Effect of trace rare earth element Er on Al-Zn-Mg alloy

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Abstract: Al-6Zn-2Mg and Al-6Zn-2Mg-0.4Er alloys were prepared by cast metallurgy. The effects of trace Er on the mechanical properties, recrystallization behavior and age-hardening characteristic of Al-Zn-Mg alloy were studied. The effect of Er on microstructures was also studied by OM, XRD, SEM, EDS and TEM. The results show that the addition of Er on Al-6Zn-2Mg alloy is capable of refining grains obviously. The addition of Er can improve the strength considerably by strengthening mechanisms of precipitation and grain refinement. With the addition of Er into Al-6Zn-2Mg alloy, the aging process is quickened and the age-hardening effect is heightened. Er additive can retard the recrystallizing behavior of Al-6Zn-2Mg alloy and cause the increase of recrystallization temperature due to the pinning effect of fine dispersed Al_3Er precipitates on dislocations and subgrain boundaries.

Key words: erbium(Er); Al-Zn-Mg alloy; Al_3Er; precipitation strengthening; fine grain strengthening; mechanical properties; recrystallization

1 Introduction

Remarkable effects of rear-earth elements on aluminium alloys, such as eliminating impurities, purifying melt, refining as-cast structure, retarding recrystallization and refining precipitated phases, have been widely researched for a long time[1−3]. But most of those studies focused on their metamorphism and the application of misch metal to aluminium alloys[4,5]. The action mechanism of single rare earth element in aluninium alloys is scarcely studied and the only study is restricted to La, Ce, Y and Sc and especially to Sc, while the effects of other single elements are scarcely referred[6]. There are also some studies dedicated to the influences of rare-earth on superplasticity and texture of Al-Zn-Mg alloys[7, 8], but the effects of single element Er on Al-Zn-Mg alloys are absent. In this paper, Er is added to Al-Zn-Mg alloys and the effects of trace Er on the mechanical properties, recrystallization behavior, age-hardening characteristic and microstructures of Al-Zn-Mg alloy have been studied. The action mechanism of Er in Al-Zn-Mg alloys is also discussed.

2 Experimental

The alloys are prepared by cast metallurgy with high purity aluminium (99.99%), industrially pure zinc (99.9%), industrially pure magnesium (99.9%), and master alloy Al-6.2Er. The chemical composition of the alloys is tested using LEEMAN SPEC-E atomic emission optical spectrometer and the results are shown in Table 1. Al-6Zn-2Mg and Al-6Zn-2Mg-0.4Er will be referred to as Al-Zn-Mg and Al-Zn-Mg-0.4Er respectively.

Table 1 Chemical composition of alloys (mass fraction, %)

Alloy	Zn	Mg	Er	Al
Al-6Zn-2Mg	5.28	1.78	0	Balance
Al-6Zn-2Mg-0.4Er	5.65	1.71	0.37	Balance

Crucible-type electrical resistance furnace was used to melt the alloys at 780 . The melt was cast by a steel mould. The as-cast alloys were homogenized at 470 for 24 h, then top cropped, face milled, hot rolled and

subsequently cold rolled with the reduction amount to 60%. The experimental alloys were solution treated at 470   for 30 min and aged at 120   for different times in salt-bath furnace. Annealing was conducted in box-type electrical resistance furnace for 1 h. The hardness of the experi- mental alloys was tested using HBWUV-187.5 hardnessmeter, the tension test was completed on MTS810 material testing machine. The samples for metallographic examination were electrolytically polished and anodized and observed in polarized light on NEOPHOT-21 metallographic microscope. Phase analysis of as-cast alloys was completed on D/MAX-3C rotary-target X-ray diffractometer. The distribution of the second-phases in as-cast alloys was observed on HITACHI S-650 scanning electron microscope and EDS was performed to measure the constitution of the second- phase qualitatively. Thin foils for TEM were prepared by twin jet polishing in a 70% carbinol plus 30% nitric acid solution. The thin foils were observed in H-800 TEM.

