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Effect of trace rare earth element Er on high pure Al[①]

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Abstract: The influence of trace Er addition on high pure aluminum was studied by mechanical properties measurement, hardness measurement, optical microscope, transmission electron microscope and energy spectrum analysis. The results show that minor Er in the studied alloy exists in the form of Al_3Er, only a few of Er in α-Al based solid solution. Primary Al_3Er particles formed during solidification were often found at the center of aluminum grains and acted as heterogeneous nucleus, also increased the rate of nucleation, therefore the grain are remarkably refined. Trace Er addition to high pure aluminum is able to increase the mechanical properties of high pure Al, which is caused by fine grain strengthening, sub-structure strengthening and precipitation strengthening. The recrystallization temperature of Er-doped aluminum increases above 50 ℃, which is caused by the pinning effect of highly dispersed fine Al_3Er precipitates on dislocations and sub-grain boundaries.

Key words: rare-earth element Er; mechanical properties; recrystallization; Al_3Er
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1 INTRODUCTION

As it's well known, China is rich in rare earths, whose proved reserves are 80% of the total reserves of the world, ranking first in the world. At present, the research and application of RE in steel & iron are rather profound in China. Though the application and studies about RE in aluminum and its alloys began early, it's not until late in the 1970's that the investigation and exploitation began on a large scale and gradually came to a climax[1-3]. In the past, the research of RE aluminum mainly focused on the application of some elements such as La, Ce, Y and mischmetal in aluminum alloys and their effect mechanisms. As for other RE elements, there's little investigation. In fact, overseas especially in Russia, the useful effect of Sc on Al alloys was found early in the 1970's[4], and has been fully studied; furthermore, a series of advanced Al alloys containing Sc has been exploited. But Sc is a strategic metal and is very expensive. Therefore, a breakthrough of the selection of RE is expected. That is, a cheaper RE that has never been tried, when adding to Al alloys through a traditional cast way, has the familiar modified function as Sc. This study focuses on the addition of Er to high pure Al. The result shows that with the addition of Er, the grains can be remarkably refined, the mechanical properties can be improved, and the recrystallization can be inhibited apparently. Meanwhile, RE element Er can also improve the corrosion resistance and weldability of Al and Al alloys[5]. Adding Er to the Al-3Mg alloy, the eutectic compound can be refined better and disperses more homogeneously, which improves the quantity of the casts[6]. In a word, the element Er has similar effect with Sc on Al and Al alloys, but its price is only 1/40 of that of Sc, so it's very significant to have further investigation about it.

2 EXPERIMENTAL

Al-Er alloys containing 0.1% and 0.76% Er respectively were prepared by a casting metallurgy method, with high pure Al (99.99%) and Al-6.2Er master alloy. To do comparison conveniently, a sample of high pure Al was prepared under the same condition. All the casts were homogeneously annealed at 470 ℃ for 13 hours, then their ends were cut down, surfaces were milled, and then hot rolled and cold rolled afterwards, the deformation degree of cold rolling being 70%. The samples which were cold rolled into 2 mm sheets were put into a box-type resistance furnace to carry out annealing treatment at a temperature range of 150-400 ℃ (got a temperature point every other 25 ℃), keeping for 1 h, then cooling down in the air. Samples for tensile properties testing were prepared according to the requests of GB6397-86. The tensile properties were tested in an

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INSTRON4302 Material Testing Machine; the hardness of each sample was measured in an HBWUV-187.5 hardness tester. Samples for optical microscope observation were electrolytically polished and anodized in Baker's reagent. The observation was carried out in a NEOPHOT-21 optical microscope made in Germany under polarimetric light condition. Samples for TEM examination were prepared by double-spray electropolishing method (the electropolishing solution was mixture of HNO_3 and CH_3OH, the ratio was 1∶3) and anlysed by H-800 TEM.

3 RESULTS

3.1 Effect of Er on mechanical properties of high pure Al

The comparison of tensile properties at room temperature between high pure Al free of Er and those containing 0.1% and 0.76% Er respectively, under cold rolled and annealed state (375 ℃ for 1 h), is shown in Table 1. It can be seen that a small amount of Er can improve the tensile strength and yield strength of the alloys, furthermore, with the increase of Er amount, the increasing extent of the strength also increases, but the increasing tendency reduces. Er addition has little effect on the plasticity of high pure Al at room temperature.

