Effects of Three-Step Aging on Microstructure and Stress Corrosion Cracking of 7N01 Aluminum Alloys

Shuai Wang, Binghui Luo*, Yaya Zheng, Sizhi Tan, Gen Jiang and Guochao Cai
School of Materials Science and Engineering, Central South University, Changsha 410083, PR China
Correspondence: lbh@csu.edu.cn

Abstract. The precipitation of 7N01 alloy after three-step ageing treatment at 65°C, 100°C and 150°C has been investigated. The SAED results show that at 65°C pre-aging the GPI zones were precipitated from the quenched solid solution and aging at 150°C results in evolution of the GPI zones formed during under ageing into the η' phase. It was found that compared with the two-stage aging (T74) and T6 aging, pre-aging at 65°C significantly increased number density of η' phase. The modified microstructure results in tensile properties comparable to that of the T6 temper, but with significantly improved the resistance of stress corrosion cracking performance.

1. Introduction
Al–Zn–Mg(Cu) alloys are used for structural applications in the aerospace and high-speed train industries. Due to their high specific mechanical properties, they have a wide range of potential applications. The present study is related to alloys used in load-bearing beams for high-speed trains. The usual precipitation sequence of 7xxx series Al alloys can be summarized as: Solid solution → Guinier Preston zones (GPZs) → Metastable η' phase → Stable η' phase (MgZn2). GPZs and Metastable η' phase is believed to be responsible for peak hardening of 7xxx series Al alloys. Therefore, in order to obtain the best performance, proper control of early precipitation, especially the size and density of these precipitates is crucial. It has also been generally acknowledged that two types of GP zones may form in 7xxx series Al alloys [1 -6]. GPI zones are reported to form as ordered and coherent layers of Zn and Mg/Al atoms on {100}Al and these ones generally exhibit spherical morphology [2 -6]. GPI zones are easily observed by bright field transmission electron microscopy (BFTEM). Probably due to its incomplete internal order [4], GPI zones have not been observed by High resolution transmission electron microscopy (HRTEM). These precipitates form from 25°C up to about 140°C and they serve as the precursor of the η' phase and η phase [4]. GPII zones are believed as Zn-rich layers on {111}Al planes and formed after quenching from temperatures above 450°C and ageing at temperatures above 70°C[7,8]. GPII zones also can be served as the precursor of the η' phase and η phase. Positron annihilation spectroscopy (PAS) investigations indicate that the interaction between solute atoms and vacancies, especially Mg-vacancy, Zn-vacancy or Zn2-vacancy complex, have a significant effect on GP zone formation [1–3]. The small angle X-ray scattering (SAXS) experiment [9,10] has suggested that the coexistence of two types of particles with different sizes aged between about 60°C and 100°C in 7xxx series Al alloys, one of which is smaller GP zones and the other is larger η' particles. Although the existing researches [11,12] have done a lot of works on the precipitation behavior of industrial alloys such as 7N01 Alloy, 7050 Alloy and 7075 Alloy, our understanding of all-stage precipitation is still limited, and especially there is a lack of quantitative information regarding the morphology, chemistry, size and density evolution. The bright field TEM and its corresponding selected area
electron diffraction patterns (SAEDPs) are often used to observe the size and type of precipitate phases. In the present work, the effect of duplex ageing treatments (100°C and then 150°C) on the precipitation and properties of the Al-Zn-Mg(Cu) alloys were investigated, with the main aim of understanding the evolution of precipitation phase. The industrial heat treatments of 7N01 alloy, usually conducted by ageing at 100°C and then at 150°C, which reduce susceptibility to stress corrosion cracking (SCC), but at the expense of strength simultaneously [13]. In this paper the investigation of precipitation in 7N01 alloy after three-step ageing treatment (PT74) at 65°C, 100°C and 150°C was studied, which aims at understanding the effect of 65°C pre-aging on the phase transformation and the resistance of stress corrosion cracking of 7N01 aluminum alloy.

