

Glass-forming ability of the Al–Ce system: a thermodynamic approach

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Abstract

The Miedema model and results from a phase diagram calculation are used to predict amorphization in Al–Ce. The results of the computing procedure have been successfully compared with experimental data for $\text{Al}_{91}\text{Ce}_9$ and $\text{Ce}_{70}\text{Al}_{30}$.

1. Introduction

The formation of amorphous metallic materials either by rapid solidification or by solid state reactions involves an interplay between thermodynamic and kinetic factors. The thermodynamic properties may be viewed as necessary conditions for amorphization to occur. If the kinetic requirements are fulfilled (*i.e.* the amorphization technique inhibits the nucleation and growth of the energetically more favoured intermetallic compounds), then the difference between the free enthalpies of the amorphous phase and solid solutions constitutes the main factor that designates which phase will prevail. Therefore a detailed thermodynamic analysis may shed light on the glass-forming tendency of a given system.

Binary metallic systems prone to form a glass show, in general, a considerable degree of short-range order in the undercooled regime [1, 2]. The presence of a deep eutectic represents an indication of stability of the liquid relative to crystal phases. Also, these alloys display enhanced viscosity at and below the melting point [3] which provides a kinetic resistance to partitioning into a mixture of phases during rapid solidification. In some cases [4], amorphization could even occur at compositions where compounds are found to be stable in equilibrium, as long as kinetic constraints inhibit the creation of crystal nuclei of critical size. It should not be surprising to

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find a highly ordered liquid in the vicinity of an intermetallic compound. In fact, the tendency to unlike nearest-neighbour interactions which leads to compound formation can persist in the liquid state. If the presence of the intermetallics is ignored, extrapolation of the liquidus curves in the phase diagram would usually give rise to an "effective deep eutectic" [5].

Amorphous alloys of potential interest for their mechanical properties have been obtained in the aluminium-rich corner of many Al-RE and Al-RE-TM systems [6, 7] (RE \equiv rare earth and TM \equiv transition metal). The Al-RE binaries display a very shallow eutectic between aluminium and an intermetallic compound having a high melting point (*e.g.* Al₁₁Nd₃ and Al₃Sm) at aluminium content exceeding 90 at.%. A deeper eutectic exists on the RE-rich side. So, the systems are likely to contain a potentially glass-forming ordered liquid.

In the present work we focus our attention on the thermodynamics of the Al-Ce system, investigating the possibility of its amorphization. The glass-forming range of a metallic system is limited by the compositions at which the free enthalpies of competing metastable crystalline phases become more negative than that of the amorphous phase. As usual (see for example refs. 1, 4 and 5), we treat the amorphous phase as an extension of the liquid down to temperatures in the undercooled regime. Here we present and compare two different frameworks to deal with the problem of amorphization. The first is a semiempirical treatment that combines Miedema's model for the heat of formation of alloys [8] and classical elasticity theory [9] (Section 2). The second approach is based on the extrapolation of calculations of the equilibrium phase diagram (CALPHADs) to the metastable regime, adding to it, if necessary, an excess specific heat for the liquid phase that accounts for the temperature dependence of the thermodynamic functions observed in glass-forming systems (Section 3).

2. Glass-forming range from extension of Miedema's model

The free enthalpy of formation of binary A-B solid solutions is given by

$$\Delta G^{ss} = \Delta H^{ss} - T \Delta S^{ss} \quad (1)$$

where ΔH^{ss} and ΔS^{ss} are the enthalpy and entropy of formation respectively. To determine the glass-forming range of the alloy, ΔG^{ss} must be compared with the free enthalpy of the amorphous phase (considered as an undercooled melt) with the pure crystalline metals as reference state, ΔG^{l-s} , *i.e.*

$$\Delta G^{l-s} = \Delta G^{l-1} + x_A \Delta G_A^{l-s} + x_B \Delta G_B^{l-s} \quad (2)$$

where ΔG^{l-1} is the free enthalpy of the amorphous phase with respect to liquid elements and ΔG_i^{l-s} is the difference between the free enthalpies of the undercooled liquid and crystalline phase of pure element *i*, *i.e.*

