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ARTICLE

Effect of Pre-aging Treatment on Room Temperature Stability of Al-5.2Mg-0.45Cu-2.0Zn Alloy Sheet

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Abstract: Pre-aging treatment was performed on Al-5.2Mg-0.45Cu-2.0Zn alloy. Results show that pre-aging treatment not only improves the stability of the alloy sheet at room temperature and avoids the paint-baking softening, but also enhances the age hardening response during subsequent artificial aging at 180 °C. The microstructure of the T4 sample in peak aged condition consists of coarse lath-like T-$Mg_{32}(Al, Zn)_{49}$ phase and needle-like S-Al_2MgCu phase. However, the microstructure of the T4P sample in peak aged condition only consists of high density of finer and equiaxed T phase and S phase disappears. Unstable clusters formed during natural aging dissolve when imposed at 180 °C, which retards the precipitation process of the alloy. Stable clusters formed during pre-aging treatment serve as the nuclei of the T phase during aging at 180 °C, which enhances the age hardening response of the alloy.

Key words: aluminum alloys; phase transformation; transmission electron microscopy

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Recycling Al alloys has been seriously considered with the continuous increase in the use of Al alloys in automotive applications. Developing one or two "unialloys" which have balanced properties such as good dent resistance, corrosion resistance and good formability to meet all the requirements of a variety of automotive components has been an effective way to improve the Al scrap recycling[1]. Non-heat-treatable Al-Mg alloys are used in the automotive inner panel due to their excellent formability and corrosion resistance. However, the yield strength after baking of the Al-Mg alloy sheets is not so high to satisfy future safety standards. In addition, high-strength Al-Zn-Mg-Cu alloys of the 7xxx series (Zn/Mg atom ratio exceed 2.5) have been increasingly used in body-in white structure because they possess higher strength than other series Al alloys. Despite this advantage, the high-strength Al-Zn-Mg-Cu alloys still lag behind in their application due to poor formability. Though complex forming process at elevated temperatures has been applied for the high-strength Al-Zn-Mg-Cu alloy sheet, degradation of high

strength[2] and delayed fracture sensitivity[3] which may be caused by hydrogen induced cracking under internal stress state[4,5] are also major problems associated with the Al-Zn-Mg-Cu alloy sheets. However, it has been found that the addition of Zn to the Al-Mg alloy is effective in inhibiting hydrogen segregation and diffusion to form hydrogen induced cracks[6]. In our previous study, the precipitation hardening response of a newly developed Al-5.2Mg-0.45Cu-2.0Zn alloy was investigated, and results indicated that pre-aging treatment significantly improves the age hardening response of the alloy by modifying the microstructure of the alloy.

The alloy sheet is often stored for a considerable period of time before it is finally stamped in the automobile plant and natural aging. Cluster formed during this period may have adverse effect on the paint-baking response that happens in the Al-Mg-Si alloys[7-11]. Pre-aging treatment has been used to avoid this detrimental effect. Therefore, in this study, the effect of natural aging on the artificial age hardening response in the Al-5.2Mg-0.45Cu-2.0Zn alloy was explored. Pre-aging

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treatment was also used in this study to improve the stability of the alloy at room temperature and to enhance the subsequent artificial aging response. The detailed investigation of the microstructure of the alloy in different states will be conducted by transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

