Effect of pre-deformation on the mechanical properties of pre-aging AA7093

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Abstract. To improve the mechanical properties of T6 AA7093, this work investigated the effect of 4% pre-stretching on mechanical properties of the 20 min pre-aging AA7093. The results show that after taking 20 min pre-aging + 4% pre-stretching treatment, the hardness of AA7093 reached the peak after taking 9 hours aging. The yield strength and ultimate tensile strength of the pre-aging + pre-stretching + re-aging AA7093 are 631 MPa and 665 MPa, respectively. Comparing with T6 AA7093, the increase of yield strength and ultimate tensile strength are 75 MPa and 29 MPa, respectively. Kinetic analysis of DSC shows that the activation energy of precipitates in T6 and pre-aging and pre-aging + pre-stretching AA7093 alloys are 216.6 kJ/mol and 129.6 kJ/mol, respectively, this results in easier nucleation and growth of precipitates after pre-deformation. TEM shows a lot of precipitates generated on dislocations in pre-aging + pre-stretching + re-aging alloy, a lot of dislocation plugs generated by pre-deformation and precipitates will impede dislocations slip is the main reason that the yield strength of it is higher than T6 AA7093.

1. Introduction
AA7093 is a new high Zn-containing 7XXX aluminium alloy developed for the Large Aircraft Project in recent years, and it has the characteristics of high strength and high toughness. As the requirement of components for large aircraft preparation is higher, and 7XXX aluminium alloys are gradually applied in automobile industry [1], it is less that the traditional T6 7XXX aluminium alloys are applied directly into the aircraft and automotive. Combining the high performance of 7XXX aluminium alloys, new forming technologies have been developed quickly.

Thermomechanical treatment is a comprehensive process of deformation and heat treatment, it combines the deformation strengthening of plastic deformation with the phase transformation strengthening of heat treatment. In the forming process of large-scale components, the thermomechanical treatment still plays an irreplaceable role. Previous studies of AA7093 were more about spray deposition forming and preparation of articles reinforced AA7093[2], little research has been done on the thermomechanical treatment of AA7093. In this paper, used pre-stretching to simulate the forming process of alloys, the work investigated the effects of solution quenching, pre-aging, pre-deformation and final aging on the structure and mechanical properties of AA7093, it provides a reference for AA7093 forming by thermomechanical treatment.

2. Material and methods
The experimental alloys were prepared by using Al (99.99%), Zn (99.99%) and Mg (99.99%), Al-50Cu, Al-10Ti and Al-10Zi master alloys and grain refiner Al-5Ti-B, the concentrations of Fe and Si
in the alloys was controlled below 0.01 wt.%. The melt was cast into a water-cooled steel mold with a size of 200 × 120 × 90 mm at 700 ℃. The compositions of three alloys were measured by optical emission spectrometer ARL 4460 (ThermoFisher Scientific, Waltham, MA) as shown in Table 1.

| Alloy | Zn   | Mg   | Cu   | Zr   | Si   | Fe   | Al   |
|-------|------|------|------|------|------|------|------|
| 7093  | 9.18 | 2.54 | 1.87 | 0.15 | 0.1  | 0.1  | Bal. |

The as-cast ingot was homogenized in an air furnace at 470 ℃ for 48 h, then the ingot was hot-rolled at a threshold temperature of 450 ℃ from 90 to 4 mm. After annealed at 430 ℃ for 1 h, the 4 mm sheet was cold-rolled to 2 mm. The solution treated in a salt bath furnace at 470 ℃ for 1 hour then quenched to room temperature. Subsequently, different heat treatment processes were listed in Table 2.

| Temper process No. | Heat treatment process                                    |
|--------------------|-----------------------------------------------------------|
| S                  | Solution treatment 470 ℃ × 1 h + quenching                |
| SP                 | 470 ℃ × 1 h + 120 ℃ pre-aging 20 min                      |
| SPD                | 470 ℃ × 1 h + 120 ℃ pre-aging 20 min + 4% pre-stretching  |
| T6                 | 470 ℃ × 1 h + 120 ℃ × 24 h                                |
| SPDT6              | 470 ℃ × 1 h + 120 ℃ pre-aging 20 min + 4% pre-stretching + 120 ℃ × 24 h |

3. Results

Figure 1 is the age hardening curves and mechanical properties of tested alloys after different process states. From Figure 1 (a), it can be found that the hardness of SPD sample is about 175 HV, it is about 30% higher than that of the S sample. This is because the precipitates formed during pre-aging and dislocations introduced by pre-stretching hinder the deformation of the alloy and increase the strength of the alloy. The hardness of SPD sample reached the peak value after taking 9 h aging treatment, the needed time is 17 h shorter than the S sample, to explain this The DSC dynamics analysis will be carried out in Section 4.1.

Figure 2 is the Differential Scanning Calorimeter (DSC) results of SP and SPD samples, the heating rate of DSC experiment is adopted 10 ℃/min. From Figure 2, it can be seen exothermic peaks emerged on DSC curve, it corresponds to the precipitates generation during heating process. Three main exothermic peaks can be judged according to the precipitation sequence of Al-Zn-Mg-Cu alloys: first exothermic peak indicates the GP zones precipitation, second exothermic peak indicates the η’ phase precipitation, third exothermic peak indicates the η phase precipitation. By comparison with DSC curve of SP sample, it is found that the precipitation peaks of the SPD sample DSC curve appear in the front positions.
Figure 2. DSC thermogram of AA7093 alloys treated with SP and SPD.

