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High Strength Magnesium Alloys Through Precipitation Hardening and Micro Alloying: Considerations for Alloy Design

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Magnesium alloys are generally not age hardened due to low age-hardening response. Recent work shows that microalloying may be a path to develop high-strength precipitation-hardening magnesium alloys. Here, we provide examples where microalloying has been used to enhance the age-hardening response through an increase in number density and through modification of the precipitate orientation. Some important considerations when selecting microalloying elements for future alloy development are also discussed.

INTRODUCTION

Magnesium-based alloys, being the lightest of the structural metallic alloys, continue to attract attention from automotive and personal electronic applications where light weight is of an importance. The use of magnesium alloys in the automotive industry has increased over the last decades, but the number of applications is limited especially for wrought applications where the final product is made from extruded profiles or rolled sheets. In the last decade, there have been significant research efforts into the development of Mg alloys for casting applications; some alloys were introduced to commercial applications due to the developmental work done. Mg has significant potential to be used in transport (automotive and aerospace), personal electronics, and medical applications (bioimplants) in either the cast (e.g., powertrain applications in automobiles) or wrought form (space frames in automobiles or body panels). However, a recurring theme in all such applications is the development of alloys with an appropriate property profile for the application envisaged. The property profile can only be achieved by controlling the microstructure of the alloys developed. The microstructure control relies on the following:

1. Grain boundary engineering: the control of the grain size, grain size distribution, and the distribution and morphology of the intermetallic particles at the grain boundaries.
2. Solute strengthening: the strengthening due to interactions between solute atoms and dislocation structures or twin boundaries during thermomechanical processing or in service.
3. Precipitation strengthening: strengthening due to the formation of nanoscale solid-state precipitates that hinder dislocation motion and nucleation and growth of twins during deformation.

The majority of the Mg alloys used in commercial applications today, such as AZ91, AZ31, and AM50, are processed by die casting. However, the strength and ductility profiles of Mg alloys available are currently not sufficient for many applications. For the development of high-strength alloys with stable elevated temperature properties, it is essential that interdendritic region and the grain boundaries contain some intermetallic phases to prevent grain growth and to withstand elevated temperature deformation associated with grain boundary motion. The development of alloys containing intermetallic particles at the grain boundaries, which can be further strengthened via the formation of solid-state precipitate formation during subsequent heat treatments, as illustrated in Fig. 1, provides a viable pathway to developing high-strength Mg alloys through a combination of grain boundary, solute strengthening, and precipitation strengthening.

Even though many magnesium alloys show a potential for precipitation hardening, the increase in the strength due to isothermal aging is not sufficiently high to warrant heat treatment.[1] Thus, unlike aluminum alloys, which are generally

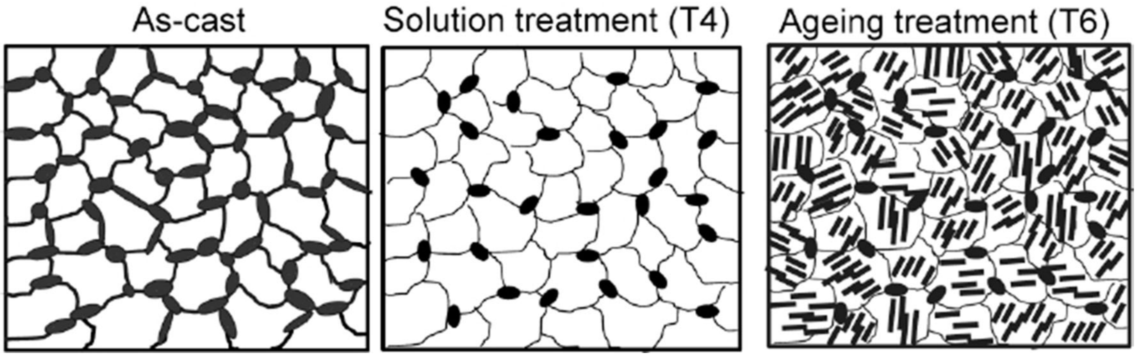

Fig. 1. Schematic representation of microstructures required for the development of high-strength cast Mg alloys.

