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Thermodynamic investigation of atomic order in AlMg liquid alloys

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Abstract. The grand partition function has been used to obtain analytic expressions for the excess free energy of mixing, the activity, the small-angle partial structure factors and the chemical short-range order parameter for weak interacting compound-forming molten alloys. It has also been applied to explain the asymmetry in the properties of mixing of AlMg molten alloys by assuming that the chemical complex Al_3Mg_2 exists in the liquid phase. It is concluded that a reasonable degree of chemical order may exist in the concentration range $0.2 \leq C_{\text{Al}} \leq 1.0$, being greatest at 60 at. % of Al. In the Mg-rich end ($C_{\text{Mg}} \geq 0.8$), however, the melt is close to the ideal mixture. The topological order, at least at the long-wavelength limit, has been found to depend only weakly on concentration.

1. Introduction

Phase diagrams, which are fundamental sources of information on alloy systems, and in particular the liquidus line [1] of AlMg alloys contrasts sharply with many other Al-based alloys. The melting temperatures of both the constituent metals are very close ($T_{\text{Al}}^{\text{m}} = 933.25 \text{ K}$, $T_{\text{Mg}}^{\text{m}} = 922 \text{ K}$) but the melting point of alloys at every composition is lower than that of the metals. It decreases linearly in the terminal region of concentration and exhibits a flattened minimum (see figure 1) in the intermediate region ($0.4 \leq C_{\text{Mg}} \leq 0.7$). The excess free energy of mixing (G_{M}^{xs}), the excess entropy of mixing (S^{xs}) and volume of mixing (V_{M}) are asymmetric around the equiatomic composition ($c = \frac{1}{2}$). S^{xs} is observed to be positive at around 10% Mg content, whereas G^{xs} shows a minimum at around 60 at. % of Al. The concentration fluctuations at the long-wavelength limit $S_{\text{CC}}(0)$, computed directly from the observed activity data, exhibit maximum deviation at $C_{\text{Al}} = 0.6$ from the ideal solution value. The size effect ($\Omega_{\text{Mg}}/\Omega_{\text{Al}} = 1.34$, Ω is the atomic volume) and the electronegativity difference ($E_{\text{Mg}} = 1.2$ and $E_{\text{Al}} = 1.5$) in AlMg are too small to account for the observed asymmetry in the properties of mixing.

We have, therefore, considered a simple statistical mechanical model [2] based on complex formation to study the concentration dependence of G_{M}^{xs} and the activity, the chemical short-range order parameter (SRO) and the long-wavelength values of the partial structure factors of both Bhatia–Thornton ($S_{\text{CC}}(0)$, $S_{\text{NN}}(0)$, $S_{\text{NC}}(0)$) and Faber–Ziman forms ($a_{\text{AlAl}}(0)$, $a_{\text{MgMg}}(0)$, $a_{\text{AlMg}}(0)$). To be more specific, SRO and $S_{\text{CC}}(0)$ are useful in the visualization of the nature of chemical order in the alloy at a given concentration. The notion of heterocoordination (i.e. preference of unlike atoms to pair as

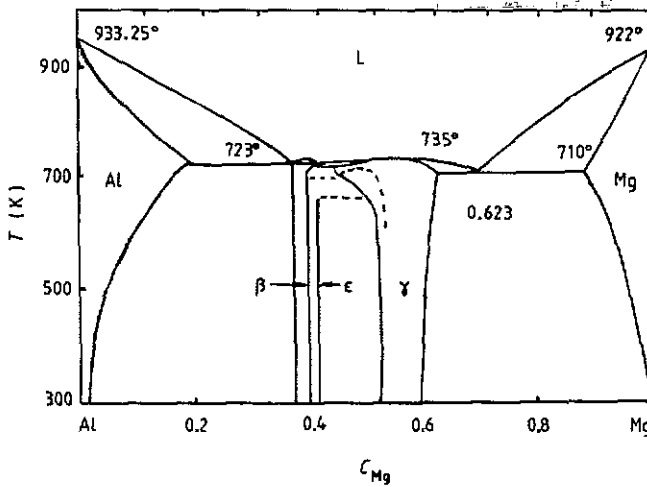


Figure 1. Phase diagram of an AlMg alloy (Hultgren *et al* [1]).

nearest neighbours) and self-coordination (i.e. preference of like atoms to pair as nearest neighbours) follow readily [3–5] from the knowledge of $S_{CC}(0)$ and SRO. The number-density fluctuations $S_{NN}(0)$ has been used to interpret the topological order in AlMg at the long-wavelength limit.

