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Effects of Al and Ca on microstructure and surface defect of magnesium alloy thin strip

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Abstract: Mg-Al-Zn alloy thin strips were prepared by vertical twin-roll casting. Effects of Al and Ca on the microstructure and the surface defects of the thin strips were investigated. The results show that with the increase of Al content, the quantity of surface cracks of the thin strips increases rapidly and their locations are moved to the center of the thin strips. The alloy melts with more than 0.10% Ca (mass fraction) stick on the roller and a poor surface quality of the thin strips appears. With the increase of Al content, the microstructure of the thin strips evolves from single *α*-Mg phase, characterized by the uniform and equiaxed recrystallization grains, to the combination of dendritic *α*-Mg with Al supersaturated *α*-Mg. The minor addition of Ca can obviously refine the grains of Mg-3Al-1Zn thin strip because the formation of Al_2Ca and the finest grains are obtained by adding 0.08% Ca.

Key words: magnesium alloy; twin-roll casting; thin strip; grain refinement

1 Introduction

The conventional hot rolling processes of magnesium alloy strips take many steps, including multi-hot rolling and multi-heat treatment, with higher energy cost and lower efficiency[1]. The short procedure processes for magnesium alloy strips, such as extrusion-rolling[2], coiling rolling[3], and twin-roll casting[4], were developed in order to save cost and enhance efficiency.

Twin-roll casting can prepare the 1−8 mm thick magnesium alloy thin strips directly from the melt, with the reduction of some medium procedures. In recent years, twin-roll casting for magnesium alloy has attracted increasing attention from both industry and academy. A mass production lines of magnesium alloy thin strip were established in China[5], and testing production lines of magnesium alloy thin strip were also built in Australia[6], Korea[7], and Turkey[8]. In order to improve the process of twin-roll casting for magnesium alloy, numerical simulation for flow field and temperature field[9], casting process[4], the optimization of rolling parameters[10] of magnesium alloy thin strips was investigated, and some new techniques were developed[5].

In general, the thickness of magnesium alloy thin strip is 1−8 mm, and during its following rolling the total reduction is much smaller than that in conventional hot rolling. Therefore, fine and uniform microstructure of the thin strips is very important to ensure that large reduction can be easily carried out in the following rolling. Unfortunately, the research of microstructure evolution, grain refinement and surface defect of magnesium alloy thin strips is not enough[4, 7−8, 11]. On this background, in this work, Mg-Al-Zn alloys containing different contents of Al and with additions of Ca were used for vertical twin-roll casting in order to evaluate the effects of Al and Ca on microstructure and surface defect of magnesium alloy thin strips, which can be used for reference in the future research and development of magnesium alloy thin strips.

2 Experimental

The materials used in the research were pure magnesium, pure aluminium and pure zinc with the purity of 99.9%, Mg-2Mn master alloy, and Mg-20Ca

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master alloy. Mg-3Al-1Zn, Mg-6Al-1Zn, and Mg-9Al-1Zn alloys were melted, respectively, which corresponded to the commercial AZ31, AZ61, and AZ91 alloys in ASTM standard. All values are in mass fraction. Minor Ca was added into AZ31 alloy melt using Mg-20Ca master alloy. All the alloys were melted in a mild steel crucible in an electric resistance furnace. When the required casting temperature and stewing time were reached, the melt was poured into a vertical twin-roll caster (250 mm in diameter and 150 mm in width) at the casting speed of 10 m/min. For the purpose of comparison, all the alloy melts were held at the same superheat of 30 ˚C, therefore, the casting temperatures of AZ31, AZ61, and AZ91 alloys were 670, 650 and 625 ˚C, respectively. During melting and casting, the melt was protected by SF_6 and CO_2 mixed gas to prevent the oxidation and burning of the melt.

Surface defects of the thin strips were evaluated by the quantity of the surface cracks that were counted in three random segments of the thin strip (200 mm in length). The samples for optical observation of cross sectional microstructure were cut from the center of the thin strips. X-ray diffraction (XRD) test was made using Rigaku D/max-3C with Co K_α.

