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As-cast microstructure of Al-Zn-Mg and Al-Zn-Mg-Cu alloys added erbium ①

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Abstract: The effects of different contents of rare earth element, and erbium, on the as-cast microstructures of Al-6Zn-2Mg and Al-6Zn-2Mg-1.8Cu alloys were studied by optical microscopy, scanning electron microscopy, X-ray diffractometry, transmission electron microscopy and EDS analysis. The results show that the netlike structure of as-cast alloys can be remarkably refined, and the distance of dendritic structure decreases, with Er addition. However, the improvement results on Al-Zn-Mg-Cu are not better than that of Al-Zn-Mg. Er and Al can interact to form Al_3Er phase, which is coherent with α(Al) matrix, with trace Er addition to the Al-Zn-Mg alloy. The refinement effect of Al-Zn-Mg alloys is familiar with the formation and precipitation of coherent Al_3Er phases. The ternary compound AlCuEr, similar with AlCuSc phase, will form when Er is added to Al-Zn-Mg-Cu alloy, which suppresses the formation of Al_3Er phase and doesn't solve in the following heat treatment.

Key words: Al-Zn-Mg alloy; Al-Zn-Mg-Cu alloy; rare earth; Er; microstructure; aluminum alloy; refinement
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1 INTRODUCTION

Many researches show that the properties of aluminum and its alloys can be remarkably improved with reasonable rare earth additions. The actions of rare earth elements in the aluminum alloys consist in alterant-agent, micro-alloying and so on[1-3]. By far element scandium is the most effective rare earth element which improves the aluminum alloys properties[4-6]. However, the price of scandium is very high. Therefore, it's very essential to find a new rare earth element, which acts on the aluminum alloys like or better than element Sc, chiefly, whose price is relatively low. The research team composing of the author, has done many researches with regard to the erbium effects on the high pure aluminum and Al-Mg alloys[7-9]. The research results show that Er has quite a few positive and resemblance effects like element Sc and its price is only 1/40 as that of Sc (Year 2001). So far the literatures and reports about the effect of element Er on the aluminum and aluminum alloys are quite few. The effects of Er on the as-cast microstructure of Al-6Zn-2Mg and Al-6Zn-2Mg-1.8Cu alloys, and the interaction of Er with the primary elements of aluminum alloys were mainly investigated in this paper. A good reference for developing new kinds of rare earth aluminum alloys with excellent performance is provided.

2 EXPERIMENTAL

Four kinds of different experimental alloys were prepared, whose chemical components were measured by ICP-AES analytical method, as listed in Table 1.

Table 1 Chemical components of experimental alloys(mass fraction, %)

Alloy No.	Zn	Mg	Cu	Er	Al
1	5.92	1.90	0	0	Bal.
2	5.62	1.74	0	0.38	Bal.
3	6.17	1.88	1.84	0	Bal.
4	5.91	1.81	1.78	0.22	Bal.

Apart from aluminum, zinc and magnesium, the other alloying elements were added using master alloys. Melting was carried out with a graphite crucible in a common type crucible furnace, with melting temperature of 740-800 ℃. Samples for optical microscope observation were mechanically polished and etched by Kellor reagent, and the observation, analysis and photograph were done on Olympus-PMG3 optical microscope.

The existing states of phases and effects of

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trace Er on the microstructure of Al-Zn-Mg (-1.8Cu) alloys, were investigated using BRUKER D8 X-ray diffractometer, FEI/QUANTA 200 scanning electron microscope, JEM2010 transmitting electron microscope and energy spectrum analysis.

3 RESULTS

3.1 Phases of experimental alloys

The XRD patterns of the four different kinds of as-cast alloys are shown in Fig. 1.

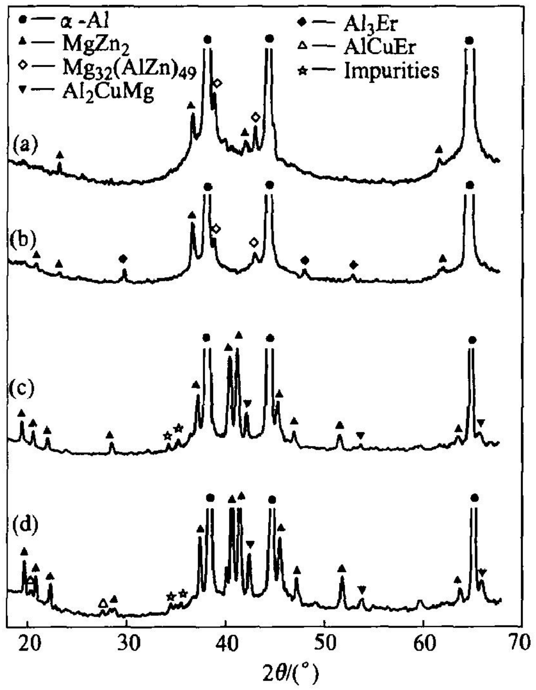

Fig. 1 XRD patterns of experimental alloys
(a) —Alloy 1; (b) —Alloy 2;
(c) —Alloy 3; (d) —Alloy 4

