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ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) s331−s335

Transactions of Nonferrous Metals Society of China
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Effects of RE and Sr additions on dendrite growth and phase precipitation in AZ91D magnesium alloy

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Received 23 September 2009; accepted 30 January 2010

Abstract: To develop AZ91D alloys with fine microstructure, effects of the addition of rare earth (RE), Sr and RE + Sr on the dendrite growth and phase precipitation in AZ91D magnesium alloy were studied, respectively. The results show that the microstructure is refined and the morphology of β-$Mg_{17}Al_{12}$ phase is modified with RE or Sr addition, especially with the RE+Sr composite addition which can reduce the average grain size of AZ91D alloy obviously to 141 μm. The needle-like or block-like new phases adhering to β-$Mg_{17}Al_{12}$ phase form at interdendrites during solidification. The enrichment of RE or/and Sr elements in front of the solidification interface, especially at the tips of α-Mg dendrite, which restricts the growth of α-Mg dendrite, changes the preferential growth of α-Mg and finally results in the grain refinement and the blunting of α-Mg dendrite.

Key words: magnesium alloy AZ91D; strontium (Sr); rare earth; grain refinement; precipitation; dendrite growth

1 Introduction

The solidified microstructures, especially the grain size, morphology of dendrite, secondary dendrite arm spacing and precipitates are influencing factors of the properties of as-cast magnesium alloys[1]. Compared with other alloys, magnesium alloys have greater potential to be refined[2] and their properties depend more on the grain size. Therefore, the grain refinement and modification of the morphology of the primary α-Mg are important ways to improve the microstructural uniformity and mechanical properties. Recently, many methods of grain refinement including super-heating [3−4], electromagnetic rheocasting[5−6], thermo-mechanical processing[7], rapid solidification[8−9] etc have been developed for Mg-Al alloys.

In addition, it is found that addition of alloying elements has positive effects on the solidification microstructure and grain refinement[10]. Recently, rare earths (RE) and Sr have become the focus of researchers. Rare earths are important alloying elements to magnesium alloys, which can improve the casting characteristics, high temperature properties and corrosion resistance[11]. WANG et al[12] and PETTERSEN et al [13]. reported the benefit of adding RE elements to magnesium die casting alloys containing aluminium, and suggested that $Al_{11}RE_3$ particles at the grain boundaries were related to the improvement of high temperature creep resistance of AE (Mg-Al-RE)-alloys. According to the research by ZHOU et al[14] and KINJI et al[15], Sr additions could refine the grains of Mg-Al alloys.

However, no systematic research about the effects of Sr and RE composite addition on casting characteristics was reported. In this work, effects of RE, Sr and RE+Sr composite additions on the crystal growth and phase precipitation in AZ91D magnesium alloy were studied and the mechanism was analyzed.

2 Experimental

The experimental alloys were prepared from commercial AZ91D alloy, RE and Al-10Sr (mass fraction, %) master alloy. RE was added in form of cerium-rich misch metal (Ce 50.65%, La 36.52%, Nd 6.38% and Pr 4.78%, mass fraction). AZ91D ingot was melted in an electrical resistance furnace at 750 ˚C with protective atmosphere (0.5% SF_6 + 99.5% CO_2, volume fraction). After the ingot was melted, 0.1% RE or 1% Al-10Sr or 0.1% RE and 1% Al-10Sr (mass fraction) were added to the melts, respectively. Then, the melts

Foundation item: Project(50774075) supported by the National Natural Science Foundation of China; Project(2007CB613705) supported by the National Basic Research Program of China
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were manually stirred for about 5 min and held at 750 ˚C for 30 min. After that, the melts were poured into a steel mold preheated at 200 ˚C to produce bar samples with a size of *d* 40 mm×100 mm.

The microstructures were investigated by optical microscopy and scanning electron microscopy (SEM) equipped with energy-dispersive spectrometry (EDS). Grain sizes were measured by SISCIAS8.0 software after the samples were solid solutionized at 400 ˚C for 20 h.