2. Materials and Methods
The raw material used in this study is 10mm thick 7N01 plate with the chemical composition of Al-4.23%Zn-1.47Mg-0.12Cu-0.34Mn-0.18Cr-0.16Zr-0.09Ti (wt.%) provided by Northeast Light Alloy Co., Ltd.. The samples were solution treatment at 475°C for 1.5 hours and then quenched in water at room temperature (25°C), which was followed by varied heat treatments including T6, T74 and three-step ageing (P-T74) respectively. The detailed heat treatment processes were listed in Table 1. The alloy sheets were cut into sample pieces of 10mm x 10mm x2mm in dimensions to test hardness and 50mm x 50mm to test conductivity. The hardness was tested using the HV-5 Vickers hardness tester with a load of 0.5 kg holding for 15s. The conductivity tests were carried out by the D60K digital metal eddy current conductivity meter. The development of microstructure during the aging treatments was studied by means of TEM (FEI Tecnai G2 20ST) operating at 200 kV. Specimens for all TEM observations were electro polished in a solution of 25% HNO3 in methanol at -30°C and 18.5 V. The slow strain rate tensile specimen size standard is shown in Figure 1 and the slow strain rate was 6.67×10^-6 s^-1. In this experiment, the resistance of stress corrosion cracking (Rsc) of 7N01 aluminum alloy in 3.5%NaCl aqueous solution was evaluated by the following formula:

\[ R_{SCC} = \frac{\sigma_{b(NaCl)}}{\sigma_{b (air)}} \]

Table 1. Heat treatment processes applied for the 7N01 aluminum alloys.

| Temper | Heat treatment                        |
|--------|--------------------------------------|
| T6     | 120°C/98h                            |
| T74    | 100°C/24h+150°C/8h                   |
| P-T74  | 65°C/24h+100°C/24h+150°C/8h          |

Figure 1. Specimen geometry used for mechanical properties testing

3. Results

3.1. Hardness and Conductivity
The age-hardness and the conductivity curves of the 7N01 aluminum alloys are shown in Fig 2. As shown in Fig 2(a) we can see that there are two peak points of T6 state of the 7N01 aluminum alloy, namely peak 1 and peak 2, respectively. Peak 1 is mainly composed of GP zones, however at present there is unified conclusion that the first peak in the double peak aging of 7xxx aluminum alloys is mainly by GPII zones [14-17]. The peak 2 is dominated by the η′ phase and the hardness value of the peak 2 is higher than that of the peak 1. In addition the peak 2 is generally referred to as the peak aging point. From Fig 2(a) we can see that the hardness of the two peak points were 137.6HV
and 148.2HV and the electric conductivity of the two peak points were 32.5 IACS.% and 33.5 IACS.% respectively. Fig 2(b) shows age-hardness and the conductivity curves of the 7N01 aluminum alloys in over-aged state (T74). The hardness curve of the alloy after T74 heat treatment don't show two peak points, which is different from the result of T6 heat treatment. The highest hardness value of the alloy after T74 heat treatment is only 133HV, but the conductivity is higher than the T6 state and the average value is 33.8 IACS.%, which indicates that the resistance of stress corrosion cracking of the alloy may be better than the alloy after T6 heat treatment. Fig 2(c) shows age-hardness and the conductivity curves of the 7N01 aluminum alloys in three-step aging state (P-T74). As shown in Fig 2(c) we can see that the highest hardness value of the alloy after P-T74 heat treatment is 145HV, which is almost the same as the highest hardness value of the alloy after T6 heat treatment. In addition, the average electrical conductivity value of the alloy after the P-T74 heat treatment is 34.2 IACS.%, which is the highest among the three. The results of electrical conductivity indicate that the P-T74 heat treatment may be the best of the three heat treatments of the stress corrosion cracking resistance of the alloys.

Figure 3. TEM micrographs of the 7N01 aluminum alloys of three different aging treatments: (a, d) T6; (b, e) T74 and (c, f) P-T74

3.2. Microstructures and Precipitation Behaviors
Figure 3 shows the TEM micrographs of the 7N01 aluminum alloys of three different aging treatments in <001> zones axis. (a), (b) and (c) in Fig 3 are comparisons of precipitated phases in the alloy after three different heat treatments. After 98 hours of peak aging, the density of precipitated phase in the crystal is significantly higher than that of the other two aging heat treatments and the size of the precipitated phases is the smallest. Comparing (a) and (b) of Fig 3, we can see that their precipitated phases are about the same size, which value are about 10nm up to 20 nm, but the precipitated phase size of the T6 aging heat treatment is only 3nm up to 10 nm. According to the literatures [18,19], for aging-strengthened aluminum alloys, precipitations contribute most to the strength of alloy and the strength is mainly determined by the volume fraction, size and distribution of precipitate phase. It can be seen from Fig 3 that the density of the precipitated phase of the three aging heat treatments is T6 P-T74 and T74 in the end and the size of the precipitated phase after T6 aging heat treatment is the smallest, and the size of the precipitated phase after heat treatment of T74 and P-T74 is almost the same. However, it can be clearly seen from Fig 3(a) that most of the precipitated phases are in a state of aggregation after the alloy has been aged for 98h and thus this aggregated precipitation phases can't fully exhibit the effect of dispersion strengthening. In the other hand after the T74 and P-T74 aging heat treatments, the degree of dispersion of the precipitated phase is significantly higher than that of
T6 aging heat treatment. Therefore, compared with the microstructure, the alloy has higher strength after aging treatment with T6 and P-T74.