$$\Delta G_i^{l-s} = \frac{\Delta H_{f,i}(T_{f,i} - T)}{T_{f,i}} - \int_T^{T_{f,i}} \Delta C_{p,i} dT + T \int_T^{T_{f,i}} \Delta C_{p,i} d(\ln T) \quad (3)$$

where $\Delta H_{f,i}$ is the heat of fusion of i , $T_{f,i}$ is the melting temperature and $\Delta C_{p,i}$ is the heat capacity difference between the undercooled liquid and the crystalline pure element i .

In the present work we have estimated the free enthalpy of an amorphous phase for the pure elements with respect to the stable solid phases by extrapolating the behaviour of C_p down to temperatures below T_f . The specific heat for the liquid was assumed to follow the linear Regnaut–Bretonnet [10] extrapolation on undercooling, which leads to a glass transition temperature around a quarter of the melting temperature [11] (in agreement with the commonly accepted Turnbull's criterion for T_g of pure metals [12]). The same criterion to obtain the T_g of pure cerium was followed.

To calculate ΔG^{ss} and ΔG^{l-1} the expressions for the enthalpy and entropy of mixing of both solid and amorphous phases need to be known. The simplest form for the entropy is that corresponding to an ideal solution. Usually ideality is a reasonable approximation but, if there are reasons to believe that the chemical short-range orders (CSRO) are different in the amorphous (liquid) phase and in the solid solution, we are led to the conclusion that an excess entropy of mixing exists in the undercooled liquid; so the ideal entropy approximation becomes unsuitable, as it is the case in the system that we are analysing. We must remark that, if it is assumed that CSRO exists to some extent in the amorphous phase, the dependence on temperature of the degree of order must be linked to a temperature dependence of the thermodynamic functions, and therefore one must be very careful when using a model such as that of Miedema at temperatures other than 0 K.

The next step is to set up expressions for the enthalpies of mixing of competing phases. We follow here a semiempirical approach proposed by Miedema and coworkers [8, 13] and used successfully by other workers to compute the glass-forming range of binary transition metal alloys [14, 15]. The enthalpy of formation of a substitutional solid solution contains three additive terms: a chemical term ΔH^c due to electron redistributions that occur when the alloy is formed; an elastic contribution ΔH^e arising from differences in atomic volume between the constituents; a structural contribution ΔH^{st} taking into account the difference in valence and crystal structure of solute and solvent.

Following Miedema and coworkers [8] we write the chemical term as

$$\Delta H^c = H^{int} x_A V_{A(\text{alloy})}^{2/3} f_{AB} \quad (4)$$

where H^{int} is a term which combines proportionality constants and parameters concerning the magnitude of the chemical interaction, $V_{A(\text{alloy})}$ is the atomic volume of metal A in the alloy, and f_{AB} is a function which accounts for the degree to which atoms of type A are surrounded by atoms of type B. For statistically ordered solutions it is given by

$$f_{AB} = x_B^s \quad (5)$$

where x^s are surface concentrations. Miedema and coworkers assume that, for ordered intermetallic compounds, f_{AB} takes the form

$$f_{AB} = x_B^s [1 - \delta(x_A^s x_B^s)^2] \quad (6)$$

with $\delta=8$. Weeber [16] has modified the function f_{AB} for the calculation of the enthalpy of formation of an amorphous alloy, taking $\delta=5$ in order to account for the tendency to CSRO of glass-forming systems. Note that the introduction of CSRO implies a deviation from regular solution behaviour, which in Miedema's model arises because the total interaction energy is assumed to be proportional to the total surface area of contact between A and B atomic cells.

