Article

Effect of Natural Ageing on Subsequent Artificial Ageing of AA7075 Aluminum Alloy

Cheng-Ling Tai 1, Po-Jui Tai 1, Ting-Jung Hsiao 1, Po-Han Chiu 1,*, Chien-Yu Tseng 1, Tzu-Ching Tsao 1, Tsai-Fu Chung 2, Yo-Lun Yang 3, Chih-Yuan Chen 4, Shing-Hoa Wang 5 and Jer-Ren Yang 1,*

1 Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan
2 Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Taipei 112304, Taiwan
3 Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan
4 Graduate Institute of Intellectual Property, National Taipei University of Technology, Taipei 10608, Taiwan
5 Department of Mechanical Engineering, National Taiwan Ocean University, Keelung 20224, Taiwan
* Correspondence: tedchiu20@gmail.com (P.-H.C.); jryang@ntu.edu.tw (J.-R.Y.)

Abstract: The effects of natural ageing treatment prior to artificial ageing treatment on the microstructures and mechanical properties of AA7075 Al-5.7Zn-2.6Mg-1.5Cu-0.18Cr-0.08Mn-0.05Si-0.17Fe (wt.%) aluminum alloy have been investigated. The hardness of solution-treated samples (91.0 HV) profoundly increased to 146.8 HV after 7 days of natural ageing. The purpose of the present work was to examine the kinetic hardening evolution in subsequent artificial ageing treatments of samples naturally aged for 7 days and their counterparts without natural ageing. The former were labelled as NA-7d samples, and the latter, NA-0d samples. After artificial ageing at 120 °C for 2 h, the hardness of NA-0d samples increased rapidly to 148.2 HV, which was approximately the same as that of the specimens with natural ageing for 7 days, compensating for the prior state of lower hardness without natural ageing. After being treated at 120 °C for 16 h, the ultimate tensile strength (UTS) and yield strength (YS) of NA-7d reached the highest value, respectively, 601 MPa and 539 MPa, followed by a slight decrement of UTS when aged to 24 h. On the other hand, NA-0d specimens aged at 120 °C for 16 and 24 h showed nearly the same UTS (598 MPa); the former possessed YS of 538 MPa, and the latter, 545 MPa. The results presumably reveal that the peak ageing condition for NA-0d samples can be achieved under 24 h ageing at 120 °C. Under the same treatment at 120 °C for 24 h, the size of η' phase in NA-7d sample (with a length of 4.96 nm) coarsened and grew larger than that in NA-0d sample (with a length of 3.46 nm). In addition, some η' phase in the NA-7d sample was found to be transformed into the η phase. The results indicated that the naturally aged specimens (NA-7d) reached the peak ageing condition earlier, but did not significantly enhance the UTS in AA7075 aluminum alloy, as compared to the samples without prior natural ageing (NA-0d).

Keywords: AA7075 aluminum alloys; natural ageing; η' and η phase; mechanical properties; high-resolution transmission electron microscopy

