Magnesium Technology 2013
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Phase Formation

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BOUNDS TO HARDENING BY SOLID SOLUTION, PRECIPITATION AND SHORT RANGE ORDER IN Mg BINARY ALLOYS

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Abstract

Miedema's coordinates are used to rank 4 model binary alloys considering the respective values of enthalpy of formation and the tendency to developing random solid solution, precipitation, short range order (SRO) and intermetallic compounds. The terminal solid solubility generally increases whereas the tendency to order decreases with decreasing heat of formation, and hardening by near-random solid solution and/or precipitation is expected to be dominant for solutes with low tendency to order, such as Al. For solutes with an intermediate tendency to order, hence solubility, such as Zn, or to form compounds, such as Gd, SRO is predicted to dominate the hardening. For solutes whose very large heat of formation leads to very high melting point intermetallics forming congruently, such as Sb, the terminal solid solubility is too low for any solute based hardening to be feasible. Implicancies for alloy design and selection regarding solute or precipitation hardening, SRO and creep resistance are discussed.

Introduction

Magnesium's locus on the group IIA manifests in highly attractive pairing with most other metals, i.e., the interaction energy of mixing is strongly negative. A strongly negative interaction energy normally [1] leads to a high melting point intermetallic bounded by two eutectics, of the type illustrated by Fig. 1-a, and to which many binary Mg alloys closely conform to. Cases in point are, in order of increasingly negative interaction energy, Mg-Al, Mg-Zn and Mg-Sb alloys. In the opposite case, i.e., strongly positive energy, limited solubility and a single eutectic is observed, as in Fig. 1-b. An example for this case is Mg-Th.

When the interaction energy is negative, the ensuing tendency to pairing between unlike atoms in a solution of X atoms in Mg introduces an ordering effect in an otherwise random solid solution, with pre-eminence of pairs Mg-X in detriment of X-X or Mg-Mg pairs [2]. In a dilute alloy the net result is the development of short range order (SRO), whereas in the concentrated ones it leads to compound formation. In some alloys SRO is observed already in the liquid, leading to highly viscous melts, and a propensity to form metallic glasses [1] (pp. 81–82). SRO has been confirmed by X-ray diffraction in a number of Mg-based solid solutions, namely: Mg-Sn, Mg-Gd, Mg-In and Mg-Er [3,4], whereas indirect evidence has been presented for Mg-Zn [5] and Mg-Y [6,7]. SRO has also been predicted from first principles and experimentally confirmed in liquid Mg-Zn [8]. The formation of SRO in a solid solution leads to increased hardening well above that of random solid solution [5,9,10]. For a metal like Mg whose alloys are reluctant to develop precipitation hardening [11-13], the exploitation of SRO as a strengthening mechanism is an important alternative.

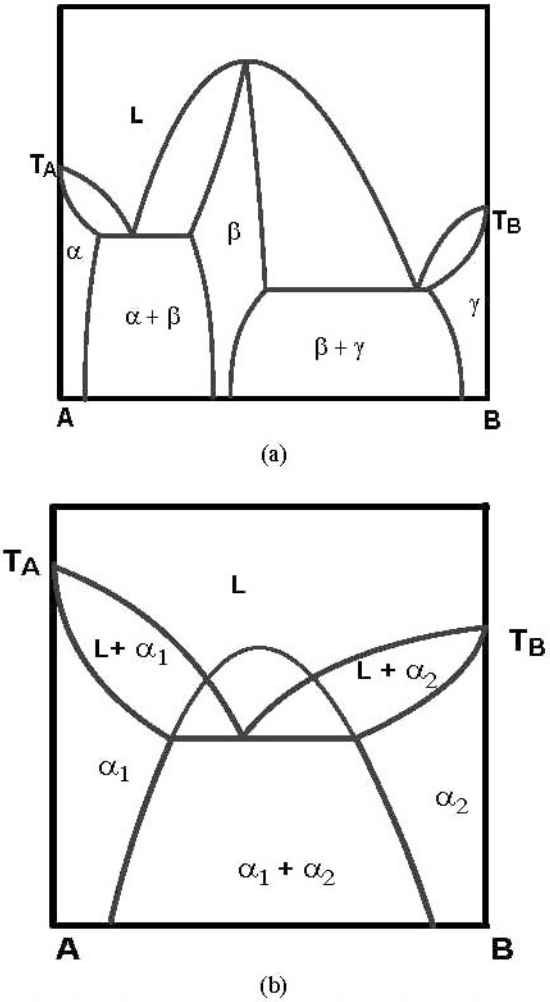

Figure 1: The phase diagrams for (a) highly negative and (b) highly positive interaction energy between solute and solvent.