3 Results and discussion

3.1 Microstructure of alloys

Figs.1 and 2 indicate the influences of RE and Sr additions to AZ91D alloys on the grain size. It was found that the RE and Sr additions, especially RE and Sr composite addition, refined the grains of AZ91D alloy significantly. Addition of 0.1% RE and 1% Al-10Sr reduced the grain sizes of AZ91D alloy from about 1 140 to 290 and 230 μm, respectively. When 0.1% RE and 1% Al-10Sr were added together, the average grain size of AZ91D alloy obviously decreased to 141 μm, as shown in Fig.2.

According to Mg-RE and Mg-Sr phase diagram, the solubility of RE and Sr in Mg is low. The solidification processes belong to non-equilibrium freezing due to the high solidification rates. During the solidification, the primary *α*-Mg crystals first formed and grew, and the remaining Sr or RE solute atoms in the melts diffused to the liquid/solid interface, restricting the grain growth. Therefore, the RE, Sr and RE+Sr composite additions, especially the RE+Sr composite addition, contribute to significant grain refinement of AZ91D alloys as illustrated in Figs.1 and 2.

Fig.3 shows the influence of RE and Sr addition on the morphology of primary phase. AZ91D alloy showed a typical equiaxed dendrite structure and the primary phase presented a six-fold symmetrical shape. RE and Sr additions made the primary phase transform from the six-fold symmetrical shape to a petal-like shape, where less developed dendrites showed radiating structure growing from the grain centers to grain boundaries. Especially, when RE and Sr were added simultaneoustly, the primary *α* phase became blunted and the secondary dendrite almost disappeared.

During the growth of the primary phase contrasted with Mg, Sr or RE solute atoms are easier to concentrate at the tips of dendrites with high curvature, which depresses their growing predominance. Because of this, the preferred growth manner of the primary crystal is depressed and *α*-Mg dendrites are blunted by RE or Sr or RE+Sr composite additions, as shown in Fig.3.

3.2 Morphology and distribution of *β*-$Mg_{17}A1_{12}$ and precipitates

The microstructure of AZ91D alloy was composed

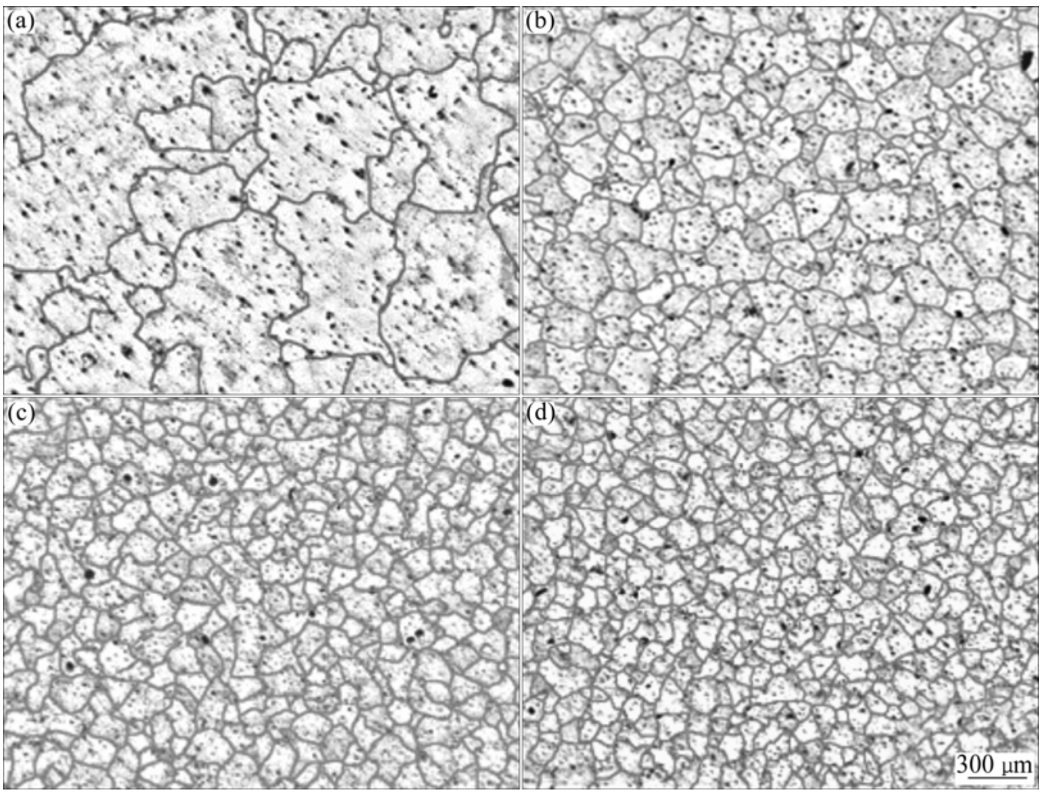

Fig.1 Microstructures of AZ91D alloy (a) and AZ91D alloys with addition of 0.1% RE (b), 0.1% Sr (c) and 0.1% RE + 0.1% Sr (d) after solution-treatment at 400 ˚C for 20 h