1. Introduction

Light-weight 7xxx aluminum alloys have been widely used in the aerospace and automotive industries because of their high specific strength, which is attributed to nanoscale precipitates that grow in the aluminum matrix under appropriate heat treatment [1–3]. Other properties like good stress corrosion crack (SCC) resistance can also be obtained through different heat treatments [4–6]. The evolution of 7xxx precipitates has widely been accepted as follows: supersaturated solid solution → GP zones (GPI and GPII zones) → semi-coherent η’ → incoherent η (MgZn) [7–9]. In 1938, Guinier [10] and Preston [11] first discovered GP zones in Al-Cu alloys, and the ultrathin-plate morphology of these
zones was confirmed in X-ray images, which presented streaks along the <100>\text{Al} direction. As for 7xxx Al-Zn-Mg-Cu aluminum alloys, GP Zones have been found in many works to be of two types having different morphologies: GPII and GPIII zones. The former has been presumed [7,12,13] to be Mg-rich spherical precipitates with a few Zn atoms aggregated on the {111}\text{Al} plane, forming a small particle (less than 3 nm) which is coherent with the aluminum matrix. The latter, the GPIII zone, has Zn-rich lamellar precipitates forming on the {111}\text{Al} plane [7,12,14]. On the other hand, a previous work [15] on Al-7.55Zn-2.65Mg-1.97Cu-0.10Fe-0.02Si-0.11Zr-0.07Ti (wt.%) alloy treated by natural ageing for 1500 h reported that both blocky-like GPII and elongated-shaped GPIII zones, with a Zn/Mg atomic ratio of around 1.2, developed on the {111}\text{Al} plane. Since the short-range Mg-Zn enriched GP zones generated by natural ageing play an essential role in the subsequent artificial ageing treatment, many previous works [7,8,15–19] have investigated how to select the optical ageing parameters to control the state during natural ageing treatment. Some previous works [15,18,20] have suggested that natural ageing treatment might be more conducive to improving the strength in the subsequent artificial ageing treatment. It has been reported [20] on Al-6.22Zn-1.8-Mg-2.0Cu-0.04Ti-0.04-Zr-0.01Fe-0.07Si alloy that GP zones that formed during 1 day of natural ageing were beneficial to the subsequent artificial ageing at 80 °C for 34 h, which improved UTS (19 MPa increment) and total elongation (1.1% increment). One previous work claimed [18] on Al-6.5Zn-2.3-Mg-2.1Cu-0.16-Zr alloy that one week of natural ageing before artificial ageing could increase the strength by suppressing the grain boundary precipitates (GBP) and reducing the width of the particle-free zone (PFZ). However, it has also been reported [17] on Al-4.62Zn-0.9Mg (wt.%) alloy that the samples without (0 days) and with prior natural ageing (for 7 days) had nearly the same hardness when the subsequent artificial ageing was treated at 120 °C for 20 h. The exact effects of natural ageing on microstructures and mechanical properties need to be further investigated.

During artificial ageing, the main strengthening \(\eta'\) phase may form from GPII zones [7,21]. The plate-like meta-stable \(\eta'\) phase on the {111}\text{Al} plane possesses a semi-coherent boundary with the aluminum matrix [7,22,23]. With continued ageing treatment, the \(\eta'\) phase transforms into one of the 14 types of \(\eta\) phases [9,24,25], which possess various morphologies, such as rod-like, disc-like, and hexagonal plate [9,24,26]. The \(\eta'\) phase and \(\eta\) phases are both hexagonal in structure and have a space group of P6₅/mmc; however, equilibrium \(\eta\) phases possess non-coherent boundaries with the aluminum matrix [22,23]. The 14 types of \(\eta\) phases adopt different orientation relationships with the aluminum matrix [9,24,25,27,28], and only one of them, the \(\eta_2\) phase, possesses the same orientation relationships as the \(\eta'\) phase [1,28]. It has been determined by in-situ HR-TEM analysis that the \(\eta'\) phase transforms into the \(\eta_2\) phase [22].

The aim of this present work was to explore whether natural ageing treatment affects the microstructures and mechanical properties of AA7075 aluminum alloy in the subsequent artificial ageing treatment. Tensile tests and TEM analysis were performed on samples that either were not naturally aged or were naturally aged for 7 days before being artificially aged at 120 °C for up to 24 h.

2. Materials and Methods

The chemical composition of the AA7075 aluminum alloy used in this work is listed in Table 1. As-received 2.0 mm thick sheets of AA7075 alloy were provided by the China Steel Corporation, Kaohsiung, Taiwan. The sheets were first solid solution treated at 490 °C for 30 min and then, immediately water quenched, followed by natural ageing treatment. Here, two types of specimens were prepared for the subsequent artificial ageing treatment. One type received a natural ageing treatment of 7 days and was denoted as NA-7d, while the other was not naturally aged (i.e., naturally aged for 0 days) and denoted as NA-0d. These two types of specimens were subsequently artificially aged at 120 °C for holding times of 2 to 24 h. Vickers hardness tests were performed on an FM-700 (Future-Tech Corp, Tokyo, Japan) with a load of 500 g for 8 s. Each sample was tested more than
20 times to obtain an average value with a standard deviation. The stress–strain curves of the tensile tests for the as-received specimen and 0 h, 2 h, 10 h, 16 h and 24 h ageing treated NA-0d and NA-7d specimens were conducted on an MTS Landmark 370.02 Dynamic Test System (MTS Systems Corporation, Eden Prairie, MN, USA) with a laser displacement sensor. The tensile test specimens were prepared according to ASTM E8/E8M-11 [29], and the strain rate was $10^{-3}$ s$^{-1}$; at least three samples for each artificial treatment were tested and the corresponding data were presented by the average value with the standard deviation value. For different heat treatment conditions, the corresponding specimens for TEM observation were ground to a thickness of 60 μm with 800# to 2500# SiC sandpaper and then electropolished at −25 °C in an electrolyte solution of 33% nitric acid and 67% methanol. The electrolytic polishing was performed with a twin-jet polisher with a voltage of 10 V and a current of 40 mA until the test specimen became perforated. The TEM specimens were examined on a FEI Tecnai G2 F20 (Thermo Fisher Scientific, Waltham, MA, USA), operated at 200 kV to investigate the size and morphology of nano-precipitates. Furthermore, HR-TEM and corresponding fast Fourier transformation (FFT) were utilized to identify η’ and η phases.

