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Revisiting the precipitation sequence in Al–Zn–Mg-based alloys by high-resolution transmission electron microscopy

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The precipitation process in Al–Zn–Mg-based alloys has been revisited using high-resolution transmission electron microscopy. It was found that there is an intermediate phase between the η′ phase and the η phase. This intermediate phase with a hexagonal structure can be termed the η precursor, since its *a* lattice parameter is the same as that of the η′ phase and its *c* lattice parameter is approximately the same as that of the η phase. Transformation from the η′ phase to the η phase occurs smoothly with this η precursor existing between them.

Keywords: Aluminum alloys; Ageing; Precipitation; High-resolution electron microscopy

Al–Zn–Mg-based alloys are not only technologically important (as high strength light metals), but also scientifically interesting (with various precipitation phases formed from the supersaturated solid solution of these alloys), and, therefore, have been extensively studied for decades [1–3]. There is an inseparable relationship between their improved combination of mechanical properties and the large number of fine precipitates formed during artificial ageing. Hence, understanding the precipitation sequence in these alloys is fundamental to their application.

For Al–Zn–Mg alloys with relatively low Mg concentrations the generally accepted precipitation sequence is [2,3]:

$$\text{solid solution} \rightarrow \text{GP zones (GPI and GPII)} \rightarrow \eta' \text{ phase} \rightarrow \eta \text{ phase.}$$

The equilibrium η phase ($MgZn_2$) [4] has a hexagonal structure with lattice parameters $a = 0.521$ nm and $c = 0.860$ nm, which is incoherent with the Al matrix and exhibits numerous crystallographic orientation relationships with the matrix [5,6]. The GP zones and the η′ phase, on the other hand, are believed to be responsible for age hardening in this system. As a consequence, a great deal of research has been carried out in an attempt to understand their composition, structure and evolution using indirect or direct measurements. It was believed from a high-resolution transmission electron microscopy (HRTEM) study that two types of GP zones, termed GPI and GPII, respectively [7], exist in these artificially aged alloys. The GPI zones were believed to be formed via solute-rich clusters and to be internally ordered with a structure similar to AuCu(I), as suggested by Schmalzried and Gerold [8]. The GPII zones [9] were thought to be linked to the vacancy-rich clusters (VRC) or vacancy-related clusters [10], despite no direct evidence being provided [3]. Their crystallographic structures have been described as the zones with zinc-rich layers on the Al {1 1 1} atomic planes, when viewed along the $\langle 1\,1\,0\rangle_{Al}$ directions [7]. The GP zones are fully coherent with the matrix and are regarded as the nuclei of the metastable η′ phase, although nucleation of the η′ phase remains controversial [7,9,11–14].

The structure of the metastable η′ phase has usually been considered to have a hexagonal structure with lattice parameters $a = 0.496$ nm and $c = 6d_{111Al} = 1.402$ nm, despite several different η′ structures having been reported [5,15–18]. The η′ phase is coherent with the Al matrix and exhibits a well-defined crystallographic orientation relationship with the matrix, $(0\,0\,0\,1)_{\eta'}//\{1\,1\,1\}_{Al}$, $[11\bar{2}0]_{\eta'}//\langle 1\,1\,2\rangle_{Al}$, $(10\bar{1}0)_{\eta'}//(1\,1\,0)_{Al}$. It is interesting to note that using X-ray diffrac-

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tion Mondolfo et al. [12] found that a transition hexagonal structure with lattice parameters $a = 0.496$ nm and $c = 0.868$ nm existed between the GPII zones and η-$MgZn_2$ in an Al–6.17% Zn–2.13% Mg–0.03% Cu alloy. This structure was in doubt without HRTEM confirmations and lately has been considered to be the η′ phase [2].

In this study, through detailed HRTEM investigations, we have more precisely re-examined the precipitation sequence for Al–Zn–Mg alloys, revealing that a coherent intermediate phase exists between the coherent η′ phase and the incoherent equilibrium η phase. The impact of the existence of this intermediate phase on the hardness–time curve is also discussed.

An in-house made Al–6.5 Zn–1.6 Mg–2.0 Cu (wt.%) alloy with the dimensions 10 × 10 × 3 mm was heated at 470 °C for 1 h for solution treatment and then quenched in water at room temperature. The as-quenched alloy samples were then immediately aged at 120 and 150 °C (±1 °C) in an oil bath for up to 400 h. A series of samples were taken at different ageing times to investigate the precipitation sequence. The hardness measurements were carried out with a Vickers hardness tester. Each hardness value was obtained by averaging five measurements. The microstructures of aged alloys were systematically studied using HRTEM (a FEI Tecnai F20 HRTEM operating at 200 kV and a JEOL JEM-3010 operating at 300 kV). The TEM specimens were prepared first by mechanical polishing and then by electropolishing.

Figure 1 shows the result of hardness measurements, with the error bars indicating the deviations of individual measurements. The hardness increased rapidly with ageing time before reaching a first peak hardness. In fact, the hardness–ageing curve can be roughly divided into three regions: region I with a rapid increase in hardness; region II with two hardness peaks accompanied by slight hardness decreases over a long ageing duration; region III with a further hardness decrease. Samples from different annealing regions were prepared for HRTEM observations in order to investigate precipitate evolution with respect to annealing time.