The elastic term ΔH^e can be computed using classical elasticity theory [9]. The result can be written in the following simple form [17]:

$$\Delta H^e = x_A x_B [x_A \Delta h^e(\text{B in A}) + x_B \Delta h^e(\text{A in B})] \quad (7)$$

where $\Delta h^e(\text{A in B})$ is the size mismatch contribution to the enthalpy of solution of constituent A in B given by

$$\Delta h^e(\text{A in B}) = \frac{2K_A \mu_B (V_A - V_B)^2}{3K_A V_B + 4\mu_B V_A} \quad (8)$$

where μ_B is the shear modulus of the host, K_A is the bulk modulus of the solute metal, and V_A and V_B are the atomic volumes of A and B. Because Gschneidner [18] gives the elastic coefficients at 300 K, we introduce a temperature dependence in the enthalpy of formation of the solid solution via an extrapolation of the elastic coefficients from room temperature to the working temperature [19].

The size mismatch contribution can be neglected in computing the heat of formation of intermetallic compounds and amorphous alloys [14, 17].

The structural contribution ΔH^{st} can only be used when dealing with systems formed by two transition metals because in the model that we follow, it arises from the formation of a common d electronic band [13]. The non-applicability of the electronic rigid-band model in the Al-Ce system leads to an overvalue of the enthalpy of formation of the solid solution coming from the neglect of the structural term that we cannot compute. The almost total absence of terminal solubilities in the phase diagram and the limited extent of supersaturation achieved by rapid solidification [20] suggest that the free enthalpy for the solid solution must be less negative than that obtained here.

Figure 1 shows the enthalpy of formation of the Al-Ce solid solution taken as statistically ordered ($\delta=0$), the amorphous phase as possessing a certain degree of CSRO ($\delta=5$) and the intermetallic compounds assumed to be line compounds with $\delta=8$. All calculations were carried out at 0 K. If the quenching technique is able to avoid the formation of the thermodynamically more favoured intermetallics, the common tangent construction opens a broad range of complete amorphization. The appearance of partial amorphization in the cerium-rich part of the calculated diagram is against our experimental finding of a single glassy state at a cerium content of 70 at.% (see Section 4). The forced neglect of a structural contribution to the

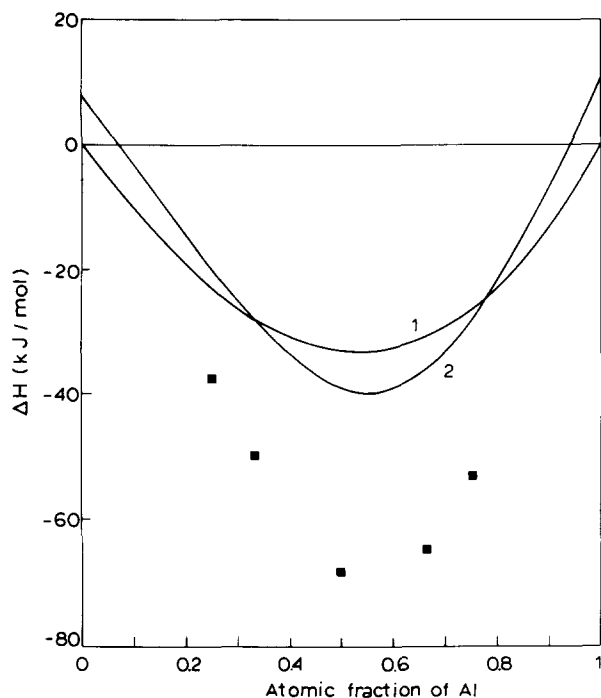


Fig. 1. Heat of mixing for the Al–Ce system obtained from Miedema's model: curve 1, f.c.c. solid solution; curve 2, liquid phase; ■, equilibrium intermetallic compounds.

heat of formation of the solid solutions seems to be the main cause of this discordancy as it would raise the solid solution curve. In the aluminium-rich region, the model predicts the appearance of the amorphous phase in the presence of a solid solution of cerium in aluminium up to around 90 at.% Al, in keeping with the experimental observation of an inhomogeneous mixture of amorphous phase and crystalline material at an aluminium content of 91 at.%. The two regions analysed in this paper are borderline cases in which the relative differences between the free enthalpies of amorphous and solid solution phases are relatively small; so slight modifications of the parameters involved would change the predictions of the model. A more detailed treatment therefore seems to be required to describe the experimental observations on this system.