Though G_M^* is not very large ($\approx -0.15 \text{ J mol}^{-1}$), Pearson [6] suggested that the intermediate phase Al_3Mg_2 exists in the solid state. We therefore, assume that the chemical complexes $A_\mu B_\nu$ ($\mu A + \nu B \rightleftharpoons A_\mu B_\nu$, $\mu = 3$ and $\nu = 2$, $A \equiv \text{Al}$ and $B \equiv \text{Mg}$) exist in the liquid state close to the melting temperature. Thus the binary A–B alloy consists of a mixture of A atoms, B atoms and a number of chemical complexes, $A_\mu B_\nu$, all in chemical equilibrium with one another. The concept of complex formation has been successfully used to explain the asymmetry in the thermodynamic properties [7–12] of a number of binary alloys. In section 2, we describe the formulation of the activity and the free energy of mixing based on the grand partition function that has been used to compute them as a function of concentration. The results of partial structure factors in the long-wavelength limit are discussed in section 3. The expression for the chemical short-range order parameter has been derived and applied in section 4. In section 5 we conclude.

2. Statistical thermodynamic model

If we consider that a binary alloy consists of $N_A (= NC_A)$ atoms of the element A and $N_B (= NC_B)$ atoms of the element B so that there are $N = (N_A + N_B)$ atoms in all, then the grand partition function for the alloy can be expressed as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp(\varphi_A N_A + \varphi_B N_B - E) / K_B T. \quad (1)$$

where $q_i(T)$ are partition functions of atoms i ($= A$ or B) associated with inner and vibrational degrees of freedom. It has been assumed that q_i remain the same whether the atom i is located in a pure state or in the alloy. φ_A and φ_B are the chemical potentials, and E is the energy of the alloy for a given configuration of N_A A atoms and N_B B atoms

due to nearest-neighbour interactions. The sum is over all configurations and over all possible values of N_A and N_B .

By considering atomic clusters of different sizes and by characterizing the existence of a privileged group of atoms, say chemical complexes $A_\mu B_\nu$ ($\mu A + \nu B \rightleftharpoons A_\mu B_\nu$, μ and ν are small integers), Bhatia and Singh [2] solved equation (1) to obtain analytic expressions for thermodynamic functions. In doing so, they assumed that the energy (ϵ_{ij}) of a given nearest-neighbour bond (AB, AA or BB) is different if it belongs to the complex than if it does not. The ratio of the two activity coefficients, $\gamma = \gamma_A/\gamma_B$, becomes

$$\ln \gamma = Z \ln \sigma + (Z/2K_B T)(P_{AA} \Delta \epsilon_{AA} - P_{BB} \Delta \epsilon_{BB}) + \mathcal{F} \quad (2)$$

where Z is the coordination number and

$$\ln \sigma = \frac{1}{2} \ln(C_B/C_A)(\beta + 1 - 2C_B)/(\beta + 1 - 2C_A) \quad (3)$$

where

$$\beta = [1 + 4C_A C_B (\eta^2 - 1)]^{1/2} \quad (4)$$

$$\eta^2 = \exp[(2W/Z + 2P_{AB} \Delta \epsilon_{AB} - P_{AA} \Delta \epsilon_{AA} - P_{BB} \Delta \epsilon_{BB})/K_B T]. \quad (5)$$

$\Delta \epsilon_{ij}(i, j = A, B)$ represents the difference in the energy of an ij bond between that when it belongs to the complex $A_\mu B_\nu$ and that when it does not. $W = \{Z[\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2]\}$ is the interchange energy. ϵ_{ij} denotes the energy of an ij bond if the ij bond is a free bond and thus $\epsilon_{ij} + \Delta \epsilon_{ij}$ denotes the energy if the ij bond is one of the bonds in the complex $A_\mu B_\nu$. P_{ij} denotes the probability that an ij bond belongs to the complex and is expressed [2] as

$$\begin{aligned} P_{AA} &= C_A^{\mu-2} C_B^\nu (2 - C_A^{\mu-2} C_B^\nu) & \mu \geq 2 \\ P_{BB} &= C_A^\mu C_B^{\nu-2} (2 - C_A^\mu C_B^{\nu-2}) & \nu \geq 2 \\ P_{AB} &= C_A^{\mu-1} C_B^{\nu-1} (2 - C_A^{\mu-1} C_B^{\nu-1}). \end{aligned} \quad (6)$$

P_{AA} and P_{BB} are respectively zero for $\mu < 2$ and $\nu < 2$. \mathcal{F} in equation (2) is a constant independent of concentration but may depend on temperature and pressure. Its determination is discussed shortly.

