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Theoretical calculation of the amorphous alloy range of the Mg–Cu system

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The enthalpy and free energy of competing phases–metastable solid solution, amorphous alloy and structurally simple compounds–of the Mg–Cu system were calculated by using a semi-empirical theory by Miedema and Niessen and by Lopez *et al.* which is based on thermodynamic considerations. These enthalpy and free energy diagrams reproduce well the range of complete amorphization caused by rapid quenching from the melt, as experimentally measured in a previous work by Sommer *et al.*

1. Introduction

Using a semi-empirical theory [1, 2] we have calculated the composition range where Mg–Cu alloys form glasses by rapid quenching from the melt. Theoretical results are compared with experimental results reported elsewhere in the literature [3].

Theory predicts the glass-forming-composition range of a binary alloy by comparing the Gibbs free energy of mixing of competing crystalline solid solution and amorphous alloy. This theory considers the competition of structurally simple compounds [1, 4]. The following thermochemical and physical properties that influence glass-forming ability are taken into account: heat of liquid alloy formation and differences in atomic size, valence and electronegativity between the alloy's constituents [1, 2].

Mg–Cu glasses were prepared by rapid quenching from the melt, using the splat-cooling method [3]. Measured crystallization temperatures are not less than 0.5 times the temperature of the deepest eutectic reaction of Mg–Cu system: $L \rightleftharpoons (Mg) + Mg_2Cu$, where (Mg) stands for the primary solid solution [3, 5]. As experimentally measured, the partial-glass-formation composition range varies between 9 at % Cu and 42 at % Cu and the range of complete-glass formation is 12 at % Cu to 22 at % Cu [3].

2. Application of the model to the Mg–Cu system

2.1. Enthalpy

We have applied a model developed by Miedema and coworkers [2, 6] to define the region of compositions where Mg–Cu glasses form. The amorphization range consists of those compositions where the formation enthalpy of the amorphous alloy is lower than that of the substitutional solid solution. The range could be further limited by the presence of structurally simple compounds.

Using the model of A. R. Miedema [2, 5–7] we have calculated the formation enthalpy of the statistical crystalline Mg–Cu solid solution.

This enthalpy is given by the sum of three contributions

$$\Delta H_S = \Delta H_{c,s} + \Delta H_e + \Delta H_{str}, \qquad (1)$$

where the subscripts represent: S, solid solution; c, chemical; s, solid; e, elastic; and str, structural. The chemical enthalpy of mixing, $\Delta H_{c,s}$ is due to the electron redistribution that occurs when the alloy is formed. The elastic contribution (or elastic energy) ΔH_e is always positive. It arises from the difference in atomic sizes between the atoms occupying equivalent lattice sites. ΔH_e is calculated by using classical elasticity theory [5, 6] and relates to the Hume–Rothery rule of atomic size effect, which states that extended substitutional solid solubility is prohibited when the absolute value of the difference between solute and solvent atomic sizes exceeds 15 % of the solvent atomic size [4, 8]. Size mismatch being considerable in Mg–Cu system [8], a large value of ΔH_e is to be expected. ΔH_{str} is a structural contribution that reflects the influence exerted on solid solubility by the difference in valences and crystal structures of solute and solvent. At present, ΔH_{str} can be calculated theoretically only for solid solutions of transition metals of the three d-series [6, 9]. The chemical and elastic contributions to the formation enthalpy of a Mg–Cu solid solution of composition x are given by

$$\Delta H_{c,s} = x(1-x)\,[(1-x)\Delta H_{c,s,o}(\text{Cu in Mg}) + x\Delta H_{c,s,o}(\text{Mg in Cu})] \qquad (2)$$

$$\Delta H_e = x(1-x)\,[(1-x)\Delta H_{e,o}(\text{Cu in Mg}) + x\Delta H_{e,o}(\text{Mg in Cu})] \qquad (3)$$

where x and $(1-x)$ are the atomic fractions of Cu and Mg and the subscript o refers to the infinitely diluted solution. The term enclosed in brackets is the regular solution parameter [2].