3 Results and discussion

3.1 Surface defects of Mg-Al-Zn thin strips with different contents of Al and Ca

The surface cracks in the thin strips with different compositions were statistically analyzed by taking account of the quantity and the location. The results are listed in Table 1. It is shown that with the increase of Al content in the thin strips, the quantity of surface cracks increases and the distributions of surface cracks in the thin strips are different. The location changes from the edge to both the edge and the center. The addition of minor Ca into AZ31 thin strips has little influence on the quantity of surface cracks. However, when the addition of Ca increases to more than 0.10%, the AZ31 alloy melt has higher viscosity[12] and thus it is stuck on the surface of the roller and the surface quality of the AZ31 thin strip is worsened rapidly, as shown in Fig.1(a).

From Fig.1(b), it is seen that the microstructure near the surface cracks of the AZ31 thin strips consists of the recrystallization grains, which shows that the surface cracks of the AZ31 thin strips result from the larger rolling deformation[13]. It is shown in Fig.1(c) that the microstructures near the surface cracks of the AZ61 thin strips are the coarse and nonuniform dendrites, which means that during casting the temperature at the center of the AZ61 thin strips is high and nonuniform. Therefore, the surface cracks in the AZ61 thin strips are caused by the thermal stress that is much higher than the strength of the interface between the dendrites[14]. Because AZ91 alloy has a wider solidification range than AZ61 alloy, the thermal stress in the AZ91 thin strips is larger and thus more surface cracks appear.

Table 1 Surface defects of Mg-Al-Zn thin strips with different contents of Al and additions of Ca under superheat degree of 30 ˚C

Composition of thin strip	Casting temperature/ºC	Quantity of surface cracks	Location of surface cracks in thin strips
AZ31	670	5	Edge
AZ31+0.05%Ca	670	4	Edge
AZ31+0.08%Ca	670	5	Edge
AZ31+0.10%Ca	670	Sticking on roller	−
AZ31+0.15%Ca	670	Sticking on roller	−
AZ61	650	9	Edge and center
AZ91	625	12	Edge and center

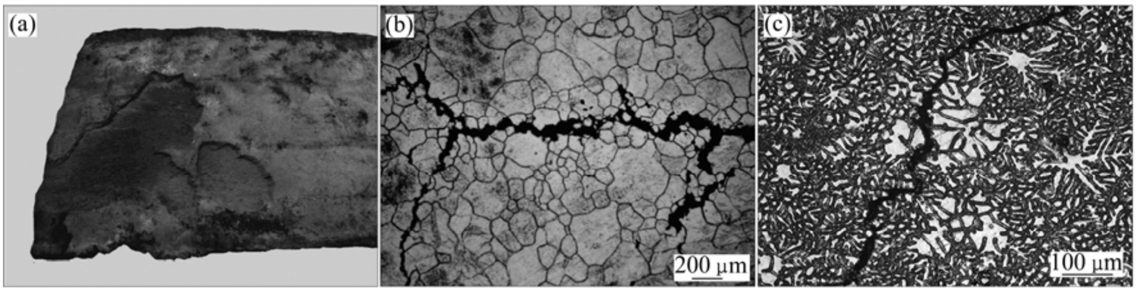

Fig.1 Surface defects of AZ31+0.10%Ca thin strip(a), and microstructures near surface crack of edge(b) and center(c) of AZ61 thin strip

3.2 Effect of Al content on microstructure of Mg-Al-Zn thin strips

The optical microstructures of AZ31, AZ61 and AZ91 thin strips are shown in Fig.2. It is seen that there are hardly β-$Mg_{17}Al_{12}$ compounds in the thin strips because the high cooling rate of vertical twin-roll casting[4] can make excessive Al element dissolve into the α-Mg matrix and form the fine Al supersaturated α-Mg, therefore leads to little segregation of the Al element in the thin strips. As shown in Fig.2(a), the microstructure of AZ31 thin strip consists of the equiaxed grains of single α-Mg phase. When the Al content is higher than 6%, because of the wider solidification range of AZ61 and AZ91 alloys, during twin-roll casting, their mushy melts consist of primary crystallized α-Mg and the residual melt. And then the residual melt will be solidified as the Al supersaturated α-Mg and no β-$Mg_{17}Al_{12}$ compounds appear. Therefore, the microstructures of both AZ61 and AZ91 thin strips consist of the primary α-Mg and the Al supersaturated α-Mg. Meanwhile, it is shown that in AZ91 thin strip there is more volume fraction of primary α-Mg, resulting from the wider solidification range of AZ91 alloy, and the size of primary α-Mg is coarser.