Let us now obtain an expression for the excess free energy of mixing:

$$G_M^{xs} = G_M - NK_B T \sum_i C_i \ln C_i. \quad (7)$$

The expression for G_M^{xs} can be obtained from equation (2) using the thermodynamic relations,

$$\begin{aligned} \ln \gamma_A &= (1/K_B T)(\partial G_M^{xs}/\partial N_A)_{T,P,N_B} \\ \ln \gamma_B &= (1/K_B T)(\partial G_M^{xs}/\partial N_B)_{T,P,N_A}. \end{aligned} \quad (8)$$

Since we have

$$N = N_A + N_B \quad C_A = (N_A/N) \quad (9)$$

equation (8) can be expressed as

$$\ln \gamma_A = \zeta + C_B \zeta' \quad \ln \gamma_B = \zeta - C_A \zeta' \quad (10)$$

where $\zeta = G_M^{xs}/NK_B T$ and the prime indicates differentiation with respect to C . Therefore, one has

$$\frac{G_M^{xs}}{NK_B T} = \int_0^C \ln \gamma dC. \quad (11)$$

Now using equation (2), we get

$$\frac{G_M^{XS}}{NK_B T} = Z \int_0^C [\ln \sigma + (2K_B T)^{-1} (P_{AA} \Delta \varepsilon_{AA} - P_{BB} \Delta \varepsilon_{BB})] dC + \mathcal{F}_C. \quad (12)$$

The constant \mathcal{F} is determined from the condition that $\zeta_{C=0} = \zeta_{C=1} = 0$. For weak interacting systems, AlMg is an example ($G_M^{XS} = -0.15 \text{ J mol}^{-1}$), equation (12) can be further simplified. The interaction energies for such systems should be sufficiently small that only the linear terms need be retained. We recall expression (5):

$$\eta^2 \equiv e^Y \quad (13)$$

with

$$Y = (1/ZK_B T)(2W + 2P_{AB} \Delta W_{AB} - P_{AA} \Delta W_{AA} - P_{BB} \Delta W_{BB}) \quad (14)$$

where for convenience we have introduced, $\Delta W_{ij} = Z \Delta \varepsilon_{ij}$ ($i, j = A, B$). Since $Y \ll 1$, for linear terms in Y , we write

$$\eta^2 \approx 1 + Y \quad (15)$$

$$\beta \approx 1 + 2C_A C_B Y \quad (16)$$

and

$$\ln \sigma \approx (Y/2)(1 - 2C_A). \quad (17)$$

Therefore, equation (2) becomes

$$\ln \gamma = (K_B T)^{-1} [(1 - 2C_A)(W + \Delta W_{AB} P_{AB}) + C_A \Delta W_{AA} P_{AA} - C_B P_{BB} \Delta W_{BB}] + \mathcal{F}. \quad (18)$$

The value of \mathcal{F} is determined by setting $\int_0^1 \ln \gamma dC = 0$, which using equation (6), yields

$$\mathcal{F} = \frac{\Delta W_{AB}}{K_B T} b_{AB}(B) + \frac{\Delta W_{AA}}{K_B T} b_{AA}(B) + \frac{\Delta W_{BB}}{K_B T} b_{BB}(B) \quad (19)$$

where $b_{ij}(B)$ are functions of the beta function, i.e.

$$b_{AB}(B) = 2B(\mu + 1, \nu) - 2B(\mu, \nu + 1) + B(2\mu - 1, 2\nu) - B(2\mu, 2\nu - 1) \quad (20)$$

$$b_{AA}(B) = B(2\mu - 2, 2\nu + 1) - 2B(\mu, \nu + 1) \quad (21)$$

$$b_{BB}(B) = 2B(\mu + 1, \nu) - B(2\mu + 1, 2\nu - 2) \quad (22)$$

with

$$B(n, m) = B(m, n) = \int_0^1 C^{m-1} (1 - C)^{n-1} dC = \frac{\Gamma(m)\Gamma(n)}{\Gamma(m+n)} \quad (23)$$