Figure 3 is the Transmission Electron Microscope pictures (TEM) showing microstructure of SP, T6 and SPDT6 7093 alloys. It can be seen from figure 3 (a), lots of fine precipitates were precipitated in the alloy after pre-aging, the size of precipitates is 2-5 nm, is about half of T6 precipitates (figure 3 (b)). From figure 3 (d), it can be testified that the precipitates is η' phase. Figure 3 (c) shows the microstructure of SPDT6 7093 alloys, it can be seen a lot of dislocations in the microstructure, and some precipitates generated on the dislocations, the size of the precipitates is about 15-20 μm.
4. Discussion

4.1. Kinetic analysis of η’ phase precipitation

The formation of precipitates needs to overcome a certain energy barrier, the smaller the activation energy required for the phase formation is, the easier the formation and growth of precipitates is. According to the literature, Avrami-Johnson-Mehl model combining with DSC can be used to calculate the activation energy of η’ phase [3]. The relevant dynamics equations are as follows:

\[ Y = 1 - \exp(-k^n t^n) \]  
\[ k = k_0 \exp\left(-\frac{Q}{RT}\right) \]  

Where \( Y \) is the volume fraction of precipitation at time \( t \); \( k \) is the rate constant and \( n \) is the growth parameter, which depend on the nuclei density and precipitate growth modes, respectively; \( k_0 \) is frequency factor; \( Q \) and \( R \) are the activation energy of the reaction and gas constant; \( T \) is the thermodynamic temperature.

The logarithmic form of Eq. (1) yields is:

\[ \ln \ln\left[\frac{1}{1-Y}\right] = n \ln t + n \ln k \]  

The rate constant \( k \) and the growth parameter \( n \) are the constants for a process mechanism. Therefore, for a specific value of \( n \), the term \( n \ln k \) in Eq. (3) remains constant. The plot of \( \ln \ln\left[\frac{1}{1-Y}\right] \) vs. \( \ln t \) from Eq. (3) yields a straight line function, from which the value of \( n \) (slope) and \( k \) (from the intercept) can be obtained.

For non-isothermal transformation, it is more expedient to use Eq. (1) in developing transformation rate and related expression. The rate of transformation can be expressed as:

\[ \frac{dY}{dt} = k(T)f(y) \]  

Where \( f(y) \) is the implicit function of \( Y \) combining with Eq. (3) and the derivative of Eq. (1) results in:

\[ f(y) = n(1-Y)[-\ln(1-Y)]^{n-1} \]  

The non-isothermal kinetic data stated in the DSC analysis can be written as:

\[ \frac{dY}{dT} = \frac{1}{\phi} \frac{dY}{dt} = \frac{1}{\phi} k(T)f(Y) \]  

\( Y \) VS \( T \) can be written as:

\[ A(T) \]  

\[ \frac{A}{A_i} \]  

\( A(T) \) is the area between the baseline from the starting point of the peak to the temperature \( T \) and the DSC curves, \( A_i \) is the area of the whole peak. \( \phi \) is the heating rate, and is 10 °C/min in this work. Substituting \( k(T) \) from Eq. (2) into Eq. (6), combining with Eq. (5) and Eq. (7), the result is simplified as:

\[ \ln\left[ \frac{dY}{dT} \frac{\phi}{f(Y)} \right] = \ln k_0 - \left(\frac{Q}{RT}\right) \left(\frac{1}{T}\right) \]  

The Eq. (8) shows that it is the linear relationship between \( \ln\left[ \frac{dY}{dT} \frac{\phi}{f(Y)} \right] \) and \( \frac{1}{T} \), activation energy \( Q \) can be calculated from the slope, the calculation results are shown in the figure 4, the results show that the activation energy of precipitates in SPD alloy is only 60% of that in SP alloy, this lead the precipitates in SPD alloy is easier to precipitate and grow, and it can greatly shorten the time of the hardness reaching peak value during aging treatment.
4.2. Effect of dislocation strengthening and precipitates pinning role on of the Mechanical properties Alloys

The strengthening mechanisms of 7xxx Al alloys mainly include precipitation hardening, grain boundary strengthening, dislocation strengthening and solid-solution strengthening [4]. By comparing figure 3 (a), (b) and (c), it can be seen that with the introducing of pre-deformation, the dislocation density increases greatly in the matrix, the generation of dislocations can provide a fast diffusion channel for heterogeneous nucleation of precipitated phase in subsequent final aging process, comparing with precipitates in homogeneous region, the precipitates on dislocations have a faster growth rate, this led to they grew bigger in the same time. The precipitates on these dislocations can pin the dislocation clusters in the subsequent deformation process, this improves the concentration of stress in these dislocation entanglement areas during deformation, and this will be beneficial to the plastic deformation of the alloy to a certain extent. Therefore, due to the dislocation strengthening and precipitates pinning role in the dislocations, comparing with T6 AA7093 alloy, the strength of the SPDT6 AA7093 alloy has been significantly improved.

5. Conclusions

1. After taking 20 min pre-aging + 4% pre-stretching treatment, the time to reach peak aging strength of AA7093 is shortened to be 9 h, and is 17 h less than T6 AA7093.

2. Kinetic analysis of DSC shows that the activation energy of precipitates in T6 and SPDT6 AA7093 alloys are 216.6 kJ/mol and 129.6 kJ/mol, respectively.

3. Due to the dislocation strengthening and precipitates pinning role in the dislocations, the yield strength and ultimate tensile strength of the SPDT6 AA7093 are 631 MPa and 665 MPa, which are 75 MPa and 29 MPa higher than T6 AA7093, respectively.
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