### Table 1. Chemical composition of the studied Al-Zn-Mg-Cu alloys (in wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 7075</td>
<td>5.74</td>
<td>2.55</td>
<td>1.47</td>
<td>0.18</td>
<td>0.008</td>
<td>0.05</td>
<td>0.17</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

#### 3.1. Vickers Hardness Test

Figure 1a shows the progressive increase in the Vickers hardness (HV) of Alloy 7075 when it was naturally aged from 0 to 7 days. During the beginning of natural ageing (6 h), the hardness rapidly increased, rising from 91.0 HV to 119.2 HV, presumably due to the rapid generation of GP zones. At 1 day of natural ageing, the hardness increased to 132.8 HV, followed by slow increases between 2 d and 7 d. Figure 1b presents the hardness (HV) of NA-0d and NA-7d specimens as a function of subsequent artificial ageing at 120 °C, with holding times ranging from 2 to 24 h. During artificial ageing at 120 °C from 0 h to 2 h, the hardness of NA-0d increased from 91.0 HV to 148.2 HV. This increment was much higher than that of NA-7d, which rose from 146.6 HV to 148.4 HV. The former was an increment of 63%, and the latter, one of only 1.2%. From 2 h to 10 h, the hardness of both NA-0d and NA-7d increased slowly, and the hardness of NA-7d was slightly higher than that of NA-0d. After ageing for 12 h up to 24 h, the hardness values of NA-0d and NA-7d remained almost the same. Immediately after the solid solution heat treatment, NA-0d specimens were artificially aged, which caused the rapid formation of precipitates in the early stage of the artificial ageing. These precipitates tremendously strengthened the alloy within a short period of time. On the other hand, NA-7d specimens underwent a 7-day natural ageing process, in which the clusters and GP zones were generated and substantially strengthened the alloy. As a result, the subsequent artificial ageing treatment slowly increased the hardness. After artificial ageing for 12 h, the strengthening effects of the precipitates were almost the same in the NA-0d and NA-7d specimens.
3.2. Tensile Test

