Effect of pre-recovery heat treatment on microstructure and mechanical properties of cold extruded 2219–0.89Ti aluminum alloy

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2219 aluminum alloy mainly focuses on solid solution and aging treatment. The pre-recovery means that the deformation metal has changed during the heating, some mechanical properties, physical properties and intercrystalline substructures have changed, but the new recrystallization grain has not yet appeared in the annealing process. The pre-recovery heat treatment is a method to increase the nucleation rate of recrystallization in high stacking fault energy (SFE) materials and refine the final grains. It has been reported that the large sub-grains generated during an extended recovery can act as a new nuclei to promote nucleation during subsequent recrystallization. The recovery at low temperature was dominated by point defect movement, and the fine structures such as cellular substructure remained basically unchanged. At higher temperatures, the main changes in the recovery process are dislocation motion and dislocation recombination. It includes the cancellation of heterogeneous dislocations, the transformation of plurilateral subcrystals and deformed cellular structures into typical subcrystalline structures. The microstructure of the metal will be changed obviously by the above process, and the microstructure and structure of the metal will be transformed to the equilibrium state [6, 7].
Table 1. Actual compositions of alloy (wt%).

| Cu  | Mn  | Zn  | Zr  | Sr  | Ti  | Al  |
|-----|-----|-----|-----|-----|-----|-----|
| 6.76| 0.38| 0.10| 0.19| 0.09| 0.89| Bal |

Table 2. Pre-recovery and solution treatment routes for alloys.

| Alloy No. | Pre-recovery and solution treatment routes |
|-----------|-------------------------------------------|
| C1        | 535 °C × 3 h                               |
| C2        | 250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h + 535 °C × 3 h |
| C3        | 250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h + 500 °C × 2 h + 535 °C × 3 h |

Previous efforts have been carried out in order to study the pre-recovery heat treatment fully. As recovery occurs, dislocations annihilation and rearrangement, sub-grains formations and growth will take place in a small scope. The pre-recovery heat treatment can not only reduce the stored energy subsequently for nucleation and growth of the recrystallized grains, but also retards recrystallization. It has been proved by Xu et al. that the strength and toughness of the 7xxx Al-Zn-Mg-Cu aluminum alloy can be effectively improved by pre-recovery heat treatment before the solution treatment. In the stage of pre-recovery heat treatment, by slowly increasing the heat treatment temperature and holding time of the material, the solid solubility of the elements in the alloy increases, which can promote the internal strengthening phase of the alloy to dissolve fully in the matrix without intergranular overburning, and prevent the abnormal grain growth in the alloy. At present, there is little information available in the literatures about pre-recovery heat treatment on the microstructure and properties of 2xxx aluminum alloy with high content of Ti.

Based on the cold extruded 2219–0.89Ti aluminum alloy, the purpose of this article is to investigate the effects of two pre-recovery treatment systems (250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h and 250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h + 500 °C × 2 h) on the microstructure and properties of the alloy before the solid solution treatment at 535 °C × 3 h, in order to provide a theoretical basis for the optimization of heat treatment strengthening of 2xxx heat resistant aluminum alloy with high content of Ti.

2. Experimental

2.1. Materials
The experiment was carried out on the 2219 aluminum alloy with high content of Ti, the main actual chemical compositions were given in details in table 1.

2.2. Specimen preparation
The alloy prepared in advance was smelted by an electromagnetic induction furnace. Mg and Zn were added as a master alloy. The temperature of melting reached as high as 900 °C. Casting started when the temperature dropped to 750 °C. The cold extrusion was carried out in the room temperature and this process will improve the mechanical properties of the alloy. The set tonnage of the hydraulic press is 100 tons, and the extrusion ratio is 7. After cold extrusion, the diameter of the extruded alloy is 12 mm. Then the alloy was investigated in the pre-recovery and solution condition and subjected to artificial aging at 191 °C for 6 h. The purpose of solid solution treatment was to fully dissolve the alloy phase in the matrix and make the alloy composition more uniform.

