# THERMODYNAMICS OF ALLOY FORMATION

Edited by
Y. Austin Chang
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THERMODYNAMICS

OF

ALLOY FORMATION

Proceedings of a symposium sponsored by the Alloy Phase Committee
of the joint EMPMD/SMD of the Minerals, Metals, and Materials Society, held
at the Annual Meeting in Orlando, Florida, USA, February 9-13, 1997
to honor the W. Hume-Rothery Award recipient, Professor Bruno Predel
of the Max-Planck Institut für Metallforschung at Stuttgart, Germany.
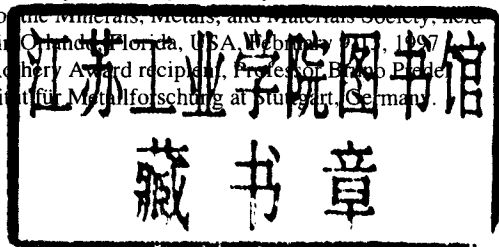
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FOREWORD

The symposium on the Thermodynamics of Alloy Formation was organized by the Alloy Phase Committee of the joint EMPMD/SMD of the Metals, Minerals and Materials Society (TMS) to honor the 1997 W. Hume-Rothery Award recipient, Professor Bruno Predel of the Max-Planck Institut für Metallforschung at Stuttgart, Germany. The primary objective of this symposium was to demonstrate the impact of key experimental measurements on our understanding of alloy behavior, in not only the stable but also the metastable state. Moreover, the results obtained from these measurements provide data essential in developing thermodynamic models of alloy phases to calculate/predict phase diagrams for related materials research and for practical applications in industry. Prof. Predel has, of course, been a key world leader in the use of traditional and innovative experimental methods to generate reliable data in the effort to better understand the energetics of alloy formation, a field pioneered by the late W. Hume-Rothery.

This symposium consists of three sessions. The first session is devoted to experimental measurements of thermodynamic properties of alloys, in both liquid and solid states. The second session focuses on the structure and thermodynamics of liquid and amorphous states; a paper on diffusion is included in this session, since attainment of the metastable state is due to the relative kinetics of atom movement. The third session is devoted to thermodynamic models and phase diagram calculations.

All of the symposium participants were invited to submit chapters for this volume. Of the seventeen participants, one is from Austria, one from France, eight from Germany, one from Italy, one from Japan, one from India, and four from the United States. It is our belief and hope that this publication will serve as a valuable reference for future generations of researchers in the field of materials science.

We wish to thank all invited participants, and several of our colleagues, for their contributions to this symposium. We want to specifically mention the help of Prof. J. F. Smith of Iowa State University for the early planning of the symposium. We would like to also mention the help of David Chen in Prof. Chang's group working with John Couper in editing and formatting the manuscripts for publication. We also thank Dr. S.-L. Chen, Ms. Helen Liang, Dr. Zi-Kui Liu, Mr. Fanyou Xie and Ms. Fan Zhang, all in Prof. Chang's group, for reading and reformatting many of the manuscripts and Ms. Lynn Neis for re-typing one of the manuscripts. Without their help, we would not have been able to publish the book in time for the symposium at the 1997 TMS Annual Meeting.

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CONSTITUTION AND THERMODYNAMICS OF

MONOTECTIC ALLOYS - A SURVEY

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Abstract

As is well known, melts that have passed a miscibility gap in the liquid state will, on cooling, solidify to a regulus consisting of two layers. Such bodies are not interesting for technical applications, and have rarely been investigated. Genuine interest in demixing systems only arose once it seemed possible to prevent layer formation in zero gravity. However, experiments in space have shown that, even under migro-g conditions, phase seperation occurs, though in a different way than on earth. This resulted in an intensive disclosure of the thermodynamics and the kinetics of the separation of liquid immiscible phases. After a discussion of the results obtained, the paper suggests how to prevent layer formation, and how to effect a finely-dispersed structure to enable technical use.