Table 1 Tensile properties of high pure Al and Al-Er alloys

Materials	Cold rolling			375 ℃ for 1 h		
	σ_b/ MPa	$\sigma_{0.2}$/ MPa	δ/ %	σ_b/ MPa	$\sigma_{0.2}$/ MPa	δ/ %
High pure Al	119.2	114.6	10.1	55.8	16.7	62.0
Al-0.1Er	130.3	125.1	7.6	61.4	20.8	61.4
Al-0.76Er	133.2	127.5	10.1	73.3	30.5	68.3

3.2 Effect of Er on recrystallizing temperature of high pure Al

The cold-rolled sheets of high pure Al and the Al-0.1Er alloy were annealed at different temperature (150-400 ℃, got a temperature every other 25 ℃), and the hardness of every annealed sample was tested. The curve of hardness-annealing temperature relationship was shown in Fig. 1 (the first point in the figure corresponding to the hardness at room temperature), T_s and T_f corresponding to the starting and ending recrystallizing temperature, respectively.

Seen from the figure, the addition of Er not only improves the hardness of high pure Al, but also increases the starting and the ending temperature of recrystallization 50 ℃ or more, which suggests that Er can prevent the recrystallization of high pure Al, and also improve the thermal stability. This is in agreement with the microstructure observation.

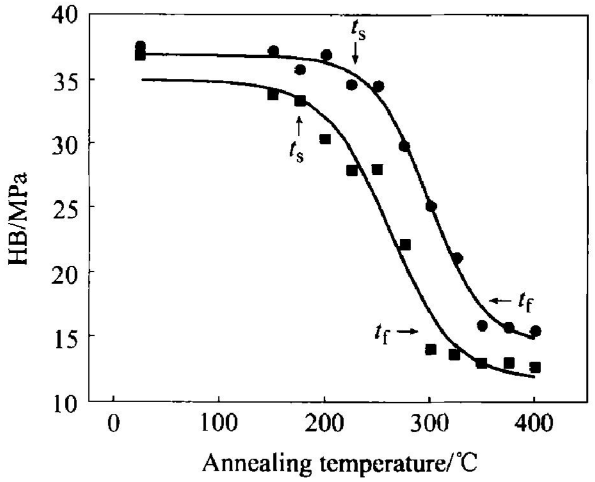

Fig. 1 Curves of hardness vs annealing temperature of high pure Al and Al-0.1Er

3.3 Effect of Er on microstructure of high pure Al

The addition of Er to high pure Al has a remarkable effect on the microstructure. The cast structures of high pure Al and the Al-0.76Er alloy are shown in Figs. 2(a) and (b), respectively. It can be seen that the grains of high pure Al are rather coarse, but those of Al-0.76Er alloy are much finer, which reveals that Er addition to high pure Al really can refine the grains. The microstructure of high pure Al and that of the Al-0.1Er alloy, annealed at 225 ℃ and 400 ℃ for an hour, is shown in Figs. 3(a)-(d). From Fig. 3, recrystallization has begun clearly in high pure Al after annealed at 225 ℃ for 1 h (Fig. 3 (a)), but recrystallization didn't appear in the Al-0.1Er alloy (Fig. 3(b)). And after being annealed at 400 ℃ for 1 h, the grains of high pure Al is apparently coarsened (Fig. 3 (c)). Although full recrystallization has also happened in the Al-0.1Er alloy, fine equiaxial grains still exist in the Al-0.1Er alloy (Fig. 3 (d)), which suggests that Er addition can refine the recrystallized grains.

The effect of Er on microstructure of high pure Al can be further demonstrated by TEM observation. The TEM photographs of high pure Al and the Al-0.76Er alloy under different conditions are shown in Figs. 4 (a)-(f).

Compared with the cast structure of high pure Al (Fig. 4(a)), the cast grains of the Al-0.1Er alloy are much finer, and containing a plenty of sub-structures, which is consisted of dislocation cell structure (Fig. 4(b)). Fine dispersed grains are also found in the alloy, Fig. 4(c) is a highly magnified photography, the bean-petal-like contrast in which is caused by the coherent strain field of the precipitation particles and the matrix. From the selected area electron diffraction (Fig. 4(d)), it can be deduced that this kind of particle is Al_3Er phase. The structure of Al_3Er phase is the same as Al_3Sc, belonging to a $Pm3m$ space group (simple cube), its crystal lattice parameter a = 0.421 5 nm, close to that of Al and can form particles coherent with Al matrix. Those fine particles shown in Fig. 4(c) are Al_3Er particles precipitated from α-Al, which can pin up dislocations. The cold rolling structure of the Al-0.1Er alloy is shown in Fig. 4 (e). Due to a rather big lattice distortion of matrix during cold rolling, the coherent strain is concealed, therefore it's difficult to find the Al_3Er particles. The structure of the Al-0.1Er alloy after annealing at 275 ℃ for 1 h is shown in Fig. 4(f). Fine dispersed Al_3Er particles can be found, because the matrix lattice distortion disappears little by little after annealing, the effect of contrast between Al_3Er particles and the matrix being apparent, so Al_3Er particles can be re-found.