The values of the elastic constants which were used to calculate ΔH_e: shear moduli and bulk moduli of Mg and Cu, are taken from reference [10].

The formation enthalpy of the amorphous alloy from the crystalline pure component metals is

$$\Delta H_a = \Delta H_{c,l} + x\Delta H_{a-s,\,Cu} + (1-x)\Delta H_{a-s,\,Mg} \quad (4)$$

where a stands for amorphous alloy and l stands for liquid. The formation enthalpy of the liquid alloy from pure liquid metals is

$$\begin{aligned}\Delta H_{c,l} &= x(1-x)[(1-x)\Delta H_{c,l,o}(\text{Cu in Mg}) \\ &\quad + x\Delta H_{c,l,o}(\text{Mg in Cu})] \quad (5)\end{aligned}$$

and ΔH_{a-s} is the enthalpy difference between the amorphous pure metal (or undercooled melt) and the crystalline pure metal, and is given by

$$\Delta H_{a-s,i} = \alpha T_{m,i} \; (i = \text{Mg, Cu}) \quad (6)$$

with $\alpha = 3.5 \times 10^{-3}$ kJ mol^{-1} [2]. T_m is the melting temperature of the pure metal. T_m values were taken from reference [11]. The elastic contribution is not important in the amorphous alloy and there is no structural contribution [1].

Model parameters and constants needed to calculate $\Delta H_{c,s,o}$ and $\Delta H_{c,l,o}$ have been taken from reference [7]. Within the frame of the Miedema model we are using, the chemical enthalpy of formation ΔH_c ($\Delta H_{c,s,(l)}$) [7] is expressed as

$$\Delta H_c = \Delta H_{ampl} x f_{CuMg} V_{Mg}^{2/3}(\text{alloy}) \quad (7)$$

or, equivalently, as

$$\Delta H_c = \Delta H_{ampl}(1-x) f_{MgCu} V_{Cu}^{2/3}(\text{alloy}) \quad (8)$$

ΔH_{ampl} is an amplitude concerning the magnitude of the chemical interaction between different atoms (Mg and Cu atoms). It is calculated by means of model parameters and constants and it is used to calculate $\Delta H_{c,s,o}$ and $\Delta H_{c,l,o}$ [7]. The following physical properties of the pure metals are the parameters used in the model: molar volume V_m, electron density at the boundary of the Wigner–Seitz cell n_{WS}, and electronegativity Φ^* [7]. f_{CuMg} is the degree by which atoms of one type (Cu) are surrounded by neighbours of the other type (Mg). For statistical solutions $f_{CuMg} = 1 - x_s$, whereas for ordered crystalline compounds, such as $MgCu_2$, an empirical relation is used instead:

$$f_{CuMg} = (1-x_s)\{1 + 8[x_s(1-x_s)]^2\} \quad (9)$$

where x_s is the surface-area concentration of Cu. V_{Cu} (alloy) is a metal molar volume which is calculated by taking into account changes in atomic volume upon alloying, due to charge transfer effect [7].

2.2. Free Energy

Metastable free-energy diagrams used to predict the range of amorphization of binary alloys can be constructed by adding entropy effects to the enthalpies of phase formation.

The amorphization region is limited by the compositions at which the free energy of its competing crystalline solid solution becomes more negative than the free energy of the amorphous alloy [1]. When the crystalline solid solution is unstable (i.e. when its free energy is positive in all compositions), the amorphization region will be limited by the compositions where the free energy of the amorphous alloy itself becomes negative.

The possible presence of compounds with simple crystalline structure can subsequently reduce the amorphization range [1].

