Effects of homogenization process on precipitation of Al₃Zr and recrystallization resistance in Al-Cu-Li-Zr alloy

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Abstract: The effects of homogenization treatments on the precipitation behavior of Al₃Zr particles and their effects on recrystallization resistance in X2A66 alloy have been investigated. The high recrystallization resistance can be attributed to the larger \( \frac{f_v}{r} \) ratio of Al₃Zr particles. During hot rolling and the subsequent thermal process, higher Zener drags can effectively resist the recrystallization in the experimental alloy.

1. Introduction

With excellent performances of low density, low anisotropy, high elastic modulus, high specific strength and excellent damage resistance, Al-Cu-Li alloys are regarded as notable competitive structural materials[1]. Aluminum-Lithium alloys have been successfully applied in aeronautic and astronautical industry, such as Airbus 350/380, Boeing 777 and C919 aircraft [2]. Compared with the first and second generation Al-Li alloys, the composition of the Al-Cu-Li alloy is consistent with that of the third-generation, of which the content of lithium (<2%, wt.%) reduced and the content of copper (>3%, wt.%) increased. China has developed a fourth-generation Al-Li alloy (X2A66) with independent intellectual property rights by adjusting the contents of Cu and Li and adding other micro-alloying elements (such as Mg, Zn, Zr, Mn) in aluminum-lithium alloys.

During the industrialized casting process, the interdendritic segregation cannot be avoided due to the complexity and high content of elements of the alloys, along with a considerable amount of massive non-equilibrium eutectics in the ingots. These factors severely restricted the workability of the alloys. Homogenization would optimize the microstructures and improve the mechanical properties of aluminum alloys compared with casting ingots. In Al-Zn-Mg-Zr alloys, H. Wu[3], Pikee Priya[4] indicated that the double-stage homogenization can induce the precipitation behavior of Al₃Zr particles and influence the recrystallization resistance and width of precipitation free zone, thus provide an additional strengthening effect. Many studies [5-7] had reported the distribution and precipitation regulation of Al₃Zr particles in the Al-Cu-Li alloys during homogenization. But researches of how Al₃Zr inhibits the recrystallization behavior of alloys during subsequent deformation and heat treatment is limited, especially in X2A66 alloys.

In this paper, X2A66 alloys were laboratory-made. Binary intermediate alloys of Al-Ti, Al-Zr and Al-Mn and pure elements of Cu, Mg, Zn, Li and high purity ingot of Al were melted in a vacuum
induction melting furnace under a controlled atmosphere of argon gas, using high pure graphite crucible. The liquid metal were then poured into a steel mold under argon. The precipitation behavior of Al₃Zr particles during the homogenization process was studied. The effect of Al₃Zr particles on recrystallization of alloy during subsequent deformation and heat treatment is also studied.

2. Material and experimental procedure
The chemical composition of the X2A66 alloy examined in this investigation is shown in Table 1. Using SG-XS high temperature box type muffle furnace (temperature error ±5°C) to homogenize the ingot. The cast ingots homogenization conditions were as follows. The first one was a single-stage homogenization treatment. The samples were homogenized at 510°C for 24 h (respectively denoted as S-1). The second one was a double-stage homogenization treatment. The samples were homogenized at 460 °C for 16 h followed by steps at 520 °C for 24 h (denoted as D-1). All the homogenized samples were air-cooled to the room temperature.

Same samples were prepared as a standard sample to investigate the features. The majority of the samples then encounter multi-pass hot-rolled at 400°C to plate of 4mm in thickness by the Φ400*1000 two-roll hot rolling mill, each test sample was given a solution heat treatment (1h at 510°C), then water quenched and followed artificially aging (175°C) by the DHG9030 digital display thermostatic dryer (temperature error ±3°C). Microstructures were studied with the help of electron backscattering diffraction (EBSD, ZEISS MA10) and transmission electron microscopy (TEM, FEI TECNAI G² 20) methods. Specimens for EBSD analysis were carefully polished with mechanical polishing followed by electro polishing with Struers A2 solution containing perchloric acid, ethanol, butoxy ethanol and distilled water. The scanning area of surface is 400×320 μm² with a scanning step size of 2.5 μm at the center of each sample and the magnification of the images is 200 times. The foils for TEM observations were prepared by mechanical polishing to less than 80 μm, subsequently punched into 3 mm disks and final twin-jet polishing with an electrolyte solution of 30% nitric acid and 70% methanol at the voltage of 10~20 V DC and the temperature below −20°C.

| Alloys  | Cu    | Li    | Mg    | Mn    | Zn    | Zr    | Ti    | Fe    | Si    | Al    |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| X2A66   | 3.5–4.1 | 1.3–1.8 | 0.2–0.6 | 0.2–0.6 | 0.2–0.8 | 0.08–0.16 | < 0.1 | < 0.1 | < 0.1 | Bal.  |

3. Results and discussions

3.1 Precipitation behavior of Al₃Zr particles during homogenization
Microscopic analysis shows that the diffusion is a migration process within the material due to thermalmotion of atoms or molecules, which can be described by law of diffusion. Generally, the supersaturation of the solid solution (driving force for nucleation) and the diffusivity of the solute in the matrix (driving force for growth and coarsening) acts as the two main factors to affect the dispersoids precipitation behavior during homogenization. Therefore, use of a lower homogenization temperature can be expected to lead to a modest reduction in particle size and a significant increase in number density.

