Effects of Cu element and heat treatment process on microstructures and properties of 6016 aluminum alloy

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Abstract—The 6016 aluminum alloy was artificially aged at different aging temperatures and time. The effects of Cu on microstructures, hardness, tensile properties and corrosion resistance of 6016 aluminum alloy were studied. The results show that the grains of the alloy added Cu are refined and new phase Q (AlCuMgSi) appears, and the mechanical properties of the alloy in T4p state are improved and the time to reach the strength peak is shortened. The intergranular corrosion resistance of the alloy decreases with the aging time, and turns to pitting corrosion in the later stage, and it suggests that the intergranular corrosion resistance of 6016 aluminum alloy added Cu is reduced.

1. Introduction

Energy and environmental protection are two major problems that need to be continuously improved until solved with social development. To promote the progress of the automobile industry, exploration must be made in the direction of new energy and lightweight so as to meet the strict requirements of energy conservation and emission reduction [1-3]. Studies have proved that for every 10% reduction in vehicle weight, fuel consumption will be reduced by 6% ~ 8% and gas emissions by 4% [4]. At present, 6016 aluminum alloy, as a typical heat treatment strengthening alloy, has been successfully applied in some major parts of automobiles.

Microalloying is an effective way to increase the comprehensive properties of 6XXX aluminum alloy. By adjusting the alloy composition, the precipitation type and sequence of the second phases in the
artificial aging process can be modified to achieve the purpose of changing the performance of the aluminum alloy. Liu et al. [5] studied the effects of trace elements Mn, Cr and Zr or Sc on the microstructures and properties of 6016 aluminum alloy, and the results showed that all these elements had the effect of grain refinement to a certain extent, produced new dispersion phase, changed the type and distribution of the second phase, and improved the properties of 6016 aluminum alloy to different degrees. He et al. [6] showed that under the condition of peak aging, adding Cu could aggravate the corrosion degree of the alloy. Ding L. [7] studied the natural aging and precipitation hardening behavior of Al-Mg-Si-Cu alloys with different Mg/Si ratios and Cu additions, and the results showed that Al-Mg-Si-Cu alloys with high Cu content had better thermal stability than their counterparts with high Si.

In this paper, 6016 aluminum alloy was taken as the research object to explore the effect of Cu, aging temperature and time on the structures and properties of it. The aging temperature was 160 ℃, 180 ℃, 200 ℃ and 220 ℃.

2. Experiment

The experimental material was 6016 aluminum alloy sheets produced by a domestic company. The T4p sheet was obtained after solid solution by air cushion furnace and artificial aging treatment by pre-aging furnace. The weight percentage of alloy components is shown in Table 1.

| Alloy | Si     | Mg     | Cu     | Mn     | Fe     | Cr     | Ti   | Al     |
|-------|--------|--------|--------|--------|--------|--------|------|--------|
| A     | 1.1201 | 0.4775 | 0.0189 | 0.119  | 0.1644 | 0.025  | 0.026| 97.974 |
| B     | 1.069  | 0.4578 | 0.0945 | 0.118  | 0.1758 | 0.0191 | 0.029| 97.965 |

Artificial aging experiment was carried out on the alloy in T4p state after 7 days of natural aging. The aging temperature was selected as 160 ℃, 180 ℃, 200 ℃ and 220 ℃, and different time of heat preservation was carried out at the corresponding aging temperature. After that, the microstructures and the mechanical properties were analyzed. In this experiment, these microstructures of the 6016 alloys were analyzed by DM2500M metallographic microscope (with polarized light), S-3400n scanning electron microscope, X-MAX energy spectrometer and FEI Tecnai G2 F20 transmission electron microscope. DSC was carried out on the DIFFERENTIAL thermal analyzer STA 449 F3 Jupiter synchronous thermal analyzer scanning. Hvs-1000 Vickers hardness tester was selected for hardness test. The load during the test was 0.5kGF and the pressure was maintained for 15 s. Z100THW tensile testing machine was used for tensile test. Two side and center samples were selected for the test. Three parallel samples were taken from each part, and each sample was selected along the direction perpendicular to rolling. The size is shown in Figure 1, and the thickness of sample is 1mm.

