Properties of Al-Zn-Mg-(Cu) Alloy After Linear Heating Aging (Postprint)

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Abstract

The precipitation behavior of precipitates, property variations, and the influence of Cu on Al-Zn-Mg-(Cu) alloys subjected to linear heating aging were investigated by means of differential scanning calorimetry (DSC), hardness analysis, transmission electron microscopy (TEM), three-dimensional atom probe (3DAP) analysis, and other characterization techniques. The results demonstrate that with increasing aging temperature, the hardness of both Al-Zn-Mg and Al-Zn-Mg-Cu alloys initially increases to a peak value before subsequently decreasing, wherein the hardness of the Al-Zn-Mg-Cu alloy exceeds that of the Al-Zn-Mg alloy. Following linear heating peak aging, the primary precipitate phase in both alloys is the ’ phase, with both alloys containing minor amounts of GP zones and phase. Cu addition modifies the chemical composition and structure of the precipitates, retarding the transformation from metastable phases to equilibrium phases.

Full Text

Preamble

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Properties of Al-Zn-Mg-(Cu) Alloy After Linear Heating Aging Treatment

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Abstract: The precipitation behavior, property evolution, and influence of Cu in Al-Zn-Mg-(Cu) alloys during linear heating aging were investigated using differential scanning calorimetry (DSC), hardness testing, transmission electron microscopy (TEM), and three-dimensional atom probe (3DAP). The results show that with increasing aging temperature, the hardness of both Al-Zn-Mg and Al-Zn-Mg-Cu alloys first increases to a peak value and then decreases, with the Al-Zn-Mg-Cu alloy consistently exhibiting higher hardness than the Al-Zn-Mg alloy. After peak aging via linear heating, the primary precipitate in both alloys is the ’ phase, with small quantities of GP zones and phase also present. Cu addition modifies the chemical composition and structure of the precipitates and retards the transformation from metastable to equilibrium phases.

Keywords: metallic materials, Al-Zn-Mg-(Cu) alloy, linear heating, aging, precipitate

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Introduction

Al-Zn-Mg-Cu series alloys are important structural materials in aerospace and transportation applications due to their low density, high specific strength, and excellent hot workability and weldability [1-3]. The precipitates formed during aging treatment play a decisive role in the high strength and stress corrosion resistance of these alloys. Since Al-Zn-Mg-Cu alloys are primarily used for large aerospace components, non-uniform heating rates between the interior and exterior during heat treatment can lead to non-isothermal effects that prevent the core from achieving the same microstructure and properties as the surface [4]. Therefore, studying non-isothermal phenomena during aging is crucial for understanding microstructural and property evolution in large components. Additionally, Cu significantly influences precipitate nucleation and growth during aging. Marlaud et al. [5] found that during isothermal aging of Al-Zn-Mg-Cu alloys, Cu substitutes for Zn atoms in precipitates, and the Cu content in precipitates increases with aging time and precipitate size, correlating with the overall Cu content in the alloy. This study employs 3DAP analysis combined with DSC, hardness testing, and TEM to investigate precipitate evolution, property changes, and the mechanism of Cu effects during non-isothermal aging of Al-Zn-Mg-(Cu) alloys.

Experimental

The chemical compositions of the two experimental alloys are listed in Table 1 . Pure aluminum (99.98 wt%), pure zinc (99.98 wt%), pure magnesium (99.75 wt%), Al-42.3%Cu master alloy, and Al-4.21%Zr master alloy were used to prepare Al-7.8Zn-1.6Mg-xCu-0.14Zr (x = 0, 0.8, 1.6) alloys, which were melted and continuously cast into cylindrical billets 72 mm in diameter. The billets were heated to 420°C and rolled to 90% deformation.

The rolled samples were solution-treated at 470°C for 2 h and water-quenched to room temperature. The quenched samples were immediately placed in a constant-temperature oven at 40°C for linear heating aging treatment at a rate of 20°C/h to 220°C, followed by water quenching to room temperature. Subsequent DSC, hardness, TEM, and 3DAP analyses were performed on these samples.