1 Experiment

The experimental Al-5.2Mg-0.45Cu-2.0Zn alloy was prepared by melting and chill casting into a steel mould. The ingot was homogenized, scalped, and then hot rolled and cold rolled to a final thickness of 1 mm. The samples were solution treated at 525 °C for 10 min in a salt bath, followed by immediate quenching in cold water. Two different thermal treatments were performed after the quenching. In the first condition, the solution treated samples were natural aged at room temperature for 7 d (T4 state), and then artificially aged at 180 °C for various time. In the second condition, the samples were stored at room temperature for 7 d after pre-aging at 80 °C for 12 h (T4P state), and then artificially aged at 180 °C for various time. For comparison, the age hardening response of the as-quenched sample was also provided. Hardness measurements were performed by a macro Vickers hardness tester with 200 g load and a dwell time of 10 s. Each reported hardness value is the average of 10 individual measurements. The mechanical properties of the alloy sheet during simulated paint-baking were investigated using MTS810 testing machine. Thin foils for TEM were prepared from 3 mm discs by double jet electropolishing in a 25% nitric acid/75% methanol solution at −35 °C. Bright field TEM images and corresponding selected-area electron diffraction (SAED) patterns were obtained with FEI Tecnai F20. DSC tests were carried out on NETZSCH 404F1 DSC instrument in argon atmosphere with a heating rate of 10 °C/min.

2 Results and Discussion

2.1 Age hardening response and mechanical properties

Fig.1 shows the age-hardening response of the alloy in different states. It can be found that natural aging occurs for the as-quenched sample after a period of incubation. For the sample in T4 state, age-softening occurs in the early stage when aging at 180 °C, and then the hardness increases gradually to the peak, which is similar to that of the as-quenched sample. For comparison, the hardness of the sample after pre-aging treatment keeps constant when aging at room temperature, and the hardness increases dramatically when aging at 180 °C for the sample in T4P state. The mechanical properties of the alloy during paint-baking are provided in Fig.2. The strength increment of the paint-baking for the sample in T4P state (57 MPa) is much higher than that of the sample in T4 state (9 MPa). Thus it can be concluded that pre-aging treatment not only improves the stability of the alloy at room temperature but also enhances the age hardening
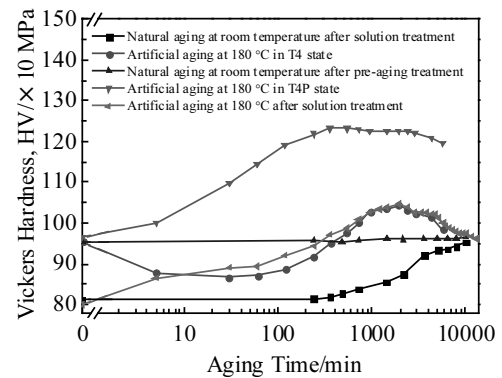

Fig.1　Age hardening response of the Al-5.2Mg-0.45Cu-2.0Zn alloy in different states
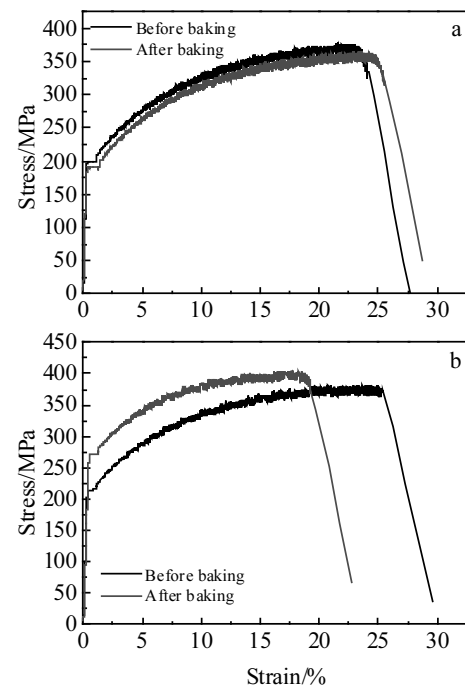

Fig.2　Mechanical properties of the alloy sheet in T4 (a) and T4P (b) states during paint baking

response of the alloy at 180 °C.

