

Microstructure and mechanical properties of Mg-5Sn-5Zn-xCa alloys

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Abstract

Mg-5Sn-5Zn-xCa(x=0.5, 1, 2) alloys were melted by the vacuum melting furnace. The microstructures and phase compositions were analyzed by the scanning electron microscope (SEM) and X-ray diffraction (XRD). The mechanical properties were tested by the electronic universal test machine. The fracture surface were observed by scanning electron microscope (SEM). The results indicate that the microstructures of Mg-5Zn-5Sn-xCa alloys are composed of CaMgSn phases, layer MgZn₂ phases and Mg₂Sn phases. Matrix precipitates onset Mg₂Ca phase, when the content of Ca is 2 wt%. With the increasing of the Ca content, the needle CaMgSn phases become rods gradually, the layer MgZn₂ phases and plate Mg₂Sn phases become continuous, ultimate tensile strength decrease. The ultimate tensile strength obtained by Mg-5Zn-5Sn-0.5Ca alloy is 184MPa.

1 Introduction

Magnesium alloys have greatly potential applications as the lightest structural material due to their inherent properties such as acceptable mechanical properties, low density, superior damping capacity and castability [1]. Nowadays, all of the researcher devote to improve the strength of the Mg alloys. The ultimate tensile strength (UTS) of Mg-RE alloys can reach 300MPa to 400MPa, but the high cost restricts these alloys from being extensively used. It is necessary to develop a new type Magnesium alloy [2]. Compared to Mg-Al and Mg-Zn alloys, the intermetallic phase Mg₂Sn in Mg-Sn alloys has a much higher melting (770°C) than the Mg₁₇Al₁₂ phase (462°C) of Mg-Al alloys and MgZn phase (347°C) of Mg-Zn alloys. The solubility of Sn in the α -Mg solid solution drops sharply with the temperature decreasing. It provides a fundamental basis for improving the mechanical properties of these alloys through aging [3-4]. According to Liu, the

microstructure of as-cast Mg-Sn alloys consisted of dendrite α -Mg and second Mg₂Sn phases and the secondary dendrite arm spacing (DAS) of the α -Mg phase was decreased with the increase of tin content. The micro-hardness of the alloys increased when tin content rised, while the great tensile 123MPa were obtained by Mg-5 wt% Sn [5]. As one of the two major alloy element, Zn has strong strength effect. Solid solution strengthening and compounds to strengthening are two main way of Zn reinforced Mg alloys. Add 1wt% Zn to Mg-Al alloys will improve the comprehensive properties of the Mg alloys. Under the condition of tin, Zn solution reinforcement will be strengthened [6]. Ca is an important alloying element of Mg alloys; it is well know that Ca can behave as a grain refiner of magnesium alloys and form a stable Mg₂Ca compound with Mg [7]. In addition, it also form intermetallic stable phase CaMgSn with content of tin [8-9]. Therefore, research on Mg-Sn-Zn-Ca alloys has important significance. This paper mainly investigate that the effect of 0.5 wt%, 1.0 wt%, 2.0 wt% Ca on as-cast microstructure and mechanical properties of Mg-5Sn-5Zn alloy.

2 Experimental

Mg-5Sn-5Zn-xCa(x=0.5,1,2) alloys were prepared using pure magnesium (99.99 wt%), tin (99.99 wt%), zinc (99.99 wt%), and calcium added in the form of Mg-30 wt% Ca master alloy. The experimental alloys were melted in a crucible under the protection of the nitrogen gas at 700°C. (The melting point of all metals is less than 700°C except to Mg-Ca alloy. The melting point of intermediate phase of Mg-Ca alloy is 715°C, but it will react with other metals in the smelting process) The melt was homogenized by mechanical stirring and held at 700°C for 30min, then it was poured into a preheated permanent mould in order to obtain a casting. The slices (shown in Fig.1) were cut by an electrodes

charge wire-cut machine for tensile tests and structural characterization. The specimens were studied by scanning electron microscopy (SEM) and optical microscopy to examine the as-cast microscopy. The specimens were polished with chromium oxide solution. Etching was carried out using a 2% nitric acid and 98% ethyl alcohol solution at room temperature. The X-ray diffraction (XRD) and energy-dispersive X-ray (EDS) analysis were carried out on selected samples to identify the phases.