Introduction

In the past, systems that tend to form intermetallic phases have been of special interest. Of course, this is understandable if one is thinking of the possibilities of the technical application of these systems. On the other hand, alloys of systems that exhibit an extensive miscibility gap in the liquid state had no technical importance, at least about 40 years ago.
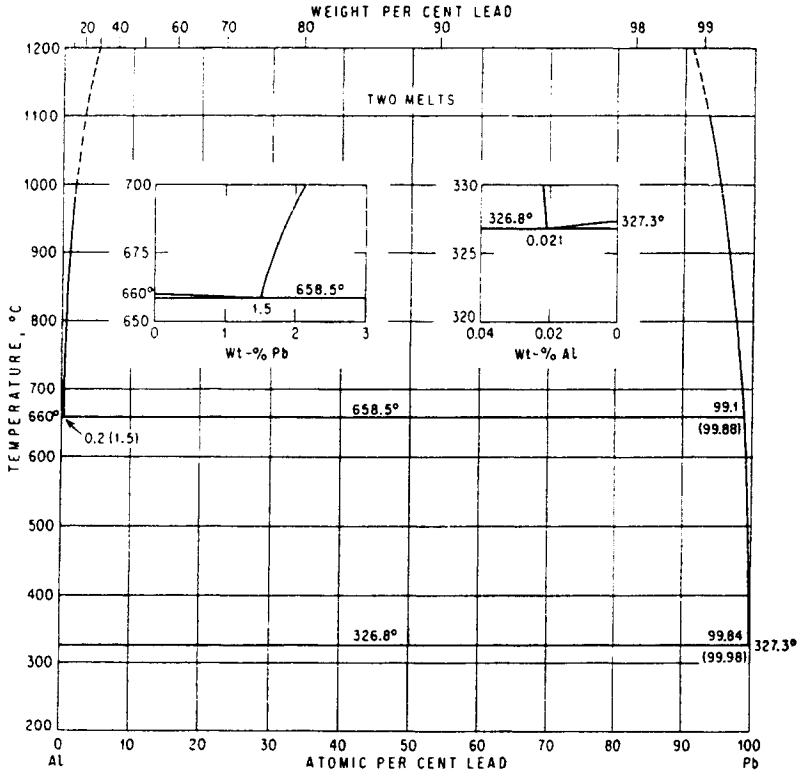
Figure 1 - Al-Pb phase diagram taken from Hansen et al. [58Han]

Fig. 1 represents the Al-Pb phase diagram, as taken from the compilation of Hansen et al. [58Han]. The miscibility gap in the liquid state is known only in the region of the monotectic temperature. An alloy which is single-phase at high temperatures passes the miscibility gap on cooling (see Fig. 2). During this process both liquid phases— due to their different densities— separate into two layers, one above the other. Subsequently, both melts solidify to a regulus, as shematically depicted in Fig. 2. Such a regulus has no value for technical applications.

Figure 2 - Schematic representation of layer formation in a system with demixing tendency

Thermodynamics of alloys with demixing tendency

With respect to their thermodynamics, systems with a miscibility gap have also been considered rather boring. To simplifying, the regular solution model has been applied. According to that, for the enthalpy of mixing, there is:

$$\Delta H = H^\circ \, x_A \left(1 - x_A\right) \qquad (1)$$

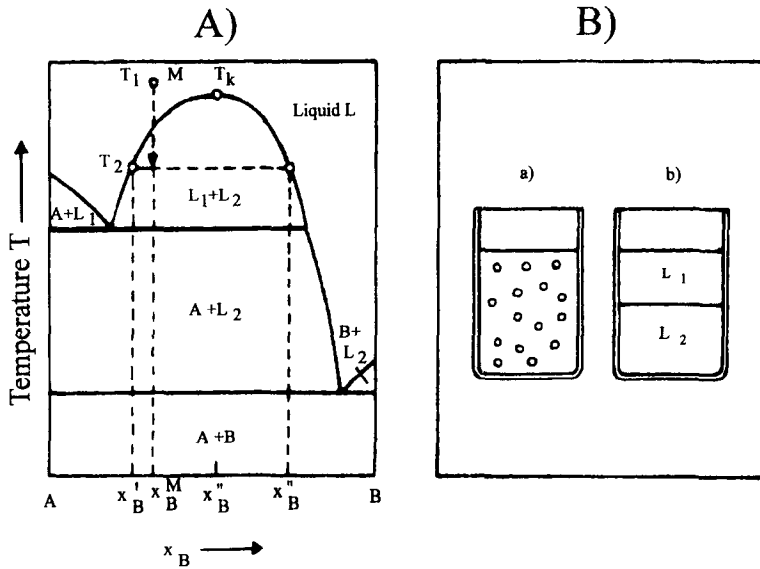x_A, $x_B = 1-x_A$ are the mole fractions.