2.2 TEM analysis

To elucidate the mechanism of improvement in stability at room temperature and enhancement of age hardening response at 180 °C after pre-aging treatment, and microstructures of the alloy in different states are characterized and shown in Fig.3~5. For the sample in T4 state, there is no indication of precipitates in the bright field (BF) image and SAED pattern (Fig.3a). According to Fig.1, however, the hardness of the sample in T4 state increases evidently compared to the as-quenched state. Thus, we can conclude that some clusters which are too small to
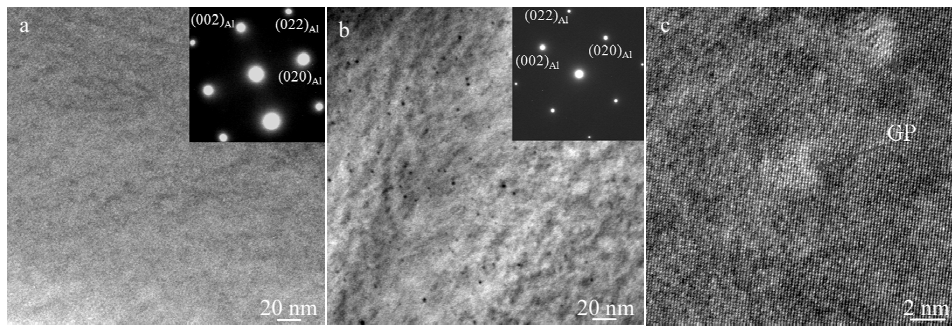
Fig.3   TEM images and corresponding SAED patterns (inset) along <100>$_{Al}$ orientation of the samples in T4 (a) and T4P (b) states; HRTEM image of GP zone in Fig.3b (c)

be observed by TEM during natural aging. For the sample in T4P state, fine and uniform distribution of precipitates are present in the matrix (Fig.3b). The corresponding SAED pattern exhibits no extra reflection, which suggests that the precipitates have no distinct structure. Thus the precipitates can be designated as GP zones. The corresponding HRTEM image of the GP zones shows that they are fully coherent with the matrix, as shown in Fig.3c.

Fig.4a shows the microstructure of the sample in T4 state when aged at 180 °C for 30 min, and sparse dotty precipitates are present in the matrix. As for the sample in T4P state, fine and uniform distribution of precipitates are present in the matrix when aged at 180 °C for 30 min. The corresponding SAED pattern (inset) exhibits intensity at 2/5 and 3/5 <220>$_{Al}$, which suggests that the precipitates have the same structure with T-Mg$_{32}$(Al, Zn)$_{49}$ phase (Im3, a=1.422 nm).

Fig.5a shows the microstructure of the sample in T4 state when aged at 180 °C for 32 h, and coarse lath-like phase and needle-like phase coexist in the matrix. The corresponding SAED pattern (inset) combines the spots at 2/5 and 3/5
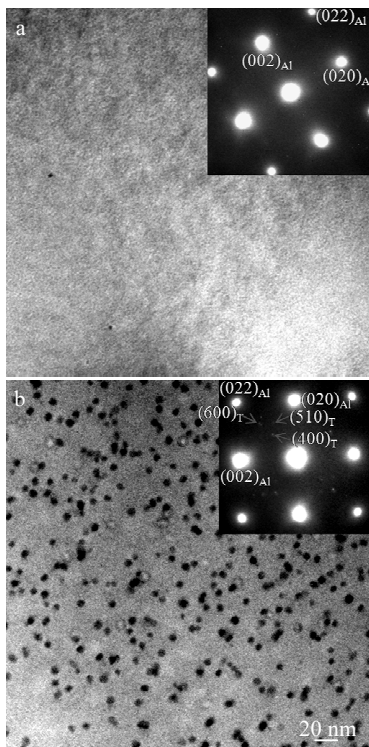