where $\Gamma(m)$ is the usual gamma function. With $\ln \sigma$ given by the approximation (17), the integration involved in the determination of G_M^{XS} (see equation (12)) can readily be evaluated in closed form for given values of μ and ν . For AlMg liquid alloys ($\mu = 3$, $\nu = 2$) one obtains:

$$G_M^{XS} = N(WC_A C_B + \Delta W_{AB} f_{AB}(C) + \Delta W_{AA} f_{AA}(C) + \Delta W_{BB} f_{BB}(C)) \quad (24)$$

with

$$f_{AB}(C) = \frac{13}{420} C + \frac{1}{3} C^3 - \frac{1}{2} C^4 + \frac{1}{3} C^5 + \frac{1}{3} C^6 - \frac{1}{5} C^7 + \frac{1}{4} C^8 \quad (25)$$

$$f_{AA}(C) = -\frac{53}{340} C + \frac{1}{3} C^3 - \frac{1}{2} C^4 + \frac{1}{3} C^5 - C^6 + \frac{1}{4} C^7 - \frac{1}{8} C^8 \quad (26)$$

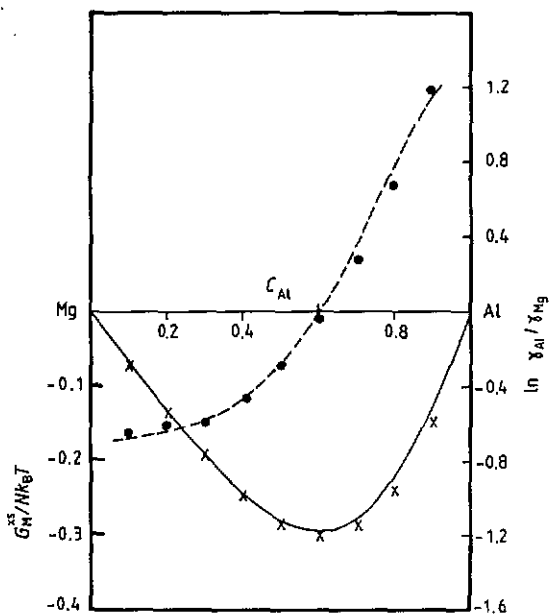


Figure 2. Excess free energy of mixing (G_M^{xs}) and activity ratio ($\ln \gamma_{Al}/\gamma_{Mg}$) of AlMg liquid alloys at 1073 K. —: theory, $\times\times\times$: experiment ($G_M^{xs}/NK_B T$) ---: theory, $\circ\circ\circ$: experiment ($\ln \gamma_{Al}/\gamma_{Mg}$).

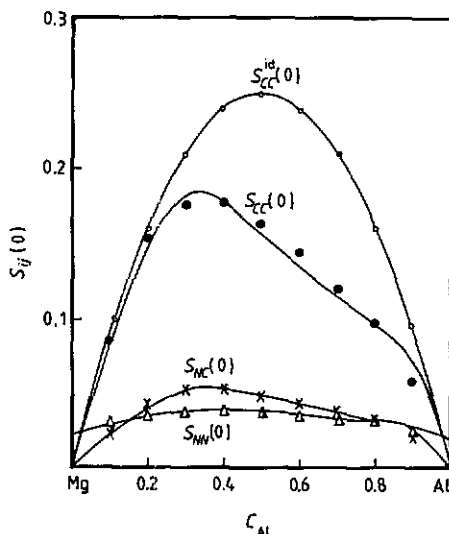


Figure 3. Bhatia-Thornton partial structure factors ($S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$) of AlMg liquid alloys ($T = 1073$ K) in the long-wavelength limit. The curves are from theory and the points were directly obtained from activity data.

$$f_{BB}(C) = \frac{23}{280}C - \frac{1}{2}C^4 + \frac{2}{3}C^5 + \frac{1}{7}C^7 - \frac{1}{8}C^8. \quad (27)$$

The above relationships could be used easily to study the concentration dependence of $\ln \gamma$ and G_M^{xs} provided that the energy parameters W and ΔW_{ij} were known. These energy parameters may depend on temperature and pressure but are independent of concentration. If W and ΔW_{ij} are made concentration dependent then the very structure of the complex-formation model weakens. In the actual calculation, a reasonable choice of the relevant interaction energies was made from experimental data on G_M^{xs} at a couple of concentrations. However, it then remains the same for all investigations including that of the atomic order of AlMg liquid alloys. The choice of interaction energies at 1073 K are as follows:

$$\frac{W}{K_B T} = -0.95 \quad \frac{\Delta W_{AB}}{K_B T} = 4.3 \quad \frac{\Delta W_{BB}}{K_B T} = 3.7 \quad \frac{\Delta W_{AA}}{K_B T} = 0. \quad (28)$$

