Unique strengthening mechanisms of ultrahigh pressure Mg alloys

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ABSTRACT

Ultrahigh pressure technique remarkably extends solid solubility limitation of Al alloying element (~25 at.%) in Mg alloys, resulting in unique solid-solution strengthening and age hardening response. Microhardness, yield strength and ultimate compressive strength are improved simultaneously without degrading plasticity by forming homogeneous and globular-shaped Mg17Al12 precipitates of 10–30 nm. In addition, thermal resistance is enhanced by eliminating the dominant growth of (101) plane and anchoring dense stacking faults in phase interface.

Precipitation strengthening is an effective approach to improve strength of Mg alloys until now [1,2]. However, it is invalid for the most widely used Mg-Al-based alloys. Basically, except for the absence of metastable lattice of Mg17Al12 precipitate [3], two intrinsic characteristics account for weak age hardening. Firstly, it is difficult to attain large supersaturate solid solubility due to insensitive variation of Al solubility dependent on temperature [4], resulting in an inadequate volume fraction of strengthening phase. Secondly, even if it forms Mg17Al12 which lies in the basal plane during aging process, it readily became a coarse plate with a dimension of microns by preferential growth along basal direction, resulting in large inter-particle spacing [5]. Consequently, strain hardening instead of solid-solution strengthening or precipitation strengthening is performed to improve their mechanical properties of Mg-Al-based alloys [6].

Recently, we confirmed that ultrahigh-pressure technique was an effective method to tailor microstructure of Mg alloys, especial twin formation [7] and phase [8–10], analogous to chemical composition and temperature. Compared with other approaches, it bestows at least two distinctive features: increasing solubility and varying phase microstructure. In this regard, it is expected to be a potential pathway to prepare high-performance Mg alloys by compensating the shortcomings of conventional precipitation strengthening mentioned above.

Herein we firstly reported that the max solid solubility of Al in Mg matrix can be doubled to ~25 at.% with a ultrahigh-pressure solid solution (USS) technique, which overwhelms all the theoretical solid solubility values of binary Mg-X (X: alloying elements) alloys (Fig. 1a). Subsequently, an obvious age hardening response is achieved, and the peak hardness is far higher than those of binary Mg-X alloys. More importantly, a high plasticity of aged ultrahigh pressure Mg-25 at.%Al alloy with high strength remains, whilst its thermal resistance is improved.

Mg-xAl (x = 4–25 at.%, thereafter in at.%) alloys were prepared by chilling casting [11], and actual compositions were confirmed by following elemental analysis. The atmospheric-pressure solid solution (ASS) was conducted under Ar flow (420 °C, 12 h), and then quenched. The Mg-25Al alloy was undergone USSed treatment under 4 GPa (800 °C, 0.5 h) according to our previous method [7]. USS-aged (USSA) Mg-25Al alloy and ASS-aged (ASSA) Mg-10Al alloy were aged in an oil bath at both 120 and 150 °C.

Microhardness (HV) was measured by a Vickers hardness tester, and the load and dwelling time were 100 g and 15 s, respectively. One sample was continuously used to decrease the error. High-temperature microhardness in a temperature range of 60–350 °C was performed under glove-box using a MHT Vickers tester with a heating rate of 20 °C/min. Compressive tests were performed on a Gleeble-3500 thermomechanical simulator at a strain rate of.
1.7 \times 10^{-3} \text{ s}^{-1}. The diameter and height were 8 and 12 mm, respectively. The phases were identified by an X-ray diffraction (XRD) system (Rigaku D/MAX2500/PC) with Cu Kα radiation at a scan from 30 to 72° with a step size of 0.02° and a dwell time of 1.5 s. The residual stress was calculated by the sin²ψ-method [12].

The microstructure was observed using optical microscopy and field emission scanning electron microscope (FE-SEM) equipped with energy dispersive X-ray analysis. The standard metallographic procedures were applied, including grinding, polishing and etching. The samples were etched in a picral solution to reveal grain boundaries. The transmission electron microscopy (TEM) observation was carried out using a FEI-Titan ETEM G2 at 300 kV. Thin foil specimens for the TEM observations were prepared by ion-milling at 4.0 V from 10° to 4°.

Unlike the as-cast (AC) Mg-10Al alloy (Fig. 1b), more Mg17Al12 phases are homogeneously distributed along dendrites/grain boundaries for the AC-Mg-25Al alloy (Fig. 1c). However, similar equal-axed grain morphologies are confirmed in both the ASS-Mg-10Al (Fig. 1d) and USS-Mg-25Al alloys (Fig. 1e), revealing that Al solid solubility increases with increasing pressure and temperature. In addition, compared with the ASS-Mg-10Al alloy, the USS-Mg-25Al sample shows a smaller grain size, demonstrating a refining role of Al. The effect of Al solid solubility on microhardness is shown in Fig. 1f. The polygonal-shaped trend is divided into two stages. When it is below ~11.6 at.%, the linear equation is fitted as follows:

\[ H_1 = 3.37C + 29.8 \]  \hspace{1cm} (1)

where H and C are microhardness and solid-solution amount of Al, respectively. The strengthening factor of 3.37 is near to the value (3.14) reported by Cellotto et al. [13].