For instance, three samples were named as C1, C2 and C3. The methods of pre-recovery and solid solution treatment of the three alloys are given in table 2. The sample C1 was directly treated with 535 °C × 3 h solid solution treatment, sample C2 and C3 were treated with two kinds of pre-recovery treatment (250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h, 250 °C × 6 h + 350 °C × 6 h + 450 °C × 2 h + 500 °C × 2 h) to make a comparison with C1 to explore the effect on the microstructure and properties of the alloy respectively. Low temperature recovery (0.1 ~ 0.3T_m) (T_m represents the melting temperature) mainly involves the movement of point defects. Vacancy or gap atoms move to grain boundaries or dislocations to disappear, or they can be aggregated to form empty pairs, vacancy groups, and can interact with gap atoms to disappear. Since the mechanical properties are not sensitive to the change of point defects, the mechanical properties are almost unchanged at this time. The middle temperature recovery (0.3 ~ 0.5T_m) mainly involves the slip motion of dislocation. With the increase of heating temperature, the atomic activity is enhanced, and the dislocation can slip or cross slip on the slip surface, which makes the dislocations attract each other and counteract each other. The dislocations in the entanglement are rearranged and combined, and
the subgrains grow and normalize. The high temperature recovery (higher than 0.5 $T_m$) mainly involves the slip and the climbing movement of the dislocation. With the further increase of the temperature, the ability of the atomic activity is further enhanced, and the dislocation can be moved in addition to the slip. The main mechanism is the vertical arrangement of dislocations (sub-grain boundary), and the second is the multilateralization (sub-grain), so that the elastic distortion can be reduced. At each temperature, the recovery degree has a limit, and the higher the temperature, the faster the performance recovery, and the shorter the time to reach this limit. So the temperature and the time interval of this pre-recovery heat treatment was ranging from 250 °C to 500 °C and 2 hours to 6 hours respectively [12].

2.3. Microstructure examination and properties behavior testing
Samples for Vickers hardness test with a size of 10 mm × 10 mm × 5 mm were prepared. Hardness tests were carried out on an HV-1000 hardness tester with a load of 0.2 kg, the dwell time was 25 s and 3 ∼ 5 measurements were made for each sample to obtain an average value. Tensile properties were tested at room temperature at a strain rate of 0.5 ∼ 1 mm min$^{-1}$, and three measurements were tested for each sample.

Figure 1. SEM image of three alloys: (a) and (b) C1; (c) and (d) C2; (e) and (f) C3.
The electrical conductivity was measured on the 3 specimen for each condition for 4 ~ 6 times. The conductivity measured was present in the unit of % IACS (International Standard, 1% IACS = 0.58 MS⁻¹ [13]). Mean value was calculated to describe the conductivity of the alloy. An optical metallurgical microscope was used to obtain the metallographes. The metallographic corrosive solution was composed of 2 ml HF + 5 ml HNO₃ + 3 ml HCl + 190 ml H₂O in order to study the grain structure. The intergranular corrosion solution was composed of NaCl 57 g L⁻¹ + H₂O₂ 10 ml L⁻¹. The microstructure of the specimens and dislocation enhancement were observed on a JSM-6360LV scanning electron microscope (SEM) and x-ray diffraction (XRD) respectively to study the grain boundaries and adjacent regions as well as the phases of the three samples.

3. Results and discussion

3.1. SEM analysis
The micro SEM diagram of C1, C2 and C3 alloys are shown in figure 1 respectively. As can be seen from the figure, the proportion of undissolved phases inside the three alloys is very small. Cold extrusion can promote the insoluble phase to dissolve in the matrix. Compared with C1 alloy, it is found that the proportion of insoluble phase decreases gradually (figure 1(b)) after the first kind of pre-recovery treatment, only some scattered and fine insoluble phase is distributed in the alloy. After holding at 500 °C for 2 h, there are still some undissolved phase residues in C3 alloy, the quantity of which is slightly smaller than that of C2 alloy, which indicates that most of the intergranular second phase has been dissolved in the matrix before holding at 500 °C, and only a small amount of insoluble phase has been dissolved in the matrix at 500 °C. At this time, the internal solid solubility of the alloy has approached saturation, if the holding time or temperature is further increased, the effect is not improved apparently. The grey undissolved phase of the matrix in the matrix (figure 2) is the θ (Al₂Cu) phase (the solution temperature is about 360 ~ 510 °C) according to the EDS, and the white region is the insoluble Al₃Ti phase (the solution temperature is about 600 ~ 750 °C).

