The effect of Er and Zr ratio on microstructure evolution and mechanical properties of 6061 aluminum alloy

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Abstract: In the present study, the 6061 alloy was chosen as base alloy, and micro-alloying effect of different ratios of Er and Zr (2:1, 1:1) on microstructure evolution and mechanical properties was examined after T6 heat treatment. Hot rolling deformation was carried out at 450℃, then a solution aging heat treatment process was adopted at 570℃/0.5h + 180℃/5h. The precipitation, recrystallization behaviors were characterized using transmission electron microscopy(TEM), scanning electron microscope(SEM) and electron backscattered diffraction(EBSD) techniques, the mechanical properties were tested using tensile tests. The results shown that recrystallization behavior was inhibited by co-additions of Er and Zr. With the increase of Er and Zr content, the recrystallized grain size and coarse Fe-rich phases at the grain boundaries decreased, the recrystallized grain distributed uniformly, the number of needle-like Mg2Si and granular Al3(Er, Zr) phases gradually increased. In 6061 alloy with Er/Zr ratio of 1, the distribution of precipitates were finer and more uniform, The uniformly distributed Al3(Er, Zr) phases pinned the grain boundaries, which effectively hindered the movement of grain boundaries. The tensile tests exhibited that the properties of 6061 alloy with Er/Zr ratio of 1 reached the highest level, i.e., tensile strength of 344.0MPa, the yield strength of 296.0MPa, and elongation of 17%.

1. Introduction
Al-Mg-Si series alloy has been an attractive candidate for lightweight automobile body owning to their favorable combination of low specific density, good corrosion resistance, strength, and formability [1,2]. However, for most Al-Mg-Si sheets, their formability and strength still need to be further improved[3,4]. The most common method to optimize the comprehensive properties of aluminum alloy was to add rare earth elements into the alloy. S. Costa et al. shown that Sc micro-alloying had a significant strengthening effect on the aluminum alloy, and the role of Sc in the alloy was: (1) Refined the grain; (2) Formed Al3Sc phase to play the role in precipitation strengthening[5,6]. However, the price of Sc is particularly high, which will greatly increase the cost of materials. Micro-addition of Er in the aluminum alloy is known to form stable Al3Er (L12) nanoparticles, which have higher melting point and relatively larger lattice misfit with α-Al (Δd=+4.08%) compared with Sc, thereby improving the mechanical properties.
at room and high temperature. So, the relatively cheap rare earth Er can be used to replace the expensive Sc. It indicated[7] that when both of the Er and Zr were added to pure Al, the density of precipitated phases during the aging process were higher than that in Al-Zr and Al-Er with single addition, and they distributed uniformly and densely. The new Al3(Er, Zr) precipitates were coherent with the matrix, which could effectively prevent the movement of dislocations, the migration of grain boundaries, and the merging and growth of sub-grains, and improve the performance of the alloy. Moreover, it was reported[8] that the recrystallization temperature of Al-Er-Zr alloy was high as 450℃, it was significantly higher than that of Al-Er alloy. The main reason was that the precipitate of the Al3(Er, Zr) phase had good thermal stability. Compared with Al3Er, the Al3(Er, Zr) precipitate was not easy to coarsen or dissolve into the matrix at high temperature, which could limit the movement of dislocations and high angle grain boundaries.

In the present study, two kinds of 6061 alloys with different Er/Zr ratios were prepared by the traditional casting process. The ingots were homogenized, followed by hot rolled. The effects of Er and Zr addition on the grain refinement and precipitation were studied after the solution and aging process. The interaction between the precipitated phase and the grain boundary, especially, the evolution of Al3(Er, Zr) precipitate were investigated in the alloys with Er and Zr. In addition, the effects of Er and Zr addition on microstructure, precipitated phase distribution, morphology, and mechanical properties were discussed in detail.