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Predicting the presence of SRO is immediate from a phase diagram like that of Figure 1-a, but not all phase diagrams of Mg alloys are so amenable of interpretation even when the interaction energy with the solute is manifestly negative. This is the case of Mg-Gd, Mg-Y or Mg-Nd alloys, amongst others, which are characterized by a sequence of intermetallic compounds, some forming from the solid solution and some forming congruently from the liquid. These intermetallics are often associated with particular size ratios between host and solute, i.e., the formation of intermetallic compounds at given concentrations normally takes pre-eminence; the same applies for particular electron concentrations [2,14]. That is, electronegativity is not the only factor at play.

The sign and magnitude of the enthalpy of mixing can be used to sort out alloys of a given host, Mg in this case, predicting, among other things, the relative solubility. These predictions can be made regardless of the details of the alloy's phase diagram, i.e., regardless of whether it conforms to those of Figure 1 or exhibits a complex sequence of compounds. This sorting method, developed on the principles laid out in the 1970's by Miedema *et al.* [15-18], will be used in this work to try and anticipate which alloy systems are more amenable of developing either strong solid solution, precipitation, short range order or, in some extreme cases, no solute-based hardening at all. Four model alloys will be used for the analysis: Mg-Al, Mg-Zn, Mg-Sb and Mg-Gd. The phase diagrams of the first three systems closely conform to that of Fig. 1-a, whereas the Mg-Gd is meant to represent the many intermetallic compound forming alloy systems.

Miedema's cellular model

Miedema *et al.*'s [15-19] phenomenological approach, in its simpler form involves only two parameters, and is valid for alloys of the transition metals with divalent metals such as Mg and Zn. It combines a work function, ϕ^*, (closely related to Pauling's electronegativity value), and the electron density at the boundary of the Wigner–Seitz (WS) cell, $n_{WS}^{1/3}$. The approach enables calculating the enthalpy of formation of dilute solutions in the liquid state, predicting the sign and magnitude of the interaction, hence the relative tendency to form either ordered, random or immiscible solutions. *Ab-initio* and Calphad calculations normally reproduce closely Miedema *et al.*'s, providing the approach with strong independent support. A limitation often pointed out is its fundamentally isotropic nature, i.e., the method applies most accurately to metals in the liquid state, where size related elastic energy effects can be neglected. Further developments in the *ab-initio* methods enabled overcoming some of these limitations (e.g., see Zhang *et al.* [20]).

The enthalpy of formation [17], ΔH, of a given alloy is the balance between a negative contribution from the difference between the host's and solute's work functions, and a positive contribution stemming from the need to smooth any discontinuity of the electron density at the boundary of the WS cell between solute and solvent. The difference in electronegativity is of course the main driving force either to form a solution or an intermetallic compound by charge transfer.

Using values from [18,21] (see Table 1 for specific values for Al, Zn, Gd and Sb), a diagram using Miedema's coordinates was created for Mg and a number of solutes in Figure 2. The two perpendicular lines through Mg sort out solutes as follows: elements sitting right on the lines have no enthalpy of mixing with Mg; the upper (or "north) and lower, (or "south") sectors identify solutes with a negative energy of mixing; those lying on the east or west sectors have a positive energy of mixing.

Solutes located right on the lines are expected exhibit complete miscibility, those on the north or south sections alloy readily with the host and show a tendency to develop phase diagrams similar to that of Fig. 1-a, whereas diagrams for solutes on the east-west sections should form simple eutectics akin to that of Fig. 1-b. The correctness of these predictions can be easily verified for the solutes considered in this work, as well as for many others.

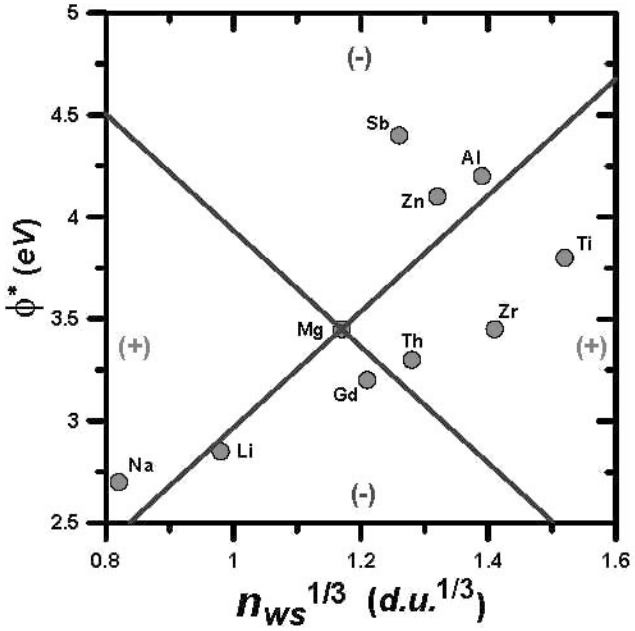

Figure 2: Miedema plot for Mg with the work function, ϕ^*, and the electronic density, $n_{WS}^{1/3}$, as coordinates (see Table 1).