Fig 3(d), (e) and (f) show the TEM bright field images of the precipitated phase in the grain boundaries of the alloy after three different heat treatments. Comparing the precipitation phases in Fig 3(d), (e) and (f), it can be observed that the grain boundary precipitated phases of T6 aging treatment are mostly in small size and continuous distribution, moreover the width of precipitate free zones (PFZ) is the most narrowest and the average value is only 30.72nm. The Fig 3(e) shows that the grain boundary precipitated phases of T74 aging treatment are mostly in larger size than that of T6 treatment and basically in intermittent distribution. The PFZ width of the alloy is the largest of the three heat treatments and the average value is up to 41.56 nm. At last we can see from the Fig 3(f) that the grain boundary precipitated phases of P-T74 aging treatment are in the largest size of the three heat treatments and discontinuous distribution of the precipitated phase is more obvious than other aging heat treatments. According to the literature [20], it is not easy of such microstructure to form corrosion channels, so they have better resistance to stress corrosion cracking.

3.3. Mechanical Properties and Resistance of Stress Corrosion Cracking

Fig 4 shows the results of slow strain rate tests (SSRT) of the alloy in the air and 3.5% NaCl aqueous solution respectively. The yield strength of the alloy after T6 heat treatment in the air is about 350 MPa and the elongation is approximately 15.8%. The yield strength of the alloy after T74 heat treatment is lower than that of T6 and the value is 317 MPa, but the elongation of T74 is higher than that of T6 and the value is 16.08%. It is obvious to observe that the yield strength of P-T74 alloy is almost same as that of T6 and its value is approximately 345MPa. Moreover, the elongation of P-T74 with the value of 16.12 % is highest among all the three heat treatments. Comparing (a), (b) and (c) in Figure 5, It is obvious to observe that the fracture surfaces all of the alloys exhibit numerous dimples and it is a typical ductile fracture. This indicates that the alloys after T6, T74 and P-T74 aging heat treatments mainly exhibit ductile fracture in the air. However, when the alloy is placed in 3.5% NaCl aqueous solution for tensile testing, the yield strength of the alloy after T6 heat treatment is only 315 MPa and the elongation is down to 15.4% and the strength loss reached 10% and elongation loss is about 2.5%. We can also see from the fracture surfaces micrograph of Figure 5(d) that a lot of cleavage areas (shown in red dashed box) are in the fracture surface of the alloys. Compared to Fig 4(e) and (f), It is obvious to observe that the yield strength loss and elongation loss of T74 and P-T74 alloy are lower than that of T6, especially P-T74, the strength loss and elongation loss of which is only 2.9% and 0.77% respectively. The analysis above indicates that the alloy after T6 aging heat treatment has a poor resistance of stress corrosion cracking and the alloy after P-T74 aging heat treatment will get an excellent corrosion resistance performance.

![Figure 4. The SSRT test of the 7N01 aluminum alloys (strain rate 6.67x10^-6 S^-1)](image-url)
4. Discussion

From the above discussion and analysis, it can be seen that the alloys after three aging heat treatments have great differences in strength and elongation. And from the TEM photograph, it can be found that the precipitation phase of the alloy after three aging heat treatments is \( \eta' \) phase, so we should analyze the type of precipitated phase and transformation behavior of the alloy at various stages of the three aging heat treatments. In the part of introduction we have stated that the type of precipitated phase and the process transformation behavior of the alloy are generally analyzed by means of selected area diffraction patterns (SADPs) in TEM. Observing the zone axis of electron diffraction of aluminum alloys is generally \( <001>_{\text{Al}}, <110>_{\text{Al}} \) and \( <112>_{\text{Al}} \) zone axis. This study selects \( <100>_{\text{Al}} \) zone axis for observation because the evolution of \( \eta' \) phase can be clearly observed in the \( <100> \) projections.

