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Review

Recent developments in rare-earth free wrought magnesium alloys having high strength: A review

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ABSTRACT

To further expand industrial application of Magnesium alloys, developments of the low-cost, Rare-Earth free Magnesium alloys with high strength were strongly desired. In this review, recent researches on the Rare-Earth free Magnesium alloys will be critically reviewed from the viewpoint of the novel alloying designs, e.g. Magnesium–Zinc, Magnesium–Tin and Magnesium–Calcium systems, and advanced processing technologies to summarize the experimental progresses in pursuing high strength. Considering the large strength gap between the current Rare-Earth free Magnesium alloys and state-of-the-art Magnesium-Rare-Earth alloy or high strength Aluminum alloy, the new strengthening mechanism, such as the solute clustering which was recently observed in Magnesium-Rare-Earth alloys and the other Rare-Earth-free Magnesium systems, was suggested. Accordingly, the new alloy design and processing routes, and also the future research directions for Rare-Earth-free Magnesium alloys would be proposed.

Contents

1. Introduction

There has been a great research interest in enhancing mechanical properties of Magnesium alloys, especially the strength, to further expand their industrial applications in aircrafts, automotives products and etc., owing to their well-known high specific

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strength [1–6]. In the past decade, researchers made full use of the grain refinement hardening, precipitation hardening and the texture hardening to improve their strengths, and the novel Magnesium alloys with 300–500 MPa were readily developed [7–13]. For example, yield strength (YS) and ultimate strength (UTS) of as-extruded Magnesium-10.0Gadolinium-5.7Yttrium-1.6Zinc-0.6Zirconium (wt.%) alloy could reach 419 MPa and 461 MPa, respectively [14]. Xu et al. [15] produced Magnesium-8.2Gadolinium-3.8Yttrium-1.0Zinc-0.4Zirconium (wt.%) alloy with ultra-high YS of 426 MPa and UTS of 517 MPa by large-strain hot rolling and aging. However, disadvantages of the Magnesium-Rare-Earth based alloys above are apparent: (i) the high cost and natural resource scarcity of Rare-Earth elements, especially for heavy Rare-Earths, make their large-quantity usage (usually ~10 wt.%) unpractical in industry applications; (ii) the advantage of high specific strength of Magnesium alloys compared with Aluminum alloys gradually losses due to the increased density of the Magnesium-Rare-Earth alloy [16,17]. In this regard, the developments of low-cost, Rare-Earth free Magnesium alloys with high strength are strongly desired [18–20].

In this review, recent development in the past decade on the Rare-Earth free wrought Magnesium alloys will be critically reviewed from the viewpoint of both novel alloying designs, e.g. Magnesium–Zinc, Magnesium–Tin and Magnesium–Calcium based alloy systems, and advanced processing technologies, in particular, for their experimental progress to pursue high strength. Considering the large strength gap between the current Rare-Earth free Magnesium alloys and state-of-the-art Magnesium-Rare-Earth alloys or high strength Aluminum alloys, the new strengthening mechanism, such as the solute clustering which were recently observed in Magnesium- Rare-Earth alloys and the other Rare-Earth -free Magnesium systems, is suggested. Accordingly, the new alloy design and processing routes, and also the future research directions for Rare-Earth free Magnesium alloys will be proposed.

2. Promising Rare-Earth free magnesium alloy systems for high strength

2.1. Magnesium–Zinc based alloys

Magnesium–Zinc alloy is regarded as the most promising one among various Magnesium alloy systems, considering the fact that the rod-like $MgZn_2$ phases would precipitate along [0001] direction and the precipitates located on non-basal planes could contribute more effectively to the dispersive strengthening, as confirmed theoretically by Nie et al. [21]. However, the commercial ZK60 alloy, developed based on the Magnesium–Zinc alloy, exhibits a moderate strength of ~240 MPa [22]. The age hardening response of this alloy is relatively not significant because of the coarse dispersion of the $MgZn_2$ phases. In this regard, numerous studies have been conducted to promote the precipitation density, including the multi-alloying (Copper [23], Cobalt [24], Vanadium [25], Chromium [26]) and two-step aging [27]. For example, Copper addition permits the Magnesium–Zinc based alloys to be solid-solution treated at a higher temperature, thus to increase the content of Zinc element in matrix and finally to result in more amounts of precipitations [23]. The time to reach the peak hardness could also be obviously shortened, and the additions of other elements, such as Cobalt, Vanadium and Chromium, have similar effects. Moreover, Oh-ishi et al. [27] found that addition of Aluminum and the following two-step aging could refine the precipitates in Magnesium-6Zinc-1Mangenese (wt.%) alloy significantly, thus the Magnesium–Zinc-Mangenese-Aluminum sample exhibits a much higher peak-hardness of ~90 HV than that of the counterpart sample (~50 HV). Based on the innovations above, Wang et al. [28] produced a novel cast Magnesium-8Zinc-1.0Aluminum-0.5Copper-0.5Mangenese (wt.%) alloy with a YS and UTS of 228 MPa and 328 MPa, and high ductility of 16%, respectively. The additions of Copper and Aluminum elements results in a great deal of refined and dispersive rod-like Mg_4Zn_7 phases along [0001] direction and thus the good mechanical properties.