Fig.4   TEM images and corresponding SAED patterns (inset) along <100>$_{Al}$ orientation of the samples aged at 180 °C for 30 min in T4 (a) and T4P (b) states
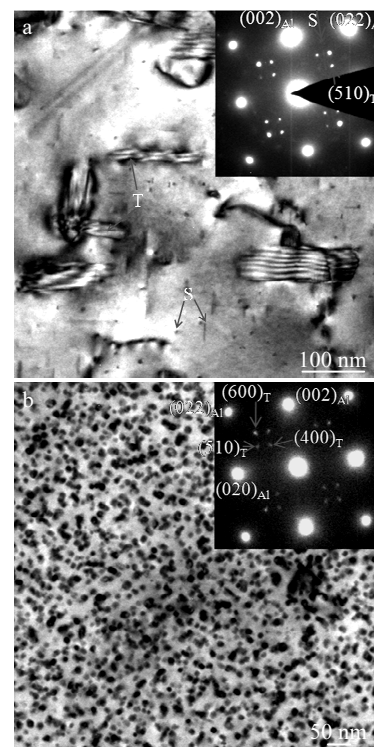

Fig.5   TEM images and corresponding SAED patterns (inset) along <100>$_{Al}$ orientation of the samples in peak aged condition: (a) T4 state and (b) T4P state

$<220>_{Al}$ which can be described as T phase and the spots situated at the corners of a cross centered at the $\{110\}_{Al}$ matrix position and elongated along the $<100>_{Al}$ directions, which can be attributed to the S-Al$_2$MgCu phase. Importantly, the microstructure of the sample in T4P state when aged at 180 °C for 6 h consists of finer and equiaxed precipitates, and the corresponding SAED pattern indicates that the precipitates can be designated as T phase.

2.3 DSC analysis

The DSC curves of the samples in different states are shown in Fig.6. For the sample with solution treatment, the peaks correspond to the following precipitation events: GP precipitation, 75~135 °C; (S+T) precipitation, 230~320 °C. For the sample in T4 state, endothermal peak appears at 80~130 °C, which correspond to the dissolution of clusters formed during natural aging. The exothermal peak of (S+T) precipitation for the sample in T4 state shifts to higher temperature compared with that of the sample with solution treatment. This indicates that natural aging retards the subsequent artificial aging. As for the sample with pre-aging treatment and in the T4P state, no endothermal or exothermal peaks are observed at low temperatures, which indicates that stable clusters form during pre-aging treatment. Additionally, the exothermal peaks corresponding to the T phase precipitation shift to lower temperature compared with those of the samples without pre-aging treatment, which suggests that stable clusters formed during pre-aging treatment enhance the precipitation of T phase. Moreover, two DSC curves of the samples with pre-aging treatment and in the T4P state are almost the same. Thus we can conclude that the alloy becomes stable after pre-aging treatment.