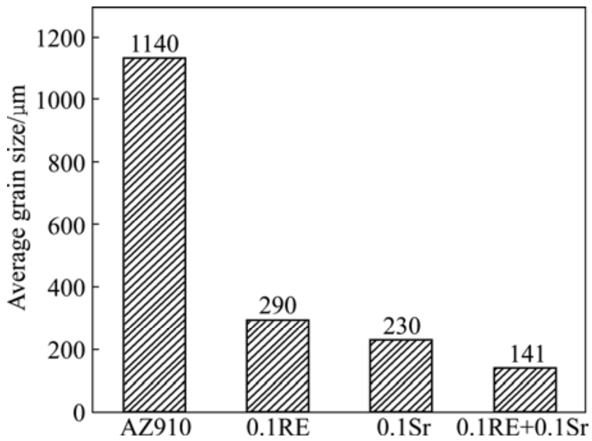

Fig.2 Average grain sizes of AZ91D alloys with different additions

of the primary α-Mg and β-$Mg_{17}Al_{12}$ phase that precipitated along interdendries. Fig.4 shows the morphology and distribution of the β-$Mg_{17}Al_{12}$ phase in the alloys. As shown in Fig.4, with the addition of RE or RE and Sr, the volume fraction of β-$Mg_{17}Al_{12}$ phase decreased obviously, the β-$Mg_{17}Al_{12}$ phase became finer and its distribution was more dispersive. However, β-$Mg_{17}Al_{12}$ phase in AZ91D alloy with Sr addition turned coarse and continuous due to the fact that Al element was added in the form of Al-10Sr.

In Fig.5, it was found that addition of Sr and RE resulted in the formation of some pole-like or block-like new phases adhering to the β-$Mg_{17}Al_{12}$ phase during the solidification of AZ91D alloys. Table 1 shows the composition analysis result by EDAX in Fig.5. It was indicated that position A and E were enriched with Al, RE and Mn, which were supposed to be composed of Al_4RE compound[16] and O-Al-Mn compound. Position B was enriched with RE, which was supposed to be Al_4RE. Position C was supposed to be Al_4Sr[14] because it was enriched with Al and Sr. Positions D and F were supposed to be O-Al-Mn compound due to its enrichment of O, Al and Mn. Therefore, the RE and Sr additions resulted in the formation of Al_4RE and Al_4Sr compound, respectively.

At the end of solidification, the RE and Sr contents were rich along interdendrites, resulting from the segregation of these elements. RE or Sr atoms combined with Al atoms as precipitates along the grain boundaries. The formation of Al_4RE or Al_4Sr consumed some aluminum atoms, which greatly reduced the amount and size of β-$Mg_{17}Al_{12}$ phase, as shown in Fig.4. However, β-$Mg_{17}Al_{12}$ phase in AZ91D alloy with addition of Sr appeared continuous due to the fact that Al element was added in the form of Al-10Sr alloy which promoted the formation of β-$Mg_{17}Al_{12}$ phase.