As is well known, the concentration dependence of the ideal entropy of mixing, ΔS_i as it is given for a random atomic distribution, is composed in the following way:

$$\Delta S_i = -R \left[x_A \, \ln x_A + x_B \, \ln x_B\right] \qquad (2)$$

ΔH° is a constant containing the coordination number. R = General Gas Constant.

Applying the regular solution model, the enthalpy of mixing has to be symmetrical, as is demonstrated; an example for $\Delta H^\circ = 10^4$ J/g-atom in Figure 3. The same is true for the ideal entropy of mixing. Accordingly, the miscibility gap has to be symmetrical (Fig. 4).

The simplifying treatment has changed somewhat during recent years.
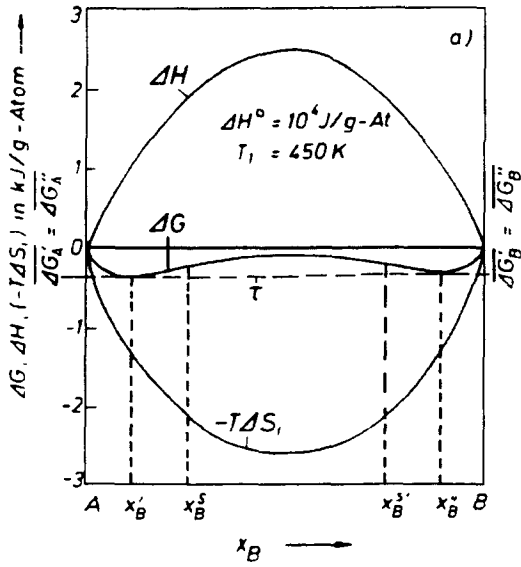
Figure 3 - Thermodynamic functions of a regular solution with $\Delta H° = 10^4$ J/g-atom at $T_1 = 450K$.
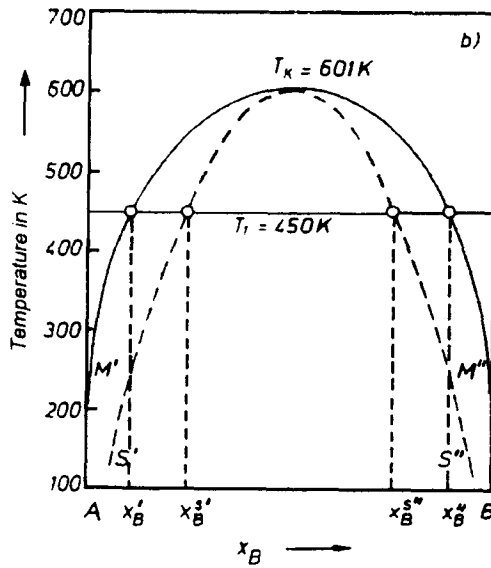
Figure 4 - Miscibility gap of a regular solution with energetic data of Figure 3.