It can be seen from Fig. 1 that owing to alloys 1 and 3 belonging to the hard aluminum, their typical phases are almost the same, the former including three phases, α-Al, Zn_2Mg and Mg_{32}(Al, Zn)$_{49}$, besides few impurities and yet in the latter Al_2CuMg substitutes for the Mg_{32}(Al, Zn)$_{49}$. However, for alloy 2 with Er addition, besides the above-mentioned basic phases, Al_3Er phase can be observed. Yet for alloy 4 with Er addition, no Al_3Er is found, while a new ternary phase AlCuEr can be rooted out, which came into being during the melting body crystallization. The effects of AlCuEr on the alloys are familiar with the known AlCuSc, a low melting point eutectic compound.

3.2 Effects of Er on microstructure of experimental alloys

For better observation of effects of Er, optical microscope was carried out. The as-cast microstructures of four kinds of experimental alloys are shown in Fig. 2.

It can be seen that the sizes of the dendritic structure of alloys 1(Fig. 2(a)) and 3 (Fig. 2(c)), without Er addition, are rather bigger and the grains are coarse. Comparatively, respectively with 0.38% Er and 0.22% Er, the sizes of the dendritic structure of alloys 2(Fig. 2(b)) and 4(Fig. 2(d)) remarkably decrease and the grains become rather smaller. Furthermore, the effect of Er on the former alloy (Al-Zn-Mg) is much better than the latter one (Al-Zn-Mg-Cu). From these results, one can see that the rare earth element Er really has refining and modifying effects on the microstructures of the Al-Zn-Mg (-Cu) alloy.

At the same time, some compounds exist in the grain boundary of the as-cast microstructures of alloys 2(Fig. 2(b)) and 4 (Fig. 2(d)), and that there are a few small particles distributing within the grains of (Al-Zn-Mg) alloy 2. The SEM images of the two kinds of alloys containing Er are shown in Fig. 3. It can be seen that some shinning piece-like phases locate on the boundaries, and shinning round particles within the grains, of alloy 2(Fig. 3(a), arrow mark). Besides, there are some shinning stick-like phases situating on the grain boundaries of alloy 4 (Fig. 3(b), arrow mark). Depending on the energy spectrum analysis (Figs. 3(c), 3(d)), it is indicated that there are only three elements, Al, Cu and Er in the shinning stick-like particles, and yet Al, Er in the piece-like phases and round particles. Combined with the X-ray diffraction analysis, it can be concluded that stick-like particles is the AlCuEr ternary phase, and those piece-like phases and round particles are Al_3Er phases.

3.3 TEM observation of alloys

TEM photographs of solid solution alloys are listed in Fig. 4. One can see that alloys 1 and 3 without Er are quite neat, for almost precipitated phases have solved in the α(Al) solid solution, which can be determined from the SAD patterns (Figs. 4(a) and (c), right upper corner). Whereas, for alloy 2 with Er addition, there are some bigger and accumulating second-phases particles, which can be regarded as the Al_3Er particles (Fig. 4(b)) precipitating from the supersaturated solid solution, based on the SAD patterns (Fig. 4(b), right upper corner) and Ref. [10]. Although Al_3Er phases gradually lose the coherency with the Al matrix, they can still hinder the movement of grain boundary or sub-boundary in a certain extent. Yet for alloy 4 likewise Er addition, a huge rectangle compound (Fig. 4(d)) is found within the matrix, which is regarded as the AlCuEr ternary phase whose construction presently is unknown, through the energy spectrum analysis (Fig. 4(e)).

