.4	5.3	77.2	146.6	5.7

### Mechanical properties

The room and high temperature tensile properties were performed when the cooling rate was different according to the thickness of as-cast samples, 6 mm and 40 mm, respectively. The yield strengths at room and high temperature were increased by increasing cooling rate. It is well known that tensile yield strength is increased with presence of fine phases and effect of grain refinement by increasing cooling rate.

In the case of thickness of 6 mm, the elongations at room temperature of ASO5105 and Sr, Ti, Y added ASO5105 were measured 4.0, 5.2, 5.1, 5.3 %, respectively. Therefore, the elongations at room temperature of Sr, Ti, Y added ASO5105 are increased about 30 % compared with ASO5105. Because the needle type CaMgSi phases were modified with the addition of Sr, Ti, Y elements in ASO5105 and the cooling rate was increased by thin thickness. Also, the tensile yield strength at high temperature, 6 mm is increased about 23 % with the addition of Sr, Ti, Y in ASO5105. Because modified CaMgSi phases have high thermal stability at high temperature, this intermetallic phase at high temperature does not diffuse easily in the matrix ( $\alpha$ -Mg) [19]. On the basis of the result, modified CaMgSi phase can act as a significantly role in increasing creep resistance. Therefore, in the future, in the order to application of high temperature Mg alloy, creep test of Sr, Ti, Y added ASO5105 is required.

### Conclusion

In this study, effects of alloying elements and cooling rate on morphology of phase in CaO added Mg-Al-Si alloys were investigated. The conclusions are as follows:

- (1) The needle type CaMgSi phases were modified Mg<sub>2</sub>Si with the addition of Sr, Ti, Y elements having negative enthalpy with Si element and with the increase of cooling rate.
- (2) The elongation at room temperature was increased about 30 % due to modification of needle type CaMgSi with the addition of Sr, Ti, Y elements in ASO5105. The tensile yield strength at high temperature, 6 mm of Sr, Ti, Y added ASO5105 was increased about 23 % compared with ASO5105.

In order to application of high temperature Mg alloys, these applications require superior creep resistance. In the result of microstructure and tensile properties, creep test of Sr, Ti, Y added ASO5105 might be required before application of die-casting process.

Table 5. Tensile properties of the as-cast ASO5105 and Sr, Ti, Y added ASO5105 at high temperature

Alloy ID	at 150 °C					
	6 mm			40 mm		
	TYS(MPa)	UTS(MPa)	E(%)	TYS(MPa)	UTS(MPa)	E(%)
ASO5105	57.2	93.9	19.2	69.6	97.6	14.8
ASO5105+0.3Sr	70.9	102.9	7.8	61.6	90.3	11.3
ASO5105+0.3Ti	71.2	104.9	14.4	60.1	88.4	12.5
ASO5105+0.3Y	70.6	103.2	11.7	60.8	89.3	10.5

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