2. Experimental procedures

The composition of three different Er/Zr ratios of 6061 alloys were shown in Table 1 (hereafter marked as 1#, 2#, and 3# alloy). The contents of Er and Zr of 2# alloy and 3# alloy were 0.2% Er and 0.1% Zr, 0.2% Er and 0.2% Zr, respectively. 1# alloy was a base 6061 alloy without Er and Zr. The ingots were homogenized at 570℃ for 12h, subsequently slow air cooling to room temperature. The ingots were then hot rolled to 3mm thick sheets. The hot-rolled samples were solution heat-treated at 570℃ for 0.5h, and subsequently were aging treated at 180℃ for 5h.

|     | Mg  | Si  | Cu  | Cr  | Mn  | Er  | Zr  | Fe  | Al  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1#  | 0.96| 0.77| 0.16| 0.07| 0.15| 0   | 0   | 0.037| Bal |
| 2#  | 1.04| 0.623| 0.16| 0.10| 0.14| 0.20| 0.08| 0.033| Bal |
| 3#  | 0.97| 0.67| 0.20| 0.09| 0.15| 0.21| 0.22| 0.029| Bal |

The size, morphology and distribution of precipitates were characterized using JEOL-2100 transmission electron microscope (TEM) with a working voltage of 200kV. The rolling direction of the plate was the length direction of the sample, Figure 1 showed the dimension of the tensile specimens. The tensile tests were performed with the stretching speed of 2mm/min at room temperature, and three tests were repeated for each specimen to ensure accuracy, the fracture surface was observed by means of the FEI Quanta200 scanning electron microscopy(SEM). The composition of the second phase were analyzed by EDS. The electron back-scattering patterns (EBSD) measurements were carried out on the ND-RD plane using a JEOL-JSM6480 scanning electron microscope and the statistic orientation analysis were carried out using HKL 5.0 software. The effects of Er and Zr addition on the recrystallization grain size and misorientation diagram of the alloy were studied.

Figure 1. Dimension of the specimen for tensile test(unit: mm)
3. Results

3.1. Microstructure evolution during solution and aging process

Figure 2 showed the grain boundary misorientation maps of the alloy with different Er/Zr ratio in solution and aging treatment, where the thick blue lines indicated high angle grain boundaries and the thin red lines indicated the low angle grain boundaries. The recrystallization grain size of the alloy with Er and Zr additions obviously decreased. According to statistics, the average grain size of base alloy without Er and Zr was 183.0 μm, and the alloys with Er/Zr ratio of 2 additions was 22.0 μm, and that with Er/Zr ratio of 1 was 20.0 μm. It clearly showed that the recrystallized grain size of 6061 aluminum alloy with Er/Zr ratio of 1 was smaller than that of the alloy with Er/Zr ratio of 2, and the recrystallization grain size distribution was more uniform.

Figure 2. Grain boundary misorientation maps of 6061-T6 alloy with different contents of Er and Zr: a) 1# alloy, b) 2# alloy, c) 3# alloy.

The TEM morphology of precipitates before and after adding Er and Zr is shown in Figure 3. The number of precipitates in the alloy began to increase after adding Er and Zr, and with the increase of Er and Zr content, i.e., Er/Zr ratio of 1, the number density of precipitates gradually increased, and the precipitated phases were more uniform and finer. These precipitated phases were mainly short rod and granular. Figure 4 showed that microstructure and selected area diffraction pattern in the region of precipitate phases. From Figure 4b, it could be seen that there were two sets of diffraction patterns. The index showed that the main spot was α-Al, and the weak spots were also a face-centered cubic structure corresponding to the precipitate phase of Al3(Er, Zr). Figure 4c-d depict the corresponding dark field and bright field image. The precipitate phase was fine and granular, and the size of the granular Al3(Er, Zr) phase were coherent with the Al matrix, which were about 3nm, the size of the needle-like precipitated Mg2Si[22,23] phase was about 10nm. Furthermore, the composition of precipitate phase at grain boundary were shown in Figure 5. The composition of the granular precipitates at the grain boundary contained Er and Zr in 2# and 3# alloy. The number of precipitated phases on the grain boundary increased with the addition of Er and Zr, and the distribution was more uniform. The EDS analysis of the precipitate phase at grain boundary showed that the phase composition was changed after adding Er and Zr, i.e., it was Fe-rich compound in the base alloy, Fe concentrations in compounds were 2.58 wt%. While it was a compound containing Al, Mg, Si, Er, and Zr in the 2# and 3# alloy, the Mn and Cr disappeared, the concentrations of Fe and Er in the compounds were 5.29 wt% and 0.8 wt% in 2# alloy with Er/Zr ratio of 2, respectively. The concentrations of Er and Zr were 4.99 wt% and 0.29 wt% in 3# alloy with Er/Zr ratio of 1, respectively, and the Fe disappeared, which indicated with the increase of Er and Zr content the Fe-rich phase decreased.
Figure 3. TEM images of 6061-T6 alloy with different Er and Zr content: a) 1# alloy, b) 2# alloy, c) 3# alloy.