There are indeed miscibility gaps that are nearly symmetrical, just as the regular solution model demands. An example is the following Hg-Ga phase diagram (Fig. 5).
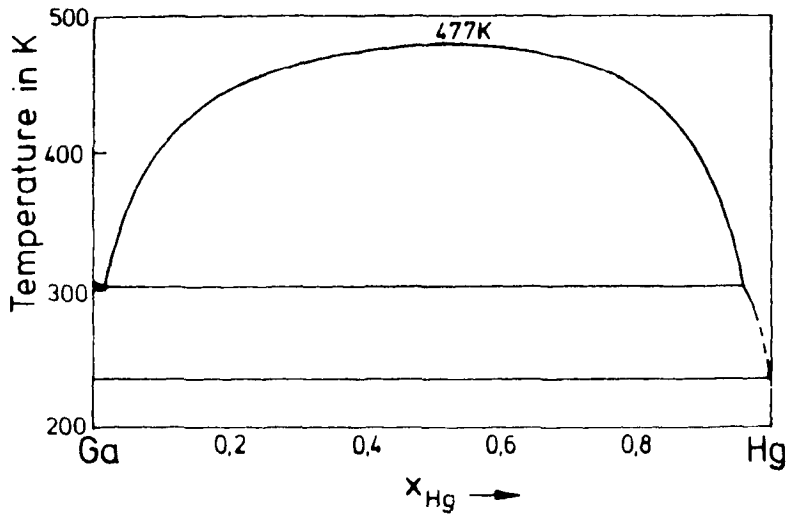
Figure 5 - Phase diagram of the Hg-Ga system [60Pre].

The Bi-Ga and Bi-Zn systems ought to be mentioned as examples of asymmetrical miscibility gaps (Fig. 6, Fig. 7). This shape of miscibility gaps cannot be described by the simple regular solution model.

Figure 6 - Phase diagram of the Bi-Ga system [60Pre, 65Ell].

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Figure 7 - Phase diagram of the Bi-Zn system [65Ell].

An important factor is the influence of the difference between the atomic radii of the components. In order to emphasize this influence, the critical demixing temperature Tc is considered. In Fig. 8, it is plotted as a function of the difference of the atomic rad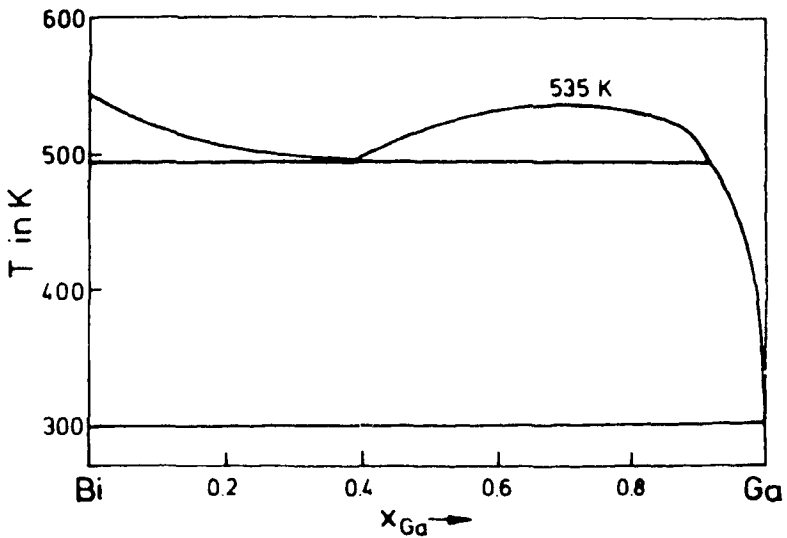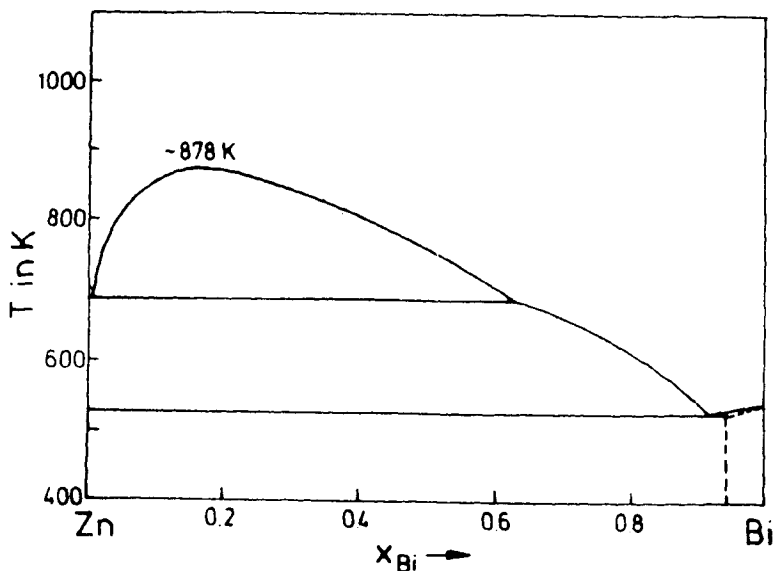ii. For simplification, systems were chosen in which one partner always remains the same, to maintain constant possible bonding influences. Fig. 8a represents such a plot for lead systems. With increasing difference of the radii, the critical demixing temperature Tc also increases. This is immediately connected with the maximal enthalpy of mixing ΔH^L, which, in Fig. 8b, is plotted against the difference of the atomic radii. The bigger the atomic radii difference d, the bigger the positive maximum enthalpy of mixing. Therefore, the bigger the misfit energy, the smaller the mutual solubility of the components [66Pre, 80Pre].
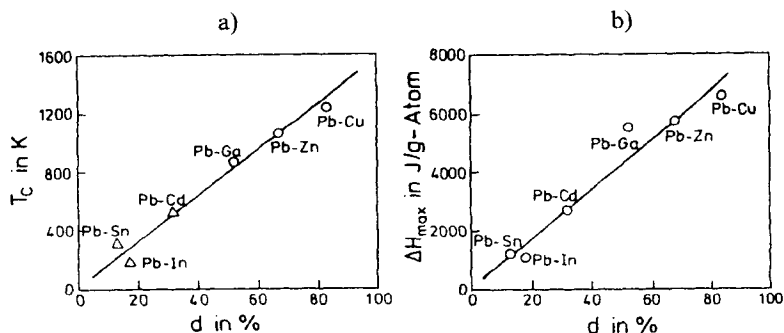