![Figure 1. Size of the tensile sample (unit: mm)](image)

According to GB/T 7998-2005 standard, the corrosion liquid was (30 g/LNaCl+10 mL/L H2O2), and the sample size was 20 mm (vertical rolling direction) ×40 mm (along the rolling direction) ×1 mm rectangular sheet.
3. Results and analysis

3.1. As-cast microstructure

The (a) and (b) in Figure 2 are the metallographic structure of the original as-cast A and B alloy. It shows that there are more dendrites in these alloys. Compared with A alloy, the grain boundary of B alloy is more obvious. The (c) and (d) in Figure 2 respectively show the microstructures of the alloys after the same corrosion. It can be seen that the grain boundary of B alloy is clearer, and the dendrite network structure is more obvious than that of A alloy, and the grain size of B alloy is smaller than that of A alloy. In order to further verify the comparison of grain size between the samples, the microstructures of the two kinds of alloys obtained by electrolysis polishing and anodic coating (shown as figure 2 (e) and (f)) were analyzed and counted (the statistical results are shown in Table 4). It shows that the alloy added Cu is refined, and the average size of grain decreases about 47μm, while the average grain size increases 1 grade.

![Figure 2. Microstructure of as-cast 6016 aluminum alloys](image)

A alloy: (a), (c), (e); B alloy: (b), (d), (f)

| The sample | Average intercept/μm | Average grain grade index/G |
|------------|----------------------|-----------------------------|
| A          | 149.89               | 2.19                        |
| B          | 102.76               | 3.27                        |

Table 2 Grain size statistics of as cast samples A and B

The microstructures of the alloys in as-cast state by SEM are shown as Figure 3. It can be seen that there are several shapes of precipitates: long white stripes of different thickness, irregular white polygons, round or oval shapes, and black polygons. The different thickness of stripes or irregular white polygons are β phase (AlFeSi) (as shown A, B, C, E, H, J, K in Figure 3). The grey-black polygons are excess eutectic Si and Mg2Si (as shown D, F, L in Figure 3). The gray round or elliptic containing Cu is Q(AlCuMgSi) phase (as shown G, I in Figure 3), and this phase appears in the B alloy with high copper content.
content. The formation of this new phase hinders the growth of grains and plays an important role in refining grains.

![Figure 3. SEM of as cast 6016 aluminum alloy A alloy: (a), (b); B alloy: (c), (d).](image)

3.2 As-cast microstructure

Figure 4 (a) and (b) are the original metallographic photos of the alloys in T4p state. It shows that, after solution treatment and artificial aging, the coarse phase is dissolved back into the matrix, however, there are black spherical precipitates and irregular precipitated phases. It is preliminarily determined that they are Fe phase, or Si particles without solution treatment, or Mg₂Si. There is no obvious difference in microstructure between A and B alloys. The (c) and (d) in Figure 4 are the metallographic photos after electro polishing and anodic coating. It shows that after solution treatment and artificial aging of plate alloy, the grains are polygonal in uniform distribution, and the fiber structure basically disappears after rolling. The grain sizes of A and B alloys are calculated, and the results are shown in Table 3. After Cu is added, the grain size of B alloy is smaller than that of A alloy, which is consistent with the results obtained in the as-cast state.

![Figure 4. SEM of as cast 6016 aluminum alloy A alloy: (a), (c); B alloy: (b), (d).](image)
Table 3 Grain size statistics of A and B alloy samples in T4p states

| Alloy | Average intercept /μm | Average grain grade index /G |
|-------|------------------------|----------------------------|
| A     | 29.32                  | 6.9                        |
| B     | 25.72                  | 7.3                        |

Figure 5 is the SEM diagram of A and B Alloy in the T4p state. After solid solution and artificial aging, the long strip β phase becomes shorter obviously, and some bright white phase and dispersed phase of different shapes and sizes are also distributed. Such small dispersed precipitation may be solute clusters is performed on some labeled points in the figure [8-10]. The results of energy spectrum analysis are shown in Table 4. It shows that after solution treatment and artificial aging, most of the precipitated phases in the alloy have been basically back dissolved and leaving the insoluble (AlFeSi) phase. It notes that the phase (AlCuMgSi) containing Cu in the B alloy (shown as G point in the Figure 5) is also insoluble.

Figure 5. Microstructure of 6016 aluminum alloy in T4p state
A alloy: (a); B alloy: (b).