3.2. Metallographic structure analysis
Figure 3 shows the metallographic structure of C1, C2 and C3 samples after solid solution treatment. It is observed by metallographic microscope after soaking in metallographic corrosion solution for 30 s. Figure 3 (a),
(b), (c) corresponds to C1, C2 and C3 alloys, respectively. After cold extrusion, the grain boundary of the alloy is clearer and most of the eutectic phase is soluble in the matrix. In figure 3(a), size of the grain is uneven, the shape is irregular and the grains are interlaced with each other, some grains even grow abnormally. After pre-recovery treatment, the grain size (figures 3(b) and (c)) is more uniform and the abnormal grain growth is not obvious. With the increase of pre-recovery temperature and time, the grain size of each alloy is C1 > C2 > C3. The grain size of C3 alloy is about 150 μm. It is shown that the low temperature soluble phase in the matrix can be fully dissolved in the matrix after pre-recovery heat treatment for a long time at lower temperature, which can inhibit the grain growth [14, 15].

### 3.3. XRD analysis and dislocation enhancement

Figure 4 shows the XRD spectra and half peak width of C2 and C3 alloys after solid solution treatment, figures 4(a), (c), (e) are the analytical spectra of C1, C2 and C3 alloys, figures 4(b), (d), (f) are the corresponding half peak widths of each alloy, respectively. The XRD analysis spectra of C1, C2 and C3 alloys are compared with those of pure Al (figure 5). It is found that the semi-peak value of figure 4(a) is quite different from that of pure Al, indicating that the proportion of internal texture of the alloy is larger. After pre-recovery heat treatment, the semi-high peak value of the alloy is closer to that of pure aluminum, among which C2 alloy is the closest (figure 4(c)), shows that pre-recovery treatment will reduce the crystal texture of the alloy. Compared with the half peak width of the three alloys, the half peak width of C2 alloy is the largest after pre-recovery treatment, and the change trend of half peak width is the same as that of half peak value.

According to the above data, the dislocation density of three kinds of materials and the corresponding contribution value of dislocation enhancement can be obtained. Coherent diffraction region size (d), lattice deformation (⟨ε²⟩) and half peak width (FWHM: obtained from XRD data) (δ2θ), X-ray wavelength (λ), the angle position of the highest peak of diffraction peak (θ₀), relationship of the physical quantities above can be expressed by the following equation [16, 17].

\[
\frac{(\delta 2\theta)^2}{\tan^2 \theta_0} = 25 \langle \epsilon^2 \rangle^2 + \frac{\lambda}{d} \left( \frac{\delta 2\theta}{\tan \theta_0 \sin \theta_0} \right)
\]
Figure 4. XRD spectrum: (a) C1; (c) C2; (e) C3; FWHM: (b) C1; (d) C2; (f) C3.