The computed values of G_M^{xs} are plotted in figure 2 and are compared with the experimental values as compiled by Hultgren *et al* [1]. Theory and experiment are in good agreement. It is expected that because the minimum value of $G_M/RT \approx -0.97$, this is an indication that the tendency to form chemical complexes is not too strong [13], and, therefore, that the approximation developed here should apply to AlMg.

The $G_M^{xs} - C$ curve is asymmetric around the equiatomic composition and exhibits a minimum around the compound-forming concentration $C_C = C_{Al} = \mu/(\mu + \nu) = 0.6$.

Though the asymmetry in G_M^{xs} (both from theory and experiment) is quite visible, the asymmetry in G_M ($G_M = G^{xs} + G^{id}$) is not equally so. This is due to the values of G^{id} ($= NK_B \sum_i C_i \ln C_i$) being large compared with those of G^{xs} .

The activity ratio computed from (18) is also plotted in figure 2. For the sake of comparison, the experimental points are also depicted; the two are in good agreement. The same set of interaction energies (28), which are independent of concentration, explain the concentration dependence of G_M^{xs} and the activity ratio simultaneously.

3. Low-angle partial structure factors

The partial structure factors of Bhatia and Thornton [14] ($S_{CC}(0)$, $S_{NN}(0)$, $S_{NC}(0)$) and Faber and Ziman [15] ($a_{AlAl}(0)$, $a_{MgMg}(0)$ and $a_{AlMg}(0)$) at long wavelengths ($q \rightarrow 0$) can easily be evaluated by using the thermodynamic equations derived in the previous section. Of these, the concentration fluctuations, $S_{CC}(0)$, are of immense help in understanding the segregation (preference for like atoms to pair as nearest neighbours) and the extent of local order (preference for unlike atoms to pair as nearest neighbours) in binary molten alloys. $S_{CC}(0)$ is also being used [16] to shed light on the phenomenon of easy glass formation where glasses are obtained by quenching the molten alloys. The necessity for and the importance of such functions have been greatly emphasized in various reviews by March *et al* [17], Chieux and Ruppersberg [18], Steeb *et al* [19], Wagner [20] and Singh [3].

The concentration fluctuation, $S_{CC}(0)$, for a binary mixture are expressed as

$$S_{CC}(0) = N \langle (\Delta C)^2 \rangle \quad (29)$$

where $\langle (\Delta C)^2 \rangle$ represents the mean square fluctuations in the concentration, which are readily derived [14] from statistical mechanics in terms of the free energy of mixing, i.e.

$$S_{CC}(0) = NK_B T (\partial^2 G_M / \partial C^2)_{T,P,N}^{-1} \quad (30)$$

Equation (7), (24) and (3) yield

$$S_{CC}(0) = S_{CC}^{id} \left/ \left[1 + C_A C_B \left(-\frac{2W}{K_B T} + f''_{AB} \frac{\Delta W_{AB}}{K_B T} + f''_{AA} \frac{\Delta W_{AA}}{K_B T} + f''_{BB} \frac{\Delta W_{BB}}{K_B T} \right) \right] \right. \quad (31)$$

where $f''_{ij} = d^2 f_{ij} / dC^2$. At this point it might be appropriate to identify $S_{CC}(0)$ in terms of the excess stability function, E^{xs} introduced by Darken [21]

$$E^{xs} = RT(1/S_{CC}(0) - 1/C_A C_B). \quad (32)$$

For ideal alloys, the interaction energies are zero ($W = \Delta W_{ij} = 0$), one readily obtains

$$S_{CC}(0) = S_{CC}^{id} = C_A C_B \quad \text{and} \quad E^{xs} = 0. \quad (33)$$

$S_{CC}(0)$ as obtained from equation (31) can, furthermore, be used to determine the other two correlation functions, namely the number-density fluctuations $S_{NN}(0)$ and the number-concentration correlation terms $S_{NC}(0)$, i.e.

$$S_{NN}(0) = \rho K_B T \chi_T + \theta^2 S_{CC}(0) \quad (34)$$

$$S_{NC}(0) = -\theta S_{CC}(0) \quad (35)$$

$$\theta = (1/V)(\partial V/\partial C)_{T,P,N} = (V_{\text{Al}} - V_{\text{Mg}})/V \quad (36)$$

where V is the molar volume of the alloy, ρ is the number density and χ_T stands for isothermal compressibility. The data for compositional dependence of V have been taken from values obtained by Pelzel [22]. For χ_T we assume that $\chi_T = C_A \chi_T^{\text{Al}} + C_B \chi_T^{\text{Mg}}$.