DSC analysis was conducted on a DIAMOND differential scanning calorimeter from room temperature to 500°C at a heating rate of 10 K/min using Φ10 mm × 5 mm samples under argon protection. Microhardness was measured using an MH-3 Vickers hardness tester with a 100 g load; five measurements were taken per sample and averaged. Precipitate evolution during linear heating aging was observed using a JEM-2010F field-emission transmission electron microscope. TEM samples were prepared by twin-jet electropolishing in a 30% nitric acid + 70% methanol electrolyte at -25°C and 15 V. A LEAP3000HR three-dimensional atom probe was used for compositional analysis. Samples with 0.5 mm × 0.5 mm cross-sections were electropolished twice: first in a thin layer of electrolyte (20% perchloric acid + 80% acetic acid) floating on a dense inert liquid, and second in a solution of 2% perchloric acid + 98% butoxyethanol.

2.1 DSC Results Analysis

Figure 1 [Figure 1: see original paper] shows the DSC curves for the Al-Zn-Mg and Al-Zn-Mg-Cu alloys. For the Al-Zn-Mg alloy, a large exothermic peak A1 appears around 100°C, corresponding to ’phase nucleation [6]. No peaks for GP zone precipitation or dissolution were observed due to the rapid transformation of GP zones. The ’ phase coarsens between 160-185°C and dissolves at 209°C (endothermic peak B1). The equilibrium phase nucleates at 236°C (exothermic peak C1) and dissolves at 252°C (endothermic peak D1).

In contrast, the Al-Zn-Mg-Cu alloy exhibits markedly different DSC results. A large exothermic peak A2 corresponds to GP zone precipitation in the early aging stage, with a GP zone dissolution peak B2 around 70°C. The ’ phase nucleates near 130°C, coarsens between 180-204°C, and dissolves around 214°C. The phase nucleates at 231°C (exothermic peak E2) and subsequently dissolves near 246°C. Previous research indicates that Cu addition stabilizes GP zones in the early aging stage and retards the ’→ transformation [7], which is consistent with our findings that Cu stabilizes GP zones and delays ’ phase coarsening and growth in later aging stages.

2.2 Hardness Evolution During Linear Heating Aging

The hardness variation of Al-Zn-Mg-(Cu) alloys during linear heating from room temperature to 220°C at 20°C/h is shown in Figure 2 [Figure 2: see original paper]. Both alloys exhibit similar hardness trends: an initial increase to a peak value followed by a decrease, with the Al-Zn-Mg-Cu alloy consistently harder than the Al-Zn-Mg alloy. In the early aging stage (70-90°C), GP zones form predominantly and hardness values remain low, though the Al-Zn-Mg-Cu alloy shows a higher hardening rate due to accelerated early-stage strengthening and favorable GP-II zone nucleation promoted by Cu. During the intermediate aging stage, the ’ phase becomes the main strengthening phase, and both alloys show rapid hardness increases. The Al-Zn-Mg alloy reaches peak hardness at 180°C, while the Al-Zn-Mg-Cu alloy peaks at 190°C, demonstrating that Cu addition delays the peak temperature and retards the transformation from metastable to stable phases. In the later aging stage, the ’ phase begins to coarsen and transform to the phase, causing hardness to decrease. The faster transformation between different precipitate types in the Al-Zn-Mg alloy indicates that Cu influences both the transformation rates and mechanisms during non-isothermal aging. Fang Xu [12] studied the precipitation behavior and crystal structures of Al-Zn-Mg-Cu alloys with different Cu contents, finding that Cu atoms substitute for Zn atoms in MgZn2 precipitates, forming new crystallographic features. The lower diffusion rate of Cu atoms prolongs the aging process and delays the transition from the metastable ’ phase to the stable phase, which our results confirm that Cu effectively hinders precipitate coarsening and growth at elevated temperatures.