In contrast, when the solid solubility is over 11.6 at.%, the microhardness is sharply increased, and the relationship is interpreted as:

\[ H_2 = 0.87 \exp(0.21C) + 62.5 \]  \hspace{1cm} (2)

The max hardness of 117 HV (USSed state) is achieved with the content of 25 at.%. The reason is partially related to large residual stress (Fig. 1g). Minus sign means compressive stress. Specifically, the solid-soluble Al atoms increase the atomic density per Mg lattice, resulting in the distortion of Mg lattice and the increment of internal stress. It demonstrates that the conventional solid solution strengthening of Mg alloys is weak in terms of strengthening factor.
Note that this supersaturated solid solution is unstable, and a volcanic-shaped age hardening curve is detected at 150 °C (Fig. 2a), in which it merely took ~2 h to reach the peak hardness. Thereafter, a stable value remains even aged for 1000 h. By comparison, the similar age trend is confirmed at 120 °C, and a higher peak value of 218 HV (20 h) is achieved. The peak hardness is 1.77 times higher than that of the Mg-10Al alloy (150 °C, 260 h), which is the highest one for Mg-X binary alloys reported so far [13–17]. The age hardening is associated with the reappearance of β-Mg17Al12 phase (Fig. 2b).

The compressive properties of different state Mg-Al alloys (Fig. 2c) show two main trends. Firstly, both yield strength (YS) and ultimate compressive strength (UCS) of the USS-Mg-25Al alloy are higher than those of the ASS-Mg-10Al alloy, suggesting that USS technique is an effective pathway to improve strength without an obvious loss of plasticity. Secondly, aging treatment significantly improves mechanical properties. Compared with the USS-Mg-25Al alloy, the YS and UCS of USSA-Mg-25Al alloy at peak hardness improve 57% and 17%, respectively.

TEM observation (Fig. 3a) shows that a large number of nano-scaled particles are uniformly distributed in the USSA-Mg-25Al alloy at peak hardness. The relationships of (101)_{β}/(0001)_{Mg}, (11̅1)_{β}/(1̅1̅1)_{Mg} are identified by the selected area electron diffraction pattern (Fig. 3b). The average dimension is ~32 nm (Fig. 3c). Some serrated steps are detected in the interface (Fig. 3d). Simultaneously, Mg atom is surrounded by six Al atoms along 〈10̅10〉 direction (Fig. 3e). Three planes via (101), (110) and (01̅1) dominate the growth process, resulting in the formation of globular -shaped precipitates, distinguishing from previous lath-like phases due to the dominant growth of (101) plane [18]. In contrast, some smaller β-Mg17Al12 phases with a dimension of ~10 nm are detected at 120 °C (Fig. 4a). Additionally, a dense staking faults (SFs) of 8 × 10^5 cm^-1 is detected, which is over 10 times than that of the USSA-Mg-25Al at 150 °C. The SF pattern was intrinsic fault 1_1, also known as a growth fault. It can be formed by the removal of a basal plane followed by slip of 1/3 (1010T00) in the crystal, yielding the
sequence of ... ABABABCBCB ... (Fig. 4b). Therefore, the larger peak microhardness at 120 °C is mainly relative to fine β-phase and high density of residual SFs.

To probe thermal stability of strengthening phase, the effect of temperature on microhardness was performed (Fig. 2d). The microhardness of the peak-hardness ASSA-Mg-10Al alloy remains stable below 120 °C, but it reduces continuously with further increasing the temperature. By comparison, the obvious inflection point is detected at 175 °C for the USSA-Mg-25Al alloy. TEM observation shows the lath-shaped β-Mg17Al12 dominantly grows along the (101) plane (basal plane) for the ASSA-Mg-10Al alloy after heating at 120 °C for 48 h, (Fig. 4c). In turn, the aggregation of strengthening particles has hardly been observed in the USSA-Mg-25Al alloy even after heating 175 °C for 64 h though the dimension slightly increases (Fig. 4d), relative to the formation of serrated interface and SFs. The SFs do not shear the β-Mg17Al12 phase (Fig. 4a), and terminate in the interface. Thus a complex stress field which forms around the interface (Fig. 4e) might provide additional barrier for phase growth although its detailed role is unclear. Furthermore, the arranged direction of SFs is parallel to (0002) plane, eliminating the predominant growth. Consequently, the strengthening phase maintains coarsening instead of banding growth.

In summary, USS strengthening is a more effective method to improve mechanical properties of Mg-Al alloys compared with conventional solid-solution. High strength and plasticity are achieved simultaneously by USS followed by aging due to the formation of fine globular-like β phase. The coexistence of fine strengthening phase without dominant orientation growth and dense stacking faults accounts for improved thermal resistance. This founding provides a new strategy to prepare high-performance Mg alloys.

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Fig. 4. (a) The typical HRTEM image of USSA-Mg-25Al sample after aged at 120 °C for 10 h. The inset shows the average diameter distribution of the precipitates. (b) FFT image of SF in (a). (c) The typical TEM image of the peak ASSA-Mg-10Al sample after remaining at 120 °C for 48 h. (d) The typical TEM image of the peak USSA-Mg-25Al sample after remaining at 175 °C for 64 h. (e) The HRTEM image of (d).

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