Non-isothermal Ageing of an Al-Mg-Si Alloy for Enhanced Anticorrosion Performance

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Abstract. The effects of different heat treatment processes on the comprehensive properties of Al-Mg-Si were investigated. The results show that the microstructures changes by T6, T73 and non-isothermal aging (NIA) lead to different hardness and electrochemical properties. The β” strengthening phase of T6 alloy has fine dispersion, uniform size and maximum sensitivity to intergranular corrosion (IGC). The hardness of alloy crystal is the lowest after T73 treatment. The number of β” phases in the crystals of the NIA-treated alloy is the largest, but there is a small amount of coarsened β” phase, and the grain boundary precipitates are intermittently distributed. The IGC sensitivity is the lowest. The NIA-treated alloy has both high strength and good corrosion resistance, which is related to the formation of a large amount of precipitates in the crystal at low temperatures and the growth and coarsening of intergranular precipitates at high temperatures.

1. Introduction
As a typical heat-treated reinforced alloy, Al-Mg-Si alloy has been widely used in automobiles, aircraft and ships due to its high strength, good welding and good forming performance [1, 2]. However, under some scurviness conditions, the corrosion resistance of traditional Al-Mg-Si and Al-Mg Al alloys still shows insufficient performance. This project has developed a new type of high strength and corrosion resistant Al-Mg-Si alloy. The corrosion resistance of new Al-Mg-Si is better than that of traditional 5xxx series and 6xxx series Al alloys. The corrosion resistance mechanism has been analyzed in related articles [3]. It is well known that T6 treated alloy has the best mechanical properties, but the alloy is highly sensitive to intergranular corrosion (IGC) [4, 5]. In order to further optimize the properties of the Al-Mg-Si alloy, Wang et al. successfully improved the IGC resistance of the Al-Mg-Si alloy by performing two-stage aging treatment [6]. M. Abdulwahab studied the effect of single-stage and multi-stage aging on the hardness of Al-Si-Mg alloys. The results show that little significant different exist between the role of NIA ageing and T6 as method of improving the mechanical properties [7]. Some authors termed the second stage temper condition for improving the hardness often as an over-aged temper. At the expense of mechanical properties, the IGC sensitivity is significantly decrease, but the strength is reduced by about 10% compared to the T6 state. 10% [8,9]. Therefore, a heat treatment process capable of optimizing the properties of the alloy must be developed.

Durham Staley and Durham (2007) found that the non-isothermal ageing (NIA) processes can further improve the overall performance of the alloy [10]. Some studies revealed that, a varying temperature during the ageing process can change the supersaturating condition of the matrix, the coarsening rate, and so on [11~13]. Thus, control the precipitation behavior during various steps of NIA treatments could obtain high overall properties.
Therefore, in order to further improve the overall performance of the new Al-Mg-Si alloy. The present study has employed hardness testing, electrochemical testing, and TEM to study the precipitation behavior, mechanical properties and corrosion resistance of non-isothermally treated Al-Mg-Si alloys. The relationship between microstructure and mechanical properties and IGC of alloys after different aging treatments was analyzed.

2. Materials and Methods

The studied material was used as the rolled 2 mm thin plate Al-Mg-Si alloy. The chemical composition is shown in Table 1. The sample was solution heat treated at 520°C for 2h, then water quenched at room temperature. Then, non-isothermal aging treatment (NIA) is carried out. The specific process is that the aging starting temperature is 100°C, the heating rate is 15°C/h, and the final temperature is 220°C. At the target temperature, remove and immediately cool in cold water. In order to compare mechanical properties and corrosion resistance, the effects of T6 (170°C/6h) and T73 (120°C/6h followed by 150°C/24h) on the microstructure and properties of the alloy were also compared by TEM.

| Table 1. Chemical compositions of the Al-Mg-Si Al alloy (wt %). |
|-------------------|---|---|---|---|---|---|---|---|
| Mg    | Si | Mn | Zr  | Cr  | Ti  | Ag  | Al   |
| 2.13  | 1.98| 0.33| 0.15| 0.16| 0.98| 0.07| Bal. |

Conductivity was measured using a D60K digital tester. Vickers hardness was measured at 2 kg load for 15s using a HV-5 sclerometer. Five indentations were performed for each sample and the average value was taken as the measurement value. The potentiodynamic polarization experiment was carried out in a 3.5% sodium chloride solution at a scan rate of 2 mV/s using a CHI660C electrochemical workstation. The saturated calomel was a reference electrode with a test surface of 1 cm2. The IGC test was carried out in accordance with British Standard 11846 Method B. Subsequently, the cross-section of the corrosion samples was prepared and subjected to metallographic analysis to observe the corrosion morphology and depth. TEM observations were performed on a Fei Tecnai G20 TEM operating at 300 kV. After the TEM sample is mechanically polished, it is prepared by electrolytic double jetting. The double spray is a mixed solution of nitric acid to methanol ratio of 1:3, and the temperature is -28°C. The applied electric current was set to 110 mA.