Accordingly, we have calculated the free energy of mixing of the solid solution (ΔG_S) and the free energy of formation of amorphous alloy (ΔG_a):

$$\Delta G_S = G_S - xG_{s,Cu} - (1-x)G_{s,Mg} = \Delta H_S - T\Delta S \quad (10)$$

$$\Delta G_a = \Delta G_l + [x\Delta G_{a-s,\,Cu} + (1-x)\Delta G_{a-s,\,Mg}] \quad (11)$$

and

$$\Delta G_l = \Delta H_{c,l} - T\Delta S \quad (12)$$

The ideal solution model is taken as a first approximation to the entropy effects:

$$\Delta S = -R\,[x \ln x + (1-x)\ln(1-x)] \quad (13)$$

$\Delta G_{a-s,i}$ (i = Mg,Cu) is the free energy of crystallization of the pure undercooled liquid metal. We have calculated $\Delta G_{a-s,i}$ by using the approximations of Miedema [2]

$$\Delta G_{a-s,i} = \alpha[T_{m,i} - T] \quad (14)$$

and Thompson and Spaepen [12]

$$\Delta G_{a-s,i} = \Delta H_{f,i}\,[(T_{m,i} - T)/T_{m,i}]\,[2T/(T_{m,i} + T)] \quad (15)$$

where $\Delta H_{f,i}$ is the enthalpy of fusion of the pure metal; its value is taken from reference [11].

All free energies have been calculated at $T = T_g = 380$ K, which is the glass temperature of the eutectic alloy of composition $x = 0.145$. T_g was calculated by Sommer *et al.* [3].

The free energy of formation of intermetallic compounds, Mg_2Cu and $MgCu_2$ (ΔG_{Mg_2Cu} and ΔG_{MgCu_2}) is approximated in this model by their enthalpies of formation ΔH_{form} (Equations 7, 8 and 9) [1].

3. Results

The numerical values that have been calculated for thermodynamic properties of infinitely diluted solutions, pure metals and intermetallic compounds are presented in Tables I, II and III.

Metastable enthalpy and Gibbs free energy diagrams are shown in Figs 1 and 2.

TABLE I Formation enthalpies of infinitely diluted solutions (kJ mol^{-1})

Solution of	$\Delta H_{c,l,o}$	$\Delta H_{c,s,o}$	$\Delta H_{e,o}$
Cu in Mg	− 15.4	− 17.5	42.1
Mg in Cu	− 20.3	− 23.8	33.8

TABLE II Enthalpies and free energies of crystallization of pure metals (kJ mol^{-1}). (a) Miedema approximation; (b) Thompson and Spaepen approximation

Metal	ΔH_{a-S}	ΔG_{a-S} (a)	ΔG_{a-S} (b)
Cu	4.8	3.4	4.1
Mg	3.2	1.9	3.1

TABLE III Formation enthalpies of intermetallic crystalline compounds (kJ mol^{-1})

Compound	ΔH_{form}
Mg_2Cu	− 5.6
$MgCu_2$	− 6.8

TABLE IV Limits of the complete amorphization range of Mg–Cu system. ΔG_{a-S}: (a) Miedema [2]; (b) Thompson and Spaepen [12]

Results obtained by:	$x' - x''$
Experiment [3]	0.12 – 0.22
Theory, enthalpy diagram	0.095 – 0.22
Theory, free-energy diagram (a)	0.08 – 0.28
Theory, free-energy diagram (b)	0.14 – 0.23

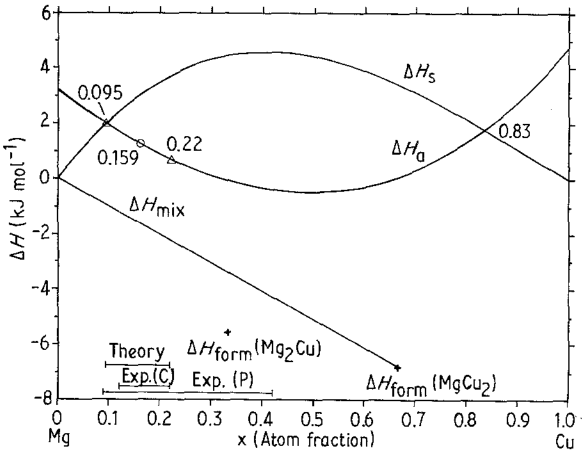

Figure 1 Metastable enthalpy diagram. (△) Limits of the calculated complete-amorphization region, (+) intermetallic compounds, (○) important points. Exp. (P): experimentally measured partial amorphization ragne. Exp. (C): experimentally measured complete amorphization range [3]. Theory: theoretically calculated complete amorphization range (this work).

