Hardening and precipitation of a commercial 6061 Al alloy during natural and artificial ageing

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Abstract. In this study, the precipitation and hardening of a commercial 6061 Al alloy during the combined natural and artificial ageing are analyzed, in order to maximize the alloy hardness by adjusting ageing time and temperature. The samples were solution-treated at 540°C for 2 hours, followed by water quenching. An artificial ageing was performed at 180, 200, and 220°C during a period from 2 min to 12 h. Natural ageing at room temperature during 12 h was performed simultaneously with the artificial one at different elevated temperatures. The Vickers hardness values of solution-treated and aged samples were measured. Precipitates were characterized via the X-ray diffraction and scanning transmission electron microscopy equipped with the energy dispersive X-ray spectroscopy. The highest hardness values were exhibited by samples that were naturally aged for 12 hours and artificially aged for 24 hours at 200 and 220°C. The hardness improvement was found to be controlled by the formation of β″ phases before the peak ageing.

1. Introduction

The 6xxx aluminum alloys combine excellent formability, weldability, and corrosion resistance features. Therefore, they have been widely used in automobile, aerospace, architecture and other domains. The precipitation sequence plays an important role in age-strengthening alloys. In particular, the ageing sequence of Al-Mg-Si alloys is generally described using precipitates with different compositions of Mg₅Si₆ [1-5]:

\[ \text{SSSS} \rightarrow \text{Mg, Si atomic clusters} \rightarrow \text{GP-zones} \rightarrow \beta'' \rightarrow \beta'' \rightarrow \beta, \]

(1)

where SSSS is the supersaturated solid solution. Meanwhile, immediately after quenching from the solidification temperature to room one, Mg, Si atomic clusters form alloys. At the earliest stage of precipitation, these clusters can be detected only using an atom probe [6-8]. The GP-zones and β″ phases are partially coherent and have needle-like shapes. These β″ phases are generally metastable with a chemical stoichiometric ratio of Mg₅Si₆ [9, 10]. However, the exact stoichiometry of β″ normally varies with changes in alloys’ overall composition. The β″ phases are presented at the peak age, whilst equilibrium β'/β are formed with a significant strength deterioration [2]. The stoichiometry of β is generally Mg₅Si. In commercial 6061 Al alloys, the addition of Mn and Fe is beneficial, since these alloying elements form α-Al(MnFe)Si dispersoids, whose stoichiometry can be variable and is generally assumed to be either Al₁₀₀(MnFe)₂₂Si₁₄ or Al₂₄(MnFe)₂₈Si₁₈ [11, 12]. In dispersoids, Mn and Fe elements can replace each other and have simple cubic or body-centered cubic lattices. The coexistence of α-
Al(MnFe)Si dispersoids may affect the strength and ductility of some Al-Mg-Si alloys by modifying their microstructure, i.e., refining the MgSi phases [3].

Al-Mg-Si alloys have been widely used in the automobile industry, in order to minimize the weight and fuel efficiency of automobiles. By stamping, aluminum alloy sheets are shaped into car parts, which are then are painted and baked at ~180°C to improve the hardness as the final heat treatment [13].

A preliminary natural ageing at the temperature of about around 170°C was found to be beneficial for the precipitation-hardening of Al-Mg-Si alloys during the subsequent artificial ageing. This finding has been well documented, i.e., in [13-16]. This study aims to reveal the optimal combination of ageing time and temperature during the combined artificial and natural ageing process, as well as to explore the precipitation-hardening in Al-Mg-Si alloys. The respective phases were characterized via the X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) equipped with energy dispersive spectrometer (EDS).

2. Experimental
We investigated the ageing behavior of a commercial 6061 Al alloy with the following composition (wt.%,): Al-0.67Si-0.85Mg-0.36Mn-0.35Fe. The alloy was solute-treated at 540°C (e.g., 813K) for 2 hours and subsequently aged at 180, 200, and 220°C for different time periods, namely 2, 10, 20, 30min, 1, 2, 4, 8, 12, 24, 36, and 48 h. In order to analyze the combined effect of natural and artificial ageing processes, a 12-hour natural ageing procedure was superimposed into the artificial ageing process. The combined natural and artificial ageing processes are illustrated in figure 1.

![Figure 1. Schematic diagram of the artificial ageing processes of an Al-Mg-Si alloy](image)

The Vickers hardness (HV) was measured at room temperature with a load of 200 g for 10 s for each heat-treated sample after water quenching. The reported HV is the average value of six indentation measurements. The XRD was performed on samples aged at 220°C using a Rigaku SmartLab3kW diffractometer with the Cu Kα radiation. Using the JADE6 software, the precipitates were identified. STEM was used to characterize the precipitates prior to or after ageing. Prior to STEM, 3mm-long specimens were prepared by mechanical grounding and polishing to 80 μm in thickness after punching from the disks. These thin specimens were dimpled using a Model 656 dimple grinder and ion-polished at -180°C in liquid nitrogen using a Gatan PIPS II Model 695 precision ion-polishing instrument.
3. Results

As seen in Figure 2, the Vickers hardness of samples aged at 220°C exceeds those of samples aged at 200 and 180°C. As compared to solution-treated samples (43.8 HV), the hardness of 2min-aged samples increased and reached 47.5 HV at 180°C, 63.6 HV at 200°C, and 80.2 HV at 220°C, respectively. At any heating temperatures, the hardness remained nearly unchanged within 1 hour. The hardness increased generally with the ageing time. The hardness of samples aged at 200 and 220°C exhibited a small peak after 4h and a sharp peak after 24h. The highest hardness values of samples aged at 200 and 220°C are close to each other (100~105 HV). The hardness values of samples aged at 180°C are much lower and exhibit the peak at 8 h. However, the highest hardness values did not appear in solution-treated samples aged for 48h.