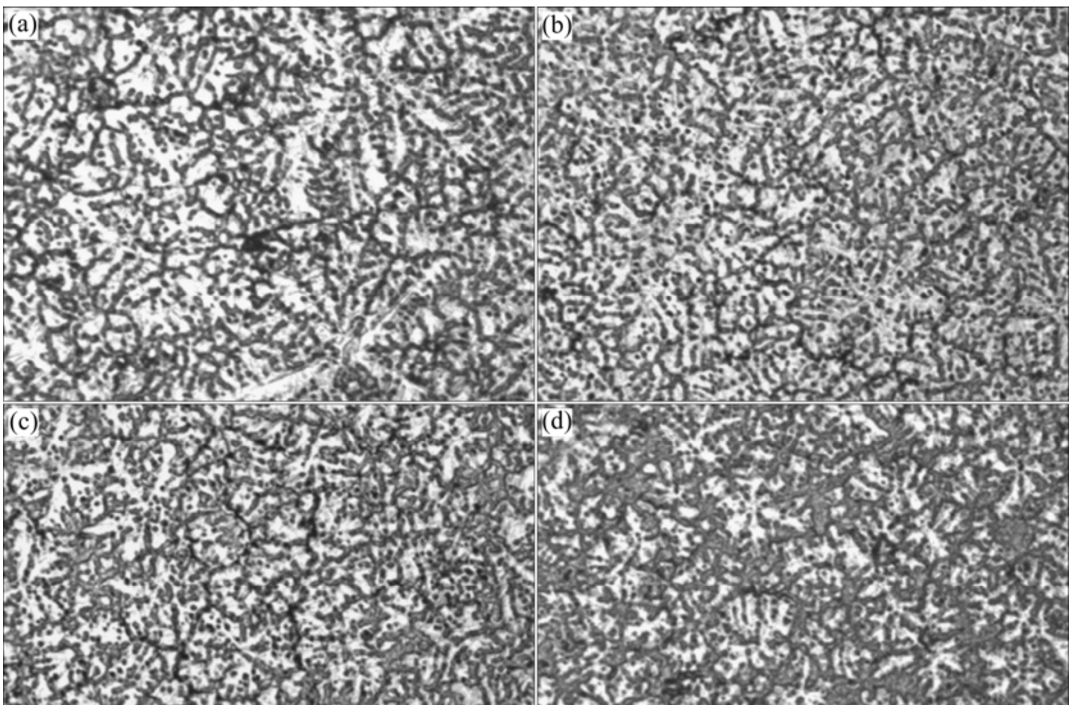

Fig.3 As-cast morphologies of primary α-Mg in AZ91D alloy (a) and AZ91D alloys with addition of 0.1% RE (b), 0.1% Sr (c) and 0.1% RE + 0.1% Sr (d)

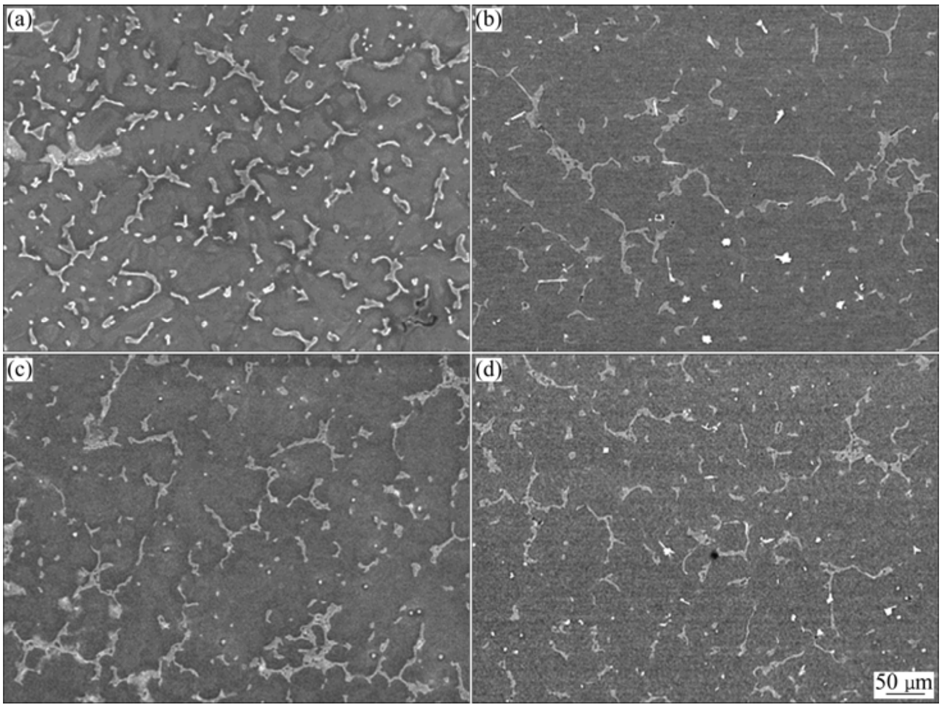

Fig.4 SEM images of β-$Mg_{17}Al_{12}$ phase in as-cast AZ91D alloy (a) and AZ91D alloys with addition of 0.1% RE (b), 0.1% Sr (c) and 0.1% RE + 0.1% Sr (d)