Mendis et al. [29] further improved YS and UTS of the Magnesium-6Zinc (wt.%) alloy to be 325 MPa and 355 MPa, respectively, by combined addition of 0.6 wt.% Zirconium, 0.4 wt.% Silver and 0.2 wt.% Calcium. The Zirconium-containing alloy showed a bimodal grain microstructure with fined and stabilized Mg(Zn, Zr) particles, thus Oh-ishi et al. proposed the bimodal grain microstructure was related to the Mg(Zn, Zr) particles [30]. However, the unique role of Mg(Zn, Zr) particle has not been well understood because the extra Silver and Calcium additions are considered to be essential. Later, Bhattacharjee et al. [31] found that Magnesium-6.2Zinc-0.5Zirconium-0.2Calcium (ZKX, in wt.%) alloy shows equivalent mechanical properties (YS of 286 MPa and UTS of 321 MPa at T6 state) as compared to the Magnesium-6.2Zinc-0.5Zirconium-0.2Calcium-0.4Silver (ZKXQ, in wt.%) alloy, even without the expensive Silver. Recently, they confirmed that small addition of Zirconium to the Magnesium-6.2 wt.% Zinc alloy could also cause the bimodal grains formation (as shown in Fig. 1), thus a substantial increase of the YS and UTS up to 275 MPa and 318 MPa, respectively [32]. In contrast, as-extruded Magnesium-6.6Zinc-0.19Calcium (ZX) alloys exhibits a low tensile YS of about 150 MPa [30,33]. The results above clarify the critical role of Zirconium alloying in the formation of Mg(Zn, Zr) precipitates (Fig. 1), which could retard the recrystallization and effectively promote the formation of sub-grains with a strong basal texture. The bimodal grains developed by the presence of the Mg(Zn, Zr) precipitates and the their good dispersion in the α-Magnesium matrix contribute to a high strength of as-extruded Magnesium–Zinc based alloys. In this alloy system, micro-alloyed Silver and Calcium could substantially refine the precipitates and increase their number density, accordingly its YS is further enhanced up to 325 MPa.

High-strength Rare-Earth free Magnesium–Zinc–Manganese wrought alloy is the other important one, because the expensive Zirconium element is absolutely replaced by Manganese element and the cost can be further reduced. Zhang et al. [34] investigated the Magnesium-xZinc-1Manganese alloy with various Zinc additions and found the optimal composition was Magnesium-6 wt.% Zinc-1 wt.% Manganese. The highest UTS of 352 MPa and 366 MPa are obtained, respectively, for the extruded samples followed by either a single- or double-aging treatment. Both the $MgZn_2$ precipitates and Guinier-Preston (G.P.) zones contribute to superior mechanical properties. Zhang et al. [35] also investigated the effect of Manganese content on mechanical properties of Magnesium–Zinc–Manganese wrought alloys and showed that the Manganese particles distributed among matrix could hinder the grain growth of α-Magnesium matrix and the dynamically recrystallized (DRXed) grains became finer with a more addition of Manganese. Qi et al. [36] also confirmed the grain refinement effect of Manganese during dynamic recrystallization of Magnesium–Zinc–Yttrium–Manganese alloys. Recently, Qi et al. [37] improved mechanical properties of extruded Magnesium-6Zinc-1 Manganese alloy by adding Tin element. The 4 wt.% Tin-containing sample in the double peak-aging state has the highest YS and UTS of 378 MPa and 390 MPa, respectively, and a moderate elongation of 4%. The achievement of high strength is considered to be mainly determined by the synergistic effect of precipitates of $MgZn_2$ and Mg_2Sn, and all the precipitates by the double aging are much finer than those by the single aging.