![Figure 2. Vickers hardness evolution of an Al-Mg-Si alloy aged at 180°C, 200°C and 220°C.](image)

Figure 3 shows XRD patterns of Al-Mg-Si samples aged at 180, 200, and 220°C for various periods of time. The main peaks can be characterized via the Joint Committee for Powder Diffraction Standards (JCPDS) for Al (00-004-0787), as (111), (200) and (222) planes [17]. No small peaks corresponding to the precipitation phases (i.e. \( \alpha \)-Al (MnFe)Si, \( \beta'' \), \( \beta' \) or \( \beta \)) were observed in the XRD patterns, due to a small amount of solute atoms in the alloy. However, the shift in the diffraction angle (2\( \theta \)) for the aged samples strongly indicates the presence of precipitation phases.

In Figure 3(a), the diffraction angle (2\( \theta \)) always shift to the left with an increase in ageing time at 180°C. Al (111) peaks shift from 38.444° for 2-min ageing to 38.416° for 48h ageing, whilst Al (200) peaks shift from 44.695° to 44.658°. The peak-aged sample (aged for 8h in figure 2) has the Al (111) peak at 38.424°, which is lower than those of a 4h-aged (38.440°) or a 12h-aged (38.436°) samples.

In Figure 3(b) and 3(c), the diffraction angle of Al (111) and Al (200) peaks stay the same when aged at 200 and 220°C within 1h. The diffraction angle shift to the right when aged for 4h at both 200 and 220°C. As the period of ageing time increases, the diffraction angles continue to shift to the right, but eventually they shift to the left. A sample aged at 220°C has a highest diffraction angle of Al (111) peak at 38.442°, which shows a 0.02° displacement to the right from either a 2-min, or a 48h samples.
Figure 3. X-ray diffraction of an Al-Mg-Si alloy aged at 180°C, 200°C and 220°C.

Figure 4(a) shows the STEM images of a solution-heated Al-Mg-Si alloy. It features numerous rounded dispersoids in the bright-field (BF) image. The EDS maps of atom distributions indicate that most of these dispersoids are pre-precipitates of $\alpha$-Al (MnFe)Si. The EDS line profiles of (Mg, Si) phases across one coarse particle suggest that the chemical Mg/Si
stoichiometric ratio is approximately equal to 2. However, the volume fraction of Mg\(_2\)Si phase is very small.

Figure 4(b) shows the STEM images of the Al-Mg-Si alloy aged at 220°C for 24h, where the hardness approaches the highest value (see figure 1). Many needle-shape precipitates are distributed homogeneously in the Al matrix. The diameters of these precipitates are approximated about 5~10 nm. The EDS line profiles across the precipitate indicates that these precipitates are \(\beta\)-type phases, which consist only of Mg and Si atoms. These phases have complex structures that contain both regions without a consistent unit cell and the \(\beta''\) phase within the needle [10]. Meanwhile, \(\alpha\)-Al (MnFe)Si dispersoids can be also observed.

Figure 4. STEM-BF images and EDS maps of Mg, Si, Mn and Fe atoms for (a) solution-treated samples, and (b) samples aged at 220°C for 24h.

4. Discussion
During precipitation, a decrease of solute concentration in the matrix occurs, leading to a variation in the lattice parameters, which, in turn, cause a gradual shift of the position of the Bragg reflections [17, 18]. XRD patterns of samples aged at 180°C show that the main peaks of Al shift to a lower angle as the periods of ageing time increase. XRD patterns of samples either at 200 or 220°C reveal an extraordinary shift to the right of the main peaks at 4h ageing. The samples aged for 24h exhibit the largest angles of the main peaks. The peak shift to a higher angle could be attributed to the structural transition of phase transformation from pre-\(\beta''\) to \(\beta''\) (i.e., from early fcc-based structures to non-fcc-based ones) [13]. The exact stoichiometry of \(\beta''\) normally varies with changes in the alloy overall composition. The latter can be normally changed via heat-treated processes, in which the solubility of Mg, Si atoms varies at different temperatures. Using advanced techniques (i.e., HAADF-STEM and APT [19]), phase parameters of needle-like \(\beta''\) phases can be quantitatively estimated in the combined process of natural and artificial ageing. It was found that needle-like \(\beta''\) precipitates increase the hardness of samples subjected to combined natural/artificial ageing [10, 20].

5. Conclusions
In this study, the commercial 6061 Al alloy was naturally and artificially aged at 180, 200, and 220°C for different periods of time from 1 min to 48h. The hardness values obtained at 220°C
systematically exceeded those measured at 200 and 180°C. The hardness increased with ageing time at different elevated temperatures. The hardness of samples artificially aged for 24 h and naturally aged for 12 h reached its highest value of 100–105 HV at 200 and 220°C. The hardness improvement is attributed to β” precipitates formed during the combined natural/artificial ageing. The structural transition associated with formation of β” precipitates plays a key role in determining the hardness during ageing.

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