Increasing values of ϕ^* are associated with a tendency to develop SRO and an attendant decrease in the terminal solubility [14]. The later follows as well from the Hume-Rothery's rule involving electronegativity. This is illustrated by Figure 3, where Al, with the smallest ΔH-value, has the largest terminal solubility, whereas Sb, with the largest one, exhibits virtually no solubility.

Solid solution hardening

In Figure 4 the room temperatures strength of Mg-Al, Mg-Zn and Mg-Gd solid solutions is compared using data from the literature. The respective rate of the solid solution hardening correlates well with the alloys' ΔH value (read from Figure 3), i.e., a rather weak hardening rate, consistent with a near random solid solution [7,10], is observed for Al, whereas the much stronger hardening in Mg-Zn and Mg-Gd is consistent with a well-developed SRO [5], expected from their increasingly negative ΔH-value.

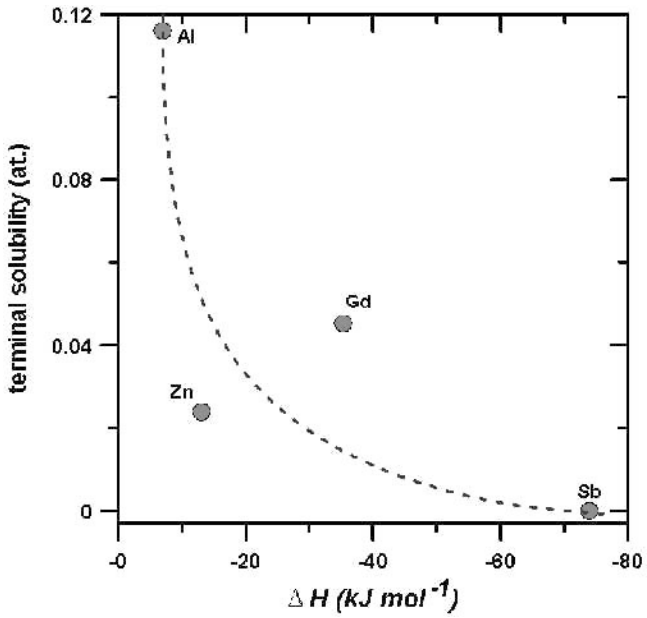

Figure 3: The terminal solid solubility as a function the enthalpy of formation for the solutes studied.

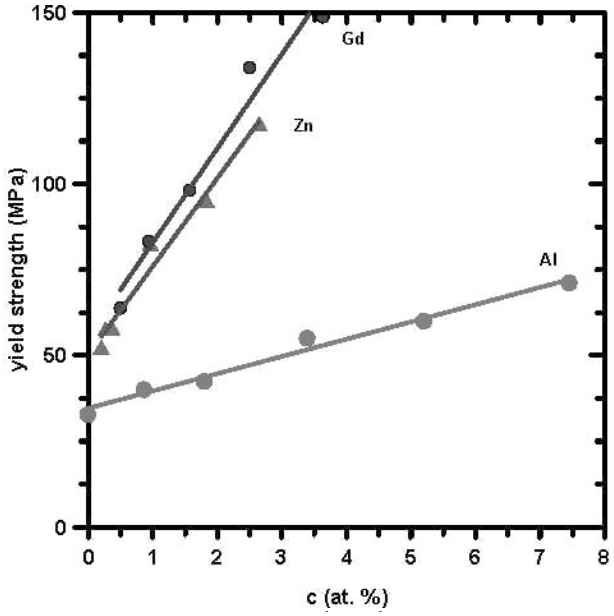

Figure 4: The strength of Mg-based solid solutions. Mg-Zn data from [22]; Mg-Al from [10] and Mg-Gd from [7].