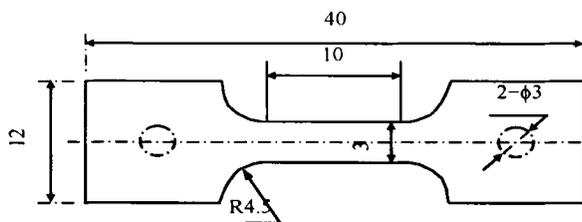


Fig. 1 The size of tensile test specimen (mm)

3 Results and discussions

3.1 Microstructure observation

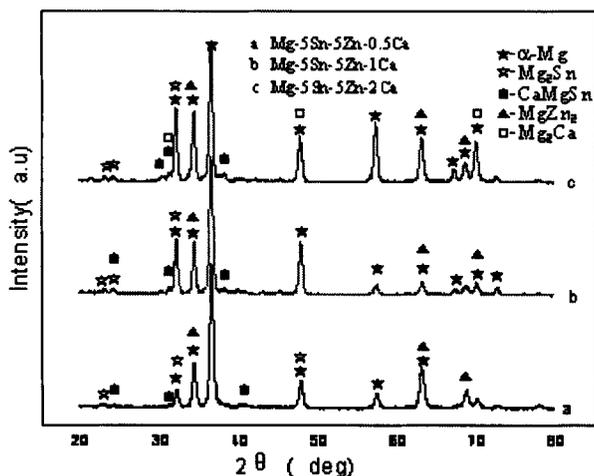


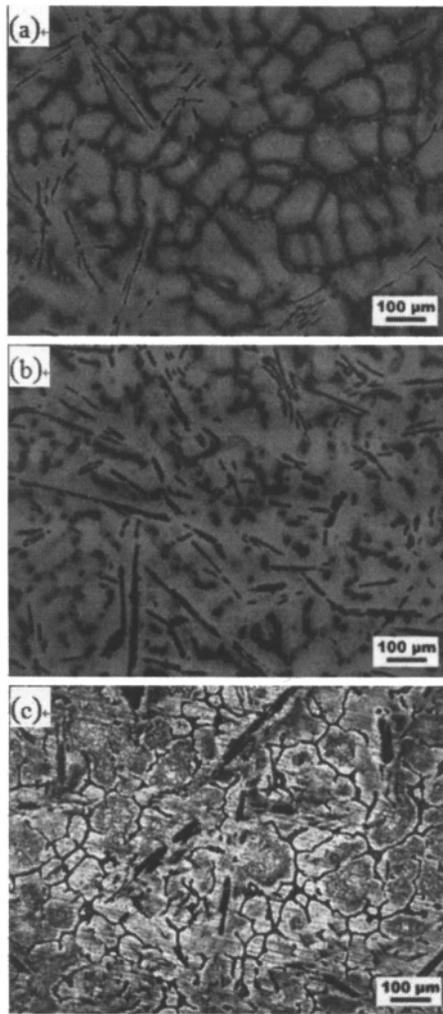
Fig.2 XRD patterns of Mg-Sn-Zn-Ca alloys

Fig.2 shows the XRD pattern of the as-cast experimental alloys. It can be observed from the Fig.2 that the as-cast experimental alloys are mainly composed of α -Mg, $MgZn_2$, Mg_2Sn and $CaMgSn$ phases with the addition of 0.5 wt% and 1.0 wt% Ca. With the Ca amount increasing, the intensity of the Mg_2Sn and $CaMgSn$ peaks become higher. The Mg_2Ca strong peak appearing in the pattern of 2.0wt% Ca alloy indicates that

there is a large number of the Mg_2Ca phase in Mg-5Sn-5Zn-2Ca alloy. It is found in Fig.1 that the addition of 0.5 wt%-1.0 wt% Ca to the Mg-5Sn-5Zn alloy results in the formation of $CaMgSn$ phase rather than Mg_2Ca phase. In general, the difficulty level in forming the intermetallics can be estimated by the electronegative difference between different elements. The higher the electronegative difference is, the more easily the intermetallics forms. The electronegative values of Mg, Sn, Zn and Ca are 1.31, 1.65, 1.96 and 1.00, respectively. Obviously, the $CaMgSn$ intermetallics is more easily formed than Mg_2Ca [10]. When Ca content is 2.0wt%, the remaining amount of Ca formed Mg_2Ca phase after the formation of $CaMgSn$ phase.

Fig.3 show the optical microstructures of the as-cast alloys. Fig.3 (a) is the microstructures of Mg-5Sn-5Zn-0.5Ca alloy. It can be observed from Fig.3 (a) that the phase precipitates along the grain boundary in the alloy with wide dendrite, and have needle-shaped precipitates in grain. Fig.3(b) is the microstructures of Mg-5Sn-5Zn-1Ca alloy. Compared with Fig.3 (a), it has discontinuous dendrite, and a part of needle-shaped precipitates change into rod-shaped. Fig.3 (c) is the microstructures of Mg-5Sn-5Zn-2Ca alloy. It has the finest dendrite in some area. The phase precipitated in grain become almost all rod-shaped. The research indicates that it has two effects with the increase of Ca content: Firstly, The increase of Ca content (2%) can effectively refine the as-cast microstructure of the alloy. Secondly, the phase precipitated in grain change to rod-shaped from needle-shaped with the increase of Ca content. This will have important effect on mechanical properties of Mg alloys.

