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Interphase boundary segregation of silver and enhanced precipitation of Mg₁₇Al₁₂ Phase in a Mg-Al-Sn-Ag alloy



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ABSTRACT

Aging-hardening response of Mg-7Al-2Sn (wt%) alloy can be remarkably accelerated by a small addition of silver (Ag). Using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) coupled with high resolution energy dispersive X-ray spectroscopy (EDS) mapping, for the first time, segregation of solute atoms (Ag in this case) was observed at the interphase boundary between continuous $Mg_{17}Al_{12}$ precipitate and magnesium matrix in Mg-7Al-2Sn alloy with 0.7 wt% Ag addition. Substantial size refinement and increased number density of $Mg_{17}Al_{12}$ precipitates may be responsible for the enhanced aging-hardening response in Mg-7Al-2Sn alloy with Ag addition.

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Magnesium alloys have attracted great interests due to the increasing demands for weight reduction and fuel efficiency in the automotive and aerospace industries [1,2]. One major limitation of commercial magnesium alloys is their low strength. Precipitation hardening is one of the most efficient ways to improve the strength of magnesium alloys, especially those targeted for casting applications [3]. Aluminum, with a large solubility up to 12 wt% in magnesium at around 437 °C, has been frequently added to commercial AZ (Mg-Al-Zn) and AM (Mg-Al-Mn) serial magnesium alloys as one principal alloying element. Upon cooling from high temperatures and aging at low temperatures, Mg₁₇Al₁₂ phase with a complex body centered cubic structure can form in Mg—Al based alloys through two competitive and simultaneous reactions: continuous precipitation and discontinuous precipitation [4,5]. Continuous precipitation nucleates and grows within grain interior, leading to a continuous change in the composition in magnesium matrix, while discontinuous precipitation forms through cellular growth at grain boundaries. $Mg_{17}Al_{12}$ phase has an Burgers orientation relationship ((0001)_{Mg}// $(011)_{Mg17Al12},\,[2\bar{1}\ \bar{1}0]_{Mg}//[1\bar{1}1]_{Mg17Al12})$ with respect to magnesium matrix [6,7]. Mg—Al based alloys have poor mechanical properties especially at elevated temperatures, mainly due to softening of discontinuous Mg₁₇Al₁₂ at grain boundaries. The addition of Sn to magnesium leads to the formation of Mg₂Sn precipitate with a face centered cubic crystal structure [8]. As compared with Mg₁₇Al₁₂ phase, Mg₂Sn has a higher melting point of 770 °C, thus having a better thermal stability. Sn addition also can effectively reduce the formation discontinuous precipitates $\rm Mg_{17}Al_{12}$ at grain boundaries, further improving alloy stability at elevated temperatures. Previous study of different Mg-Al-Sn system shows that Mg-7Al-2Sn, designated AT72, has an excellent combination of strength, ductility and corrosion resistance among different Mg-Al-Sn alloys [9].

However, one main drawback of using Mg₂Sn phase for the purpose of precipitation hardening is that its precipitation kinetics is very sluggish and thus aging hardening response is poor. Addition of Zn can substantially increase aging hardening of Mg—Sn alloys through refining Mg₂Sn precipitates and increasing its number density [10,11]. A recent study using advanced scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDXS) reveals that Zn can segregate at the interface boundary between Mg₂Sn precipitates and Mg matrix in Mg—Zn alloys [12]. Such segregation may play an important role in enhancing aging hardening response in Mg—Sn systems. Mechanical properties of magnesium alloys can be greatly influenced by the segregation of alloying elements. For example, in Mg—Gd, Mg—Zn and Mg-Gd-Zn alloys, periodic equilibrium segregation of solutes are observed at fully coherent twin boundaries, leading to unusual annealing strength through the pinning effects of solutes at twin boundaries [13].