Figure 8 - T_C and ΔH_{max} as a function of atomic radii difference do = experimental; Δ = calculated [66Pre, 80Pre].
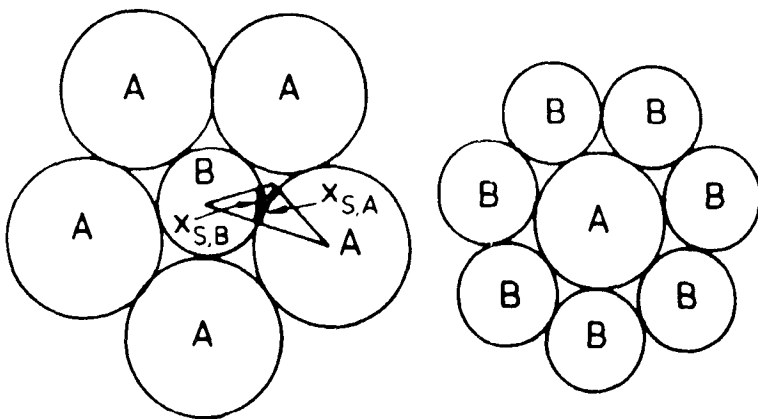
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Figure 9 - Coordination number and atomic radii differences (see [87Pre])

The influence of the coordination number depending on radii differences is shown in Fig. 9. In this case, $x_{S,A}$ and $x_{S,B}$ are the fractions of atomic surface, which are taking part in the interatomic interaction. The quantities $x_{S,A}$ and $x_{S,B}$ have to be inserted, replacing x_A and x_B, respectively, in the regular solution model. The relationship between these quantities is given by:

$$x_{S,A} = \frac{x_A\, r_A^2}{x_A\, r_A^2 + x_B\, r_B^2} \quad , \quad x_{S,B} = \frac{x_B\, r_B^2}{x_A\, r_A^2 + x_B\, r_B^2} \tag{3}$$

r_A, r_B = atomic radii.