Figure 2 demonstrates the typical appearances of the hardening particles in the samples that had been aged at 120 °C for 32, 72 and 400 h, respectively. $\langle 1\,1\,2\rangle_{Al}$ and $\langle 1\,1\,0\rangle_{Al}$ are the two viewing directions most suitable

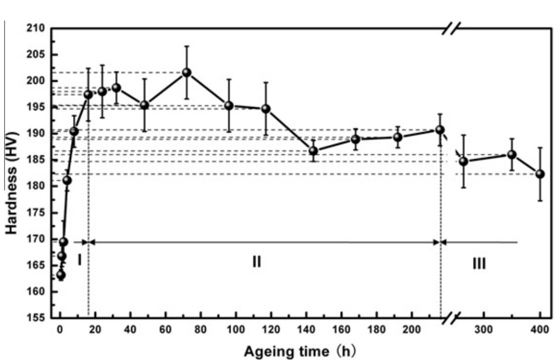

Figure 1. The hardness–time curve plotted for an Al–6.5 Zn–1.6 Mg–2.0 Cu (wt.%) alloy aged at 120 °C.

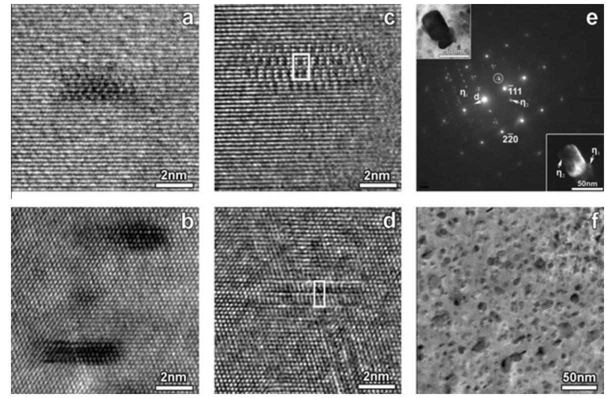

Figure 2. Crystallographic features of the three known phases formed upon precipitation in Al–Zn–Mg(Cu) alloys characterized by TEM images or diffraction patterns. (a and b) HRTEM images of the disc-shaped GPII zones viewed edge-on along the $[1\,1\,2]_{Al}$ and $[1\,1\,0]_{Al}$ directions, respectively; (c and d) HRTEM image of the disc-shaped η′ phase particles viewed edge-on along the $[1\,1\,2]_{Al}$ and $[1\,1\,0]_{Al}$ directions, respectively; (e) SAED pattern of two η phase particles (the inset in the upper left corner is a bright field image, while the inset in the bottom right corner is a dark field image); (f) an overview of the sample aged for 400 h taken along the $[1\,1\,2]_{Al}$ direction, showing that the microstructure was a mixture of η′ phase particles and the larger, short rod-shaped η phase particles.

to study disc-like hardening precipitates in Al–Zn–Mg(Cu) alloys. Figure 2a and b shows a $\langle 1\,1\,2\rangle_{Al}$ lattice image and a $\langle 1\,\mathbf{1}\,\mathbf{0}\rangle_{Al}$ lattice image, respectively, of the so-called GPII precipitates in the sample aged for 32 h (corresponding to the first hardness peak in Figure 1). The typical GPII zones were fully coherent with the matrix and were composed of disc-like particles consisting of a few atomic layers parallel to the $\{1\,1\,1\}_{Al}$ planes [7,19,20]. It is known that the first hardness peak can be mainly attributed to the existence of large numbers of GP zones (including GPI [9] or GPII zones [7]). Our extensive HRTEM investigations have confirmed that the GPII zones are the dominant particles in the samples aged for up to 32 h. The typical sizes of GPII zones are 1–6 atomic layers in thickness and 3–6 nm in width. With further ageing the increase in thickness was slower than the increase in width. No GPI zones were clearly identified in our observations.

Figure 2c and d shows typical $\langle 1\,1\,2\rangle_{Al}$ and $\langle 1\,1\,0\rangle_{Al}$ HRTEM images, respectively, taken from the sample aged for 72 h (corresponding to the second hardness peak in Figure 1), showing the morphological and crystallographic features of the so-called η′ phase particles [16]. The η′ precipitates are much larger than the GPII zones. These precipitates were 3–4 nm in thickness and 5–10 nm in width, and were the major precipitates in the samples aged for 72 h, although a small amount of GPII zone still existed. The η′ precipitates consisted of more atomic layers (>6 layers) parallel to the $\{1\,1\,1\}_{Al}$ planes, compared with the GPII zones. Having a hexagonal lattice with c parameter approximately equal to $6d_{111Al}$ (=1.402 nm), as shown in Figure 2c, the η′ phase is generally believed to be the main hardening phase. As such, the minimum thickness of an η′ precipitate should be greater than 6 $\{1\,1\,1\}_{Al}$ atomic layers. Considering their similarity in morphology and in structural arrange-