Based on the present results, it can be concluded that pre-aging treatment not only improves the stability of the alloy at room temperature, avoids the paint-baking softening, but also improves the age hardening response during subsequent artificial aging. Unstable clusters formed during natural aging dissolve during aging at 180 °C in the early aging stage, which causes the age softening. Clusters formed during pre-aging are
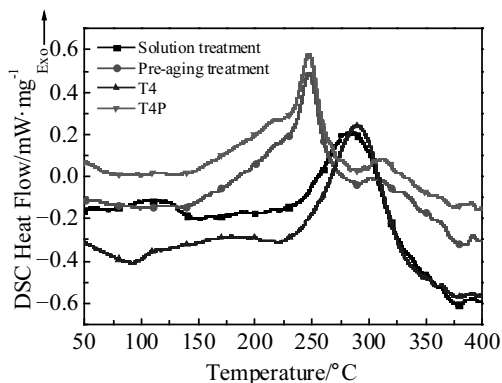
stable at 180 °C, which serve as the nuclei of T phase and enhance the age hardening response. As the thermal stability of coherent precipitates depends on their size due to the capillary effect, GP zones formed during pre-aging treatment at 80 °C for 12 h are expected to be more thermally stable than the clusters formed during natural aging. The adverse effect of natural aging on the subsequent artificial age-hardening response is given as follows. Fig.7 presents the schematic size distribution of co-clusters and GP zones formed during natural aging and pre-aging treatment. The shaded distribution diagram represents the size distribution which is expected right after heating the sample to the artificial aging temperature (T=180 °C). The size of the clusters formed during natural aging is smaller than the critical size which is necessary for nucleation at 180 °C, R_c (T=180 °C). Thus, once heating the sample to the artificial aging temperature, all clusters formed during natural aging may be reverted. The precipitation becomes slower than the as-quenched sample due to the fact that the quenched-in vacancies are annealed out at the room temperature and artificial aging temperature. The size distribution of the GP zones formed during pre-aging treatment is schematically shown in Fig.7b. Some GP zones are larger than R_c (T=180 °C), and thus only smaller GP zones are reverted at 180 °C. The GP zones larger than R_c (T=180 °C) will remain after heating to 180 °C, and they may serve as nuclei for the T phase or evolve to T phase. Thus, prior natural aging causes an adverse effect on subsequent artificial age-hardening response,
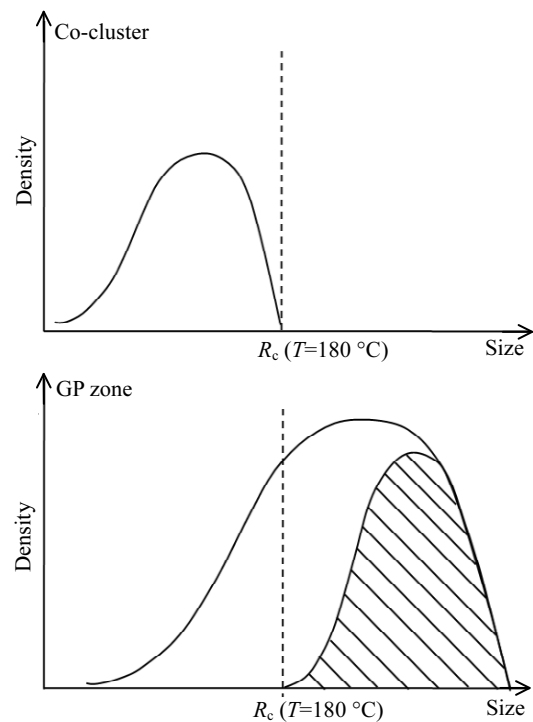

Fig.7 Schematic size distribution of clusters and GP zones formed during natural aging (a) and pre-aging at 80 °C for 12 h (b)

Fig.6 DSC curves of the samples in different states

and pre-aging at 80 °C for 12 h shows a beneficial effect on the subsequent artificial age-hardening response.

3 Conclusions

1) Pre-aging at 80 °C for 12 h can improve the stability of the Al-5.2Mg-0.45Cu-2.0Zn alloy at room temperature and enhance subsequent artificial age hardening response.

2) Unstable clusters formed during natural aging dissolve at 180 °C, which results in aging softening in the early aging stage at 180 °C.

3) Stable GP zones formed during pre-aging treatment serve as the nuclei for T phase and improve the age hardening response of the alloy.

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预时效对 Al-5.2Mg-0.45Cu-2.0Zn 合金室温稳定性的影响

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摘 要：研究了预时效对 Al-5.2Mg-0.45Cu-2.0Zn 合金时效析出行为的影响。结果表明：预时效不仅提高了合金的室温稳定性，避免了合金烤漆软化，同时提高了合金的烤漆时效响应速度。合金经 T4 处理后，再峰时效处理后的组织包括粗大的 $T\text{-}Mg_{32}(AlZn)_{49}$ 相以及针状的 $S\text{-}Al_2MgCu$ 相。然而合金经 T4P 处理后，再峰时效处理的组织只含有细小而高密度的 $T\text{-}Mg_{32}(AlZn)_{49}$ 相而不包括 $S\text{-}Al_2MgCu$ 相。自然时效后不稳定的原子团簇在 180 ℃时效后会回溶到基体中，从而抑制了合金的时效析出强化。而预时效后生成的稳定的原子团簇会成为 180 ℃时效的形核点，显著提高了合金的时效响应速度。

关键词：铝合金；相变；透射电镜

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