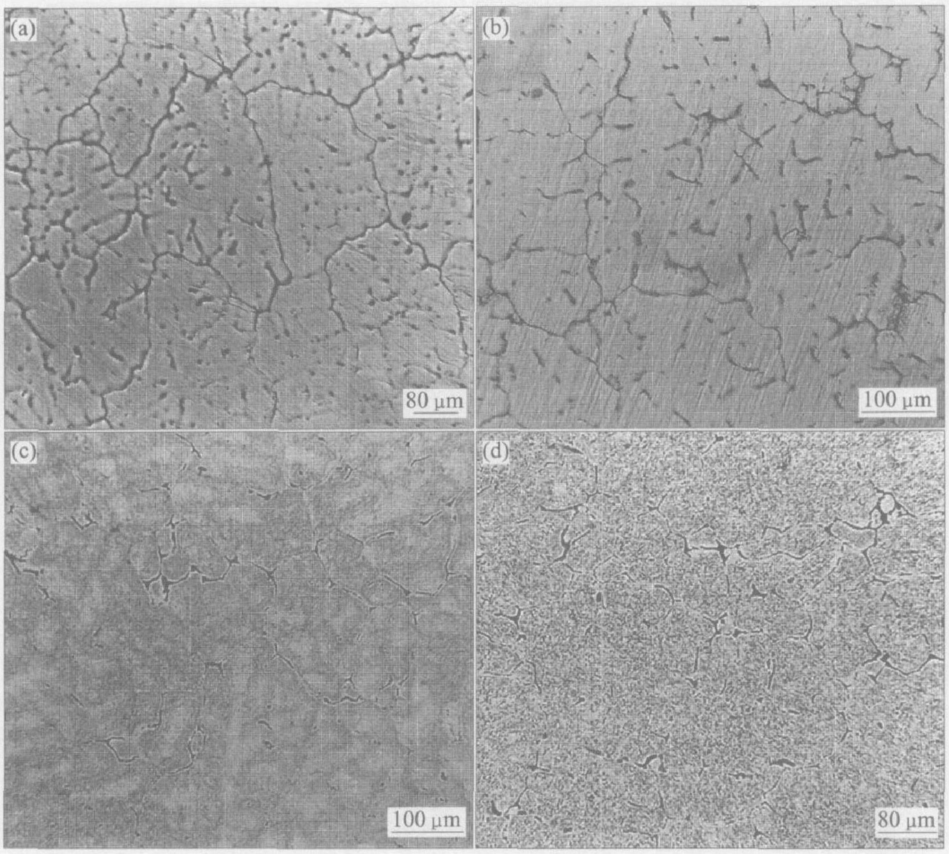

Fig. 2 Optical micrographs of as-cast experimental alloys
(a) —Alloy 1; (b) —Alloy 2; (c) —Alloy 3; (d) —Alloy 4