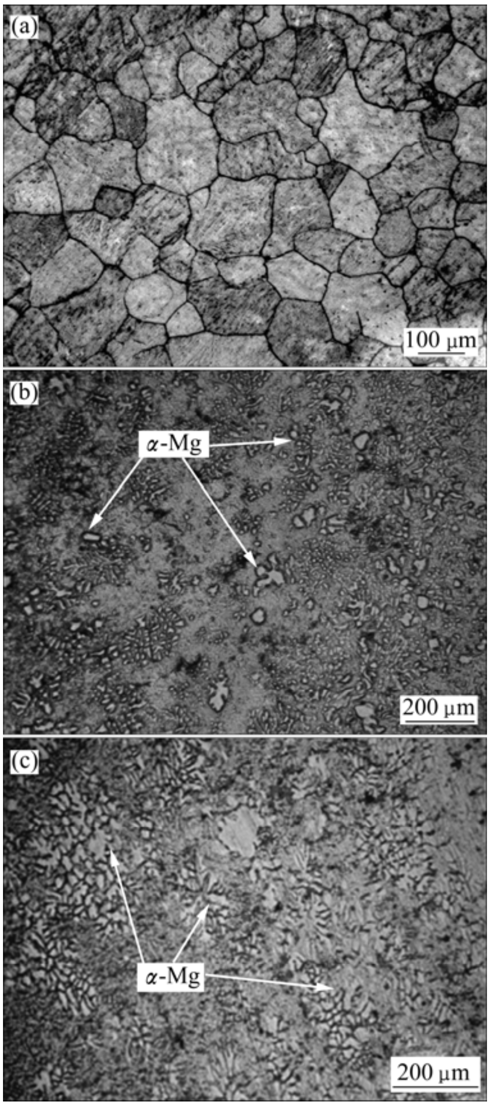

Fig.2 Microstructures of AZ31(a), AZ61(b) and AZ91(c) thin strips

3.3 Effect of addition of Ca on microstructure of AZ31 thin strips

The optical microstructures of AZ31 thin strips containing different additions of Ca are shown in Fig.3. Compared with the microstructure of AZ31 thin strips without the addition of Ca shown in Fig.2(a), the microstructures of the AZ31 thin strips with the addition of Ca, shown in Fig.3, are obviously finer and the size of the grains is reduced. With the increase of the addition of Ca, the grain size of AZ31 thin strips decreases. When the addition of Ca is 0.08%, the grain size is the smallest. But in AZ31 and Mg-5Al alloys prepared by mould casting[15−16], the optimal addition of Ca is more than 0.7% in order to get the finest microstructure. This is different from the result in this work, which may be caused by the higher cooling rate and the deformation stress during vertical twin-roll casting.

Further increasing the addition of Ca would make the grain size enhanced to a certain extent. This result shows that the addition of Ca into the AZ31 alloy has a limited efficiency of the grain refinement, which agrees with the effect of Al-4Ti-5B master alloy on the grain refinement of aluminium alloys[17−19], and there exists an optimal level of the addition of Ca for the AZ31 thin strip. It is also the same as the effect of ZnO particles or Al-4Ti-5B on the grain refinement of Mg-Zn alloy[20] or Mg-3Al-1Zn[21]. Meanwhile, Al_2Ca was found in XRD pattern of the AZ31 thin strip containing 0.08% Ca, shown in Fig.3(e). So, the grain refinement of the AZ31 thin strips may result from the contributions of Al_2Ca and Ca.

It is known that Ca is more chemically active than Mg and the electronegativity difference between Ca and Al is larger. Therefore, when being added into AZ31 melt, Ca has the priority to react with Al and then Al_2Ca compound is formed. On the other hand, the Ca-to-Al mass ratio in AZ31 containing 0.05%−0.15% Ca is 0.017−0.05, much less than 8, therefore, only Al_2Ca is found[22]. In addition, the Ca-to-Al mole ratio is 0.011−0.033, largely less than that in Al_2Ca compound, therefore, the addition of Ca in AZ31 alloy melt will completely react with Al and no Ca is dissolved into Mg matrix. Obviously, the growth restriction factor (GRF)[23] from the addition of Ca has basically no contribution to the grain refinement of AZ31 thin strips.