Figure 5. XRD spectrum for pure Al.
The data of $q_0$ and FWHM $(\Delta 2\theta)$ can be obtained according to figure 4, and these data are then used to fit the functional diagram of the 4 alloys of figure 6. The coherence diffraction region size ($d$) and the mean lattice strain ($\langle \varepsilon^2 \rangle^{1/2}$) of the XRD are calculated according to the slope of the straight line in figure 6 and the intercept parameter at the time of the intersection with the y-axis. As can be known from the following equation, the greater the lattice strain, the greater the dislocation density in the alloy [18].

$$\rho = 2\sqrt{3} \langle \varepsilon^2 \rangle^{1/2} / (d \times b)$$  

(2)

The vector (b) in this formula is 0.286 nm for aluminum alloy. In this way, the dislocation density ($\rho$) of the alloy is obtained. Dislocation enhancement ($\sigma_\rho$) can be calculated by the following equation [19].

$$\sigma_\rho = M_0Gb\rho^{1/2}$$  

(3)

In the formula, $M$ is a Taylor orientation factor, and its value is 3.06, $\alpha$ represents a numerical factor and its value is 0.24. $G$ represents shear modulus, which is 26 GPa. According to the above three equations, the related dislocation parameters are presented in table 3.

From the data in the table 3, it can be seen that the dislocation parameters after pre-recovery heat treatment are higher than that without pre-recovery, which are consist with the figure 3 that the grain size of C2 and C3 alloy are smaller than the C1 alloy. With the increase of time and temperature, the strengthening effect of dislocation density increases first and then falls, which indicates that a small amount of dislocation inside the alloy has been consumed at 500 °C × 2 h heat preservation, resulting in the reduction of contribution rate of dislocation enhancement. The process of pre-recovery and recrystallization are competing with each other, and their driving forces are the energy storage in the deformation state. Therefore, the degree of pre-recovery depends on the difficulty of crystallization. On the contrary, the pre-recovery not only reduces the driving force...
of crystallization, but also affects the crystallization. The pre-recovery does not completely release the cold deformation energy, and only the recrystallization process will completely eliminate the work hardening [20]. In addition, the lattice strain increases after pre-recovery treatment, and the larger the lattice strain is, the lower the quench sensitivity of the alloy will be [21], which indicates that the quench sensitivity of the alloy will be decreased by pre-recovery treatment.

3.4. Hardness and Conductivity

Figure 7 shows the conductivity and hardness curves of C1, C2 and C3 alloys, table 4 shows the specific parameters of hardness and conductivity, and the samples tested by hardness and conductivity are samples after solid solution aging. It can be found from the diagram that the hardness and conductivity of the alloy are increased after pre-recovery treatment, the value of C3 alloy is the highest, in which the hardness is increased by 10.18 HV, reaching 150.6 HV. The conductivity is increased to 22.53% IACS, indicates that the pre-recovery treatment will increase the hardness and stress corrosion resistance of the alloy.

![Figure 7. Hardness and conductivity curve for three alloys.](image)

| Table 4. Specific values of hardness and conductivity for C3~C5 the alloys. |
|--------------------------|--------------------------|--------------------------|
| Alloy No. | Hardness (HV) | Conductivity (%IACS) |
| C1 | 140.42 | 22.49 |
| C2 | 148.98 | 23.19 |
| C3 | 150.60 | 23.53 |

| Table 5. Mechanical properties parameters. |
|--------------------------|--------------------------|--------------------------|
| Sample | Tensile strength/MPa | Yield Strength/MPa | Elongation/% |
| C1 | 416.67 | 354.65 | 8.6 |
| C2 | 449.36 | 376.92 | 17.5 |
| C3 | 457.14 | 379.39 | 12.8 |

3.5. Room temperature tensile properties

Table 5 shows the yield, tensile strength and elongation after break of the three alloys.

Compared with the data in the table 5, the yield strength and tensile strength of the samples treated by pre-recovery heat treatment are higher than those of monopole solid solution treatment, and the strengthening effect on plasticity increases at first and then decreases, among which C3 has the best mechanical properties, the yield strength and tensile strength are 379.39 MPa, 457.14 MPa, respectively, and the extension after break is 12.8%. This is due to the long holding time of pre-recovery heat treatment at low temperature, which makes the
low temperature soluble phase of the alloy fully dissolve in the matrix, which suppresses the grain growth, and the mechanical properties of the alloy are greatly improved. Compared with C3 alloy, C2 has the best extension rate of 17.5% and little increase in strength, which increases 2.47 MPa and 7.78 MPa, respectively. According to the phase-temperature analysis, most of the eutectic phases are dissolved in the matrix before 500 °C, and only a small part of eutectic phase dissolves in the matrix at 500 °C for 2 h, so the increase is not obvious.