4 DISCUSSIONS

4.1 Strengthening mechanisms of studied alloys

When adding a small amount of Er to high pure Al, Er can react directly with Al to form primary Al_3Er particles, because the crystal lattice type ($L1_2$) and the crystal parameter of Al_3Er particles are very close to those of Al matrix (FCC, crystal parameter a = 0.404 9 nm) and the mismatch is rather small (about 4.1%), therefore, Al_3Er particles are coherent or semi-coherent to the matrix. Those fine primary Al_3Er particles can act as the heterogeneous nucleus during the process of recrystallization nucleation, thus the grains can be remarkably refined. On the other hand, the difference of atom radius between RE element and Al is 22%-41% (except Sc, the difference of radius between Al and Sc is about 14.8%).

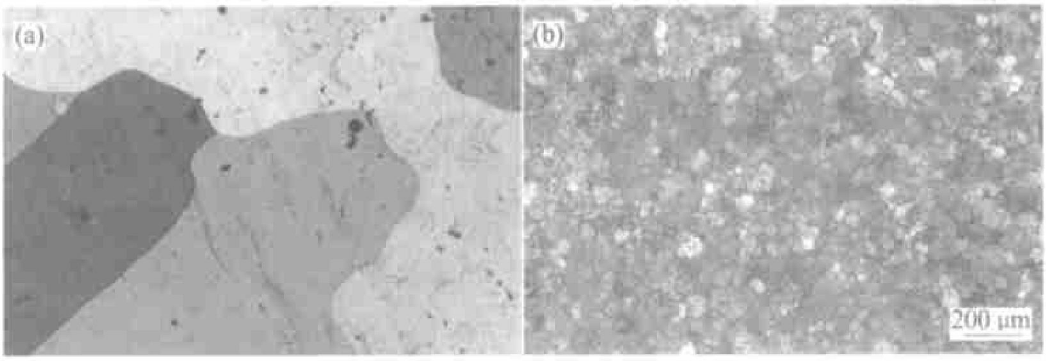

Fig. 2 As-cast structure of high pure Al and Al-0.76Er
(a) —High pure Al; (b) —Al-0.76Er