3. Survey of phase diagram calculation approach for the Al–Ce system

The CALPHAD approach is based on the optimization of many thermodynamic quantities measured experimentally (see for instance ref. 21). In order to obtain information about the behaviour of the different phases in metastable conditions, it is necessary to start from data obtained at equilibrium. In some cases, the same method has been usefully employed

to calculate phase diagrams in metastable conditions [22, 23]. Considerable success was also achieved by other workers who made use in the computing program of thermodynamic data obtained for the amorphous phase [24].

In the CALPHAD approach [21] the free enthalpy of a solution phase is expressed as

$$G_i = x_A G_A + x_B G_B - T \Delta S_{id} + \Delta G_{ex} \quad (9)$$

where G_i is the free energy of the i phase at temperature T and concentration $x_A = 1 - x_B$, G_A and G_B are the free energies of pure A and B at temperature T in the i phase, ΔS_{id} is the ideal entropy of mixing and ΔG_{ex} is the excess free energy. For line compounds the enthalpy and entropy of formation are used in eqn. (9) instead of the excess free enthalpy and ideal entropy of mixing. The equilibrium phase diagram for the Al–Ce system has recently been optimized by means of this approach [25]. The Gibbs free energies of the pure elements were derived from a fitting of collected data [26]. The liquid phase was described with ΔG_{ex} given by a Legendre polynomial:

$$\Delta G_{ex} = x_A x_B [L_{0a} - L_{0b} T + (x_A - x_B)(L_{1a} - L_{1b} T)] \quad (10)$$

with $L_{0a} = -167\,593.1$, $L_{0b} = -97.913\,27$, $L_{1a} = 36\,060$ and $L_{1b} = 11.148\,67$. The intermetallics were treated as line compounds.

As previously mentioned, the CALPHAD permits the best fitting of experimentally measured quantities at equilibrium. Therefore it must account for the presence in the Al–Ce phase diagram of liquidus equilibrium curves heavily sloping over a wide temperature range facing the two eutectics. So the Legendre polynomial which expresses the free energy of the liquid might implicitly describe its progressive ordering during cooling when extrapolated to the metastable regime.

4. Experimental details and results

In order to verify to what extent the free-enthalpy curves, computed by CALPHAD, can reproduce the actual behaviour of the liquid free enthalpy in the undercooling regime, some experiments were performed for the Al–Ce system.

Two eutectic alloys, $Al_{91}Ce_9$ and $Ce_{70}Al_{30}$, were prepared by arc melting the pure elements and were melt spun under an argon atmosphere. Their compositions lie in different parts of the phase diagram corresponding to glass-forming regions already explored [27]. The $Ce_{70}Al_{30}$ alloys were completely amorphized whereas partial formation of a glassy phase was obtained in $Al_{91}Ce_9$. Samples of the amorphous $Ce_{70}Al_{30}$ ribbon were crystallized to the equilibrium phases by heating them in a PE7 differential scanning calorimeter at 30 K min^{-1} (Fig. 2). A single exothermal crystallization peak was found to begin at 530 K, giving a heat of -6.2 kJ mol^{-1} . Bulk samples of the alloys were scanned in the differential scanning calorimeter up to their melting point. A heat of fusion of 7.9 kJ mol^{-1} at 925 K was obtained