3. Results

3.1. Hardness and Conductivity Evolution

The variation of the hardness and conductivity of Al-Mg-Si alloys during NIA process are pointed in Fig. 1. In the initial of the heating process, the hardness of the alloy increases rapidly with the heating time, and the hardness value reaches 128 HV until 6.5 hours (195 °C). As the temperature continues to increase, the hardness value of the alloy decreases rapidly. The electrical conductivity of the alloy keeps rising. During the initial stage of heating, the conductivity increased sharply, and when heated to near peak hardness stage, the conductivity remained substantially at 46.2% IACS. As the temperature continues to rise, the conductivity rises sharply. Considering that the alloy has the highest hardness and conductivity, the temperature is 195 °C (6.5 h). Higher than the 44% IACS measurement in the T73 state of the study (T6 state alloy hardness and conductivity 133 HV, 42% IACS) [3,14]. Therefore, it can be inferred that it is possible for the NIA-treated alloy to simultaneously obtain high mechanical properties and good corrosion resistance.
3.2. Corrosion Test
Fig. 2 shows the corrosion morphology of the different aging treated samples. The maximum corrosion depth is greatly affected by the aging condition. In the T6 state, the grains are separated from each other and fall off from matrix, and the corrosion depth is the largest, reaching about 71 μm. The corrosion has spread to the inside of the alloy and presents obvious IGC characteristics (Fig. 2a). As shown in Fig. 2b, there is slight corrosion in the T73 alloy, and the IGC tendency is significantly reduced. The maximum corrosion depth is 50 μm, which is lower than the T6 state. The corrosion sensitivity of the NIA alloy sample is reduced, only with slight local corrosion, and the maximum corrosion depth is 39 μm. The corrosion resistance of the alloy after NIA treatment is significantly improved. For these results, it can be further inferred that the non-isothermal aging treatment of the alloy has the potential to further improve the corrosion resistance of studied alloy.

3.3. Electrochemical Test
Fig. 3 shows the polarization curves of the alloys after different aging treatments. The curves have similar shapes, consisting of a cathode and an anode branch, with distinct polarization intervals, a passivation platform and an overpassing region. Some electrochemical parameter are listed in Table 2. For T73 and samples under NIA conditions, $E_{corr}$ and $I_{corr}$ have similar values between T73 and NIA samples. $I_{corr}$ value of T6 treated alloy was significantly higher than other samples. The alloys treated by NIA and T73 have higher corrosion resistance, and the corrosion rates of the alloys treated by the two aging processes are lower than T6.
Figure 3. Polarization curves of Al-Mg-Si alloy

| Sample | $E_{\text{corr}}$ (V vs SCE) | $i_{\text{corr}}$ (μA cm$^{-2}$) | $E_{\text{pit}}$ (V vs SCE) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) |
|--------|-------------------------------|----------------------------------|----------------------------|-------------------|-------------------|
| T6     | -0.862                        | -328±2                           | -0.696                     | 82                | 112               |
| T73    | -0.775                        | -241±2                           | -0.651                     | 76                | 124               |
| NIA    | -0.768                        | -237±2                           | -0.639                     | 78                | 119               |

3.4. Microstructures

The microstructures of the intragranular and grain boundaries of Al-Mg-Si alloys after different aging treatments are shown in Fig. 4. As can be seen from Fig. 4a, for T6 treated alloy very fine needle-like phases are uniformly distributed in the Al matrix. The length of the phases is approximately 15 to 40 nm and is arranged along the [100]$_{\text{Al}}$ and [010]$_{\text{Al}}$ directions of the Al matrix. As can be seen from the electron diffraction pattern (inserted in Fig. 4a), except for the diffraction spots of the Al matrix, there are also distinct cross-shaped stripes. According to the study by Luo et al., it can be judged that the phase is $\beta''$ phase [3]. The $\beta$ phase has a slight mismatch with the Al matrix in the b-axis direction and provides a strong strain field. It becomes the most effective strengthening phase in the Al-Mg-Si alloy. The black circular region is a $\beta''$ phase cross section. There are a large number of rod-like precipitates in the grain boundary (Fig. 4d). According to the related literature, the phase is $\beta'$ phase [14, 15], and the matrix exhibits a semi-coherent state. In the T73 state, the size distribution range of the $\beta''$ precipitation phase in the alloy crystal is increased, which is about 15 to 55 μm. At the same time, the number density of the grain boundary $\beta'$ phase decreases and the degree of continuity decreases. After NIA treatment. As shown in Fig. 4c, T73 microstructures include two kinds of phases, fine needle-like $\beta''$ and coarsened $\beta''$, which is close to 40 to 60 nm. A number of regions are randomly selected from typical brightfield images to estimate the number of precipitated phases. The number of planes can be obtained by dividing the number of precipitated phases by the area of the region. In the T6, T73, and NIA samples, the approximate plane number density of the phases were $1.6\times10^5$ m$^{-2}$, $5.4\times10^4$ m$^{-2}$, and $1.4\times10^5$ m$^{-2}$, respectively. From the above results, number density of the NIA sample was the largest. The T73 sample had the smallest number of precipitated phases and a slight increase in size. The number density of the precipitated phase of the NIA sample was significantly higher than that of the T6 sample, indicating that the nucleation of the precipitated phase in the matrix dominated the NIA process. At the same time, the precipitation phase of the grain boundary is intermittently distributed. This is beneficial for the decrease of IGC sensitivity.
4. Discussion