3 Results

3.1 Effect on mechanical properties

Tensile properties of the experimental alloys are shown in Table 2. It can be concluded that the addition of Er improves the strength of as-cold rolled alloys and as-aged alloys. The elongation is somewhat decreased, but still remains on a high level.

Table 2 Tensile properties of experimental alloys

Alloy	Cold rolled			470 , 30 min+ 120 , 30 h		
	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%
Al-6Zn-2Mg	349	286	8.71	422	379	10.96
Al-6Zn-2Mg-0.4Er	449	388	6.98	495	463	9.95

3.2 Effect on precipitation hardening

The experimental alloys were solution treated at 470   for 30 min, and then aged at 120   for different times. Fig.1 shows the variation of hardness with aging time. The hardness increases and the aging time decreases with the addition of 0.4%Er.

3.3 Effect on recrystallization temperature

The recrystallization temperature of the experimental alloys is tested by hardness-metallurgy. First the HBS of the alloys annealed at different temperatures was tested, the curves of the hardness as functions of annealing temperatures are shown in Fig.2, where T_s represents the starting temperature of the recrystallization and T_f the finishing temperature.

Through the optical microstructures of the recrystallized alloys (Fig.4), the recrystallization temperature of Al-Zn-Mg-0.4Er is 320−390   , which is improved by 40−60   when compared with that of Al-Zn-Mg alloys 280−330   . The improvement indicates that the addition of Er retards the recrystallization of the Al-Zn-Mg alloy.
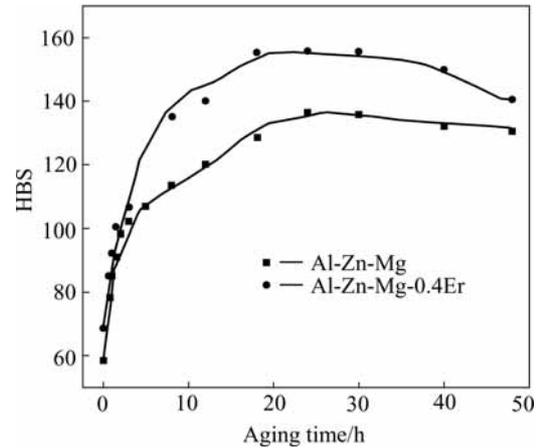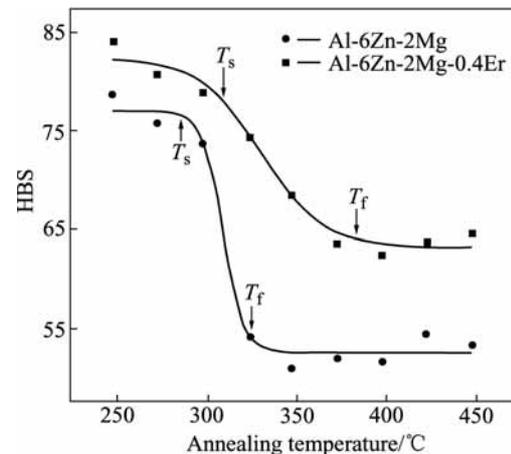

Fig.1 Variation of hardness with aging time

Fig.2 Variation of hardness with annealing temperature

3.4 Effect on microstructure

1) Optical microstructure(OM)