Ranking of alloys

A straightforward way of ranking the strength of Mg alloys within the north-south sectors of Figure 4, i.e., those with negative interaction energy, and, more importantly, regardless of whether the respective phase diagrams conform to that of Figure 1-a, can be easily developed based on the potential strength of the SRO. For a solute concentration c , the strength of the SRO, τ_{SRO}, can be assumed to obey the relationship of the form [5]:

$$\tau_{SRO} \sim [\Delta H^* c(1-c)]^2. \qquad (1)$$

SRO is a typical athermal hardening mechanism, and alloys which develop it can be expected to be more creep resistant than those exhibiting only random solid solution [23,24]. Thus, to make the ranking valid for predicting creep strength, and in order to prevent any precipitation hardening effects that might arise when testing a supersaturated solid solution at high temperature, the analysis was done for the respective solute solubilities at ~200°C. These c-values are listed in Table 2.

Table 1: Miedema's coordinates values for Figures 2, 3 and 5 .

Solute	Al	Zn	Gd	Sb
ϕ^*	4.2	4.1	3.2	4.4
$n_{WS}^{1/3}$	1.39	1.32	1.21	1.26
ΔH	-7	-13	-35.3	-74

Table 2: Approximate solute solubilities (at.%) at 200°C for the alloys studied.

Solute	Al	Zn	Gd	Sb
c @ 200°C	2.5	1.5	1.0	0.05

The ranking of the alloys as per Eq. 1 is shown in Figure 5. Accordingly, the Mg-Al alloy is expected to exhibit the lowest strengthening by SRO, in this case due to its low ΔH-value. Zn and Gd containing alloys should exhibit increased strength due to the larger ΔH despite the somewhat reduced c. At the other end, for Mg-Sb the c-value drops to nearly zero, i.e., the alloy should exhibit no solute based strengthening despite its large ΔH. The latter is obviously an upper bound, as Mg-Al is a lower bound. That is, other Mg alloy systems within the north-south sectors of Figure 2 can be expected to fit in between these two bounds, with some systems exhibiting SRO strengths matching or surpassing that of Mg-Gd.

The alloys' behavior at room temperature depicted in Figure 4 is closely consistent with the ranking of Figure 5. Regarding the creep behavior, Figure 5 suggests that Mg-Gd should exhibit a well-defined athermal behavior due to its strong SRO, whereas Mg-Al should not, and Mg-Zn should lie in between. Creep data confirming these predictions are presented in another session in this symposium [25].

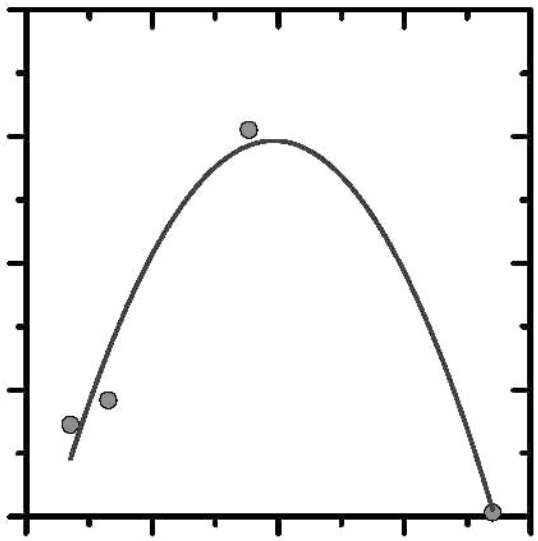

Figure 5: The predicted strength of the SRO (Eq. 1) *vs.* the heat of formation, for the alloys studied.

Figures 3 and 5 allow making predictions concerning the feasibility of precipitation hardening. A strong tendency to order, as opposed to clustering, is expected to interfere with the homogeneous nucleation of small and finely distributed precipitates upon ageing of the supersaturated solid solution [1]. The feasibility of developing strong precipitation hardening is thus expected to be opposite to the tendency to develop SRO. That is, alloys to the left of the maximum in Figure 5 should be increasingly prone to developing precipitation hardening. The classical ageing experiments on Mg-Al and Mg-Zn by Clark [11-13] support this assertion, i. e., of the alloys considered here Mg-Al exhibits the strongest (albeit mild by Al alloys' standards) response to ageing at intermediate temperatures.

Conclusions

Miedema *et al.*'s phenomenological approach has been used to rank the potential solute effects on the strength of four model Mg binary alloys considering the alloys' enthalpy of mixing.

A maximum in the random solid solutions and precipitation hardening is predicted for solutes with low heat of formation, such as Al.

Solutes with an intermediate heat of formation, such as Zn or Gd, are expected to exhibit strong SRO. These alloys are predicted to exhibit maximum strength at high temperature as a result of an extended athermal stress range.

For extreme values of heat of formation, e.g., Mg-Sb alloys, the very limited terminal solubility implies negligible solute-based hardening effects.

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