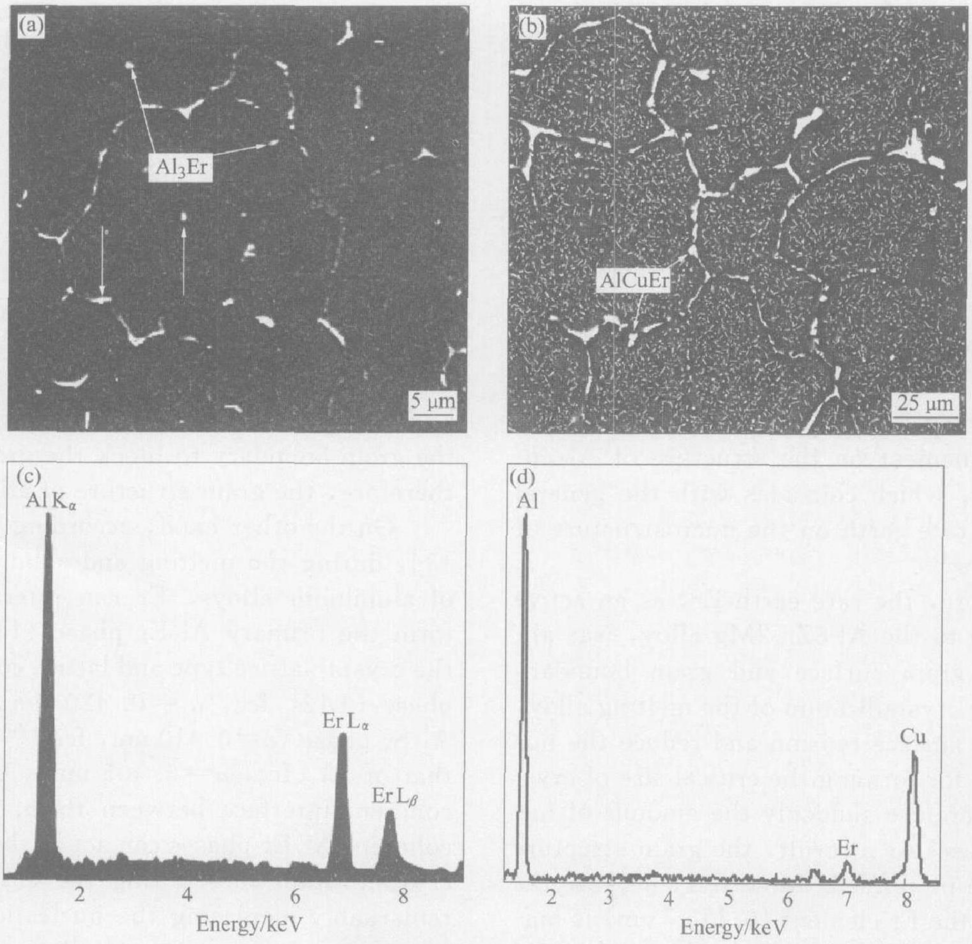

Fig. 3 SEM micrographs of as-cast alloys 2 and 4 and energy spectrum analysis results
(a) —Alloy 2; (b) —Alloy 4; (c) —Fixed-point EDS pattern of Fig. 3(a); (d) —Fixed-point EDS pattern of Fig. 3(b)