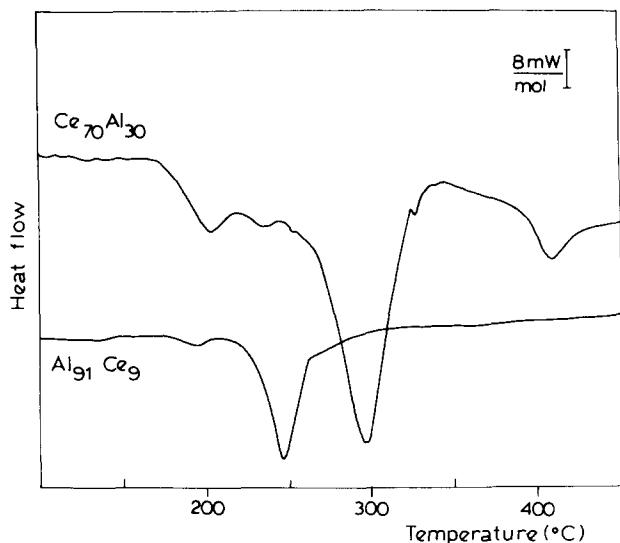


Fig. 2. Differential scanning calorimetry traces for melt-quenched $\text{Ce}_{70}\text{Al}_{30}$ and $\text{Al}_{91}\text{Ce}_9$ (heating rate, 30 K min^{-1}).

which compares well with the value of 8.6 kJ mol^{-1} reported in the literature [28]. Using the above data the average specific heat difference between liquid and crystal phases in the range from T_f to T_x was calculated from

$$\Delta C_p = \frac{\Delta H_f + \Delta H_x}{T_f - T_x} = 6.1 \text{ J mol}^{-1} \text{ K}^{-1} \quad (11)$$

An analogous calculation for $\text{Al}_{91}\text{Ce}_9$ is not possible because of partial amorphization. However, a value of $\Delta C_p = 9 \text{ kJ mol}^{-1} \text{ K}^{-1}$ was obtained for an $\text{Al}_{91}\text{Nd}_9$ alloy which crystallizes and melts at temperatures very close to those of $\text{Al}_{91}\text{Ce}_9$ with a similar heat of fusion ($\Delta H_x = -4.5 \text{ kJ mol}^{-1}$, $T_x = 450 \text{ K}$, $\Delta H_f = 9.8 \text{ kJ mol}^{-1}$ and $T_f = 918 \text{ K}$).

ΔC_p for the liquid alloy was chosen to increase with decreasing temperature up to values comparable with those reported in the literature [27, 29] (ΔC_p was around $11 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x_{\text{Al}} = 0.30$ and ΔC_p around $9\text{--}12 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x_{\text{Al}} = 0.84$) at the glass transition temperature. As commonly accepted [1, 4, 10], C_p for the liquid alloy was assumed to drop sharply at this temperature to its value in the crystalline phases.

The glass transition temperature is never manifest in our alloys, in agreement with previous findings [29]. Extrapolation of the data for ternary Al–Y–Ni [7], Al–Ce–Ni and Al–La–Ni [6, 29] to the binary Al–RE system shows that it should not exceed T_x by more than 20 K. So the usual approximation, $T_g = T_x$, seems fully justified for the binary alloys. Moreover, both the glass transition and the crystallization temperatures for systems containing different rare earths are very close; so values extrapolated from Al–La–Ni to $\text{Al}_{50}\text{La}_{50}$ (630 K) and $\text{Al}_{40}\text{La}_{60}$ (590 K) can provide a guide for

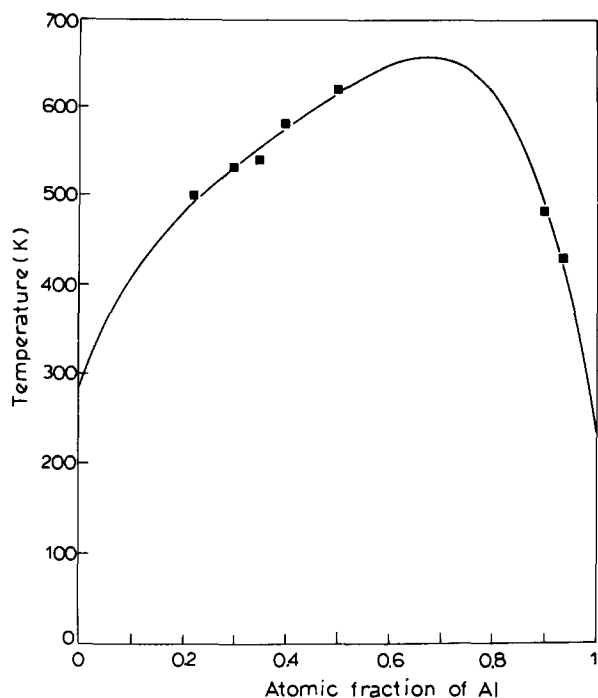


Fig. 3. Glass transition temperature for the Al-Ce system (polynomial fit).

the trend of T_g as a function of composition. In Fig. 3 the T_g trend is shown as fitted by an empirical polynomial.

