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Effects of Zn addition on the age hardening behavior and precipitation evolution of an Al-Mg-Si-Cu alloy

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ABSTRACT

The effects of Zn on the age hardening behavior and corresponding microstructure of an Al-0.9Mg-0.8Si-0.2Cu (wt%) alloy were investigated by hardness testing, transmission electron microscopy (TEM) and three-dimensional atom probe (3DAP). During aging for up to 8 h at 170 °C (peak hardness condition), the addition of Zn does not alter the precipitation sequence of the Al-Mg-Si alloy, which can be expressed as: supersaturated solid solution → solute clusters → GP zones → β″. The Zn does not significantly partition into clusters or precipitates, and the majority of Zn remains in the Al matrix, prompting the formation of solute clusters during the early stage of aging and subsequently stimulating the transformation from solute clusters to GP zones to β″ precipitates. The characterization of precipitation evolution caused by Zn addition correlates well with the observed enhanced age hardening response.

1. Introduction

The 6xxx series (Al-Mg-Si) alloys exhibit many advantageous properties, such as high strength to weight ratio, excellent formability and good corrosion resistance, facilitating their wide use as automotive skin panels [1,2]. Precipitation hardening is the major strengthening mechanism in Al-Mg-Si alloys. The precipitation sequence generally accepted for these alloys is [1,3]: SSSS → solute clusters → GP zones → β″ → β′ → β, where SSSS is the supersaturated solid solution. The solute clusters are believed to be aggregates of solute atoms, which are fully coherent with the Al matrix [4,5], and these clusters evolve rapidly into metastable precipitates during artificial aging. GP zones involve early stage precipitation, with considerably larger and more stable coherent solute aggregates exhibiting spherical morphology [6]. The needle β″ precipitates, which transform from GP zones, are considered the main hardening precipitates [7–9]. The β' precipitates form after the β″ phase with further aging, and exhibit rod-shaped morphology [10]. Finally, coarse β phases are formed as the equilibrium phases [11,12]. For automotive body panel applications, Al-Mg-Si alloys require low yield strength for good formability in T4 temper and high yield strength after the final paint-bake (PB) cycle for in-service dent resistance [13,14]. The addition of alloy elements is an efficient way to improve material mechanical properties in order to meet application requirements. For example, the addition of Cu to Al-Mg-Si alloys has been used to increase strength. During a fixed PB aging time, the presence of Cu promotes the formation of Cu-containing precipitates (L/S/C, QP and QC phase), leading to a significant hardening effect [15]. However, the increased Cu content reduces the formability of alloys during the stamping process [16]. Therefore, the control of Cu content is a key factor to attain the required properties of Al-Mg-Si alloy for automotive applications.

Most recently, Zn additions to Al-Mg-Si alloys have been studied, effectively affecting the precipitation microstructure and enhancing age hardening response. Some investigations have reported that Zn additions to Al-Mg-Si alloys lead to the formation of clusters or precipitates of the Al-Mg-Zn alloy system. These clusters or precipitates play important roles in improving the age hardening response. Cai et al. [17] suggested Mg-Zn clusters were formed together with Mg-Si clusters during the early artificial aging stage, resulting in a rapid and significant age hardening response. Guo et al. [18] reported that Mg-Zn clusters can act as nucleation sites for Mg-Si precipitates (e.g., GP zones and β″ precipitates), leading to the formation of fine and high density Mg-Si precipitates. The resulting enhancement in age hardening response was achieved. Yan et al. [19] and Ding et al. [20] confirmed the co-existence of GP zones, β″ phases, GP (II) zones and η′ phases in Al-Mg-Si alloys with different Zn contents and observed corresponding enhanced age responses. In contrast with the above studies, Saito et al. [21] did not observe precipitates of Al-Zn-Mg alloy system when Zn was added to Al-Mg-Si alloy. They suggested that the Zn addition only

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prompted the formation of β″ phases, resulting in higher peak hardness. To date, there is a lack of detailed information about precipitation evolution and solute partitioning behavior during aging in these alloys. A better understanding of precipitation microstructure is importance to establish the microstructure-hardening relationship of Al-Mg-Si alloys containing Zn.

The goals of this work are to develop a deeper understanding of the precipitation evolution of an Al-Mg-Si-Cu alloy with 0.6 wt% Zn addition and to determine the relationship between precipitation evolution and aging hardening behavior during artificial aging at 170 °C. To do this, the aging hardening curve of the Zn-containing Al-Mg-Si-Cu alloy is determined and compared with the Zn-free one. Transmission electron microscopy (TEM) and three-dimensional atom probe (3DAP) are employed to characterise precipitation microstructure formed during aging in the Zn-containing and Zn-free alloys. In addition, the solute partitioning behavior is revealed based on 3DAP quantitative analysis. Finally, the effects of Zn addition on the age hardening behavior and precipitation evolution of the Al-Mg-Si-Cu alloy are understood well by the comprehensive microstructure information obtained from the combination of TEM and 3DAP characterisations.