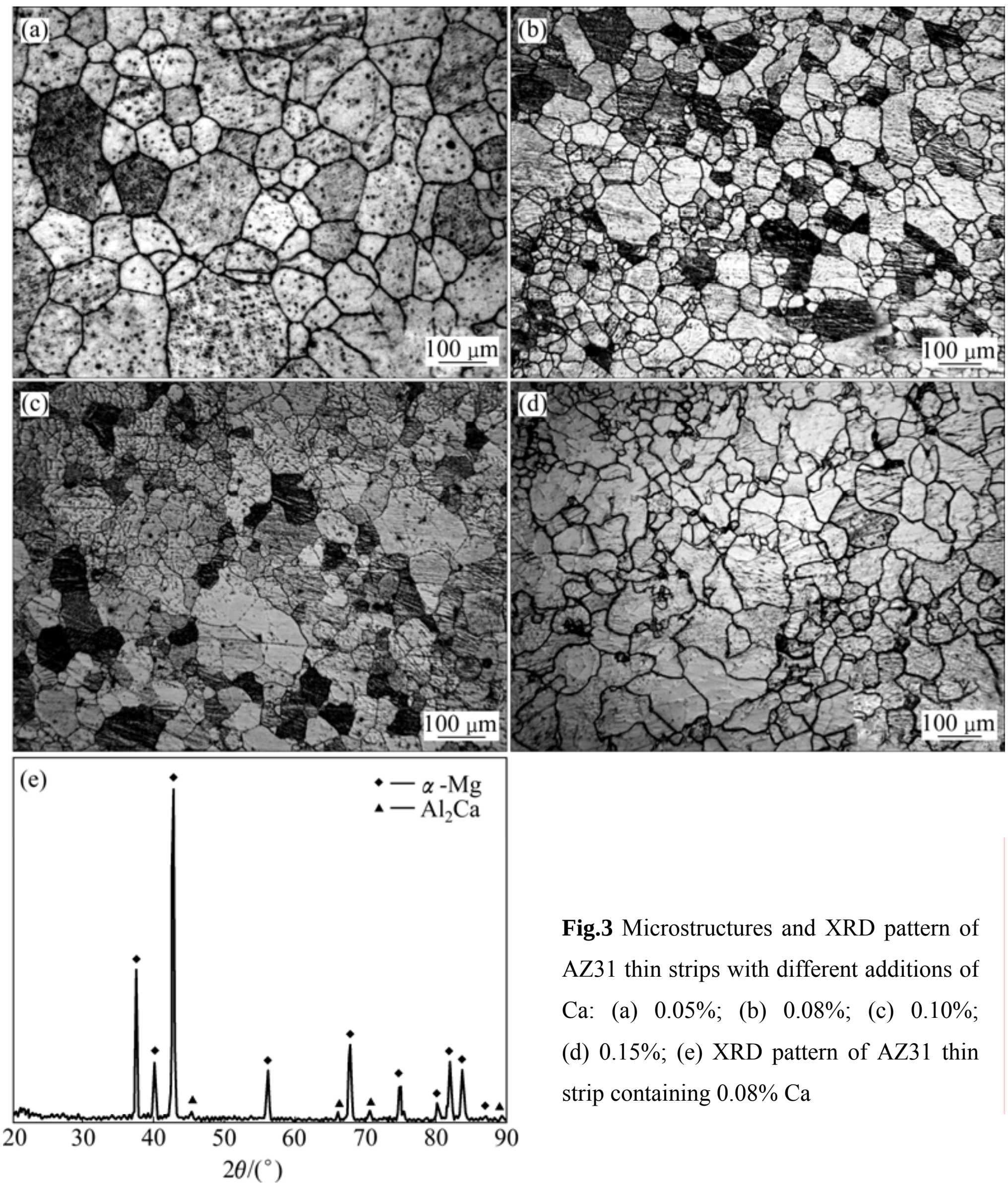

Fig.3 Microstructures and XRD pattern of AZ31 thin strips with different additions of Ca: (a) 0.05%; (b) 0.08%; (c) 0.10%; (d) 0.15%; (e) XRD pattern of AZ31 thin strip containing 0.08% Ca