The alloys treated with S-1 and D-1 were made into a standard sample and observed under a transmission electron microscope. Fig. 1 demonstrates the dark field TEM images of the Al₃Zr particles character after two different homogenization conditions, it can be seen that the size and number density of these Al₃Zr particles have obvious difference (Fig. 1a and c). Due to homogenization of air cool, part of the GP zone in the alloy precipitated (as shown in the box). And the GP zoned size is much smaller than Al₃Zr particles.
Fig. 1 Dark fields TEM images of specimens at different homogenized treatment: (a~b) S-1, (c~d) D-1

The statistics of the area fraction of Al$_3$Zr were analyzed using Image-Pro Plus software (Fig. 1b and d). After S-1 treatment, the mean diameter ($d$) of the Al$_3$Zr particles is 18.69 nm and the volume fraction ($f_v$) is 0.78%. Furthermore some Al$_3$Zr particles agglomerate seriously, as shown in red circles in Fig. 1b. Compared with the S-1, however, the D-1 can lead to a significantly decrease in the mean diameter of the Al$_3$Zr particles and a slight increase in the volume fraction, and even the corresponding distribution of the Al$_3$Zr particles are much more homogenous, as shown in Fig. 1c. The mean diameter of the Al$_3$Zr particles is 12.28 nm and the volume fraction ($f_v$) is 0.91%. It can be found that the mean diameter of the Al$_3$Zr particles decrease by at least about 34.30% and volume fraction increases by at least about 3.53%.

At the high homogenization temperature (510°C), the solubility and diffusion rated of Zr in the Al matrix are relatively high, which are disadvantageous for the precipitation of the Al$_3$Zr dispersoids, resulting in large Al$_3$Zr particles and wide none precipitation zone, both of which are undesirable and not beneficial to the recrystallization resistance of the alloy. The solubility of Zr decreases significantly, and the superaturation increases at lower temperatures (460°C, the first step), which should be advantageous for the precipitation of the Al$_3$Zr dispersoids. And a higher temperature (520°C) should be employed in the second step treatment in order to promote the controlled growth of the dispersoids.

Therefore, the D-1 sample (Fig. 1c) is the thermodynamically (lower Zr solubility) and kinetically (increased precipitation rate of Al$_3$Zr dispersoids) optimized sample compared with S-1. The experimental observation is consistent with the theoretical analysis.

### 3.2 Recrystallization behavior

A low dispersoid density within the grains in the final form of the material, which render it more prone to recrystallisation due to the localised reduction in Zener pinning. It can prevent the growth of recrystallized grains if there is sufficient Zener drag:
where \( d \) is the mean particle radius and \( f_v \) is the local volume fraction of the dispersoids. \( \gamma \) is the specific grain boundary energy between the nucleus and the deformation matrix, about 0.3 \text{ J/m}^2. \) It can be seen from this Eqs. (1), in order to achieve a high recrystallization resistance, a high Zener drag force \( P_z \), to effectively overcome the driving force for the dislocation movement and the subboundary migration, a high volume fraction of fine dispersoids (high \( f_v/d \) ratio) is necessary, that is to say the dispersoids is maximized by maximizing the volume fraction \( (f_v) \) and minimizing the particle size \( (d) \). Therefore it is necessary to increase the \( f_v/d \) ratio by optimizing the homogenization treatment.

The homogenized specimens are rolled to 4mm thickness using the same hot rolling process and equipment. After a further 1 hour solution treatment at a heating temperature of 510 °C and an aging treatment of 175 °C, samples were taken for EBSD analysis. Fig. 2 shows the EBSD images (include rolling direction, TD and normal direction, ND) of grain structure for the specimens. The black line represents the grain boundary or the subboundary and the color of each grain is coded by its crystal orientation based on inverse pole figure (IPF) as shown in inset at the lower right corner of the Fig. 2a. As can be seen from the analysis of Fig. 2, regardless of alloy TD and ND, the recrystallized and deformed degree of the sample after D-1 treatment were much lower than that of S-1 treatment. But the number of sub-grains in the alloy is more than that of S-1 treatment.

Since other conditions are the same, it can be considered that different homogenization regimes affect the degree of recrystallization of the alloy. Compared with S-1, the Al\(_3\)Zr particles in D-1 sample to possess finer particles size, much higher number density and volume fraction and resulting in their recrystallization resistance is much higher. So the recrystallized fraction of recrystallized grains in D-1 samples are much lower than that in the S-1 sample.
Fig. 2 EBSD images of grain structure of the different heat treatment samples: (a) S-1-TD, (c) S-1-ND, (e) D-1-TD, (g) D-1-ND; misorientation angle distribution and the recrystallized fraction of the samples: (b) S-1-TD, (d) S-1-ND, (f) D-1-TD, (h) D-1-ND.
4. Conclusions

Compared with single-stage homogenization treatment (S-1), the double-stage homogenization (D-1) can generate a smaller size and a higher volume fraction of the Al₃Zr particles in the sample. And the Al₃Zr particles precipitated in the homogenization process effectively inhibit the recrystallization degree of the alloy during the rolling and subsequent heat treatment.

Acknowledgements

This work is financed by the Province Natural Science Foundation of Hunan (2018JJ5066).

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