Fig.3 shows the optical micrographs of the as-cast and as-homogenized alloys. It can be seen that the dendritic structure of the Al-Zn-Mg alloy is severe and the grain is coarsening relatively (Fig.3(a)). While the microstructure of the as-cast Al-Zn-Mg-0.4Er alloy is fine equiaxial grains (Fig.3(b)), almost all of the dendritic structure is eliminated and the average grain size decreases by more than 10 times. After annealed, while the dendritic structure of the Al-Zn-Mg alloy is eliminated, its grains remain large (Fig.3(c)). The grains of Al-Zn-Mg-0.4Er alloy is very fine (Fig.3(d)). So the addition of Er to Al-Zn-Mg refines both the as-cast and the annealed microstructures remarkably.
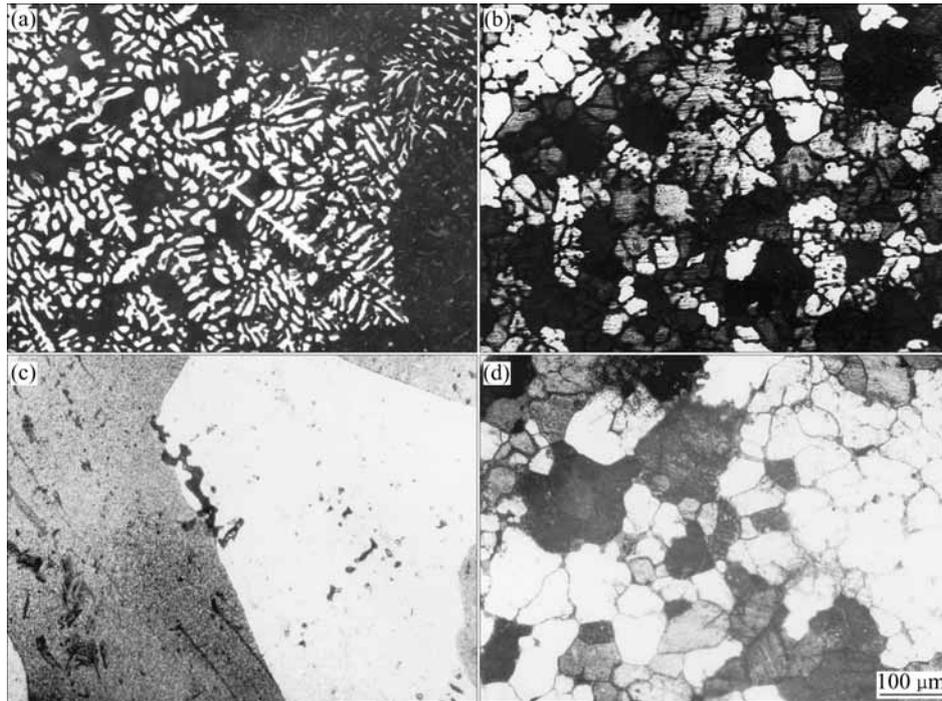
Fig.3 Optical micrographs of as-cast and as-homogenized alloys: (a) Al-Zn-Mg, as-cast; (b) Al-Zn-Mg-0.4Er, as-cast; (c) Al-Zn-Mg, as-homogenized; (d) Al-Zn-Mg-0.4Er, as-homogenized
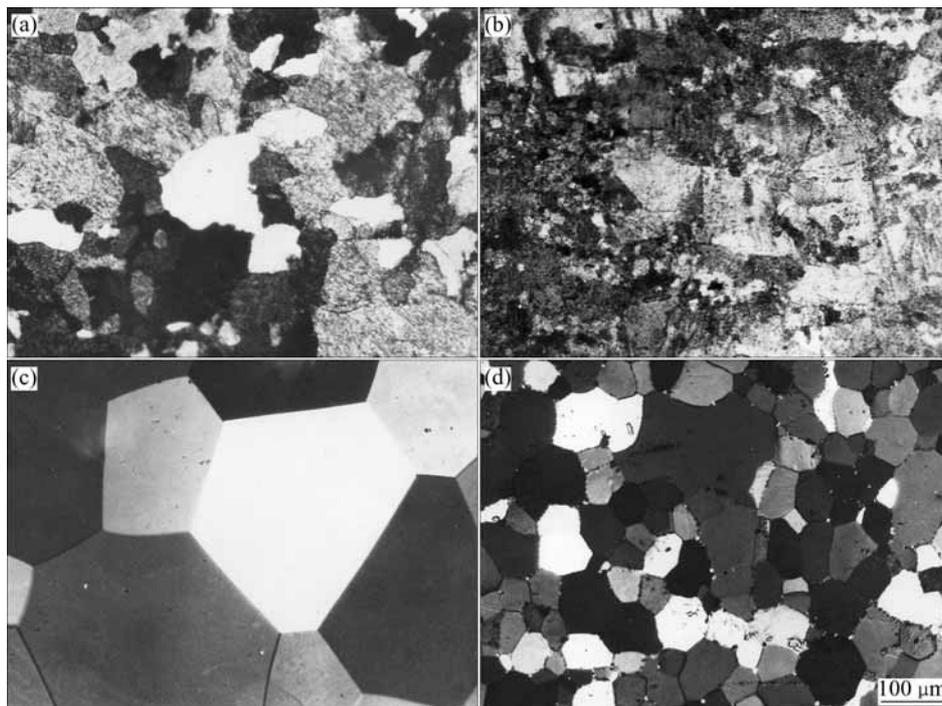