strengthened via precipitation hardening, the majority of the magnesium alloys are not precipitation hardened. The phase diagrams (e.g., the Mg-Zn system is shown as an example in Fig. 2) show a large reduction of solid solubility of Zn with the decrease in temperature. As an example, precipitation hardening or isothermal heat-treatment temperature of 150°C for example has a solid solubility of 0.5 at.%, while at a solution heat treatment temperature of 350°C, the solid solubility of Zn is approximately 2.4 at.%. However the hardening increment observed is very small (Fig. 2b).[2] The lower hardening response observed has been attributed to the relatively coarse distribution of precipitates in a nonfavorable orientation for optimized hardening, which form during isothermal aging of Mg-Zn alloys due to inherent difficulties in nucleating solid-state precipitates. Therefore, the precipitation hardening may be optimized by either increasing the number density of precipitates or by modifying their orientation. In the latter case, the precipitate orientation is modified to block slip or twinning more effectively.[3] Nie[3] considered the effect of precipitate orientation and number density on the strengthening increment due to precipitation. In this investigation, the strength increment due to precipitation was found to be inversely dependent on the interparticle spacing in the slip planes and thus dependent on the orientation of the precipitates, as shown by Orowan strengthening equation and its relationship to interparticle spacing in Fig. 3. As illustrated in Fig. 3, at a given number density, the orientation of the precipitates affects the strengthening increment by changing the inter-particle distances in the slip plane. As an example, the strengthening increment due to basal plate precipitates is much lower than that due to the prismatic plates. However, the strengthening increment due to both these types of precipitates may be increased by increasing the number density of the precipitates. In the following sections, use of increased number density of precipitates and the modification of precipitate orientation in terms of increasing the strengthening increment will be discussed with examples from the magnesium literature.

INCREASING THE NUMBER DENSITY OF PRECIPITATES

The number density of precipitates increased by providing extra sites for the nucleation of precipitates. There are three different ways this may be achieved. The first is multistage aging to provide extra sites for nucleation as demonstrated by Ohishi et al.[4] in the Mg-Zn-Al system. The lower aging temperature used initially increases the number density of nucleation sites, and the higher aging temperature in the latter stages causes the increased growth rates. The multistage aging requires significant number of experiments to optimize the process and may not be viable. The second method for increasing the number density is the introduction of extra sites for nucleation through deformation. The dislocation lines or vacancy concentrations introduced will lead to an increase in the nucleation sites and, thus, an enhanced age-hardening response. Hilditch et al.[5] showed that deformation following solution heat treatment can enhance the age-hardening response of WE54 (Mg-1.5Y-0.7RE at.%) (Mg-5Y-4RE wt.%) alloy. However, the use of deformation to enhance the age hardening response is not applicable in all applications especially where applications require parts with complex geometry.

The effectiveness of trace additions in enhancing the properties has been clearly demonstrated in many alloy systems, with Al-Cu representing the most studied system.[6] The Al-Cu and Al-Zn systems containing trace addition show a significant age-hardening response and yield strengths in excess of 500 MPa with more than half of the strengthening increment attributed to precipitation hardening.[6] However, such increment in strengthening due to precipitation hardening has not been observed in magnesium alloys. Recently, the trace additions to