Table 4 Energy spectrum analysis results of each characteristic point of as cast

|          | Al  | Si  | Mg  | Fe  | Mn  | Cu  |
|----------|-----|-----|-----|-----|-----|-----|
| A        | 75.85 | 14.50 | -   | 9.65 | -   | -   |
| B        | 72.43 | 22.30 | 4.43 | 0.43 | -   | -   |
| F        | 58.35 | 21.47 | 20.18 | -   | -   | -   |
| G        | 54.88 | 30.7  | 13.23 | -   | -   | 1.19 |

3.3. DSC analysis

The precipitation sequence of 6XXX aluminum alloy phase is as following[11]: supersaturated solid solution → clusters (Si and Mg clusters) →GP region →β″ phase →β ′ phase →β phase, and β″ phase has the best strengthening effect among them. The differential scanning calorimetry curves of the alloys are shown in Figure 6. It can be seen that both the alloys have a precipitation peak at about 225°C, according to the phase diagram, the phase of the precipitated peak is β″ phase. According to the analysis of the curve, the activation energy of B alloy and A alloy are 0.718 J/g and 0.7979 J/g respectively. Therefore, increasing Cu content can reduce the activation energy of β″ phase and promote the precipitation of β″ phase.
3.4. Effect of different aging temperature on the hardness of alloy

In this experiment, 160℃, 180℃, 200℃ and 220℃ were selected as the baking temperatures respectively. Meanwhile, samples were taken at different times during the whole baking process, and the variation law of hardness with time at different aging temperatures was obtained as shown in Figure 8.

It shows that when the aging temperature of the alloys is 160 ℃ or 180 ℃, the hardness value increases monotonously with the extension of aging time, while in the early stage the hardness of B alloy increases obviously. However, when the aging temperature reaches 360 min, neither alloy reaches the peak point of hardness, and both are in the underaging stage. B alloy reaches the peak earlier than A alloy, and the strength is higher than that of A alloy. The aging time values of A alloy and B alloy to reach the peak point are 240 min and 30 min respectively. This is because the activation energy of β″ of B alloy added Cu decreases, and β″ is easier to precipitate. When the aging temperature is 220 ℃, both A and B alloy reach the peak point at 30 min, while the peak hardness values of A alloy and B alloy are 94.83 HV and 101.93 HV respectively. In general, the hardness of B alloy added Cu is higher than that of A alloy.

It is noted that the variation of the aging curves at 200℃ and 220℃ is different from that at 160℃ and 180℃. The hardness of the former increases in zigzag in the early stage and decreases gradually in the later stage, because at the initial stage of aging, the clusters and GP regions were formed by natural aging dissolve and the β′″ phase gradually precipitated at the initial stage of aging, that results in a zigzag increase in hardness. It is known that the strengthening degree of precipitated phase is β″>β′>β, and the transformation from β″→β′→β occurs in the later stage of aging, so the hardness of the alloy decreases gradually [12-13].

3.5. Effects of aging temperature on tensile properties of alloys

The time variation curves of mechanical properties (tensile strength Rm, yield strength Rp0.2 and elongation A50) of A and B alloys at the above aging temperature are shown in Figure 9. Table 5 shows the peak points of mechanical properties of A alloy and B alloy, and the corresponding aging time. It can
be seen that the yield strength and tensile strength of the two alloys show an increasing trend when the aging temperature is 160 °C, the time of B alloy to reach the peak tensile strength is shorter than that of A alloy, and the tensile strength peak (302.37 MPa), and yield strength peak (240.72 MPa) of B alloy are both higher than those of A alloy (tensile strength 299.19 MPa, yield strength 234.72 MPa). Under the temperature of 180°C, the yield strength and tensile strength of two alloys first increases and then slowly decreases, while the time for B alloy to reach the peak of yield strength is 120 min less than that of A alloy, and the time for reaching the peak of tensile strength is 60 min less than that of A alloy, and two peak strength values of B alloy are higher than those of A alloy. When the temperature rises to 200 °C, the tensile strength and yield strength of two alloys increase first and then decrease. Yield strength: A alloy reaches the peak value (234.92MPa) at 80min, and B alloy reaches the peak value (244.17MPa) at 60min. Tensile strength: A alloy reaches the peak value(283.52MPa) at 45min, and B alloy reaches the peak value(289.93MPa) at 40min. When the temperature is 220 °C, the tensile strength and yield strength of the two alloys still increase at first and then decrease, and the peak strength values of B alloy are higher than those of A alloy. It is also shown from the table that the elongation of B alloy is slightly lower than that of A alloy except the value of 180 °C.