These considerations can be traced back to Lacman [62Lac] and Miedema [76Mie]. The enthalpy of mixing is now expressed by:

$$\Delta H = C_{reg}\, x_{S,A}\, x_{S,B} \tag{4}$$

To correctly express the entropy of mixing if there is a radii difference, Flory [42Flo] and Huggins [42Hug] have modified equation (2), (see Lück et al. [86Lüc]). In this case, the molar fractions have to be replaced by the volume fractions:

$$x_{V,A} = \frac{x_A\, r_A^3}{x_A\, r_A^3 + x_B\, r_B^3} \quad , \quad x_{V,B} = \frac{x_B\, r_B^3}{x_A\, r_A^3 + x_B\, r_B^3} \tag{5}$$

The entropy of mixing has to be written:

$$\Delta S = -R\left(x_{V,A}\, \ln x_{V,A} + x_{V,B}\, \ln x_{V,B}\right) \tag{6}$$

On the basis of the quasichemical approximation, Guggenheim [52Gug] and Münster [62Mün] have disclosed further terms for the Gibbs Free Energy. The final relationship is:

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$$\Delta G = RT\left(x_{V,A}\,\ln x_{V,A} + x_{V,B}\,\ln x_{V,B}\right) + C_{reg}\,x_{S,A}\,x_{S,B}$$

$$+ \left[\frac{2RT}{Z} + C_{reg} - \frac{2RT}{Z}\exp\left(\frac{C_{reg}\,Z}{2RT}\right)\right]x_{S,A}^{2}\,x_{S,B}^{2} \tag{7}$$

$$+ \left[\frac{6RT}{Z} + 2C_{reg} - \frac{8RT}{Z}\exp\left(\frac{C_{reg}\,Z}{2RT}\right) + \frac{2RT}{Z}\exp\left(\frac{C_{reg}\,Z}{RT}\right)\right]x_{S,A}^{3}\,x_{S,B}^{3}$$

where Z = coordination number. At high temperatures, all terms except the first two can be neglected.
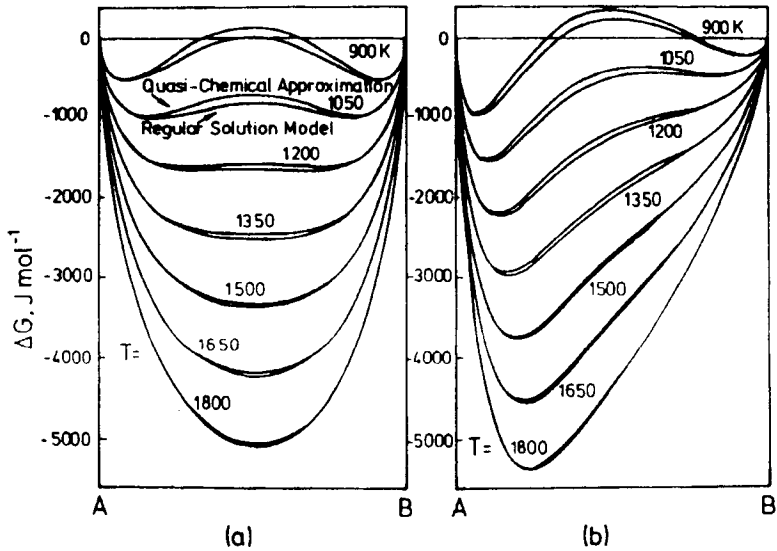

Figure 10 - Gibbs free enthalpies of mixing (see [87Pre])
a) for systems with equal atomic radii
b) for a system with $r_A/r_B = 1.33$

The effect of the atomic radii difference is shown in Fig. 10 ($\Delta H^\circ = 10^4$ J/g-atom). Fig. 10a represents ΔG-x curves at equality of the radii of the two kinds of atoms. Fig. 10b shows the asymmetry for the case where $r_B/r_A = 1.33$. With increasing temperature, in Fig. 10b the ΔG-x curves become more similar. As already stated, with increasing temperatures, the influence of the higher terms (from the 3rd term upward) is more and more decreasing.