Fig.4 Optical micrographs of alloys annealed for 1 h at different temperatures: (a) Al-Zn-Mg, 350   ; (b) Al-Zn-Mg-0.4Er, 350   ; (c) Al-Zn-Mg, 450   ; (d) Al-Zn-Mg-0.4Er, 450

The optical micrographs of the alloys annealed for 1 h at different temperatures are shown in Fig.4. The recrystallization has finished in the Al-Zn-Mg alloy annealed at 350   for 1 h and its microstructure has changed to equiaxial grains (Fig.4(a)), while after the same treatment, the recrystallization of the Al-Zn-Mg-0.4Er has only begun and some of the worked microstructure remains (Fig.4(b)). After   annealing at 450   for 1 h, the grains of Al-Zn-Mg alloy are coarse (Fig.4(c)); while in the Al-Zn-Mg-0.4Er alloy, the recrystallization has completed and the microstructure remains fine equiaxial grains (Fig.4(d)), which is much smaller than that of the Al-Zn-Mg alloy. Therefore the optical micrographs and the hardness testing results

(Fig.2) are consistent, which indicates that the addition of Er not only retards the recrystallization and improves recrystallization temperature, but also refines the recrystallization microstructure.

2) X-ray diffraction and SEM(EDS)

The X-ray diffraction patterns of the as-cast alloys are shown in Fig.5. It is found that the microstructure of the as-cast Al-Zn-Mg alloy is mainly composed of the following phases: α(Al), $MgZn_2$, Mg_{32}(Al, Zn)$_{49}$ (Fig.5(a)). The Mg_{32}(Al, Zn)$_{49}$ is an unstable phase based on T phase and it is similar to T phase[9−11]. In Al-Zn-Mg-0.4Er alloy, besides the three phases referred to the above, the Al_3Er phase is present(Fig.5(b)). In the SEM micrograph of Al-Zn-Mg-0.4Er alloy (Fig.6(a)), there are some elliptic or dendritic particles which are of the same color and have the size of 3−5 μm. In EDS the constitution of these particles is composed of two elements: Al and Er. The combination of the EDS and the X-ray diffraction pattern can confirm that these particles are Al_3Er.

