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Atomic-scale HAADF-STEM characterization of an age-hardenable Mg-Cd-Yb alloy

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ABSTRACT

Herein, we present the first report of a high-density nanoblock Laves phase that can be directly precipitated in the Mg-Cd-Yb alloy, with peak-hardness increasing from 50.9 to 66.5 Vickers hardness (HV) during isothermal aging at 200 °C. C_s-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) mapping results indicate that the nanoblock precipitate is a new, structured $(Mg, Cd)_2Yb$ ternary intermetallic compound, which has a C14 Laves structure (hcp, space group: $P6_3/mmc$, $a = 6.28$ Å, $c = 10.14$ Å). Additionally, the orientation relationship between the $(Mg, Cd)_2Yb$ precipitate and α-Mg matrix is determined to be $(0001)_p//(0001)_\alpha$ and $[1\bar{1}00]_p//[11\bar{2}0]_\alpha$. This finding is expected to guide the future design of novel, high-strength, and corrosion resistant Mg-Cd alloys.

1. Introduction

Magnesium alloys, with a density below 2 g/cm^3, such as the Mg-Al systems, Mg-Zn systems, and Mg-RE (where RE represents rare earth elements) systems [1–7], are the lightest of all commonly used structural metals. These alloys have been used for various industrial products such as portable electronic devices, automobile components and aerospace components [1,2,8]. However, poor mechanical strength, creep resistance and corrosive properties of most Mg alloys limit their practical application.

Recently, Mg-Cd alloys have attracted wide attention due to its excellent corrosion resistance [9–11]. It has been reported that the addition of Cd to Mg could reduce the hydrogen evolution reaction (HER) rate during the reduction of H^+, which is attributed to the very high overpotential and low exchange current density of Cd [9–11]. Nonetheless, the relatively low mechanical performance limits its further development.

From the Mg-Cd binary phase diagram, it can be determined that the solid solubility of Cd in Mg matrix is infinite, which means the Mg-Cd system can be developed into an age-hardenable engineering alloy *via* microalloying. One typical example is the Mg-In system [6,12], where the addition of Ca to Mg-In binary alloys leads to a remarkable age-hardening response, although the solute solubility of In in the matrix is still high during isothermal aging at 200 °C.

Yb is a well-known valence-fluctuation element. The maximum solid solubility of Yb in Mg is 0.35 at.% (or 2.44 wt%) at the eutectic temperature, and decreases to almost 0 at.% at 200 °C. The elements Yb and Cd have a strong affinity, as the enthalpy of mixing value is −31 kJ/mol for Cd-Yb, far less than the enthalpy of mixing value of Mg-Cd (−6 kJ/mol) and Mg-Yb (−6 kJ/mol) [13]. Therefore, it is feasible to increase the strength of Mg-Cd alloy by microalloying with Yb, which could lead to the Cd-Yb intermetallic compounds being preferentially precipitated and hardened.

According to this strategy, we attempt to develop an age-hardenable Mg-Cd-Yb ternary alloy. Using atomic-scale high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) techniques, we have discovered a new, structured, high-density nanoblock Laves phase formed by direct precipitation in the Mg-Cd-Yb ternary alloy aged isothermally at 200 °C. This finding deepens our understanding of the precipitation mechanism

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of the Laves phase, and provides meaningful theoretical guidance for designing and developing novel, high-strength, and corrosion resistant Mg-Cd alloys.

2. Experimental procedures

The alloy with nominal composition of Mg-1.5Cd-0.75 Yb (in at.%) was prepared by melting the pure Mg (99.9 wt%), Cd (99.9 wt %) and Yb (99.9 wt%) in the induction furnace with protection of the argon atmosphere. The molten alloy was stirred and kept at 760 °C for 5 min and poured into a steel mold preheated to 300 °C. The as-cast samples were solution treated at 500 °C for 12 h, followed by water quenching and ageing in oil bath at 200 °C for different times. Vickers hardness testing was performed by using a hardness tester (W-W-450SVD) with a loading force of 30 N and dwell time of 15 s. The TEM specimens with a diameter of 3 mm were ion-milled with Gatan 695, (5.0 kV ion gun energy under 10° milling angle, subsequently, 3.0 kV ion gun energy under 3.5° milling angle). Afterwards Gatan SOLARUS (950) Plasma Cleaning System was used to clean up the sample surface. TEM and STEM observation were then carried out using the JEM-ARM200F at an accelerating voltage of 200 kV, equipped with probe Cs corrector and cold field emission gun. The probe convergence is 25 mrad which yields a probe size of less than 0.1 nm, and the camera length was set to 8 cm which yields a collection semi-angle of 48–327 mrad. Crystal models of the Laves phase were built by Crystal Maker software.