Miscibility Gaps in Systems with Strong Tendencies toward Compound Formation

An example is the Ag-Te system (Sommer [82Som]). Fig. 11 shows the phase diagram for $x_{Te} <$
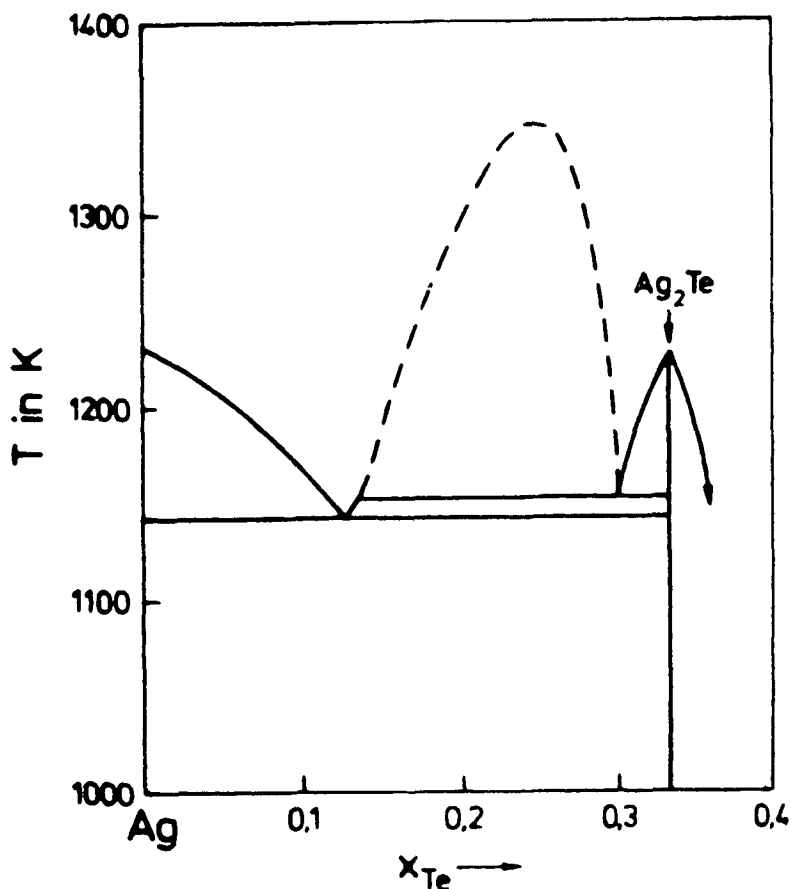
Figure 11 - Partial phase diagram of the Ag-Te system [82Som]

0.4. In addition to an intermetallic phase Ag_2Te, in the liquid state a miscibility gap occurs. Here, the atomic structure of the melt plays an important role.

In addition to the monoatomic species Ag and Te, molecule-like associations Ag_2Te are present in the melt. Generally, in such cases there is:

$$iA_1 + jB_1 \Leftrightarrow AiBj \qquad (8)$$

i and j are the stoichiometric coefficients of the associations.

For the total number of moles, there is:

$$n = n_{A_1} + n_{B_1} + n_{AiBj} \qquad (9)$$

Here, n_{A_1}, n_{B_1}, n_{AiBj} are the numbers of moles of A_1, B_1, and AiBj.

The association equilibrium must be in accordance with the mass action law:

$$\frac{x_{A_1}^i \, x_{B_1}^j}{x_{AiBj}} = \frac{1}{K_{AiBj}} \qquad (10)$$

For the concentration dependence of the enthalpy of mixing results:

$$\Delta H = \Delta H^o_{A_1 B_1} \frac{n_{A_1} \, n_{B_1}}{n} + \Delta H^o_{A_1, AiBj} \frac{n_{A_1} \, n_{AiBj}}{n}$$
$$+ \Delta H^o_{B_1, AiBj} \frac{n_{B_1} \, n_{AiBj}}{n} + n_{AiBj} \, \Delta H^o_{AiBj} \qquad (11)$$

$\Delta H^o_{A_1,B_1}, \Delta H^o_{A_1,AiBj}, \Delta H^o_{B_1,AiBj}$ are the constants of the interaction between the species characterized by indexes. In the case of the presence of an association equilibrium, the concentration dependence of the entropy of mixing may be given by:

$$\Delta S = - R \left(n_{A_1} \ln x_{A_1} + n_{B_1} \ln x_{B_1} + n_{AiBj} \ln x_{AiBj} \right) + n_{AiBj} \, \Delta S^o_{AiBj} \qquad (12)$$

where ΔS^o_{AiBj} = molar entropy of formation of the associates.