Silver is an effective alloying element for improving the strength of Mg alloys, and it can substantially enhance aging hardening response in Mg-Y-Zn alloys, through promoting the formation of the densely distributed basal precipitates [14]. Enhanced aging hardening response and significant refinement of precipitation microstructure was observed

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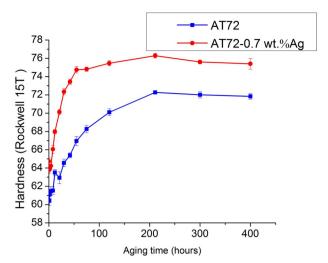


Fig. 1. Aging hardening response of AT72 alloys with and without Ag addition during isothermal aging at 200 $^{\circ}\text{C}.$

in Mg-2.4 at.% Zn alloy with the addition of trace amount of Ag and Ca [15]. The addition of Ag and Zn in Mg—Gd alloys results in the formation of nano-scale precipitates and thus significantly improve aging hardening response [16]. Similar enhanced aging hardening response due to Ag addition was also observed in other Mg alloys systems including Mg—Gd alloys [17] and Mg—5Sn alloy [18].

In this work, the effect of Ag addition on aging hardening response of AT72 alloy was investigated. Advanced transmission electron microscopy including atomic resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy coupled with high resolution EDS mapping were used to reveal detailed precipitation microstructure, especially the chemistry of the interphase boundaries. Such detailed microstructure characterization provides valuable insights to the understanding of the effect of addition of micro-alloying elements on precipitation kinetics and mechanical properties of Mg alloys.

Test alloy ingots (25 mm in diameter) with nominal compositions of Mg-7Al-2Sn and Mg-7Al-2Sn-0.7 wt% Ag were prepared through induction melting in a mild steel crucible under a protection atmosphere of 0.5%SF₆/CO₂, and casting into a steel cylinder mold. Samples cut from ingots were solution treated at 420 °C for 24 h, and then water quenched. Aging treatment was carried out in a silicone oil bath at 200 °C. Hardness tests were conducted on a Buehler Rockwell hardness tester using Rockwell superficial 15T scale. For each aging condition, a total of 10 measurements were recorded. Thin slices with a thickness around 800 µm were cut from aging specimens using a low speed diamond saw. Those specimens were mechanically ground to about 90 μm. Further mechanical polishing down to about 30 μm was conducted in a Finisone 100 dimpler. Final perforation of thin TEM foils were completed using a Finione model 1010 ion mill. Quantitative precipitation characterization was conducted using a FEI Tecnai TF20 microscope operating at an accelerating voltage of 200 keV. For each dimension of Mg₁₇Al₁₂ precipitates, about 250 precipitates were measured. The

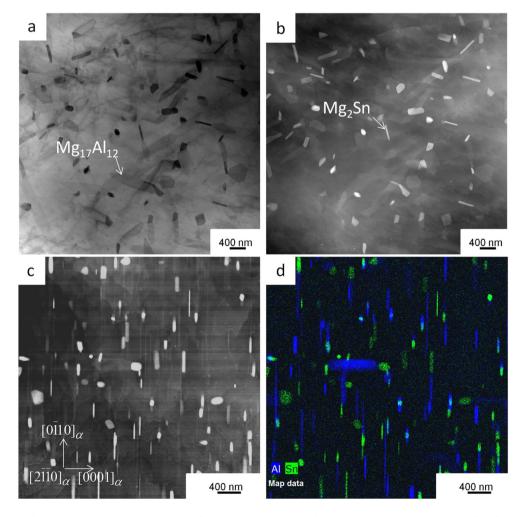


Fig. 2. STEM characterization of precipitation microstructure in AT72 alloy after isothermal aging at 200 °C for 55 h: a) BF-STEM image (beam close to [0001] zone axis); b) corresponding HAADF-STEM image; c) HAADF-STEM image showing the region for EDS mapping (α represents Mg matrix); and d) Al EDS map overlapped with Sn map.

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