If the molar volume of the two species are the same, then $\theta = 0$ and equations (34) and (35) simplify to

$$S_{\text{NN}}(0) = \rho K_B T \chi_T \quad (37)$$

$$S_{\text{NC}}(0) = 0. \quad (38)$$

Obviously the fluctuations in number density are independent of those in concentration and the expression is like that for the pure liquid ($S(0) = \rho K_B T \chi_T$). The above equations also indicate that there is no correlation between the fluctuations in number density and the fluctuations in concentration, i.e. $S_{\text{NN}}(0)$ and $S_{\text{CC}}(0)$ oscillate independently.

We recall that $S_{\text{CC}}(q)$ and $S_{\text{NN}}(q)$ are widely used [18, 20] to interpret the chemical and topological short-range order in structurally disordered systems, respectively. Thus $S_{\text{CC}}(0)$ and $S_{\text{NN}}(0)$ furnish valuable information about atomic order, at least in the long-wavelength limit.

$S_{\text{CC}}(0)$ computed from equation (31) for AlMg is plotted in figure (3) as a function of concentration. In principle, $S_{\text{CC}}(0)$ can also be determined directly from the small-angle diffraction experiments, but it poses a much more difficult experimental problem and has never been accomplished successfully. Funel-Bellissent *et al* [23] observed that the low-angle neutron scattering which leads to an abnormal scattering cannot be interpreted as being due to the density and concentration fluctuations of a classical binary liquid alloy. Thus we have no information on $S_{\text{CC}}(0)$ from the diffraction experiments, although it can be determined directly from the measured activity data following the equalities

$$S_{\text{CC}}(0) = C_{\text{Mg}} a_{\text{Al}} (\partial a_{\text{Al}}/\partial C_{\text{Al}})_{T,P,N}^{-1} = C_{\text{Al}} a_{\text{Mg}} (\partial a_{\text{Mg}}/\partial C_{\text{Mg}})_{T,P,N}^{-1}. \quad (39)$$

$S_{\text{CC}}(0)$ computed directly from the activity are usually termed experimental values. Here one needs to evaluate the first derivative of activity with respect to C . With a view to minimizing the errors involved in numerical differentiation, we make a series expansion of the observed activity data [1] at 1073 K,

$$\begin{aligned} a_{\text{Al}} = & 0.498 C_{\text{Al}} + 0.349 C_{\text{Al}}^2 - 1.478 C_{\text{Al}}^3 - 1.866 C_{\text{Al}}^4 + 39.244 C_{\text{Al}}^5 \\ & - 106.159 C_{\text{Al}}^6 + 105.542 C_{\text{Al}}^7 + 0.378 C_{\text{Al}}^8 - 66.929 C_{\text{Al}}^9 \\ & + 31.319 C_{\text{Al}}^{10} \end{aligned} \quad (40)$$

$$\begin{aligned} a_{\text{Mg}} = & 0.119 C_{\text{Mg}} + 2.046 C_{\text{Mg}}^2 - 3.824 C_{\text{Mg}}^3 + 18.869 C_{\text{Mg}}^4 \\ & - 48.868 C_{\text{Mg}}^5 + 58.799 C_{\text{Mg}}^6 - 30.638 C_{\text{Mg}}^7 + 9.076 C_{\text{Mg}}^8 \\ & + 6.098 C_{\text{Mg}}^9 - 1.609 C_{\text{Mg}}^{10}. \end{aligned} \quad (41)$$

The last two equalities of equation (39) along with (40) and (41) provide another check on the value of $S_{\text{CC}}(0)$.