3) TEM observation and analysis

TEM was used to observe the existing form and distribution of Er in Al-Zn-Mg alloy and Fig.7 shows the results. It is clear that in the as-cast Al-Zn-Mg-0.4Er
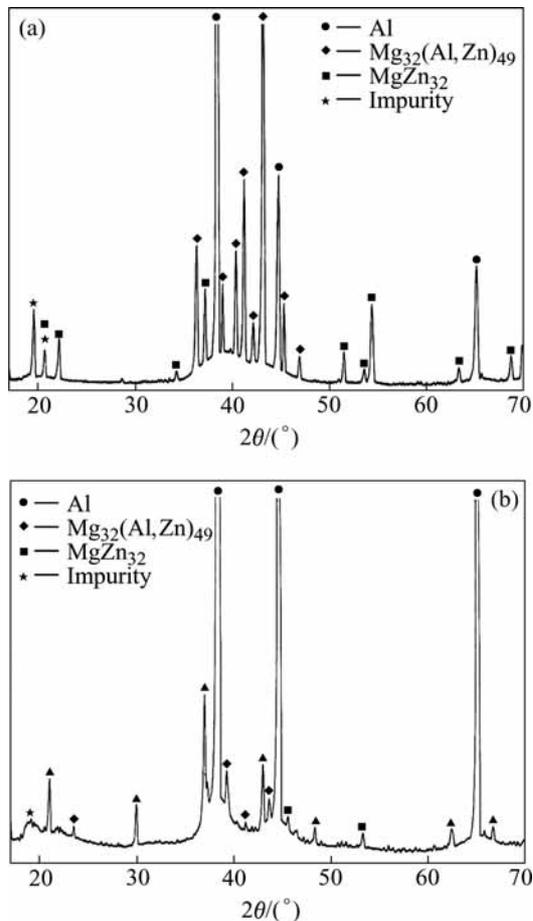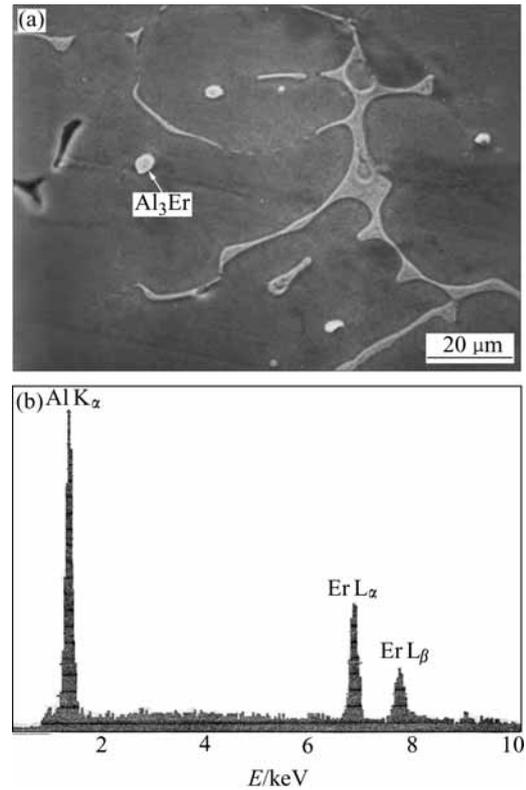

Fig.6 SEM micrograph and EDS analysis of as-cast Al-Zn-Mg-0.4Er alloy: (a) SEM micrograph of as-cast Al-Zn-Mg-0.4Er alloy; (b) EDS analysis of second phase