Figure 4. TEM images of 6061-T6 alloy with 0.2Er-0.1Zr: a) Precipitate morphology, b) Matrix diffraction spot, c) Dark field, d) Bright field.

Figure 5. Grain boundary precipitate phase in 6061-T6 alloy with different Er and Zr content: a) 1# alloy, b) 2# alloy, c) 3# alloy, d-f) EDS.
3.2. Mechanical properties after solution and aging process

The tensile properties of 6061 aluminum alloy with different Er and Zr contents in T6 state as showed in Figure 6. It could be seen that the tensile strength, yield strength, and elongation of the alloy had a certain increase with the increase of Er and Zr in the T6 state. The properties of 6061 aluminum alloy with Er/Zr ratio of 1 had the highest properties, indicated the tensile strength of 344.0MPa, the yield strength of 296.0MPa, and the elongation of 16.9%. Compared with base 6061 aluminum alloy without Er and Zr, the tensile strength increased about 6%, and the elongation increased about 10%. Figure 7 showed the tensile fracture morphology of 6061 alloys with different Er and Zr contents in solution and aging state. The fracture dimples of each alloy were obvious, which were composed of dimples and tearing edges, it was a typical ductile fracture. The base alloy without Er and Zr revealed uneven distribution of dimples and fewer dimples. However, the alloys with Er and Zr had more dimples, and they were more evenly distributed. The 3# alloy with Er/Zr ratio of 1 had denser and deeper dimples, and there were small dimples inside the large dimples, indicated better toughness.

![Figure 6. Tensile mechanical properties of 606-T6 alloy with different Er and Zr contents](image)

![Figure 7. SEM images of the fracture surface morphology of 6061-T6 alloy with different Er and Zr contents: a) 1# alloy, b) 2# alloy, c) 3# alloy.](image)

4. Discussion

4.1. Micro-alloying effect of Er and Zr on precipitate phase

With the increase of Er and Zr in the solid solution in the matrix, the stored energy in the matrix was increased. In addition, the precipitate phase hindered the movement of the grain boundary, played a role in refining the grains, and improved the performance of the alloy. After solution treatment, a part of the metallic compounds was dissolved in the matrix to form a supersaturated solid solution. Then, a large number of dispersed phases precipitated during aging treatment. As shown in Figure 5, TEM analysis showed that Al3(Er, Zr) phase appeared in the 3# alloy with Er/Zr ratio of 1, The Al3(Er, Zr) phase was a kind of core-shell structure with a small lattice constant, which hindered the coarsening of the particle and improved the strength and plasticity of aluminum alloy. These phases also could act as...
heterogeneous nucleation cores to promote the Mg2Si phase and the remaining Al3(Er, Zr) phase precipitation. Relative to the base alloy, with the addition of Er and Zr content, the Fe-rich phase decreased, which reduced the adverse effect of coarsening and Fe richening on the grain boundary. In addition, the grain boundary precipitate phase could pin the grain boundary mobility, which effectively hindered the movement of the grain boundary, inhibited the recrystallization of the alloy, reduced the grain size, and produced strong substructure strengthening and precipitation strengthening, and then improved the alloy performance.

According to the strengthening theory of the alloy, if the precipitates in the alloy were spherical, the degree of mismatch with the matrix was more than 1%, and the good coherent relationship with the matrix was maintained, then the strengthening mechanism was mainly precipitation strengthening. When the size was small, the strengthening effect on the alloy was as follows:

\[ \Delta \tau = 4.1 \varepsilon^{3/2} \mu \left( \frac{f}{b} \right)^{1/2} \]  

(1)

If the particle size was large, its strengthening effect on the alloy was as follows:

\[ \Delta \tau = 0.7 \mu f^{1/2} \left( \frac{2b^3}{r^3} \right)^{1/4} \]  

(2)

Where \( \varepsilon \) was the degree of mismatch, \( \mu \) was the shear modulus, \( f \) and \( r \) were the volume fraction and radius of precipitate particles, respectively. Where \( b \) was the burgers vector of dislocation.