3.6. Resistance to intergranular corrosion

The intergranular corrosion diagram of C1, C2 and C3 alloys is shown in figure 8. Figures 8(a)–(c) is C1, C2 and C3 alloys after solid solution aging and soaking in intergranular corrosion solution at 35 °C for 6 h. Table 6 is the evaluation table of intergranular corrosion grade.

It can be seen from the diagram that the maximum corrosion depth of the three alloys is in the range of 100 ~ 300 μm, and the grade is 4. Compared with the maximum intergranular corrosion depth of the three alloys, the corrosion depth of C1 alloy is the largest, reaching 193.9 μm. There is an uneven grain corrosion pit on the side and surface of the corrosion morphology. The corrosion solution has been corroded along the grain boundary to the inside, and the outer grain boundary begins to appear, showing a reticular structure (figure 8(a)). The intergranular corrosion depth of the alloy decreases after the first kind of pre-recovery heat treatment system, and the corrosion depth of the alloy in figures 8(b) is 162.17 μm. The corrosion depth of C3 alloy treated with the further pre-recovery heat treatment is the smallest, and the value is about 42.3 μm, which is lower than that of C1 alloy, and the intergranular penetration of corrosion solution in the surface grain is not

| Alloy No. | Maximum corrosion depth (μm) | Rank |
|-----------|-----------------------------|------|
| C1        | 193.90                      | 4    |
| C2        | 162.17                      | 4    |
| C3        | 151.60                      | 4    |

Figure 8. Intergranular corrosion diagram of alloys: (a) C1; (b) C2; (c) C3.
obvious, and some outermost grains are corroded off. It is shown that the pre-recovery heat treatment can improve the corrosion resistance of the alloy, which is due to the small degree of recrystallizing, the small amount of equiax grains as well as the large proportion of the small angle grain boundary of the alloy. Compared with the large angle grain boundary, the energy of the low angle grain boundary is lower, the enrichment degree of the aging precipitated phase is much lower than that of the high angle grain boundary, and it is not easy to form a continuous grain boundary precipitation phase, which will hinder the formation of the sensitive active channel. It is beneficial to improve the intergranular corrosion properties of the alloy [22, 23].

4. Conclusions

Based on the composition of cold extruded 2219–0.89Ti aluminum alloy with high content of Ti, the microstructure and properties of two kinds of pre-recovery treatment processes were studied in this paper. The three alloys numbered C1 were directly treated with solid solution at 535 °C × 3 h, and the pre-recovery solid solution treatment systems for C2 and C3 alloys were 250 °C × 6 h 350 °C × 6 h 450 °C × 2 h 535 °C × 3 h and 250 °C × 6 h 350 °C × 6 h 450 °C × 2 h 500 °C × 2 h 535 °C × 3 h. The main conclusions were as follows:

(1) The pre-recovery heat treatment can promote the insoluble phase of the alloy to dissolve in the matrix, inhibiting the abnormal growth of grain, further refine the grain, and the dislocation enhancement effect shows the tendency of first and then fall.

(2) The hardness and conductivity are improved after the pre-recovery heat treatment processes. The alloy with the second pre-recovery heat treatment process has the highest hardness and conductivity which are 150.6 HV and 23.53% IACS, respectively.

(3) For the three alloys after cold extrusion, the strength at room temperature increases with the increase of pre-recovery treatment time. The alloy with the second pre-recovery heat treatment process has the highest tensile strength. Compared with the alloy without pre-recovery heat treatment, the tensile strength of the alloy is increased by 40.47 MPa to 457.14 MPa, and the extension rate after break is 12.8%. At the same time, the alloy has good intergranular corrosion resistance, and the maximum corrosion depth is reduced by 42.3 μm to 151.6 μm.

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