Figure (3) indicates that $S_{\text{CC}}(0)$ computed from the theoretical expression (31) and that from (39) are in good agreement. We recall that the values of $S_{\text{CC}}(0)$ can readily be used to interpret [3] the nature of chemical order in binary liquid alloys. If, at a given

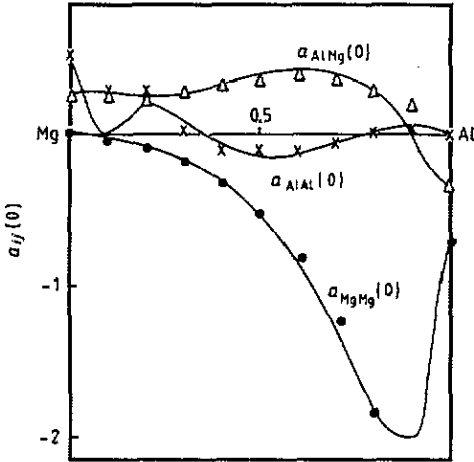


Figure 4. Faber-Ziman partial structure factors ($a_{AlAl}(0)$, $a_{MgMg}(0)$ and $a_{AlMg}(0)$) of AlMg at 1073 K. The curves show theoretical predictions and the points represent experimental values.

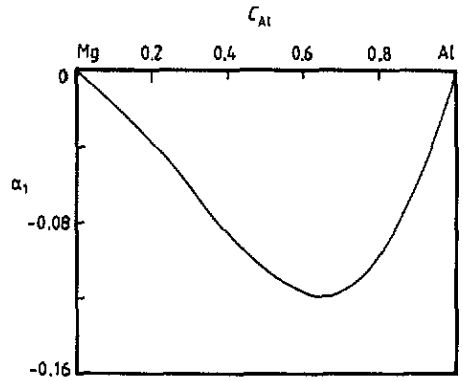


Figure 5. The chemical short-range order parameter (α_1) for the first coordination shells of AlMg alloys at 1073 K.

composition, $S_{CC}(0) \geq S_{CC}^{id}(0)$, then there is a tendency for segregation (preference for like atoms to pair as nearest neighbours) and $S_{CC}(0) \leq S_{CC}^{id}(0)$ indicates order (preference for unlike atoms to pair as nearest neighbours) in the alloys.

The values of $S_{CC}(0)$ obtained for AlMg liquid alloys at 1073 K are clearly not ideal. The maximum deviation occurs around the compound-forming concentration $C_{Al} = \mu/(\mu + \nu) = 0.6$, $S_{CC}^{id}(0) - S_{CC}(0)$ exhibits a peak at this concentration. There is order in the alloy in the concentration range $0.2 \leq C_{Al} \leq 1.0$. At the Mg-rich end ($C_{Mg} \geq 0.8$), however, the alloy behaves very much like an ideal mixture.

The number density fluctuations, $S_{NN}(0)$ in AlMg alloys are much smaller than $S_{CC}(0)$. $S_{NN}(0)$ varies almost linearly with concentration; that is to say that in contrast to chemical order, the topological order in AlMg liquid alloys depends very little on concentration. $S_{NN}(0)$ at pure ends are also approximately the same. In addition, it should be noted that the coordination numbers of Al and Mg ($Z_{Al} = 10.6$, $Z_{Mg} = 10$) near the melting point are not much different. The correlation term $S_{NC}(0)$ is also small but shows variation with concentration. Due to the linear variation of $S_{NN}(0)$, the nature of $S_{NC}(0)$ is the same as that of $S_{CC}(0)$.

The Faber-Ziman [15] partial structure factors $a_{ij}(0)$ in the long-wavelength limit can also be obtained from $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$, i.e.

$$\begin{aligned} a_{AlAl}(0) &= \rho K_B T \chi_T - C_{Mg}/C_{Al} + (1 - C_{Al}\theta)^2 S_{CC}(0)/C_{Al}^2 \\ a_{MgMg}(0) &= \rho K_B T \chi_T - C_{Al}/C_{Mg} + (1 + C_{Mg}\theta)^2 S_{CC}(0)/C_{Mg}^2 \\ a_{AlMg}(0) &= \rho K_B T \chi_T + 1 - (1 - C_{Al}\theta)(1 + C_{Mg}\theta) S_{CC}(0)/C_{Al} C_{Mg}. \end{aligned} \quad (42)$$

For ideal alloys $S_{CC}(0) = C_{Al} C_{Mg}$ and if $\theta = 0$, then (42) reduces to

$$a_{AlAl}(0) = a_{MgMg}(0) = a_{AlMg}(0) = \rho K_B T \chi_T. \quad (43)$$

Again, expression (43) is like that for a pure liquid, and there is no structural correlation between the constituent species. The computed values of $a_{ij}(0)$ for AlMg are plotted in figure 4. All three structure factors depend strongly on concentration and exhibit

complicated behaviour. Often in the calculation of transport properties it is assumed that the partial structure factors are independent of composition, but this seems a poor approximation for the case of AlMg.