Figure 2a presents the stress–strain curves of AA7075 aluminum alloy samples, as-received with NA-0d and NA-7d (i.e., naturally aged for 0 and 7 days). The corresponding values of yield strengths (YSs), ultimate tensile strengths (UTSs), and total elongation (ELS) of NA-0d and NA-7d samples are presented in Table 2. The data of the tensile tests for the as-received material (before solid solution treatment at 490 °C for 30 min) are listed below in Table 2. Followed by 7 days of natural ageing treatment, the UTS of the NA-7d specimens dramatically increased, which was much higher than that of NA-0d specimens; the former was 544 MPa, and the latter, 441 MPa. The tensile test data verified the strengthening effect of natural ageing, which enhanced by 23% the strength of Alloy 7075 which was naturally aged for 7 days. It is striking to see the NA-0d stress–strain curve (Figure 2a) with serration characteristics, which was presumably caused by the interaction between solute atoms and dislocations [30]. Figure 2b shows the stress–strain curves of NA-0d specimens treated by artificial ageing at 120 °C for 2, 10, 16, and 24 h. After 2 h, the UTS of the NA-0d specimen was 560 MPa with total elongation of 19.9%. When the ageing time was increased to 10 h, the UTS rose to 591 MPa but the total elongation slightly fell. In specimens of NA-0d treated for 16 h and 24 h, their UTSs were almost the same (598 MPa), while the yield strength (YS) increased from 538 MPa to 545 MPa, respectively. Figure 2c presents the stress–strain curves of NA-7d samples artificially aged at 120 °C for 2, 10, 16, and 24 h. After 2 h, the UTS of the NA-7d specimens reached 570 MPa with total elongation of 17.3%. Compared with the NA-0d specimens with the same treatment (aging for 2 h), the UTS of NA-7d was slightly higher (by 10 MPa), but the ductility was lower. After 10 h, the UTS of NA-7d specimens was approximately the same as that of NA-0d. NA-7d specimens artificially aged for 16 h possessed an UTS of 601 MPa, which was the peak ageing condition, while the total elongation decreased to a minimum value of 14.6%. In samples aged for 24 h, and thus, past the peak ageing condition, the UTS slightly decreased to 597 MPa. Overall, the UTSs of NA-0d specimens were slightly lower than those of NA-7d specimens, but the ductility was slightly higher. In samples aged for 2 h, the UTS of NA-7d specimens was higher than that of the NA0d specimens, probably due to a larger number of GP zones already existing in the former during natural ageing. This significantly accelerated the transformation of GP zones into the η' phase during the initial artificial ageing period. In the NA-0d specimens, in contrast, GP zones would first need to form in the aluminum matrix. The NA-7d specimen aged at 120 °C for 16 h reach its peak UTS (601 MPa) and YS (539 MPa), while the NA-0d specimen, aged at 120 °C for 24 h, achieved its highest UTS (598 MPa) and YS (545 MPa). This indicated that natural ageing for 7 days reduced the following artificial ageing time; however, the natural ageing treatment only accelerated the artificial ageing process but couldn’t be particularly effective in strengthening the alloy.

Figure 1. Age-hardenning curves of (a) natural ageing treatment during 7 days and (b) NA-0d and NA-7d samples aged at 120 °C for different holding times from 0 to 24 h.
at\[22\]. However, the discrimination of \(\eta'\) and \(\eta\) phases is difficult at low magnification because they possess the same morphology and structure, and their orientation relationships with the aluminium matrix are also the same, \([0001]_{\eta'} // [111]_\text{Al}\) and \([1012]_{\eta'} // [110]_\text{Al}\). The differences between the \(\eta'\) and \(\eta\) phases are in their chemical compositions and lattice constants \([1,9,21,24,26,31,32]\). Figs. 3a-b and 3c-d present HR-TEM micrographs of \(\eta'\) phase and \(\eta\) phase in NA-7d sample aged at 120 °C for 24 h, observed along the \([110]_\text{Al}\) zone axis, and accompanied with their corresponding FFT diffractograms and simulated diffraction patterns. The lattice constant of the \(\eta'\) phase is presumed to be \(a = 0.504\ \text{nm}, \ c = 1.303\ \text{nm}\) \([32]\). As the plane spacing of \([0002]_{\eta'}\) in the \(\eta'\) phase is around three times that of the \([111]_\text{Al}\) plane, and they are parallel to each other, \(|\tilde{g}(0006)_{\eta'}|\) is close to \(|\tilde{g}(111)_\text{Al}|\) in the corresponding fast Fourier transformation (FFT) diffractograms and the simulated
patterns in Figure 3b. On the other hand, the lattice parameters of the $\eta_2$ phase are $a = 0.504$ nm and $c = 0.828$ nm [32]. The $\{0002\}_{\eta_2}$ plane in the $\eta_2$ phase is also parallel to the $\{11\bar{1}\}_{Al}$ plane, with around double spacing of the $\{11\bar{1}\}_{Al}$ plane; therefore, $|\mathbf{g}(0004)_{\eta_2}|$ is close to $|\mathbf{g}(11\bar{1})_{Al}|$ in the corresponding FFT diffractograms and the simulated pattern in Figure 3d. Through HR-TEM analysis, whether the $\eta'$ phase has been transformed into the $\eta_2$ phase by the artificial ageing treatment can be identified.