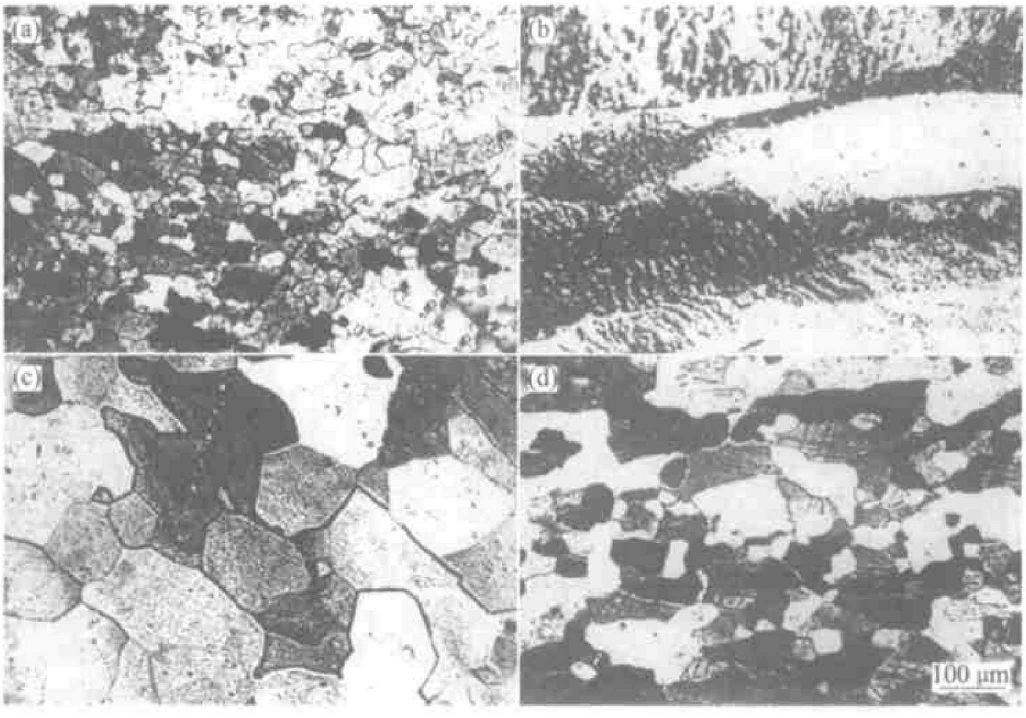

Fig. 3 Optical micrographs of high pure Al and Al-0.1Er
(a) —High pure Al annealed 60 min at 225 ℃; (b) —Al-0.1Er annealed 60 min at 225 ℃;
(C) —High pure Al annealed 60 min at 400 ℃; (d) —Al-0.1Er annealed 60 min at 400 ℃

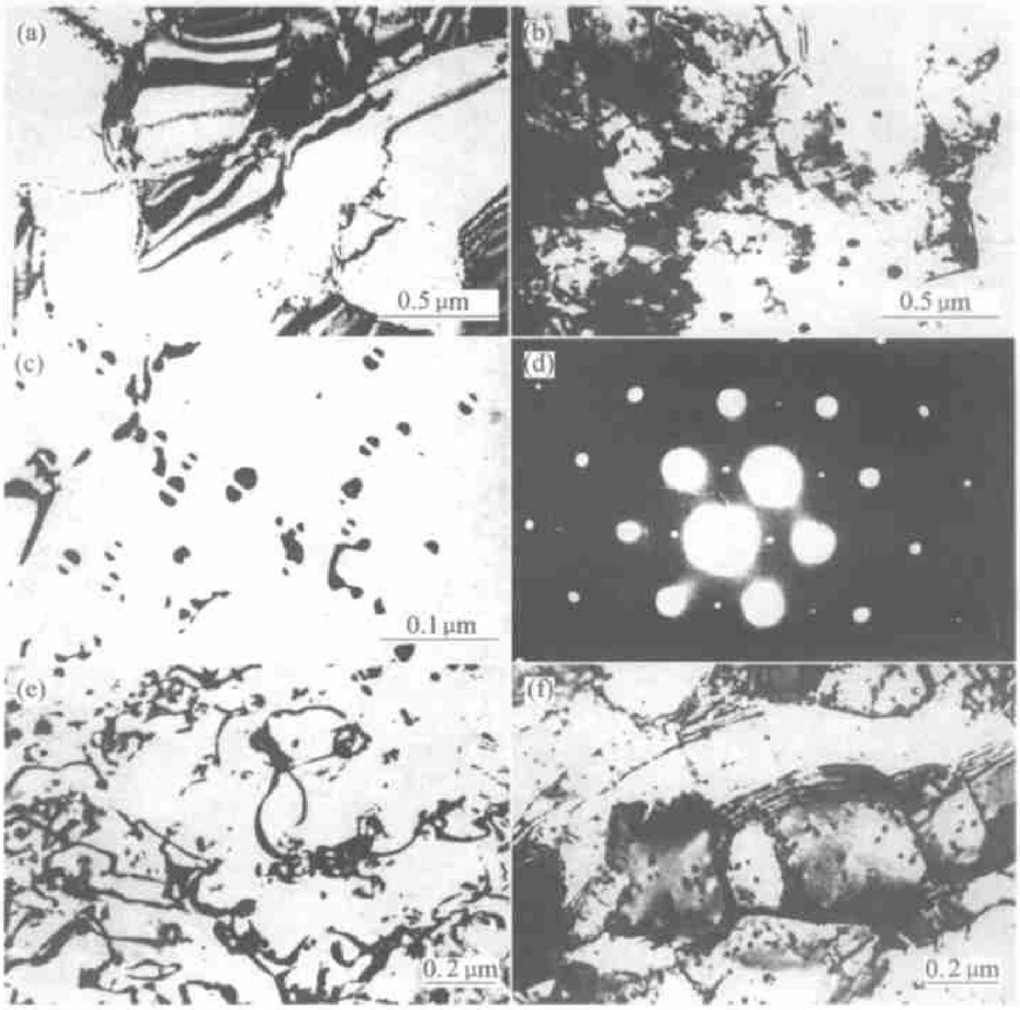

Fig. 4 TEM micrographs of high pure Al and Al-0.1Er
(a) —Cast structure of high pure Al; (b) —Cast structure of Al-0.1Er;
(c) —High magnification structure of Al-0.1Er; (d) —Selected-area electron diffraction;
(e) —Al-0.1Er cold rolled condition; (f) —Al-0.1Er annealed at 275 ℃ for 1 h