The strength of Al-Mg-Si alloy mainly depends on the size, morphology, number density and distribution of the precipitation during the aging treatment. The precipitation behavior of Al alloys includes nucleation, growth and coarsening of precipitates during aging. According to the nucleation rate relationship between Grong and Myhr [16],

\[
N^* = N_0 \exp(\frac{-G}{RT}) \exp(\frac{Q_d}{RT})
\]

Where \(N^*\) is the nucleation rate, \(N_0\) is the nucleation rate constant, \(Q_d\) is the diffusion activation energy, \(R\) is the gas constant, and \(T\) is the absolute temperature. It can be seen from Equation 1 that as the temperature increases, the critical radius decreases, the nucleation rate increases, result that more nucleation sites are formed in the matrix. Therefore, the nucleation rate obtained by NIA is higher than the nucleation rate obtained by T6 aging and T73, which is consistent with the statistical results of number density of the strengthening phases. The NIA treated alloy not only has sufficient nucleation time in the low temperature stage, but also the nucleation effects of the precipitation phase dominate the aging process, resulting in greatly improved nucleation rate. Therefore, a higher number density is observed from the NIA treated sample, but there is a slightly thicker \(\beta''\), resulting in a hardness slightly lower than T6. After reaching the peak hardness at 195 °C, the precipitate phase is coarsened and the hardness is rapidly decrease with increase in temperature. T6 sample have the highest strength because a small and more uniform \(\beta''\). The T73 sample mainly formed a large number of atomic clusters and GP regions in the pre-aging stage. Due to the low thermal stability, some of the GP regions gradually dissolve during the high temperature ageing process, and the number density of the GP regions decreases. Part of the formation of fine \(\beta''\), a large number of large-scale rod-shaped \(\beta'\) phase appeared, the sample is treated in the condition of slightly over-aging, resulting in poor mechanical properties. In the T73 sample. During the re-aging process, the diffusion process of solute atoms controls the grain boundary, therefore, the TEM image of the alloy in the T73 state shows that the precipitated phase along the grain boundary is coarse and discontinuous, while the precipitated phase in the T6 state is...
fine and continuous. During the T73 treatment process, as the temperature increases (secondary temperature of T73 condition is higher than the pre-ageing temperature), the diffusion activation energy of the solute atoms in the grain boundaries is lower than the diffusion activation energy in the matrix, resulting in the solute atoms at the same temperature. The diffusion rate in the grain boundary is higher than matrix, and this difference of diffusion rate increases with the increase in temperature. Therefore, the grain boundary precipitates easy grow by diffusing, and forming coarse and discontinuous distribution. The coarse and discontinuous precipitates on the grain boundary prevent the corrosion evolution along the grain boundary. Therefore, both NIA and T73 samples have good anti-IGC properties.

5. Conclusions
1. The fine precipitates of the T6 treated alloy has the highest hardness and the highest sensitivity to IGC. After NIA treatment, the number density of β” phase of the alloy is largest, but there is a small amount of coarsened β” phase, IGC sensitivity is lowest. After T73 treatment, the strengthened phase density and the hardness of the alloy is the lowest.
2. Changes in the microstructure of the grain boundary precipitates caused by T6, T73, and NIA lead to different IGC sensitivities. The NIA treatment can coarsen and disperse the grain boundary precipitates and improve corrosion resistance.
3. The combination of high strength and good corrosion resistance of NIA treated alloys is related to the formation of precipitates at low temperature and the growth and coarsening of intergranular precipitates at high temperatures. NIA treatment is possible to obtain an Al-Mg-Si alloy with high mechanical properties and good corrosion properties.

6. References
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