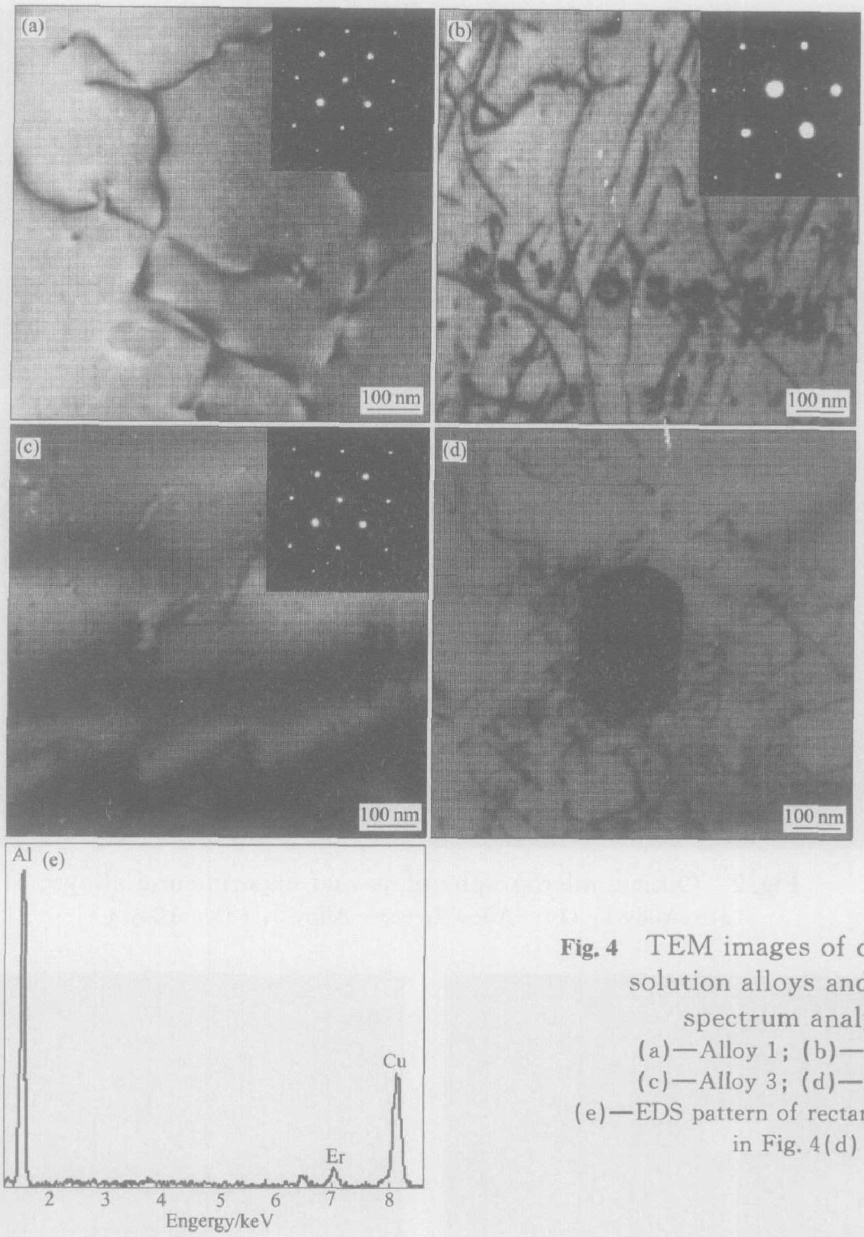

Fig. 4 TEM images of different solid solution alloys and energy spectrum analysis
(a)—Alloy 1; (b)—Alloy 2; (c)—Alloy 3; (d)—Alloy 4; (e)—EDS pattern of rectangle compound in Fig. 4(d)

4 DISCUSSION

It can be seen from Fig. 2 that Er has really remarkable refinement on the structure of Al-Zn-Mg(-Cu) alloy, which coincides with the general effects laws of rare earth on the microstructure of aluminum alloys[11].

What's more, the rare earth Er, as an active element, added to the Al-6Zn-2Mg alloy, was absorbed to the grain surface and grain boundary edge during the crystallization of the melting alloy, to decrease the surface tension and reduce the nucleating energy for forming the critical size of crystal nucleus, therefore suddenly the amount of nucleation increases. As a result, the grain structure of the alloy can be refined. Moreover, because the atom radius of the Er element (0.175 7 nm) is bigger and the solid solubility of Er in the α(Al) solid solution is too much lower, based on the absorption relation between the solid solubility and grain boundary, the lower solid solubility of the solute, the easier to be absorbed to the grain boundary[12], so Er, which dispersedly distributes, segregates to the grain boundary to block the growth of grains, therefore, the grain structure of alloys is refined.

On the other hand, according to Refs. [3, 5, 13], during the melting and solidification process of aluminum alloys, Er can interact with Al to form the primary Al_3Er phase (Fig. 3). Because the crystal lattice type and lattice constant of Al_3Er phase (L12, fcc, a = 0.420 nm), similar with Al_3Sc phase (a= 0.410 nm, fcc)[14], is a match for that of Al (fcc, a= 0.405 nm), thereby, having coherent interface between them. These primary coherent Al_3Er phases can act as the heterogeneous crystallization core during the crystal formation, remarkably increasing the nucleation ratio, to refine the grain structure of alloys. Moreover, the rare earth elements have a much lower solid solubility in the aluminum alloy, hardly solving in the α(Al) matrix, accordingly, the rare earth element will gather in the front edge of the solid liquid interface during the crystallization process, what with the restriction of non-equilibrium freezing of alloys, to decrease the distance of arborescent structure.

Just as mentioned above, the effect of Er on the Al-6Zn-2Mg-1.8Cu alloy is much worse than that of the Al-6Zn-2Mg alloy. It may be that Er interacts with Al, Cu to form the AlCuEr ternary phase, which might be connected with the Cu/Er ratio and is similar with AlCuSc phase, even as the formation of AlCuSc compound related to the Cu/Sc ratio[15, 16], during the process of solidification, when Er is added to the aluminum alloys containing Cu. So the Er concentration in the melt is very poverty due to the formation of AlCuEr phase and the electronegative action between Er and Cu atom becomes much greater, resulting in that it's not enough for element Er to form Al_3Er phase. Moreover, the high strengthening aluminum alloy belongs to the alloy whose alloying is much higher, and the other alloying agent of Al-6Zn-2Mg-1.8Cu alloy can reduce the solid solubility of Er in the α(Al) matrix, and the addition amount of element Er is low (0.22%), for as much as these, Al_3Er phase can't form.

5 CONCLUSIONS

1) With rare earth Er added to the Al-6Zn-2Mg alloy, the Al_3Er, which has rather good coherency with α(Al) matrix, acting as heterogeneous crystallization core, have better crystalloblastesis effect, as a result, the grain structure is dramatically refined and the distance of dendrite arm structure decreases.

2) The effects of Er on the super-high strengthening alloy is not better than that of the hard aluminum. The reason is that the formation of the discontinuous distribution of AlCuEr leads to the Er concentration leanness in the melt, inhibiting the formation of Al_3Er phases. AlCuEr compound, similar with the ternary AlCuSc, belongs to the low melting point eutectic compound, and doesn't solve in the following heat treatment.

3) The ternary compound AlCuEr forms when Er is added to Al-Zn-Mg-Cu alloy, which induces decrease in the solid solubility amount and is harmful to the strength of the alloy.

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