With the increase of Cu content, the activation energy of β'' phase precipitation in B alloy decreases, so at the same aging temperature, B alloy precipitates β'' phase more easily than A alloy, which makes the strength of B alloy at the peak point higher. For the same alloy, with the increase of aging temperature, the time to reach the peak point is shorter, because the higher the aging temperature, the faster the transformation rate of clusters and GP region into β'' phase. The higher the aging temperature is, the larger the size of the second phase precipitated in the alloy is, which is easier to promote the transformation from β'' phase to β' phase in the alloy, so the strength of the alloy decreases with the increase of aging temperature [14].

Figure 8. Performance change curve of A and B alloys with time at different temperatures
Table 5 Specific performance values of A and B alloys at different temperature

| The sample performance | A | B |
|-------------------------|---|---|
| Rp0.2(Mpa) | Rm(Mpa) | δ (%) | Rp0.2(Mpa) | Rm(Mpa) | δ (%) |
| 160°C | 234.72 | 299.19 | 20.49 | 240.25 | 302.37 | 19.22 |
| Corresponding time | 960min | 960min | 960min | 840min |
| 180°C | 243.09 | 293.22 | 17.48 | 243.83 | 295.95 | 18.20 |
| Corresponding time | 600min | 240min | 480min | 480min |
| 200°C | 234.92 | 283.52 | 17.30 | 244.17 | 289.93 | 16.47 |
| Corresponding time | 80min | 45min | 60min | 40min |
| 220°C | 223.28 | 264.44 | 15.45 | 234.32 | 274.09 | 14.71 |
| Corresponding time | 30min | 10min | 30min | 10min |

3.6. Effect of artificial aging on intergranular corrosion performance of alloy

The two alloys aged under 200 °C for 5 min, 30 min, 50 min, 180 min and 480 min were made accelerated corrosion test, and the intergranular corrosion depth values at different aging time are shown in Figure 10. It shows that the intergranular corrosion sensitivity of the two alloys are low, the intergranular corrosion tendency of the alloys is less, and the strength of the alloys is not high enough and is in the state of underaging. While aging 180min, the intergranular corrosion resistance of the alloy is the worst, and the corrosion depth is 124 μm for A alloy and 175 μm for B alloy. When the aging time is extended to 480min, the intergranular corrosion resistance of the two alloys is enhanced, and the corrosion type of the alloy gradually turns to pitting corrosion. In general, the corrosion resistance of 6016 aluminum alloy added Cu is weaker than that of the alloy unadded Cu.
Figure 9. Maximum corrosion depth of A alloy and B alloy selected at each stage of aging process

(a), (b), (c), (d), (e) are corrosion depth values of A alloy when corrosion time respectively are 5 min, 30 min, 50 min, 180 min, 480 min

(f), (g), (h), (i), (j) are corrosion depth values of B alloy when corrosion time respectively are 5 min, 30 min, 50 min, 180 min, 480 min

4. Conclusion
The 6016 aluminum alloy was artificially aged at different aging temperatures and time. The effects of Cu on microstructures, hardness, tensile properties, and corrosion resistance of 6016 aluminum alloy were studied. The results are as following:

(1) The as-cast microstructure of the alloys mainly includes β-(AlFeSi), hypereutectic Si, Mg2Si and other phases, but a new alloy phase Q (AlCuMgSi) is found in the alloy added Cu. The grains of the alloy added Cu are refined. After soaking-solid solution-pre-aging, most of the phases in the alloys have been dissolved in the matrix, but β-(AlFeSi) and Q (AlCuMgSi) are insoluble phases.

(2) Under T4p, the mechanical property of the alloy added Cu is better than that of the alloy unadded Cu. In the artificial aging stage, at different aging temperatures, the higher the aging temperature is, the shorter the time to reach the peak strength is. At the same aging temperature, the time for the alloy added Cu to reach the peak strength is obviously less than that of alloy unadded Cu. When aging at 160℃, 180℃ and 200℃, the time values to reach the peak point of strength are reduced by 12.5%, 25%, 11% respectively after adding Cu, and the strength values are higher than those of the alloy unadded Cu.

(3) The intergranular corrosion resistance of the alloy added Cu decreases with the aging time, and turns to pitting corrosion in the later stage, and it suggests that the intergranular corrosion resistance of 6016 aluminum alloy added Cu is reduced.

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