3. Results and discussions

Fig. 1a shows the change in hardness with aging time for the Mg-1.5Cd-0.75 Yb alloy (solution-treated at 500 °C for 12 h, followed by water quenching and aging at 200 °C). The hardness increases from ~50.9 HV in the initial solution-treated state to a maximum value of ~66.5 HV at the peak-aging time of 4 h, and then starts to decrease with prolonged aging time. Thus, the peak-aged sample with the maximum hardness was selected for the TEM and HAADF-STEM analysis to capture the morphologies, crystal structures, and chemical compositions of the main strengthening phases.

Fig. 1b and c provide bright-field TEM images of the peak-aged Mg-1.5Cd-0.75 Yb alloy with the electron beam direction parallel to $[0001]_\alpha$ and $[1\bar{1}00]_\alpha$, respectively. A high density of nanoblock precipitates can be seen to have formed along the $\{0001\}_\alpha$ planes, with a height less than 15 nm, and a diameter of ~10–15 nm. The corresponding selected area electron diffraction (SAED) patterns, as shown in the insets in Fig. 1b and c, exhibit extra electron diffraction information around the α-Mg diffraction spots, indicating the presence of the precipitates.

Fig. 2 presents the results of energy dispersive X-ray spectroscopy (EDS) analysis obtained from $[0001]_\alpha$ (Fig. 2a–d) and $[10\bar{1}0]_\alpha$ (Fig. 2e–g) directions by making use of a combined technique of HAADF-STEM and EDS. The elemental mapping images show that both the Cd and Yb elements are enriched in the nanoblock

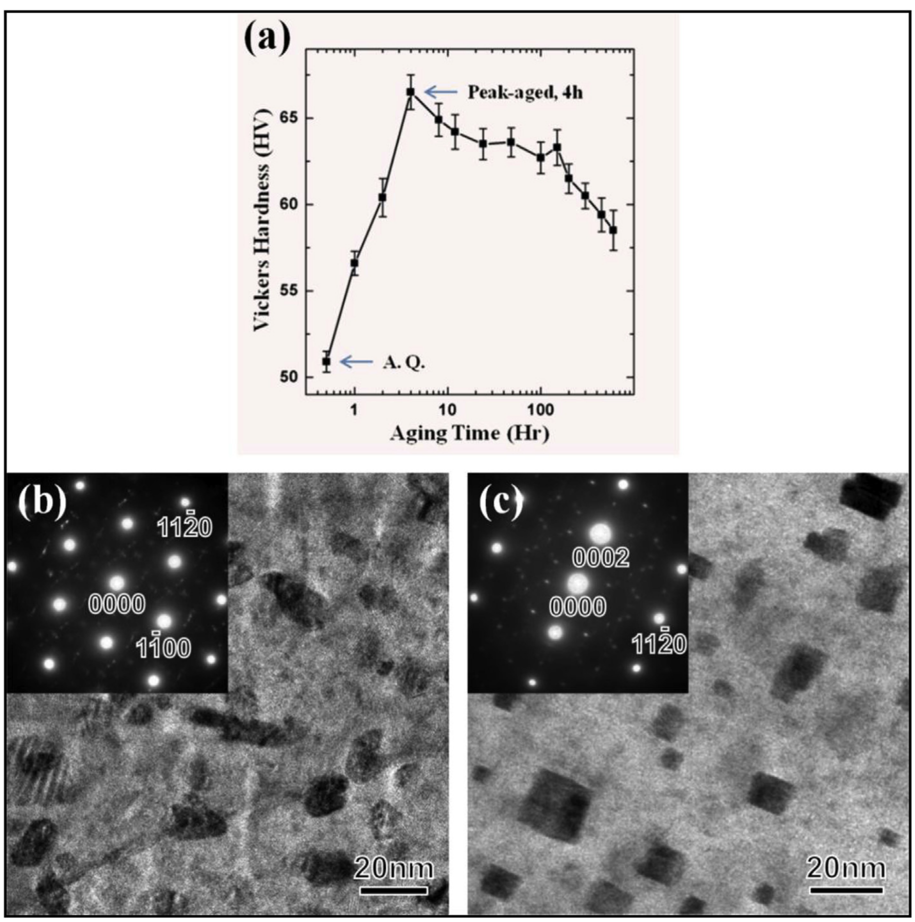

Fig. 1. **(a)** Age hardening response curve of the Mg-1.5Cd-0.75 Yb alloy during isothermal aging at 200 °C. **(b)** and **(c)** Bright-field TEM images of the Mg-1.5Cd-0.75 Yb alloy isothermally aged at 200 °C for 4 h, and the insets are the corresponding SAED patterns. The electron beam is parallel to (a) $[0001]_\alpha$ and (b) $[1\bar{1}00]_\alpha$.