The composition range where the system Mg–Cu forms amorphous alloys, calculated in this work, is presented in Table IV and in Figs 1 and 2.

4. Discussion

4.1. Enthalpies

When considering competition between amorphous alloy and solid solution, the limits of the amorphization region given by the abscissae of the points where ΔH_S and ΔH_a curves intersect are $x' = 0.095$ and $x'' = 0.83$ (Fig. 1), where x' stands for the Mg-rich and x'' for the Cu-rich limits of the amorphization range.

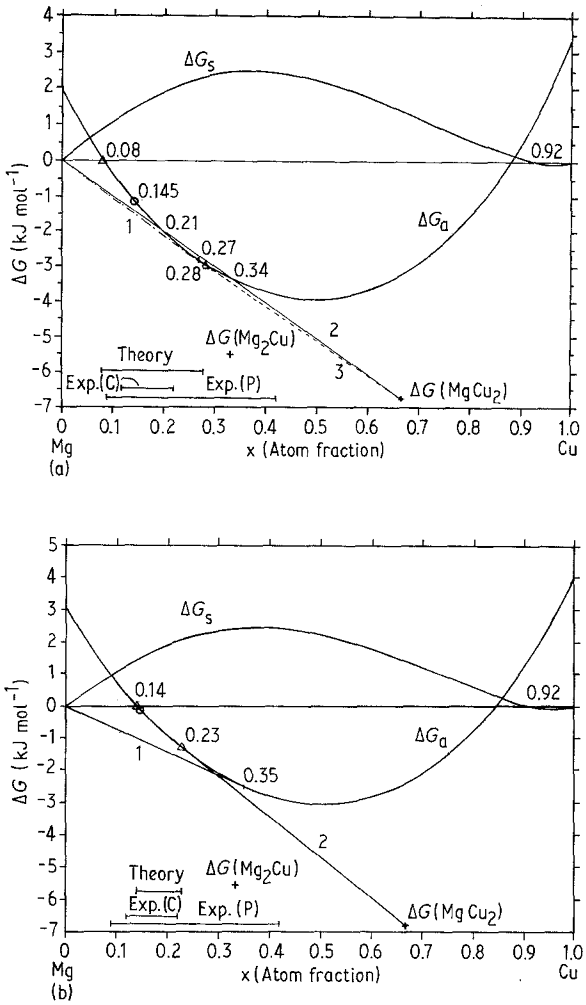

Figure 2 Metastable free-energy diagrams. (a) ΔG_{a-S} was evaluated by using Miedema approximation [2]. (- - - -) (1) a + Mg, (———) (2) Mg + $MgCu_2$, (– – – –) (3) a + $MgCu_2$. (b) ΔG_{a-S} was evaluated using Thompson and Spaepen's approximation [12]; (1) a + Mg, (2) a + $MgCu_2$. (△) Limits of the calculated amorphization region, (+) intermetallic compounds, (○) important points: $x = 0.145$. Exp. (P): experimentally measured partial amorphization range. Exp. (C): experimentally measured complete amorphization range [3]. Theory: theoretically calculated complete amorphization range (this work).

This range of amorphization is considerably wider than the experimental partial-amorphization composition range $x' = 0.09$ and $x'' = 0.42$ [3].

At the Mg-rich side, the theoretical limit agrees very well with the limit measured by experiment.