The ΔH-x curve has a triangular shape, with its apex at the stoichiometry of the associations (Ag_2Te, see Fig. 12). The ΔH-values between 0 and 33 at.% Te deviate from the straight line plotted in the figure to lower negative values. This is due to an interaction between the associations and the Ag atoms in the melt (second term in equation (11)). This indicates a demixing tendency in this concentration range. Results of thermodynamic calculations carried out by Sommer [82Som] indeed show a miscibility gap in the liquid state in this region (see Fig. 11).
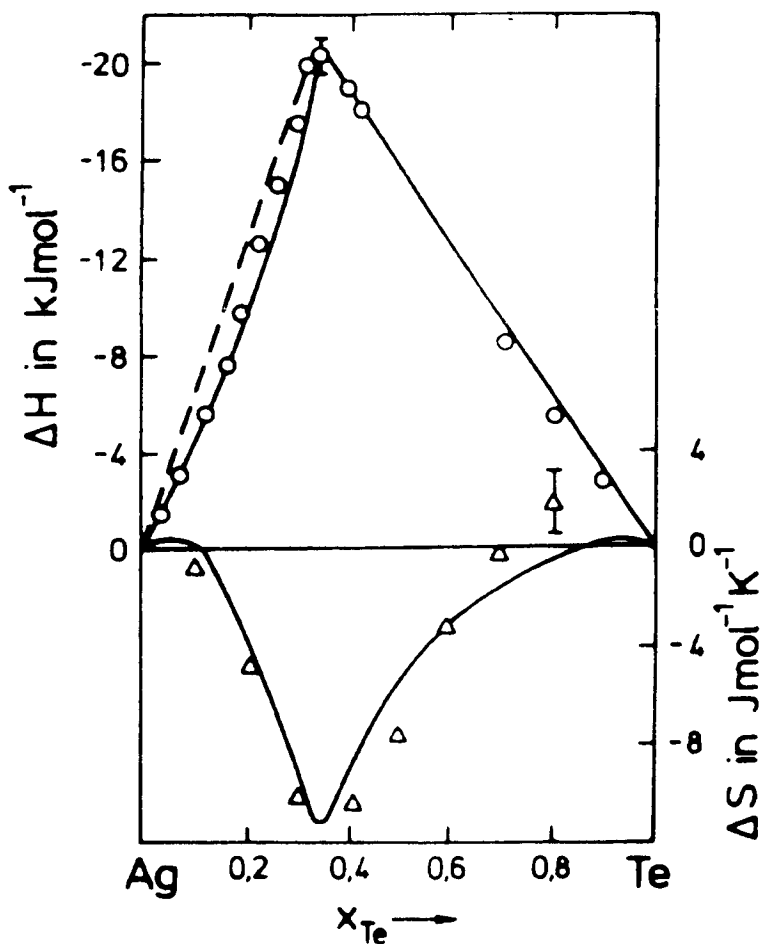
Figure 12 - Thermodynamic functions of the Ag-Te system [82Som]

Further Examples of the Occurrence of Miscibility Gaps in the Liquid State

As mentioned before, miscibility gaps in the liquid state may also occur in systems with compound formation tendency. But, in most cases, they are typical in systems that have a rather high value of positive ΔH^L. This positive ΔH^L value may result from different features. Some more examples may be mentioned.

Miscibility gaps in the liquid state occur in some systems that are composed of a transition metal and a main group element. An example is the Ni-Pb system. For many such systems, the shape of the miscibility gap is not yet known.

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