During the movement of dislocations, it encountered precipitate particles, dislocation loops might be formed around the particles or pass through the precipitate particles in the way of cutting through the particles, which further increased the dislocation density and improved the strengthening effect of the alloy. TEM analysis showed that the fine Al3(Er, Zr) phase precipitated in solution and aging treatment, which had a strengthening effect by cutting through particle mechanism. Moreover, the size of Mg2Si phase was about 10 nm, so as to play the same strengthening mechanism. Combining the two strengthening methods, they conduced to the improvement of the strength of the alloy.

4.2. Micro-alloying effect of Er and Zr on mechanical properties

The yield strength \( \sigma_{0.2} \) of alloy was consisted of three parts, first was different solid solubility, second was the grain refinement, and the last part was the precipitate phase. Among three parts, the grain refinement improved the strength and plasticity of the alloy at the same time. It could be seen from Figure 2, Figure 3, and Figure 5 that the difference in strength and plasticity of the three alloys in this experiment is mainly due to the latter two parts. Recrystallization occured in all three alloys, but the recrystallization grain size of 3# alloy with Er/Zr ratio of 1 was the smallest. The mechanical properties of 3# alloy haved the highest performance, with the tensile strength of 344.0MPa, the yield strength of 296.0MPa, and the elongation of 17.0%. Compared with base 6061 aluminum alloy without Er and Zr, the tensile strength increased about 6%, and the elongation increased about 10%. Therefore, the strength and plasticity of 3# alloy with Er/Zr ratio of 1 were better, which was caused by grain refinement. The relationship between grain size and yield strength could be explained by the Hall-Petch relationship. The smaller the grain size of the alloy, the stronger the hindrance of dislocation movement and the higher the yield strength of the alloy. According to Figure 2 and Figure 6, the Hall-Petch relationship between grain size and yield strength of three alloys could be fitted. To take “ \( \sigma_s = a + b \cdot d^{-1/2} \) ” as a straight line, then the fitting formula of the line was deduced, i.e., \( \sigma_s = 283+173d^{-1/2} \). The grain sizes of 2# and 3# alloys with Er and Zr additions were the same degree. However, there was an obvious change in strength and plasticity, so the main controlling factor of strength change of these two alloys should be precipitation strengthening. During aging treatment, a large number of dispersed and coherent Al3(Er, Zr) phase particles formed in the 6061 alloy with Er/Zr ratio of 1, These phases precipitated in the grain boundary and pinned the grain boundary mobility, which could effectively inhibit the grain boundary movement, therefor inhibited the recrystallization of the alloy. It reduced the grain size of the alloy, produced strong substructure strengthening and precipitation strengthening, and improved the properties of the alloy.
5. Conclusions
The 6061-aluminum alloy with Er and Zr composite microalloying was hot rolled followed by solution and aging treatment, showing the micro-alloying effect of different ratios of Er and Zr (2:1, 1:1) on microstructure evolution and mechanical properties. The conclusions are summarized as follows:

1) After the solution and aging treatment for 570°C×0.5h+180°C×5h, the 6061 aluminum alloy with Er/Zr ratio of 1, i.e. 0.2Er-0.2Zr, had the highest performance, which tensile strength was 344.0MPa, the yield strength was 296.0MPa, and the elongation was 16.9%.

2) The recrystallized grain size of 6061 alloy with Er/Zr ratio of 1 was the smallest, and the average grain size was 20μm. Compared with base 6061 aluminum alloy without Er and Zr, the average grain size decreased 89%, the tensile strength increased by 19MPa, about 6%, and the elongation increased by 1.5%, about 10%.

3) During aging treatment, a large number of dispersed and coherent Al3(Er, Zr) phase particles formed in the 6061 alloy with Er/Zr ratio of 1, and Al3(Er, Zr) fine particles precipitated at grain boundaries and pinned grain boundaries, which effectively inhibited the recrystallization of the alloy.

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