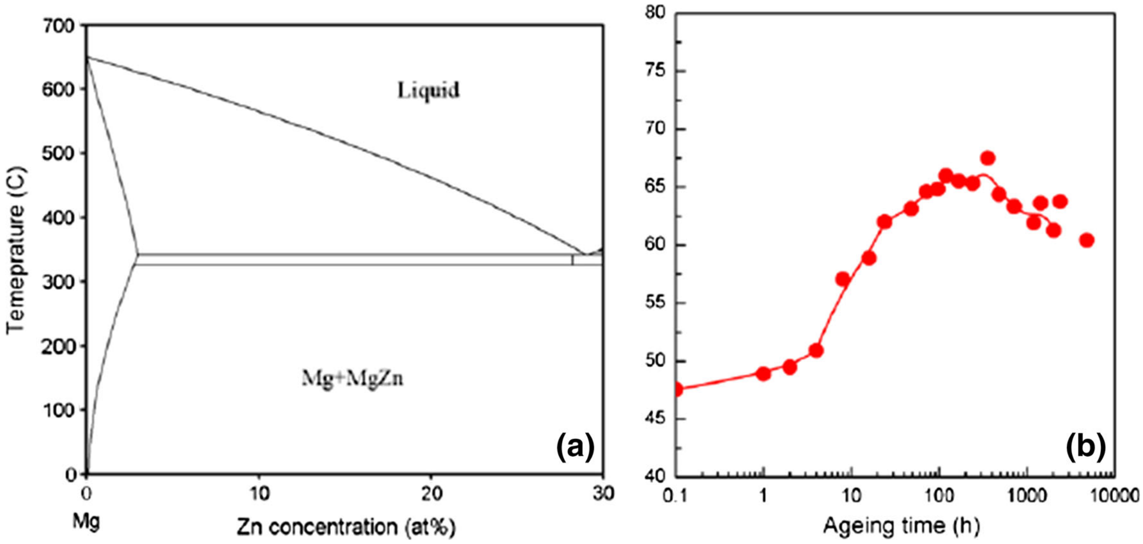

Fig. 2. (a) Binary Mg-Zn phase diagram.[1] (b) The age-hardening response of Mg-2.4Zn at.%.[2]

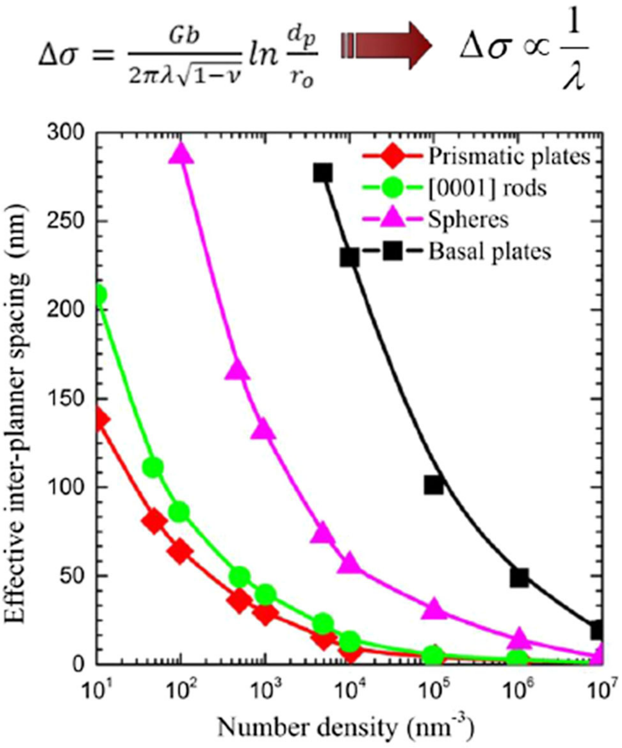

Fig. 3. The effect of number density of particles and the particle orientation in magnesium alloys on the inter-particle spacing and its dependence on the strengthening increment due to precipitation. Reprinted with permission from Ref. 3.

precipitation hardenable magnesium alloys show enhancement in age hardening response. This has been illustrated for Mg-Zn and Mg-Sn systems with the additions of Ag + Ca[2,7] and Na[8], respectively. The same enhancement was observed with the addition of Ag to Mg-Gd-Zn[9] and Mg-Y-Zn[10] systems.