2. Experimental Procedures

For our investigations an Al-Mg-Si-Cu alloy and a Zn-containing model alloy were used. The chemical compositions of the Zn-free and Zn-containing alloys are listed in Table 1. The studied alloys were prepared by induction melting of high-purity aluminum (99.9%), high-purity magnesium (99.9%), high-purity copper (99.9%), high-purity Zinc (99.9%), Al-10 wt.%Mn, Mg-30 wt.%Zr and Al-14 wt.%Si master alloys, followed by casting into a steel mould. The two ingots were homogenised at 430 °C for 10 h plus 545 °C for 16 h in an air furnace and then were hot and cold rolled to 1 mm thick sheet. The specimens were then cut into 10 × 10 × 1 mm^3 before heat treatment. The solute treatment was conducted at 550 °C for 0.5 h in a muffle furnace and water-quenched samples were subsequently artificially aged at 170 °C for various times in an air-circulation oven. Vickers hardness measurements were carried out at a load of 5 kg with a dwell time of 10 s. The data points in hardness curves are average values of at least 10 indentations.

Thin foils for TEM studies were prepared by punching 3 mm diameter discs and twin jet electro-polishing with an electrolyte consisting of 30 vol% nitric acid in methanol solution below −30 °C at an operating voltage of 15 V. TEM observations were performed on a FEI Tecnai F20 TEM microscope. The combination of the TEM bright-field images with corresponding thickness measurements allowed quantification of the average precipitate size, number density and volume fraction. The thickness of the investigated area was measured according to the contamination spot separation (CSS) method described in Ref. [22]. Briefly, focusing of a small electron beam onto the specimen causes the accumulation of contamination on both sides of the TEM foil. Tilting the foil through an angle γ causes the upper and lower contamination spots to separate, and measurement of this separation r enables the simple calculation of foil thickness t according to the following equation

$$t = \frac{r}{\sin\gamma} \tag{1}$$

Spherical GP zones and needle β″ precipitates were formed at 170 °C for different aging times. The statistical methodology of β″ precipitate has been described elsewhere [23]. Quantitative calculation of the size, number density and volume faction of the GP zone followed the Schwartz-Saltykov method [24]. The corrected size distribution (n) equals the observed size distribution (m) multiplied by a matrix X. This matrix X depends on the thickness t of the TEM specimen and the number of size classes M with a certain size Δ. To form the matix X, first the diagonal is defined by the uncut particles x_{ii}^{uncut} with $i,j = (1, \ldots, M)$, the partiles with their center within the specimen. The x_{ii}^{uncut} can be written as $x_{ii}^{uncut} = \tau/(t + i)$ with a thickness factor $\tau = t/\Delta$. Partilces x_{ii}^{cut} are cut at the specimen surface and their center is outside the specimen. The projected diameters of these particles as observed in a TEM image are smaller than their actual diameters. The x_{ii}^{cut} can be expressed as $x_{ii}^{cut} = (\sqrt{j^2 - (i-1)^2} - \sqrt{j^2 - i^2})/(\tau + j)$. Thus the matrix X is obtained by $X = X^{uncut} + X^{cut}$. The corrected size distribution n is then

$$n = \mathbf{X}^{-1}m \tag{2}$$

Once the corrected size distribution is determined, estimates for the mean diameter of particle

$$\bar{d} = \sum_{i=1}^{M} d_i n_i \tag{3}$$

and the average sphere volume

$$\bar{v} = \frac{\pi}{6}\sum_{i=1}^{M} (d_i)^3 n_i \tag{4}$$

can be determined, where d_i is the average diameter and n_i is the number fraction in the size class i.

The number density of particles is

$$\rho = \frac{N_{obs}/V}{1 + \bar{d}/t} \tag{5}$$

N_{obs} is the observed number of particles over volume $V = At$, which is corrected by factor $1 + \bar{d}/t$.

The volume fraction of particles (f_V) equals the number density multiplied by the mean volume:

$$f_V = \rho\bar{v} \tag{6}$$

Needle samples for three-dimensional atom probe (3DAP) analysis were prepared from sample bars with the dimensions of 0.5 × 0.5 × 15 mm^3 using standard two stage electro-polishing [25]. The 3DAP experiments were carried out on a LEAP 4000HR with a sample temperature of 20 K, a pulse fraction of 20%, a pulse rate of 200 kHz and a detector efficiency of 36%. IVAS 3.6.12 software was used for selection, quantification and composition analysis of the solute-rich features, such as clusters and precipitates. The maximum distance between atoms (D_{max}), the surround distance (L) and erosion distance (S) were each set to 0.7 nm for a meaningful detection of nearest neighbour atoms. Solute-rich features containing < 10 solute atoms were neglected in the analysis because these small solute-rich features were randomly distributed in the volume with solute atoms. The number density of the solute-rich features was determined as the ratio of the number of observed solute-rich features to the overall analyzed volume. The volume fraction of the solute-rich features was defined as the ratio between the number of detected atoms in the solute-rich features and the total number of collected atoms. The first nearest neighbour (1NN) analysis was employed to reveal the distribution of solute atoms in the alloys during aging [5,26].

Table 1
Chemical composition of the experimental alloys (wt%).

Alloys	Mg	Si	Zn	Cu	Mn	Zr	Fe	Al
Zn-free	0.90	0.82	0.006	0.23	0.11	0.09	< 0.1	Bal.
Zn-containing	0.92	0.78	0.64	0.23	0.10	0.12	< 0.1	Bal.

3. Results

3.1. Hardness Measurements

Fig. 1 shows the age hardening curves of Zn-free and Zn-containing