5. Excess specific heat contribution for the liquid phase

The quoted CALPHAD is limited by the number of available experimental data to a linear temperature dependence; so it cannot account explicitly for any extra temperature dependence of enthalpy and entropy. If we want to know whether it takes implicitly into account the presence of an excess specific heat in the liquid phase, we must analyse the behaviour of the free enthalpy. An analysis of the specific heat trend for various glass-forming liquids yielded upper and lower limits for the values of the thermodynamic quantities frozen in on undercooling as a function of the ratio $\Delta H_x/\Delta H_f$ [30]. With the enthalpy values obtained experimentally in the present work, it is found that the entropy difference between the liquid and solid phases must lie in the range $2.15\text{--}4.1 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x_{\text{Al}}=0.91$ [30] when calculated at T_x (480 K). Using the above values for the heat of crystallization, the free enthalpy difference between amorphous and crystal phases turns out to be between -2.5 and -3.5 kJ mol^{-1} . The difference between the CALPHAD value (-8 kJ mol^{-1}) and our own estimate is more than 100% of our value, and so we are led to the conclusion that at this composition the CALPHAD

treatment [25] does not account for the specific heat contribution to the thermodynamic properties of the liquid on undercooling. On the contrary, an analogous estimate at $x_{\text{Al}}=0.30$ shows that the difference between the free enthalpies of the liquid and crystalline phases calculated at T_x with the same two approaches are of the same order. So in this composition range it appears that the excess specific heat contribution is implicitly accounted for in the Legendre polynomial describing the CALPHAD liquid.

In the aluminium-rich region the presence of an excess specific in the liquid is taken into account by adding an extra term into eqn. (9):

$$G_{\text{ex}}^* = - \int_T^{T^{\text{ref}}} C_p^{\text{ex}} dT + T \int_T^{T^{\text{ref}}} C_p^{\text{ex}} d(\ln T) \quad (12)$$

where C_p^{ex} is the excess specific heat of the liquid phase. As the liquid and crystalline pure elements have similar specific heat and the Newmann–Kopp rule is often obeyed by solid alloys, the excess specific heat can be assimilated to the difference between the specific heats of the liquid and crystal phases. A positive value of this latter quantity means that some ordering is taking place in the undercooled liquid, which loses its excess entropy with respect to the solid phases. On cooling, the entropy of the liquid would equal that of the solid at the ideal glass transition temperature T_k ; so below this temperature the excess specific heat becomes zero. To determine this limiting temperature an entropic balance based on Kauzmann's paradox [31] may be used:

$$\begin{aligned} \Delta S_{\text{for}} - \Delta S_{\text{mix}} = & x_A \Delta S_{f,A} - x_A \int_{T_g}^{T_g^A} \Delta C_{p,A} d(\ln T) \\ & + x_B \Delta S_{f,B} + x_B \int_{T_g}^{T_g^B} \Delta C_{p,B} d(\ln T) \end{aligned} \quad (13)$$

In the present paper we have estimated the glass transition temperature trend from the experimental values on crystallization temperatures for Al–Ce and Al–La [29] (taking $T_k = T_x$). In so doing, we can calculate an approximate value for the difference $\Delta S_{\text{for}} - \Delta S_{\text{mix}}$ in the intermediate compositions. The difference between the specific heats of liquid and solid pure elements is positive on undercooling; so the integrals in eqn. (13) are positive, but smaller than $\Delta S_{f,i}$. Therefore the above difference in entropies must be greater than zero if the system shows a glass-forming behaviour (mathematically, T_g values higher than the weighted average of those of pure constituent elements). In fact, we obtain a maximum difference of $9.24 \text{ J mol}^{-1} \text{ K}^{-1}$ for an aluminium content of 77 at.%.