Fig.4 show the SEM microstructures of the as-cast alloys. The EDS results of the as-cast alloys are given in the table 1. Fig.4 (a) is the SEM microstructures of Mg-5Sn-5Zn-0.5Ca alloy. It can be observed from the Fig.4 (a) that the as-cast Mg-5Sn-5Zn-0.5Ca experimental alloys are mainly composed of three phases except α -Mg phase. According to the XRD and EDS results (Table 1), the plate phase in the grain boundary is Mg_2Sn , and the lamellar tissue is $MgZn_2$, and needle-shaped phase is identified as $CaMgSn$ phase. According to the morphology and distribution, there are two eutectic reaction in the formation process: firstly, $L \rightarrow \alpha$ -Mg+ $CaMgSn$. secondly, $L \rightarrow \alpha$ -Mg+ Mg_2Sn + $MgZn_2$.

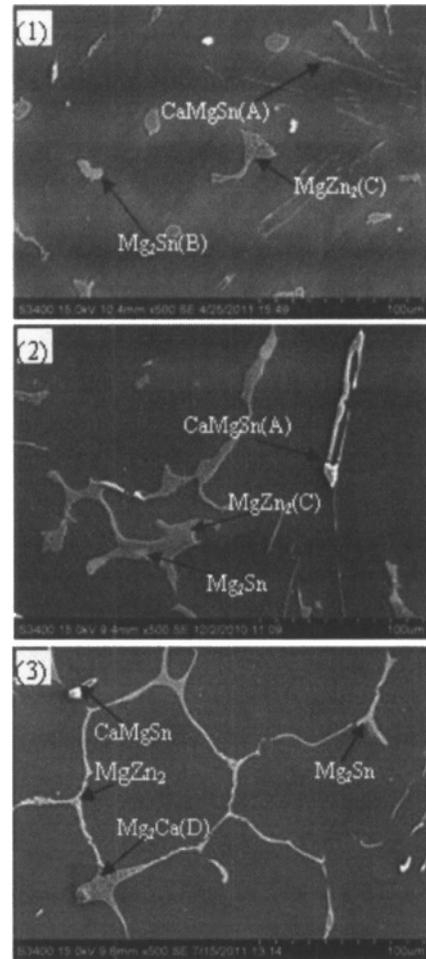


a) Mg-5Sn-5Zn-0.5Ca b) Mg-5Sn-5Zn-1Ca
c) Mg-5Sn-5Zn-2Ca

Fig.3 Microstructures of the as-cast Mg-Sn-Zn-Ca alloys

Fig.4 (b) is the SEM microstructures of Mg-5Sn-5Zn-1Ca alloy. Compared with Fig.4 (a), the Mg_2Sn phase and $MgZn_2$ are not independent, but attached with each other. The rod-shaped $CaMgSn$ precipitated in grain. According to the morphology and distribution, there are four eutectic reaction in the formation process: firstly, $L \rightarrow CaMgSn$. Secondly, $L+CaMgSn \rightarrow \alpha-Mg+CaMgSn$. Thirdly, $L \rightarrow \alpha-Mg+Mg_2Sn$. fourth, $L \rightarrow \alpha-Mg+MgZn_2$. Fig.4 (c) is the SEM microstructures of Mg-5Sn-5Zn-2Ca alloy. It differs from Fig.4 (a) and Fig.4 (b), there exist Mg_2Ca phase (arrow D) in the grain boundary, it forming a network with Mg_2Sn phase and $MgZn_2$ phase. According to the morphology and

distribution, there are four eutectic reaction in the formation process: Firstly, $L \rightarrow CaMgSn$. Secondly, $L+CaMgSn \rightarrow \alpha-Mg+CaMgSn$. Thirdly, $L \rightarrow \alpha-Mg+Mg_2Sn$. Fourth, $L \rightarrow \alpha-Mg+CaMgSn+Mg_2Ca$.



1) Mg-5Sn-5Zn-0.5Ca 2) Mg-5Sn-5Zn-1Ca
3) Mg-5Sn-5Zn-2Ca

Fig.4 SEM Microstructures of the as-cast Mg-Sn-Zn-Ca alloys

According to Mg-Sn binary diagram[11], the saturation solid solubility of tin in magnesium is relatively large with 14.85 wt% at the temperature of 561.2°C, which decreases sharply with the temperature falling with 0.45 wt% at 200°C and almost zero at room temperature. The fact that the saturation solid solubility declines fast with the decreasing of temperature case the tin atoms to precipitate, in the form of the Mg_2Sn during the solidification process. According to the XRD and EDS result (Table 1), the layer

phase (arrow C) precipitated on the grain boundary is $MgZn_2$ phase and another layer phase (arrow D) is Mg_2Ca phase. Based on the calculated vertical phase diagram section of the Mg-Sn-Ca alloys with a constant Ca composition of 2.0 wt%, during the solidification of the CaMgSn phase first forms as a primary phase when passing through L+CaMgSn region, and then at the large stage of solidification a pseudo binary eutectic reaction ($L+CaMgSn \rightarrow \alpha-Mg+CaMgSn$) and a ternary eutectic reaction ($L \rightarrow \alpha-Mg+CaMgSn+Mg_2Ca$) occur at about 638°C and 514°C, respectively [12]. It is found from the Fig.3 that Mg_2Sn and $MgZn_2$ phases in the grain boundary are refined with Ca increasing and grain size become smaller. This study is consistent with Yang [10].