The increment in number density of the solid-state precipitates due to trace additions may be illustrated by the addition of equiatomic amounts of Ag and Ca to Mg-6Zn alloy. The hardening response of the Ag- and Ca- containing alloy is significantly higher than that observed for the binary alloy (Fig. 4) following isothermal aging at 160°C. In fact, the increment in the hardness due to precipitation is three times that of the alloy containing trace additives as compared with the binary alloy (Fig. 4a). Looking at the microstructures of the two alloys (Fig. 4b and c), an increase in the number of particles in a given area may be observed. The number density of the precipitates was $\sim 1 \times 10^{19}$ m^{-3} for the binary alloy and 3×10^{21} m^{-3} for the alloy modified with trace additions.[2] This is ~300 times increase in the number of precipitates, which accounts for the strengthening increment observed. It was reported that Ag and Ca segregated on the fine scale precipitates of $MgZn_2$ in the peak-aged condition.[7] The investigation of the underaged alloys at 160°C shows the formation of clusters of Zn, Ag, and Ca after 30 min aging in Mg-2.35Zn-0.1Ca-0.1Ag (at.%) (Mg-6Zn-0.2Ca-0.4Ag, wt.%) alloy[11] (Fig. 4d). However, Zn-enriched clusters were not observed in Mg-2.35Zn (at.%) (Mg-6Zn, wt.%) alloy after 8 h of aging at 160°C[11] (Fig. 4f). The Zn, Ag, and Ca clusters observed in the Mg-2.35Zn-0.1Ca-0.1Ag alloy gives rise to the faster age-hardening kinetics and the higher number density of the precipitates observed in this alloy.

The viability of this alloy for wrought applications using extruded profiles[7] and twin roll cast and hot-rolled sheets[12] has been demonstrated. The mechanical properties of the extrusions and sheets of Mg-2.35Zn-0.1Ca-0.1Ag are enhanced following isothermal aging.[7,12]