According to the criterion put forward by Hume-Rothery, those elements whose difference of atom radius lower than 15% can be easier to form solid solution[7], therefore it is difficult for RE elements and Al to form a solid solution. It can be seen from the binary Al-Er alloy phase diagram[8] that the equilibrium solid solubility of Er in Al matrix is very low, but under experimental condition, due to a high melting temperature and cooling rate, the solid solubility of Er in Al matrix is improved to a great extent. Those Er resolved into Al matrix can be precipitated in the form of second-born Al_3Er phase during the succedent heating process. All these fine Al_3Er particles can pin up the dislocation strongly, prevent the slip of them, increase the shear stress needed for the dislocation slip, meanwhile they can also prevent the migration and incorporation of the sub-boundaries, and stabilize the sub-structure formed during deformation process. In addition, those well-dispersed fine Al_3Er particles precipitated from α-Al play a role in precipitation strengthening. Therefore, it can be concluded that the main strengthening mechanisms of the studied alloys are fine-grain strengthening mechanism, sub-structure strengthening and precipitation strengthening mechanism.

4.2 Recrystallization behavior of studied alloys

Except for a low solubility of RE in Al, experiments have found that not a very small amount of fine dispersed Al_3Er particles exist in the cast Al-0.1Er alloy (Figs. 4(b) and (f)). It can be concluded that in the cast Al-0.1Er alloy, the fine dispersed phase are mainly primary Al_3Er particles, which are compounds formed directly by Er and Al. In cold rolling structure, a substantial tangles of dislocation and cellular structure can be observed, but clear precipitation phase is difficult to find (Fig. 4(e)). However, in the alloys annealed at 275 ℃, the precipitation phase is mainly second-born Al_3Er particles which are precipitated from the matrix, of course, there are a little primary Al_3Er particles, too. These fine dispersed Al_3Er particles have a rather strong function of pinning the dislocations and sub-boundaries, thus can make sub-structure stable. In the process of recovery before recrystallization, they prevent the movement of dislocations and the incorporation of sub-boundaries, and keep a rather high dislocation density, thus delayed the beginning of the recrystallized nucleation. During the succedent growth of the nucleus, the stable sub-structure make it difficult for the migration of crystal boundaries, thus inhibit the growth of the recrystallized nucleation. As a result, the recrystallization can be prevented and the recrystallization temperature shall be improved. Only high enough temperature can make the fine precipitation Al_3Er phase gather and grow, distance between particles become large, thus the pining effect on dislocation and sub-boundaries can be reduced, and the recrystallization process is fully over.

General speaking, the mechanisms of recrystallized nucleation of metals and their alloys are as follows: boundary arced mechanism[9], sub-crystal gathering mechanism[10] and sub-crystal growing mechanism[11]. In this study, the experimental alloys being cold rolled, a substantial of dislocation cellular structure could be formed due to the cross slip of dislocations and the formation of dislocation tangles (Fig. 4(e)). During the annealing process afterwards, surplus dislocations disappear because of the recovery process and come into being sub-crystals. The adjacent dislocations incorporate constantly and the sub-boundaries disappear and then turn into the recrystallized nucleus, shown in Fig. 4 (f). What's more, from Fig. 4 (f), it also can be found that the sub-crystals incorporate at the same time a part of boundaries have become large-angle boundaries, which reveals that the nucleation process of the alloys is a corporate effect of the sub-crystal incorporation mechanism and the sub-crystal growing mechanism.

5 CONCLUSIONS

1) Grains can be remarkably refined by a small amount of Er, and the tensile strength and the yield strength of high pure Al in either cold rolling state or annealing state can be improved to different extents. The strengthening mechanisms of the studied alloys are believed mainly to be fine-grain strengthening mechanism, sub-structure strengthening mechanism and precipitation strengthening mechanism.

2) The recrystallizing temperature of high pure Al can be increased 50 ℃ higher by adding trace RE element Er. The reason is that fine dispersed Al_3Er particles can strongly pin up dislocations and sub-boundaries, which can prevent the recrystallization.

3) The addition of Er can not only prevent the recrystallization, but also refine the recrystallized grains remarkably. The two mechanismssub-crystal gathering mechanism and sub-crystal growing mechanism play corporately role in the process of the recrystallization.

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