A parabolic dependence on composition for C_p^{ex} was used. This dependence is a good approximation in the region that we are analysing because of the vicinity to pure aluminium but, as we go to compositions in the middle

of the phase diagram, the choice of this kind of fit appears arbitrary as it does not account for possible skewness of the curve. The absence of experimental information prevents us from choosing a better approximation. In Fig. 4 we show the original CALPHAD free-enthalpy curve for the liquid, the curve calculated in this work and the free enthalpy of the intermetallic compounds linked by straight lines describing two-phase equilibria. Note that, for 91 at.% Al, the difference between the free enthalpies of our calculated curve and the crystal phases is in close agreement with the expected value (-3 kJ mol^{-1}). As already stated, the CALPHAD results do not describe the undercooling behaviour of the liquid in the aluminium-rich region. The introduction of an excess specific heat contribution reconciles the calculated free-enthalpy differences between amorphous and crystal phases with experiments, in this composition range. However, if we introduce the contribution over the whole composition range, we overestimate the decreasing behaviour of the thermodynamic functions with temperature in the cerium-rich region, leading to free-enthalpy values for the liquid comparable with those for the intermetallic compounds. A CALPHAD approach making use of direct experimental information on the glassy phase will possibly give a more satisfactory description of the liquid phase also in the aluminium-rich region.

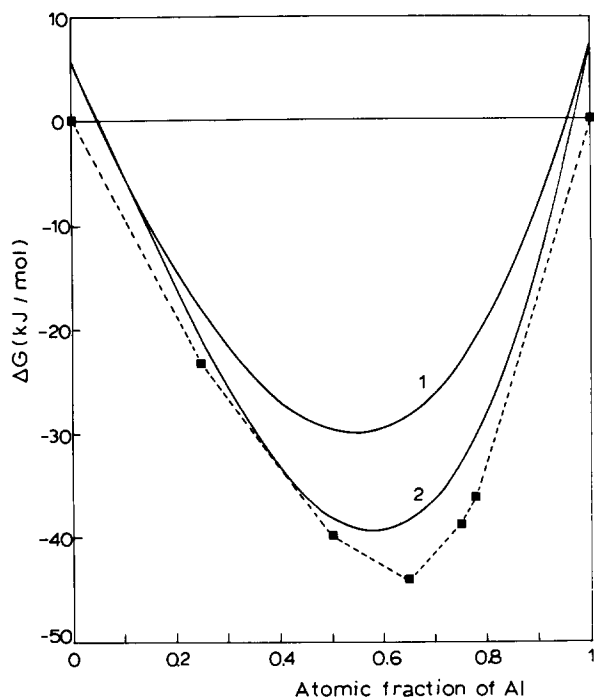


Fig. 4. Free-enthalpy diagram for the Al-Ce system at 300 K: curve 1, CALPHAD for the liquid phase; curve 2, modification of curve 1 by means of a term accounting for excess specific heat; ■, equilibrium intermetallic compounds.

6. Conclusions

To analyse the problem of amorphization in the system Al–Ce, we have used two different treatments. As a first approximation, we made use of a combination of Miedema's model for the heat of formation of alloys and classical elasticity theory. This scheme predicts a wide amorphization range at intermediate compositions but fails to describe two borderline cases under study, namely $\text{Al}_{30}\text{Ce}_{70}$ and $\text{Al}_{91}\text{Ce}_9$. A more accurate description is provided by the CALPHAD approach, which reproduces well the behaviour of the liquid phase on cooling in the cerium-rich region. This has been checked by measuring the heat of crystallization and fusion of an $\text{Al}_{30}\text{Ce}_{70}$ alloy. Analogous experiments and calculations for the aluminium-rich side show that the introduction of an excess specific heat contribution for the liquid phase is required to account for the glass-forming tendency in this region of the phase diagram.

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