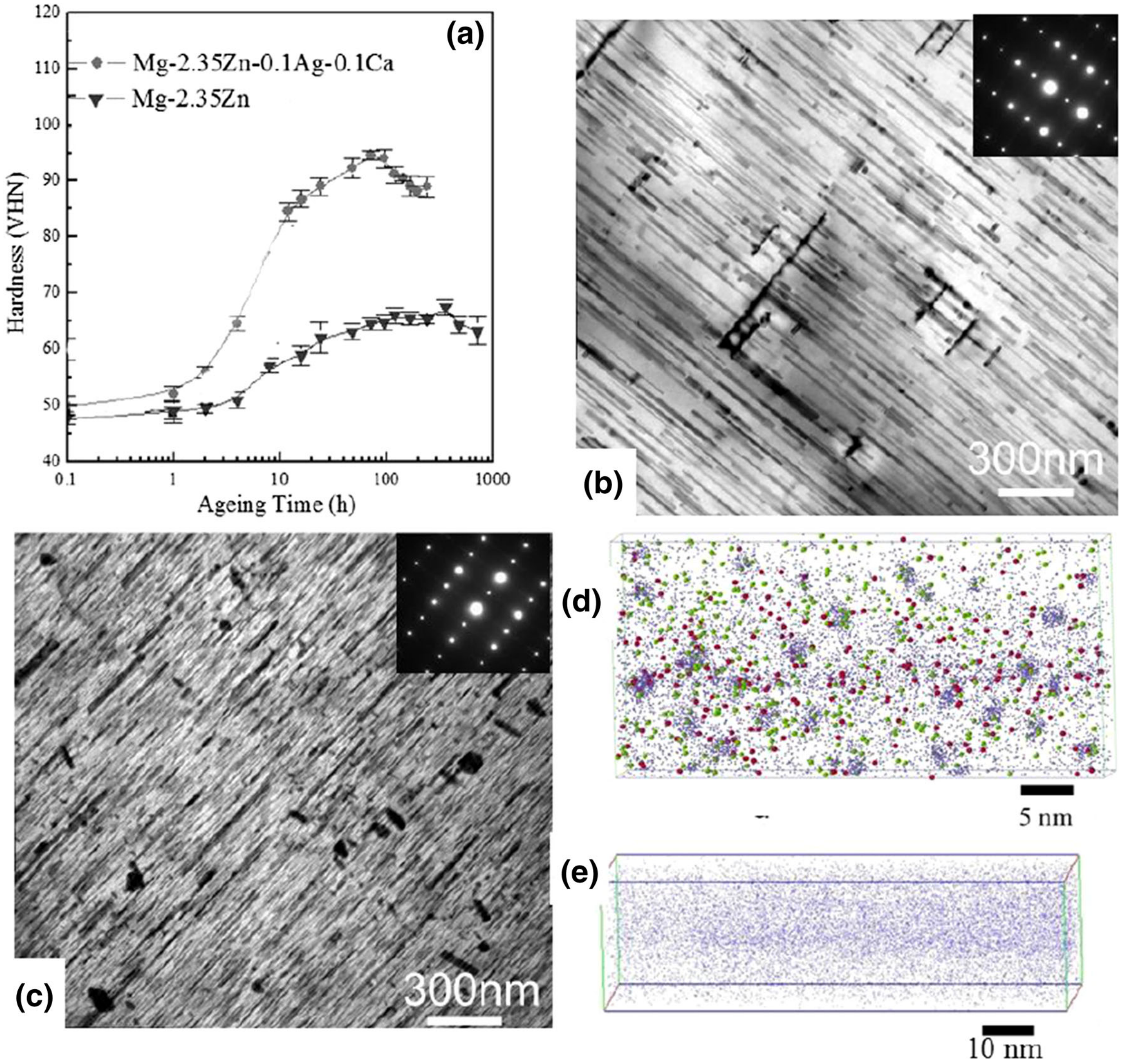

Fig. 4. (a) Age-hardening responses of Mg-2.35Zn-0.1Ca-0.1Ag and Mg-2.35Zn alloys at 160°C, the peak aged microstructures of (b) Mg-2.35Zn-0.1Ca-0.1Ag and (c) Mg-2.35Zn alloys. (d) The formation of clusters after aging at 160°C for 30 min in Mg-2.35Zn-0.1Ca-0.1Ag alloy illustrated by three-dimensional atom probe tomography. (e) Mg-2.35Zn alloy after aging for 8 h at 160°C using three-dimensional atom probe tomography showing no clusters. Adapted from Refs. 2,11.

MODIFICATION OF THE ORIENTATION OF NANO-SCALE PARTICLES

As shown by Nie[3] (Fig. 3), the optimum precipitates in Mg are lath- or plate-shaped precipitates in prismatic planes or rods with their long axis parallel to [0001]Mg direction. In previous investigations, this has been observed for the addition of Zn to Mg-Sn alloys.[13,14] Additionally, the modification of precipitate phase has been observed with the addition of Zn,[15,16] Al,[17] and In[18] to Mg-Ca system and addition of Zn to the Mg-Gd[19,20] system. The reasons behind the change in orientation and possibility of application of this concept to other Mg-based alloys are of great interest for Mg alloy development.

The modification of the orientation of the solid-state precipitates is demonstrated by the Mg-Ca and the modification of the precipitates through the addition of a ternary element. The addition of Zn and In enhanced the age-hardening response of the Mg-0.3Ca (at.%) (Mg-0.5Ca [wt.%]) alloy at 200°C.[16,18,21] The addition of 0.6 at.% Zn (1.6 wt.%) resulted in an hardness increment twice that observed for the binary alloy, whereas the increment in the hardness response was approximately four times with the addition of 1 at.% In (4.5 wt.% In) (Fig. 5a). The Mg-Ca system contained a very coarse distribution of cuboidal precipitates (Fig. 5b). The addition of Zn changes the morphology of the precipitates from cuboidal particles to monoatomic layer thick particles or G. P. zones forming on basal planes (Fig. 5c). The number density of the basal G. P. zones was found to be approximately 2×10^{23} m^{-3} (Ref. 16). The addition of In changed the cuboidal particles in the Mg-0.3Ca alloy into prismatic plates