So, Al_2Ca is probably the main factor for the grain refinement of the AZ31 thin strips. The researches in Refs.[24−25] show that the crystallography matching between an intermetallic compound and Mg matrix can make the compound be the grain refiner when the mismatch of the close or near close packed planes between the compound and Mg matrix is less than 6%. According to the X-ray powder diffraction data, the three close packed planes of Mg are defined as $(10\bar{1}0)$, (0002) and $(10\bar{1}1)$, those of Al_2Ca as (222), (220) and (311). Therefore, there are nine pairs of potential matching planes for Mg and Al_2Ca. The mismatches of the potential matching planes can be defined by the following equation:

$$M=\frac{\left|d_{\mathrm{Mg}}-d_{\mathrm{Al_2Ca}}\right|}{d_{\mathrm{Mg}}}\times 100\% \qquad (1)$$

where d_{Mg} and $d_{\mathrm{Al_2Ca}}$ are respectively defined as the interplane spacing of close packed planes of Mg and Al_2Ca.

According to Eq.(1), the mismatches of the potential matching planes are listed in Table 2. Therefore, there are three pairs of the matching planes for Mg and Al_2Ca marked by the italic because of less than 6% mismatches[25]. As a result, there are some crystallography orientation relationships between Mg and Al_2Ca, but they need to be further studied. These crystallography orientation relationships can make Al_2Ca act as the effective nucleation sites[24] and refine the grains of the AZ31 alloy during twin-roll casting. Therefore, Al_2Ca can be regarded as the heterogenous nucleation site for the grain refinement of the AZ31 thin strips containing Ca.

Table 2 Mismatches of potential matching planes for Mg and Al_2Ca

Potential matching plane	$(10\bar{1}0)_{Mg}/(222)_{Al_2Ca}$	$(10\bar{1}0)_{Mg}/(220)_{Al_2Ca}$	$(10\bar{1}0)_{Mg}/(311)_{Al_2Ca}$	$(0002)_{Mg}/(222)_{Al_2Ca}$	$(0002)_{Mg}/(220)_{Al_2Ca}$	$(0002)_{Mg}/(311)_{Al_2Ca}$	$(10\bar{1}1)_{Mg}/(222)_{Al_2Ca}$	$(10\bar{1}1)_{Mg}/(220)_{Al_2Ca}$	$(10\bar{1}1)_{Mg}/(311)_{Al_2Ca}$
Mismatch/%	16.690	2.037	12.980	11.130	8.853	7.171	5.579	15.650	1.379

4 Conclusions

1) With the increase of Al content, the quantity of surface cracks of AZ31, AZ61 and AZ91 thin strips increases obviously, the surface cracks of AZ31 thin strips are mainly located at the edge of the strip, and those of AZ61 and AZ91 thin strips at the center and edge. The microstructure near the surface cracks in AZ31 thin strips consists of the equiaxed recrystallization grains, and that in AZ61 thin strips consists of coarse dendrites. The addition of Ca into AZ31 thin strips basically has no effect on the quantity and the location of surface cracks, but when the addition is more than 0.10%, the AZ31 alloy melt containing Ca is stuck on the roller, and the surface quality of AZ31 thin strips is worsened.

2) The microstructure of AZ31 thin strips consists of the single α-Mg phase, and that of AZ61 and AZ91 thin strips consists of the primary α-Mg and the Al supersaturated α-Mg, and no β-$Mg_{17}Al_{12}$ compounds appear, because of the high cooling rate of vertical twin-roll casting. Meanwhile, the primary α-Mg in AZ91 thin strips has larger size and more volume fraction because AZ91 alloy has wider solidification range.

3) The addition of Ca into AZ31 alloy can obviously refine the grains of AZ31 thin strips. When the addition is 0.08%, the finest grains can be gotten. Further increasing the addition of Ca can make the grains of AZ31 thin strips grow to some degree. Al_2Ca formed during vertical twin-roll casting is the main factor for the grain refinement of the AZ31 thin strips because of the crystallography relationship between Al_2Ca and Mg matrix.

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