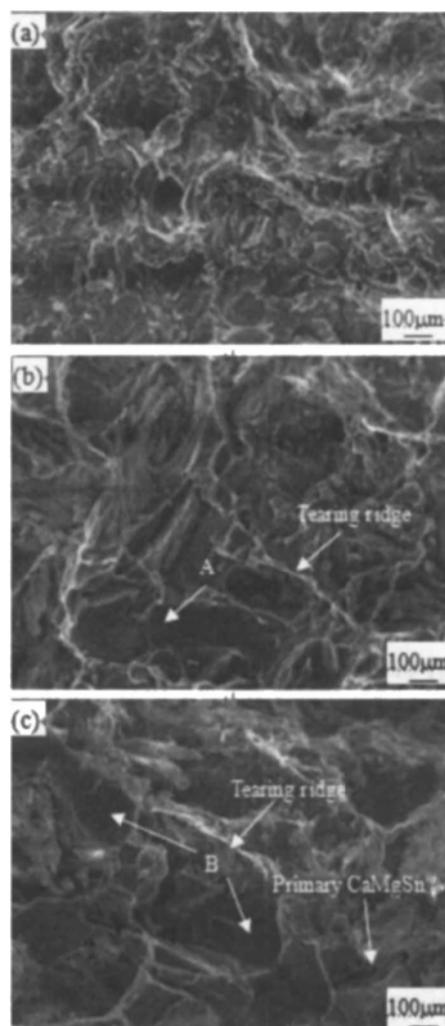
Table 1 EDS results of as-cast alloys (molar fraction,%)

element	A	B	C	D
Mg	83.22	67.15	27.15	74.31
Sn	9.72	32.85	0	19.53
Zn	0	0	72.85	0
Ca	6.96	0	0	6.61
total amount	100	100	100	100

3.2 Mechanical properties

The tensile properties including ultimate tensile strength (UTS), 0.2% yield strength (YS), elongation (Elong) are listed in Table 2. It is observed that with the Ca amount increasing, the ultimate tensile strength and elongation increase, and the 0.2% yield strength (YS) first increase and then decrease. This is possibly ascribed to that the excess Ca cases the formation of coarse primary CaMgSn phase. CaMgSn phases possibly promotes the initiation and propagation of cracks and leads to an adverse effect on the ultimate tensile strength. The maximum ultimate tensile strength and elongation in the Mg-5Sn-5Zn alloy with addition of 0.5 wt% Ca are achieved. Fig.5 shows SEM tensile fractographs of as-cast experimental alloys. It can be observed that fractograph a which are composed of a large number of little dimples is typical ductile fracture, and it has excellent toughness. As shown in the Fig.5, fractograph b and fractograph c including a number of cleavage planes (A and B) and tearing ridge indicates that the tensile fracture surfaces of the experimental alloys exhibit mixed characteristics of cleavage and quasi-cleavage fractures. The crack caused by coarse primary CaMgSn particle can be seen in the

fractograph C.



a)Mg-5Sn-5Zn-0.5Ca b)Mg-5Sn-5Zn-1Ca
c)Mg-5Sn-5Zn-2Ca

Fig 5. SEM tensile fractographs of as-cast experimental alloys

Table 2 Tensile and properties of as-cast experimental alloys

Alloy	Tensile property		
	Uts/MPa	YS/MPa	Elong/%
Mg-5Sn-5Zn-0.5Ca	184.72	85.71	3.29

Mg-5Sn-5Zn-1.0Ca	152.34	87.14	2.89
Mg-5Sn-5Zn-1.0Ca	123.28	52.13	1.05

4 Conclusions

1. The microstructures of Mg-5Zn-5Sn-xCa alloys are composed of CaMgSn phases, layer MgZn₂ phases and Mg₂Sn phases. Matrix precipitates onset Mg₂Ca phase, when the content of Ca is 2 wt%.

2. With the increasing of the Ca content, the needle CaMgSn phases gradually become rods, the layer MgZn₂ phases and plate Mg₂Sn phases become continuous.

3. With the increasing of the Ca content, ultimate tensile strength and elongation decrease.

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