4. Chemical short-range order parameter

It is clear from the previous section that chemical order exists in AlMg alloys in the concentration range $0.2 \leq C_{\text{Al}} \leq 1.0$. This can best be understood quantitatively by evaluating the Warren-Cowley [24-25] short-range order (α_1). For the first-neighbour shell, α_1 can be defined as

$$(A/B) = C_A(1 - \alpha_1) \quad (B/A) = C_B(1 - \alpha_1) \quad (44)$$

where i/j defines the probability that an i atom exists as a nearest neighbour of a given j atom. α_1 provides an immediate insight into the local arrangement of atoms in the alloy. For a random distribution of atoms (i.e. ideal alloys), (A/B) is simply C_A and (B/A) is (C_B) , then $\alpha_1 = 0$. If $\alpha_1 < 0$, then A-B pairs of atoms are preferred over A-A or B-B pairs as nearest neighbours, and for the converse case, $\alpha_1 > 0$. From a simple probabilistic approach, the limiting values of α_1 can easily be shown to lie in the range

$$\begin{aligned} -C_{\text{Al}}/C_{\text{Mg}} \leq \alpha_1 \leq 1 & \quad C_{\text{Al}} \leq \frac{1}{2} \\ -C_{\text{Mg}}/C_{\text{Al}} \leq \alpha_1 \leq 1 & \quad C_{\text{Al}} \geq \frac{1}{2}. \end{aligned} \quad (45)$$

For equiatomic composition ($C_{\text{Al}} = 0.5$) one has $-1 \leq \alpha_1 \leq 1$. The minimum possible values of α_1 , i.e. $\alpha_1^{\text{min}} = -1$, represent the complete ordering of pairs of nearest-neighbour atoms in the A-B configuration, whereas $\alpha_1^{\text{max}} = +1$ suggests segregation leading to the formation of A-A pairs or B-B pairs in the alloy.

The conditional probability (i/j) can readily be evaluated [2] from the knowledge of the grand partition function. This enables one to write

$$\alpha_1 = (\beta - 1)(\beta + 1)^{-1} \quad (46)$$

where β is defined in (4). In view of approximation (16), α_1 becomes,

$$\alpha_1 = C(1 - C)Y/[1 + C(1 - C)Y] \quad (47)$$

where Y is a function of interaction energies and is given in (14). With the help of interaction energies, as provided in expression (28), we have computed α_1 as a function of concentration; we have taken $Z = 10$. The values of α_1 are plotted in figure 5 and could not be checked by comparison, as no other experimental and theoretical results exist.

The $\alpha_1 - C$ curve is also asymmetric and exhibits a minimum around 67 at. % of Al. The negative value of α_1 indicates that there is a preference for unlike atoms (Al-Mg) to pair as nearest neighbours. Furthermore, we observe that the ordering is larger at the Al-rich end than at the Mg-rich end. It should, however, be mentioned that the magnitude of α_1 is much smaller than required for complete ordering (see (45)). For example, at stoichiometric composition ($C_{\text{Al}} = 0.6$), $\alpha_1 = -0.117$ compared with the -0.66

needed for complete ordering. Similarly, the magnitude of α_1 at other concentrations can also be used to interpret the degree of order that exists in the alloy.

5. Conclusion

Being a weak interacting system, the properties of mixing of AlMg liquid alloys are asymmetric as a function of concentration. The anomalous behaviour has been explained by assuming that the preferential ordering of atoms in the form Al_3Mg_2 exists in the melt close to the melting temperature. There is heterocoordination (preference for unlike atoms to pair as nearest neighbours) which depends sensitively on the concentration being at a maximum around $C_{\text{Al}} = 0.6$. The AlMg liquid alloys deviate most from the ideal behaviour at around 60 at.% of Al, but at the Mg-rich end ($0.8 \leq C_{\text{Mg}} \leq 1$) the alloy compositions tend towards ideal mixtures. The topological order seems to depend weakly on concentration.

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