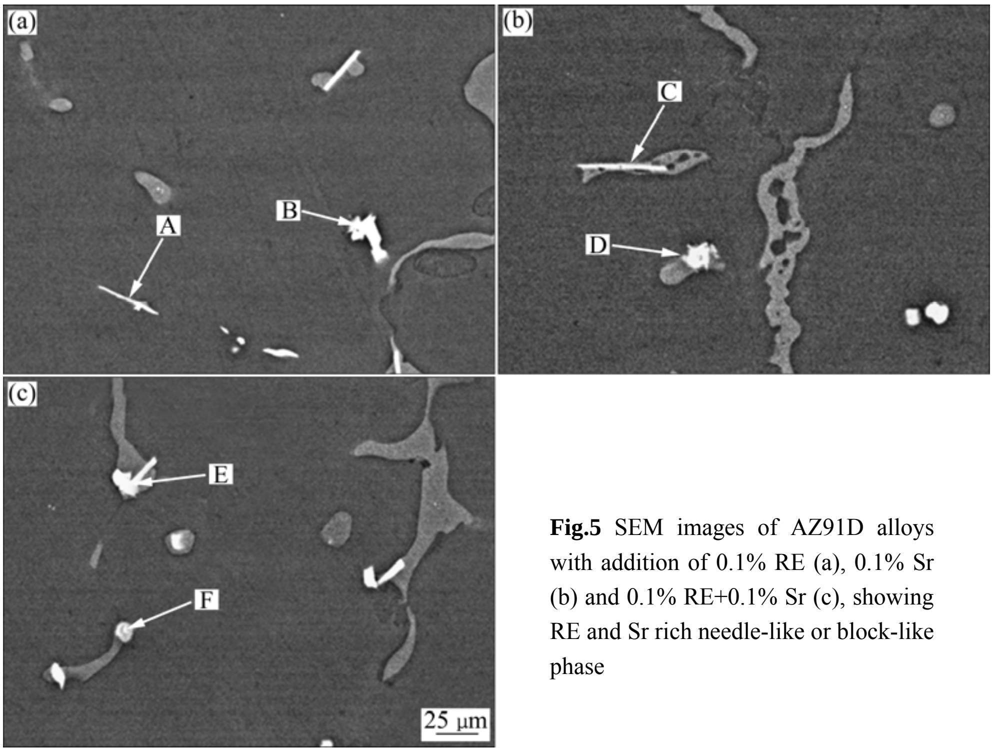

Fig.5 SEM images of AZ91D alloys with addition of 0.1% RE (a), 0.1% Sr (b) and 0.1% RE+0.1% Sr (c), showing RE and Sr rich needle-like or block-like phase

4 Conclusions

1) The enrichment of RE or/and Sr elements at solidification interface front, especially at the tips of α-Mg dendrites, restricts the growth of α-Mg dendrite and changes the preferential growth of α-Mg, which results in the grain refinement and the blunting of α-Mg dendrites.

2) The RE and Sr additions to AZ91D alloy contribute to the formation of Al_4RE and Al_4Sr phases adhering to the β-$Mg_{17}Al_{12}$ phase, which consumes Al element and consequently greatly reduces the amount and size of β-$Mg_{17}Al_{12}$ phase.

Table 1 Chemical compositions of needle-like or block-like phases in Fig.5 (mole fraction, %)

Position	O	Mg	Al	Mn	Sr	Ce	Nd	La	Zn
A	7.68	13.28	48.75	25.91	0	3.06	0.45	0.87	0
B	2.07	61.51	31.50	0	0	2.10	0.28	1.30	1.06
C	0	54.87	34.36	0	10.56	0	0	0	0
D	39.09	10.43	30.78	19.75	0	0	0	0	0
E	8.66	17.99	55.45	15.58	0	2.52	0	0	0
F	34.98	13.54	30.38	21.08	0	0	0	0	0

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(Edited by FANG Jing-hua)