(Fig.7(a)), some fine particles with the size of 20−30 nm are present. In the diffraction pattern (Fig.7(b)) of the matrix and the precipitated particles there are patterns of superlattice. According to Refs.[12−14], the crystal structure of Al_3Er phase is $L1_2$ type (AuCu$_3$ type) and the lattice constant is 0.421 5 nm which is close to that of the matrix Al (fcc, a=0.404 9 nm). So Al_3Er is coherent or half-coherent with the matrix. Therefore it is concluded that the fine particles in Fig.7(b) is the secondary Al_3Er phases precipitated from the supersaturated solid solution. During annealing the fine Al_3Er particles serve to anchor the dislocations and impede the motion of them (Fig.7(c)). At the same time these particles anchor the subgrain boundaries and hinder the formation and growth of the subgrains (Fig.7(d)). After aging at 120 for 18 h, in Al-Zn-Mg-0.4Er alloy, many fine η' phases precipitate and some biggish particles distribute in the matrix (Fig.7(e)). EDS (Fig.7(f)) of these biggish particles indicates that their constitutions are Al and Er and solid solvent Zn. Combined with the former analysis it is confirmed that these particles are Al_3Er phase. Compared with the Al_3Er phase in Fig.7(a), these are relatively coarser. This is perhaps due to the fact that the fine Al_3Er particles do not solve after solid solution treatment and so still distribute in the matrix but grow larger.
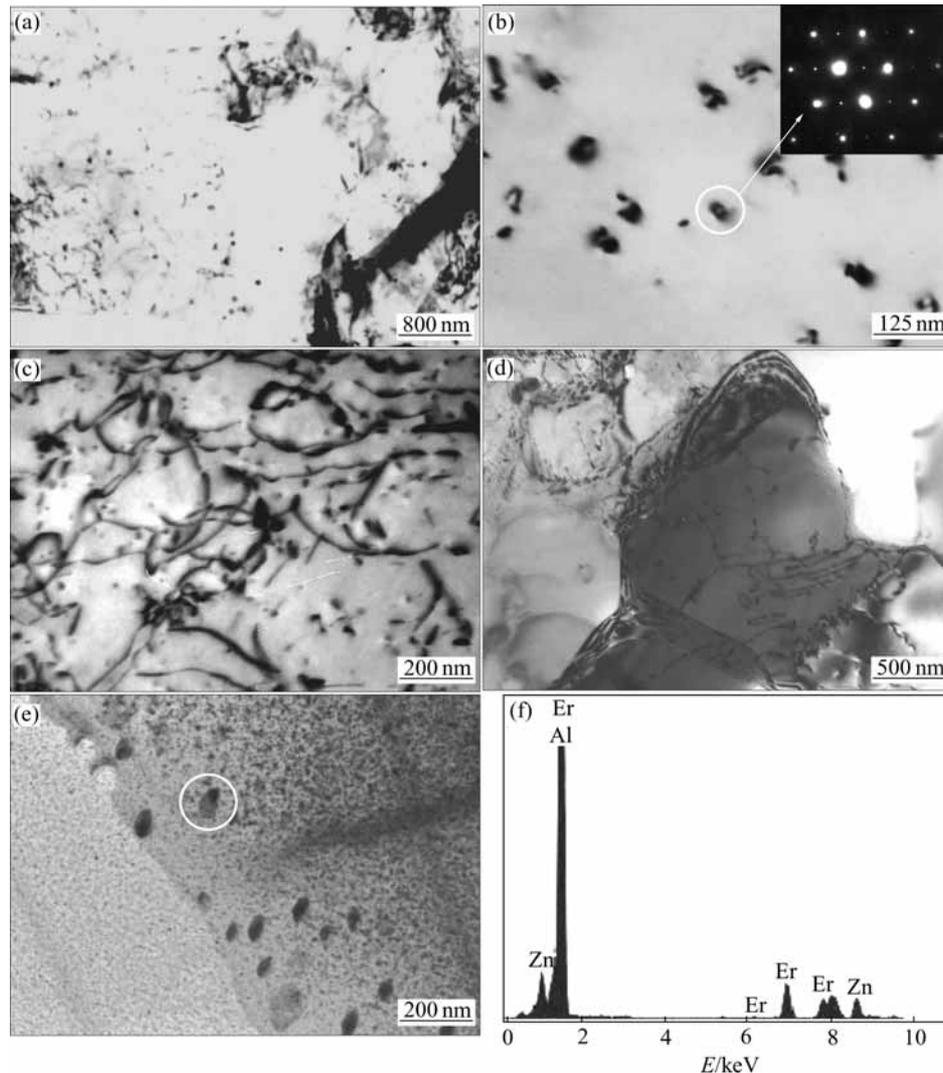

Fig.5 X-ray diffraction patterns of as-cast alloys: (a) Al-Zn-Mg; (b) Al-Zn-Mg-0.4Er

Fig.7 TEM photographs of Al-Zn-Mg-0.4Er alloy under different conditions and EDS pattern: (a) As-cast microstructure; (b) Precipitates and SADP of Al matrix and precipitate in as-cast alloy; (c) Dislocation Pinned by particles in as-annealed alloy; (d) Subgrain boundary Pinned by particles in as-annealed alloy; (e) As-aged microstructure (120 , 18 h); (f) EDS analysis of second coarse phase in Fig.7(e)