**Figure 3.** HR-TEM micrographs of (a) $\eta'$ phase (yellow square) and (c) $\eta_2$ phase (red square) in NA-7d specimen ageing at 120 °C for 24 h observed along the $[110]_{Al}$ zone axis with their corresponding FFT diffractograms and simulated diffraction patterns, (b,d). The thickness of $\eta'$ phase and $\eta_2$ phase were marked by yellow and red arrows, respectively.
3.4. Precipitate Size Analysis

Figure 4a shows a TEM image and corresponding selected area diffraction (SAD) pattern of AA7075 aluminum alloy naturally aged for 7 days, observed along the [001]_{Al} zone axis. Plentiful black dots were observed, but they were too small in size to identify by the diffraction pattern. Therefore, HR-TEM was conducted, as shown in Figure 4b. However, although many clusters were observed in this specimen, the FFT of these clusters did not reveal any detailed information from the diffractograms, so it could not be concluded that they were GPI zones. The difficulty in confirming the structure of the clusters might have been due to the thickness of the specimen. Since the clusters were less than 3 nm in diameter and fully embedded in the aluminum matrix, it was extremely hard to obtain their signals; they will need to be further investigated. Here, we can only presume that these black dots, which formed during the 7-day natural ageing treatment, contributed to the strengthening effect and the increase in UTS. Figs. 4c and d present TEM images of NA-0d and NA-7d specimens treated at 120 °C for 24 h. Under this artificial ageing treatment, the \( \eta' \) phase is considered the main precipitate that strengthens the AA7075 alloy. When observed along the [110]_{Al} zone axis, two edge-on configuration variants of the \( \eta' \) phase have a thick-line morphology with an included angle of 70.52° between them, while the other two non-edge-on configuration variants possess an elliptical-shaped morphology. Under the same artificial ageing of 120 °C for 24 h, the lengths of \( \eta' \) phases with the edge-on configuration in NA-0d specimens were shorter (3.46 ± 0.90 nm) than those of the NA-7d specimens (4.96 ± 1.62 nm). In addition, some equilibrium \( \eta_2 \) phase was also found in the NA-7d specimen (Figure 4d), indicating that under this treatment, meta-stable \( \eta' \) phase started to transform into the equilibrium \( \eta_2 \) phase.

---

**Figure 4.** (a) TEM images of AA7075 naturally aged for 7 days and its diffraction pattern observed along the [001]_{Al} zone axis. (b) HR-TEM image and the corresponding FFT of enlarged yellow square
4. Conclusions

The effects of artificial ageing at 120 °C with (NA-7d) and without (NA-0d) prior natural ageing on the mechanical properties and microstructures of AA7075 aluminum alloy have been investigated. The results show that natural ageing treatment can effectively enhance the strength of AA7075 aluminum alloy, due to the formation of clusters in the aluminum matrix, which accelerates the precipitation of η′ phase during the subsequent artificial ageing treatment. Therefore, the yield strength of NA-7d specimen reached the peak value as aged at 120 °C for 16 h (539 MPa, the same as 24 h), while the yield strength of NA-0d specimen achieved its highest value (545 MPa) as aged for 24 h. In addition, after artificial ageing of 24 h, the η′ phase in NA-7d specimens slightly coarsens and some of the η′ phase have transformed into the η phase. In summary, the peak ageing conditions of NA-7d and NA-0d specimens bring about approximately the same UTSs; the former is 601 MPa, and the latter, 598 MPa. This indicates that natural ageing prior to artificial ageing can shorten the time to reach the peak ageing condition but cannot be particularly effective in strengthening the material.

Author Contributions: Conceptualization, C.-L.T. and J.-R.Y.; investigation, C.-L.T., P.-J.T., T.-J.H., P.-H.C., C.-Y.T., T.-C.T., T.-F.C., Y.-L.Y., C.-Y.C., and S.-H.W.; supervision, J.-R.Y.; writing—original draft, C.-L.T.; writing—review and editing, J.-R.Y. All authors have read and agreed to the published version of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science and Technology Council (Taiwan) under the contract NSTC 110-2221-E-002-039.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors would like to thank China Steel Corporation (Taiwan) for providing the material.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References