Fig. 6 shows the selected area diffraction patterns (SADPs) of 7N01 Al alloy samples of T6 aging treatment in \( <001>_{\text{Al}} \) zone axis. Fig 6(a) exhibits the SADPs of quenched samples after solution treatment at 475 °C. The main strong diffraction spots were from the Al matrix and the sharp diffraction spots in \( <001>_{\text{Al}} \) zone axis was from spherical \( \text{Al}_3\text{Zr} \) dispersoids. Fig 6(b) shows the SADPs of the samples aging at 120°C for 24h. It can be seen from Fig 6(b) that the spots of \( \text{Al}_3\text{Zr} \) become blurred and there are many other small petal-like spots around the spots of \( \text{Al}_3\text{Zr} \), which may be the stage before the precipitation of \( \eta' \) phase. Fig 6(c) shows the SADPs of the samples aging at 120°C for 48h. We can clearly observe that there are many small petal-like spots around the spots of \( \text{Al}_3\text{Zr} \), which indicates that after 48 hours of 120°C aging heat treatment, the alloys have begun to precipitate the \( \eta' \) phase. Fig 6(d) shows SADPs of the samples aging at 120°C for 98h(T6). It can be clearly seen that the spots around the \( \text{Al}_3\text{Zr} \) have become larger, and the petal-like diffraction spots are clear and bright. Combined with the TEM bright field images of Fig 3(a), it can be known that after 98 hours of peak aging, the main precipitates of the alloy is small continuous \( \eta' \) phase.

Fig 7 shows the selected area diffraction patterns (SADPs) of 7N01 Al alloy samples of T74 aging treatment in \( <001>_{\text{Al}} \) zone axis. Fig 7(a) exhibits the SADPs of quenched samples after solution treatment at 475 °C. As above, we also use the \( \text{Al}_3\text{Zr} \) spot as a reference to observe changes in the...
diffraction patterns. We can see from the Fig 8(b) that there are some diffuse spots appear slightly outside \{422\}/3\textsubscript{Al} elongated in three different directions; the spots on the radial \{422\}\textsubscript{Al} direction being the strongest. According to the literature [4], this is the unique diffraction spot when GPI zones begin to precipitate. Moreover, the diffraction pattern of the alloy after aging for 24 h at 65 °C in the Fig (c) directly shows the spots in the GPI zones, which directly indicates that GPI zones is precipitated in the alloy at the pre-aging stage of 65 °C. It can be seen from the observation in Fig 8 (d) that not only the GPI zones but also the petal-like η' phase appears around the reference point of Al\textsubscript{3}Zr, which indicates that the GPI zones are going to be η' phase. In the diffraction pattern of Fig 8(e), there is only η' phase diffraction spot and it indicates that the GPI zones formed in the previous stage have all been translated to η' phase. Combined with the TEM bright field images of Fig 3(c), It can be known that the density of the precipitated phase is larger and the size is smaller than that of T74 heat treatment.

![Figure 7. SAED patterns of 7N01 Al alloy samples of T74 aging treatment](image)

![Figure 8. SAED patterns of the 7N01 aluminum alloys of P-T74 aging treatment](image)

5. Conclusions

In this paper, by studying the microstructure, hardness, electrical conductivity and mechanical properties of alloys with three different aging heat treatment systems, especially the study of stress corrosion resistance, it is concluded that the P-T74 heat treatment can effectively improve the resistance of stress corrosion resistance of the alloy. Finally, combined with the selected area diffraction patterns (SADPs) in the part of analysis, we know that the role of the 65 °C played in the P-T74 heat treatment is forming more GPI zones and preparing for η' phase of the alloys, so that the alloy has more nucleation points in the later aging process, which can form more η' phases. From the comparison in Figure 3, the aging heat treatment of P-T74 has a higher density and smaller size of η' phase. It can also be seen from the SEM fracture surfaces micrographs in the air and in the 3.5% NaCl aqueous solution that the alloys after P-T74 aging heat treatment has good stress corrosion resistance. Through the study of the 7N01 aluminum alloy in this paper, we can draw the following conclusions:

1. The strength after P-T74 aging heat treatment is much close to that of T6, but the resistance of stress corrosion of P-T74 in the 3.5% NaCl aqueous solution is much better than that of T6 aging. Moreover, the elongation loss of P-T74 heat treatment is very small in the 3.5% NaCl aqueous solution.

2. The SAED results show that at 65°C pre-aging the GPI zones were precipitated from the quenched solid solution and aging at 150°C results in evolution of the GPI zones formed during under ageing into the η' phase, so that the alloy has more nucleation points in the later aging process, which can form more η' phases.

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7. References

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