The large difference at the Cu-rich side could be attributable to the presence of the intermetallic compound $MgCu_2$. This equilibrium compound has a simple structure, of the face centered cubic type of pure Cu [13]. This similarity suggests the idea that during rapid quenching the crystallization of $MgCu_2$ would compete with the formation of the amorphous phase.

The enthalpy diagram in Fig. 1 shows a straight line representing the (Mg + $MgCu_2$) two-phase mixture (ΔH_{mix}). Within the composition range where the enthalpy of the two-phase mixture is near the enthalpy of the amorphous alloy, this amorphous alloy would easily form if the liquid alloy could not separate into two crystalline phases because of rapid solidification [14].

The minimum value of the difference between the enthalpy functions ΔH_a and ΔH_{mix} is 2.9 kJ mol^{-1} at $x = 0.159$. This value is very near the eutectic composition $x = 0.145$; so the glass will form preferably very near the eutectic composition.

As mentioned above, the origin of the amorphization region is $x' = 0.095$. The difference between ΔH_a and ΔH_{mix} amounts to 3.0 kJ mol^{-1}, which can be taken, therefore, as the largest value of the difference that allows liquid alloy amorphization. The same enthalpy difference appears at $x'' = 0.22$, which is defined, consequently, as the Cu-rich limit of the amorphization region.

To summarize, the limits of the glass-formation range as they have been calculated in the metastable enthalpy diagram of Fig. 1 are $x' = 0.095$ and $x'' = 0.22$, and they are in good agreement with the total-glass-formation composition range determined experimentally in reference [3] (Table IV).

4.2. Free Energy

It is possible to suppress to a large extent the formation of the Mg_2Cu phase by splat-cooling of Mg–Cu alloys [3]. This discussion assumes that Mg_2Cu crystallization does not compete with glass-formation during rapid solidification because of the complex crystalline structure of Mg_2Cu [13].

Fig. 2a is the metastable free-energy diagram built to assess Mg–Cu glass formation range, and where $\Delta G_{a-s,i}$ (i = Mg,Cu) was evaluated by using Miedema approximation (Equations 11 and 14) [2].

In agreement with the experimental formation of Mg–Cu glasses by rapid quenching from the melt [3], the diagram of Fig. 2a shows an interval of compositions limited by $x = 0.21$ and $x = 0.34$ where the stability of the amorphous phase is slightly larger than that of the two-phase mixture (Mg + $MgCu_2$).

The lower limit (i.e. the limit at the low Cu content) of the amorphization region is given by the composition at which ΔG_a becomes negative ($x' = 0.08$). At this limit the amorphous phase becomes more stable than the mixture of the two pure metals Cu and Mg, shown in Fig. 2a as the horizontal line at $\Delta G = 0$.

We have found that the point of contact between the curve ΔG_a and the common tangent to ΔG_a and ΔG_{MgCu_2} may be defined as the upper limit of the total amorphization region:

$$x'' = 0.28$$

The existence of a common tangent to ΔG_a and ΔG_{MgCu_2} indicates the possible existence of an equilibrium mixture of both phases, the amorphous alloy of composition $x'' = 0.28$ and the compound $MgCu_2$.

Summarizing, we have defined the following limits of the range of total amorphization: $x' = 0.08$ and $x'' = 0.28$, which agree well with the limits experimentally measured for the total amorphization range [3] (Table IV).

According to this description, in the region between $x'' = 0.28$ and $x = 0.34$ the mixture of amorphous alloy of composition $x'' = 0.28$ and crystalline $MgCu_2$ would be formed by rapid solidification. Consequently, $x'' = 0.34$ may be accepted as the upper limit of the partial-glass-formation range.

To draw the metastable free-energy diagram in Fig. 2b, we have evaluated $\Delta G_{a-s,i}$ by using the approximation of Thompson and Spaepen (Equations 11 and 15) [12].

The lower limit of the glass-formation region is the composition at which ΔG_a becomes negative $x' = 0.14$ (Fig. 2b). That is to say, the composition where the amorphous alloy becomes more stable than the two-phase mixture of pure Mg and Cu.