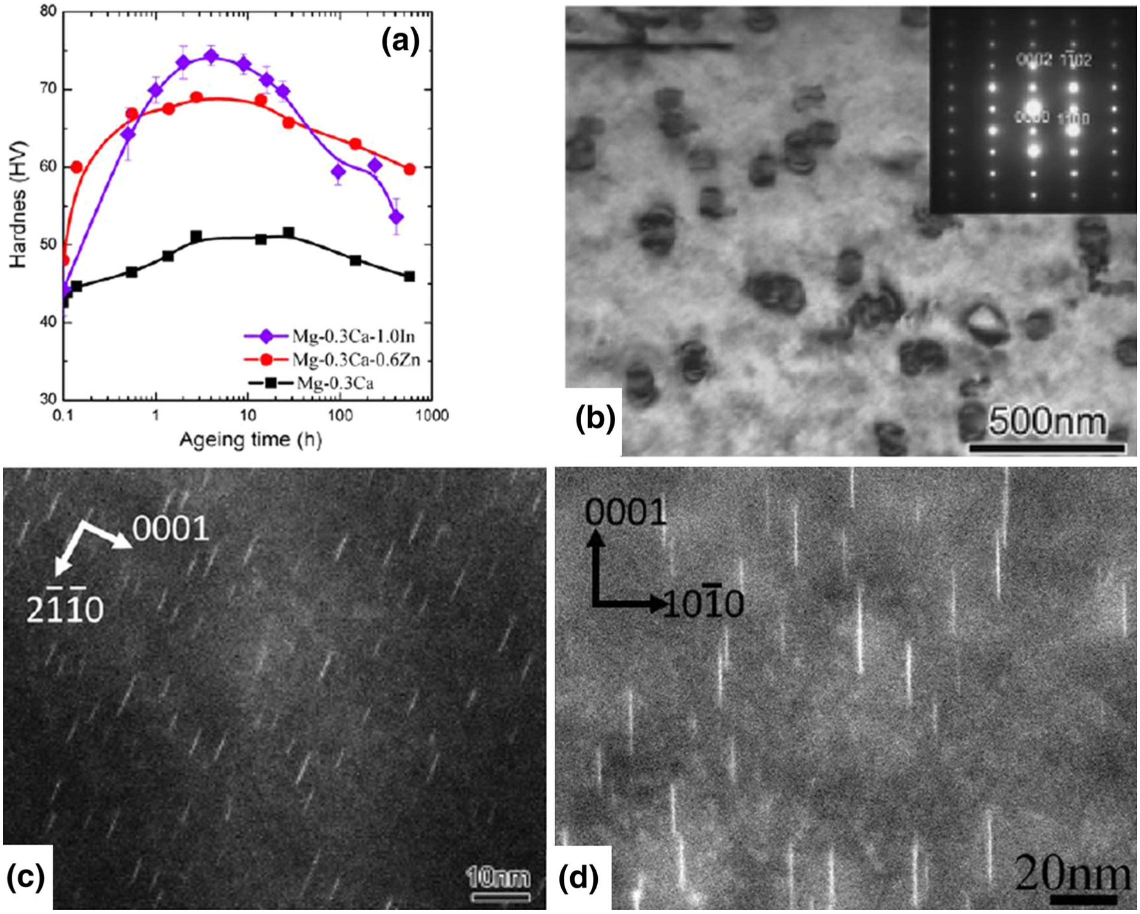

Fig. 5. (a) The age-hardening response of Mg-0.3Ca (at.%) alloy modified with Zn and In at 200°C. (b) Transmission electron micrograph showing a microstructure typical of Mg-0.3Ca alloy aged at 200°C to maximum hardness. The HAADF-STEM (high angular annular dark field-scanning transmission electron microscopy) micrographs of (c) Mg-0.3Ca-0.6Zn and (d) Mg-0.3Ca-1In alloys aged at 200°C to maximum hardness. Adapted from Refs. 16,17,21.

that are approximately three atomic layers in thickness (Fig. 5d). The number density of the prismatic plates in the Mg-0.3Ca-1In alloy was approximately 2×10^{22} m^{-3} (Ref. 17). The hardness increment due to the In additions was higher than that observed for the Mg-0.3Ca-0.6Zn alloy even though the number density of the basal precipitates was a magnitude higher than that observed for the prismatic plate precipitates observed in the Mg-0.3Ca-1In alloy.