4 Discussion

It is known that the grain refinement effect of Sc in aluminium alloys is contributed to the primary Al_3Sc particles[15, 16]. While the eutectic point of Er and Al is 6% which seems without formation of primary Al_3Er phase, but the primary Al_3Er particles were observed in our experiments. This is because in the experimental alloys, a small percent of the Er was solid solved in the matrix and most of the Er aggregated in the advancing front of the solid liquid interface. The aggregation of Er in the interface will result in the two following effects: one is to prick up the compositional fluctuation and the other is to augment the compositional over-cooling in the solid liquid interface. According to the Al-Er phase diagram, the eutectic temperature of the Al_3Er and Al is 655 and the solidification domain is very small[17]. Moreover the constitution of the eutectic point is low

(6%Er). So Al_3Er can form in the solution near the interface with the high content of Er. This kind of Al_3Er formed directly from the melt and is referred to as primary Al_3Er which differs from the secondary Al_3Er precipitated from the solid solution. Because the crystal type of Al_3Er is similar to that of the matrix Al and the misfit degree is relatively small (about 4.1%), there is preferable coherency between the Al_3Er phase and the matrix. Moreover the melting point of Al_3Er is 1 067 which is much higher than that of the matrix, so Al_3Er will not resolve and is steady. All these make the primary Al_3Er to be perfect crystal nucleus and the nucleation to be improved. So the as-cast and as-annealed alloys are refined (Fig.3).

The fine secondary Al_3Er particles precipitated from the supersaturation (Figs.7(a) and (b)) are perfectly matched in the interface with the matrix α-Al. So they anchor the dislocations strongly (Fig.7(c)) retarding the

motion of the dislocations and improve the shear stress necessary for the dislocations to slide. Thus the precipitant strengthening effect is remarkable. At the same time, the addition of Er can refine the grains remarkably (Fig.3(d)). According to Hall–Petch relation: $\sigma=\sigma_0+kd^{-1/2}$, the finer the grains, the higher the strength. In conclusion, the addition of Er to Al-Zn-Mg alloy can significantly improve its strength (Table 2).

After aging, in Al-Zn-Mg-0.4Er alloy, the Al$_3$Er particles distributed in the matrix and the resulted high-density substructures(Fig.7(e)) arouse energy relaxation. All these become the preferable nucleation position for η', and so make the η' precipitate homogeneously. The aging process is accelerated and the aging effect is improved(Fig.1).

The mechanism that Er retards the recrystallization is as follows: the fine Al$_3$Er particles anchor the dislocations and the subgrain boundaries (Figs.7(c) and (d)); all these retard the dislocations recombination and the subgrainboundaries motion, thus the nucleation and growth of the subgrains are delayed. At the same time, the addition of Er can refine the as-cast alloys and increase the grain boundaries which are preferable sites for recrystallization, and so the nucleation is improved and the grains are refined. In addition, the growth of the grain, proceeding through motion of grain boundaries, is retarded due to strong anchoring of the grain boundaries by the Al$_3$Er particles. To sum up, the addition of Er not only retards the recrystallization, but also increases the recrystallization temperature (Fig.2, Figs.4(a) and (b)) and significantly refines the recrystallized grains (Figs.4 (c) and (d)).

5 Conclusions

1) The addition of Er to Al-Zn-Mg alloy can refine the grains remarkably. The mechanism is mainly owing to the presence of the primary Al$_3$Er, which can serve as nucleus for inhomogeneous nucleation and significantly improve the ratio of nucleation and refine the grains.

2) The addition of Er improves the mechanical properties of the alloy. The reason is the precipitation of secondary Al$_3$Er particles and the remarkable refinement of the grains, namely, precipitation strengthening and fine-grain strengthening.

3) The addition of Er accelerates the aging process and improves the effect of aging strengthening. The effect arises from the Al$_3$Er particles and the resulted high-density substructures, which cause energy relaxation. All these can serve as preferable nucleation sites of η' and make the η' precipitated homogeneously.

4) The addition of Er can retard the recrystallization

of the Al-Zn-Mg alloy, increase the recrystallization temperature and significantly refine the recrystallization grains. The reason is the fine Al$_3$Er particles anchor the dislocations and the subgrain boundaries, hinder the recombination of the dislocations and the motion of the subgrain boundaries, and so delay the nucleation and growth of the subgrains.

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