2.3 Microstructure After Aging

TEM analysis was performed on both alloys after linear heating to their respective peak-aged conditions, as shown in Figures 3 [Figure 3: see original paper] and 4 [Figure 4: see original paper]. For the Al-Zn-Mg alloy aged to 180°C, relatively coarse precipitates are visible at grain boundaries with a discontinuous distribution, while finer precipitates exist within the matrix. Electron diffraction along the [211]Al direction reveals ’ phase diffraction spots at the 1/3 position and phase spots at the 1/2 position of the [220] direction. The Al-Zn-Mg-Cu alloy aged to 190°C also shows discontinuous precipitates at grain boundaries, but with smaller sizes. Additionally, numerous dislocations pinned by second-phase particles are observed at grain boundaries (Figure 4a). Diffraction along the [100]Al direction shows both ’ and phase spots (indicated by arrows). High-resolution TEM images reveal nanometer-scale precipitates in the Al-Zn-Mg alloy that are fully coherent with the matrix and exhibit low contrast, identified as GP zones (indicated by arrows). Larger spherical precipitates approximately 10 nm in size show semi-coherent interfaces with the matrix and are identified as ’ phase. The Al-Zn-Mg-Cu alloy contains more numerous fine GP zones due to Cu’ s stabilizing effect and promotion of GP zone nucleation. Comparison of the larger spherical precipitates shows that the incoherency with the matrix is more pronounced in the Al-Zn-Mg alloy than in the Al-Zn-Mg-Cu alloy, likely because Cu incorporation into precipitates modifies their composition and structure, delaying the ’ → transformation. Some researchers have identified a transitional precipitate between ’ and phases, termed a precursor phase, though its structure requires further investigation [13]. These results demonstrate that non-isothermal aging produces more complex precipitate structures than isothermal aging because precipitate nucleation and growth rates depend on diffusion coefficients, nucleation driving force, and nucleation potential, all of which vary simultaneously with temperature, creating complex competitive relationships between metastable phases during linear heating [14].

2.4 3DAP Analysis After Linear Heating to Peak Aging

Three-dimensional atom probe can resolve small atomic clusters and precipitates while providing information on particle density, composition, and morphology [15-16]. Figures 5 [Figure 5: see original paper] and 6 [Figure 6: see original paper] show the overall morphology and elemental segregation in both alloys after linear heating to peak aging. In the Al-Zn-Mg alloy, precipitates are predominantly ellipsoidal (Figure 5a), with Zn and Mg atoms co-located in the same regions (Figures 5b and 5c), indicating that precipitates consist of Zn and Mg atoms. In contrast, the Al-Zn-Mg-Cu alloy shows predominantly rod-shaped precipitates (Figure 6a), with Zn, Mg, and small amounts of Cu atoms segregated together (Figures 6b-d).

Based on differences in chemical composition and size ranges of various precipitates, G. Sha et al. [17] performed statistical cluster analysis. Table 2 presents the statistical 3DAP results for both alloys after linear heating to peak aging. The analysis reveals that both alloys primarily contain ’ phase with small amounts of GP zones and phase. However, the Al-Zn-Mg alloy contains only 8.5% GP zones, while the Cu-containing alloy contains 30.3%. Conversely, the phase content is higher in the Al-Zn-Mg alloy than in the Al-Zn-Mg-Cu alloy, confirming that Cu addition stabilizes GP zones and delays the ’ → transformation, consistent with DSC and TEM results.

The Zn/Mg ratio increases progressively from GP zones to phase, with the Al-Zn-Mg-Cu alloy showing higher Zn/Mg values than the Al-Zn-Mg alloy. Overall, Cu incorporation into precipitates during aging modifies their chemical composition and morphology.

To compare precipitate compositions between the two alloys, characteristic clusters were selected and magnified (Figures 7 [Figure 7: see original paper] and 8 [Figure 8: see original paper]). The Al-Zn-Mg alloy cluster is spherical, approximately 7 nm in size, with a Zn/Mg ratio of 1.9 (Figure 7). The Al-Zn-Mg-Cu alloy cluster is larger and rod-shaped, with a (Zn+Cu)/Mg ratio of 2.1 (Figure 8). Cu segregation is observed primarily at the precipitate-matrix interface, which reduces interfacial energy. Due to Cu’ s low diffusion rate in the matrix, Cu addition retards ’ phase coarsening and transformation to phase, thereby enhancing thermal stability.

3. Conclusions

1. During linear heating aging, the hardness of both alloys first increases with temperature, reaches a peak, and then decreases, with the Al-Zn-Mg-Cu alloy consistently harder than the Cu-free Al-Zn-Mg alloy.
2. Cu addition stabilizes GP zones in the early aging stage and delays coarsening and transformation of the ’ phase in later stages.
3. After linear heating to peak aging, precipitates in the Al-Zn-Mg alloy are predominantly ellipsoidal, while those in the Al-Zn-Mg-Cu alloy are rod-shaped. Both alloys primarily contain ’ phase with small amounts of GP zones and phase.
4. Cu atoms incorporate into precipitates in the Al-Zn-Mg-Cu alloy, primarily segregating at the precipitate-matrix interface, which modifies precipitate chemistry and structure.

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Note: Figure translations are in progress. See original paper for figures.