CHOICE OF ALLOYING ADDITIONS FOR ENHANCING THE AGE-HARDENING RESPONSE

The above sections describe the use of trace additions or ternary additions to successfully enhance the age-hardening response of Mg-Zn and Mg-Ca systems. There are number of other examples in which ternary or trace additions have enhanced the age-hardening response.[22] The selection of the trace additions require an investigation of numerous alloying additions to determine the most appropriate element that will provide the best strengthening increment. To increase the number density of the precipitates require an increase in the number of nucleation sites. This may be achieved by the provision of local heterogeneities in the composition, such as the formation of clusters of alloying additions at the earlier stages of aging. Several criteria were developed to help the choice of trace or ternary additions that will help increase the number of nucleation sites in an earlier investigation.[8] The first requirement is a driving force for the formation of heterogeneities that will act as nucleation sites during early stage of aging. The heterogeneities can come from vacancy loops stabilized by alloying elements, cosegregation of elements with negative enthalpies of mixing or segregation of elements that show a strong tendency to be immiscible with the matrix. The negative enthalpies of mixing and the elements that are immiscible in the matrix may be derived from the binary or complex phase diagrams. The information on the vacancy interactions with the alloying elements is not readily available for magnesium alloys. Recently, Shin and

Wolverton[23] justified the choice of trace additions described for Mg-Sn and Mg-Zn systems through first-principles calculations on vacancy interactions. Based on these calculations and predictions made by Shin and Wolverton[23] and by Saal and Wolverton,[24] elements that can increase the heterogeneities in the magnesium alloys through the elemental interactions with the vacancies may be predicted.

In the criteria developed, there is a requirement for the main alloying element not to segregate away from the sites of heterogeneities provided. That is, if the main alloying element does not diffuse to the sites of heterogeneities, then these heterogeneities become ineffective at providing extra nucleation sites. However, the recent investigations on Mg-Sn-Zn-Al-Na (Ref. 25) system where even though there is a strong tendency for the Al and Zn to segregate away from the Na, an increase in the number density of precipitates and enhanced age-hardening response. It is suggested that the change in the strain fields surrounding the Na rich clusters provides regions close to these clusters where preferential nucleation of Zn-, Al-, and Sn-rich precipitates occurs. Thus, mutual segregation of the main alloying addition and the trace addition is not a requirement that determines the effectiveness of the trace addition.

The final requirement for the trace or ternary additions to be effective is that the rate of diffusion and cluster formation should occur at a faster rate than the time required for the main alloying additions to form solid-state precipitates without the presence of trace additions. Thus, diffusion of the trace elements should be faster than or similar to that of the main alloying element so that clusters will form before the solid-state precipitates form. Therefore, information on the diffusion of various elements in magnesium matrix is essential but is not readily available. Significant research effort has been currently made to determine both experimentally and theoretically.

The above criteria provide for the choice of alloying elements that will increase the number of sites for nucleation through the provision of heterogeneities. However, these criteria do not consider the role of nucleation sites in modifying the orientation of precipitates so that most effective orientation for the prevention of dislocation slip and twining. The prediction of alloying elements that modify the orientation of the precipitates require further understanding of the nucleation theory and how the growth directions and habit planes of the precipitates may be modified. However, to date an experimental understanding of the role of nucleation on the modification of habit planes of precipitates and growth direction is not sufficient to predict the role of trace or additional elements in modifying the orientation of the precipitates.

There is significant potential to develop high-strength alloys through precipitation hardening through the modification of alloy chemistry by trace additives. To date, many examples (including those described here) show the potential of precipitation hardening to develop high-strength alloys. The criteria developed based on previous work and the continued expansion of diffusion data for magnesium alloy along with first-principles calculations on vacancy interactions provide a starting point for the smart selection of trace and additional elements to modify the alloy chemistry.

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