The common tangent to ΔG_a and ΔG_{MgCu_2} (line 2 in the figure) touches ΔG_a at a composition which defines the upper limit of the total amorphization range $x'' = 0.23$ (Fig. 2b). Accordingly, crystalline $MgCu_2$ and the amorphous alloy of composition $x = 0.23$ may exist in equilibrium.

Therefore, using Thompson and Spaepen's approximation to evaluate $\Delta G_{a-s,i}$ [12], we have calculated the following limits of the region of complete amorphization $x' = 0.14$ and $x'' = 0.23$. They agree well with the experimental values $x'_{exp} = 0.12$ and $x''_{exp} = 0.22$ (Table IV) [3].

The limits of the complete-glass-formation range, calculated by comparing formation enthalpies, agree well with those calculated by comparing free energies when the entropy effects were added to the enthalpies of phase formation. This can be seen in Table IV.

It was reported in reference [3] that on heating the Mg–Cu glass of eutectic alloy composition ($x = 0.145$), pure Mg forms as the first crystalline phase and then crystallization proceeds. The diagrams in Fig. 2a and b provide an explanation because they show that at $x = 0.145$ a two-phase mixture of (Mg + amorphous alloy of composition $x = 0.27$) (line 1 in Fig. 2a) and (Mg + amorphous alloy of composition $x = 0.35$) (line 1 in Fig. 2b) has lower free energy than that corresponding to the pure amorphous phase. The common tangent to pure Mg and to ΔG_a touches ΔG_a at $x = 0.27$ and at $x = 0.35$ in Fig. 2a and b, respectively.

At the Cu-rich side of the free-energy diagrams shown in Fig. 2a and b, the solid solution of Mg in Cu extends to 8 at % Mg at $T = 380$ K. This composition is of the same order of magnitude as the values of the equilibrium substitutional solid solubility, measured by experiment [15, 16]. Measured solid solubility of Mg in Cu amounts, approximately, to 5.1–5.6 at % Mg at room temperature, 6.5 at % Mg at 973 K and 6.7 at % Mg at 995 K [15]. Reference [16] reports 6.94 at % Mg at 997 K.

5. Summary

The glass-forming composition range of the Mg–Cu binary system was calculated by using a semi-empirical theory [1, 2]. This theory is based on thermodynamic considerations and was used to draw the enthalpy [2] and free-energy [1] diagrams of competing metastable phases: the metastable substitutional solid solution and the amorphous alloy. The formation enthalpy of structurally simple equilibrium compounds was taken into account to assess the glass-forming range.

The contribution of the structural stability to the formation enthalpy of the Mg–Cu solid solution cannot be calculated theoretically [6, 9].

The elastic energy makes a dominant contribution, destabilizing the solid solution in all compositions, except those in the Cu-rich end of the free-energy diagram (Fig. 2a and b).

Metastable enthalpy and free energy diagrams built for the Mg–Cu system reproduce well the range of complete amorphization caused by rapid quenching from the melt, as was measured experimentally in a previous work [3] (Table IV).

Mg–Cu glasses form preferentially near the alloy of eutectic composition $x = 0.145$. The glass of this composition starts its crystallization by forming pure Mg [3]. The metastable diagrams in Figs 1 and 2 also explain these experimental results.

The upper limit of the partial-glass-forming composition range could be assessed theoretically in the metastable free-energy diagram where $\Delta G_{\mathrm{a-s,i}}$ ($\mathrm{i} = \mathrm{Mg,Cu}$) was calculated by using Miedema's approximation [2]. Within the calculated glass-forming range there is a region which ends at this upper limit, where the amorphous alloy has the lowest free energy (Fig. 2a). This theoretical result is in agreement with the experimental formation of Mg–Cu glasses by rapid quenching from the melt [3].

Finally we stress that it was critical to include the presence of structurally simple compounds (in our case $MgCu_2$) to obtain agreement with experiment.

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