

Concentration fluctuations and surface tension in liquid Au-Sn-Zn

P. TERZIEFF

Institute of Inorganic Chemistry, University of Vienna, Währingerstrasse 42, A-1090 Wien, Austria

Experimental thermodynamic data were applied to calculate the surface tension and the long-wavelength limit of the concentration-concentration fluctuations $S_{cc}(0)$ in the ternary system Au-Sn-Zn. The fluctuations in the concentration of Zn and in particular those of Sn show marked maxima around $Au_{15}Sn_{30}Zn_{55}$ whereas for Au the fluctuations are smaller than those of a non-interacting ideal mixture. Over an extremely wide range of compositions the surface layer of the ternary is found to be primarily populated by Sn atoms. Excepting the alloys with larger amounts of Au ($c_{Au} > 0.3$) or high contents of Zn ($c_{Zn} > 0.7$) the surface tension is not very different from that of pure by Sn ($0.52\text{--}0.60\text{ Nm}^{-1}$). The progressive substitution of Sn by Zn at a constant value of $c_{Au} \approx 0.3$ leaves the surface tension practically constant up to $c_{Zn} \approx 0.5$. In sections of constant c_{Au}/c_{Sn} with $c_{Au}/c_{Sn} > 0.3$ the surface tension is observed to even pass through pronounced minima if larger amounts of Zn are added. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Over the past few years, environment-related objections to the use of conventional Pb-Sn solders in the interconnection and packaging of electronic components have led to new developments. Presently, substantial efforts are being made to eliminate lead from all kinds of applications. There are many alternative solder materials with promising properties, primarily multicomponent alloys based on the elements Ag, Cu, Sn, Sb, Bi, In and Zn. Most of them do not meet the requirement of low-cost, suitable operating temperatures, low electrical resistivity, high corrosion resistance, good wettability and appropriate mechanical properties at the same time. A comprehensive review of the current developments in the field is given by Abteu and Selvaduray [1].

Among the numerous candidates which have been investigated the most attractive group is that based on Sn-Zn, Ag-Sn and Cu-Sn. Eutectic or near-eutectic Sn-Zn (Sn-9 wt%Zn) solders, as an example, stand for low operating temperatures and inexpensive solder joints of good mechanical stability [2, 3]. However, due to the high activity of Zn the corrosion resistance of these alloys is unacceptable and the wetting properties are rather poor [2, 4]. Sn-based alloys with noble metal additions (Cu, Ag, Au) such as eutectic Ag-Sn (Sn-3.5 wt%Ag), on the other hand, are widely recommended since they combine a reasonable wetting behaviour with a high ductility [5–7]. It has been reported that the addition of Ag to alloys of Sn-Zn enhances the wetting ability and increases the ductility thus giving rise to a high mechanical stability of the solder joint [7–9]. Minor additions of Cu to Ag-Sn-Zn, in turn, were found to be useful to keep the ductility at the high level of binary Ag-Sn [7]. Furthermore, thermodynamic data indicate

that the activity of Zn and thus the sensitivity to corrosion is strongly reduced if Zn is alloyed with noble metals [10]. As a matter of fact, Sn based alloys with small additions of Zn, Ag and Cu have been taken into serious consideration as potential substitutes of traditional Pb-Sn solders [3, 7].

In some preceding papers the thermodynamic properties of liquid Cu-Sn-Zn, Ag-Sn-Zn and Au-Sn-Zn have been examined in order to provide further information on this class of systems [11–13]. So far, Au has been less taken into account as an alloying element, since its addition to Sn-Zn increases the cost and has practically no effect on the wettability of the solder [9]. However, emphasizing the corrosion resistance of these systems Au-Sn-Zn seems to be the most potential candidate since the addition of Au reduces the activity of Zn more effectively than Cu or Ag [10].

One of the key factors to minimize the contact angle between the solder and the substrate so as to improve the wettability is the surface tension of the solder. Experimental data on multicomponent systems are scarce, in particular if one of the constituents has a high melting temperature. This paper was aimed at evaluating the surface tension of the ternary system Au-Sn-Zn by combining Butler's model of surface tension [14] with the thermodynamic data of the system.

From the purely academic point of view, the ternary system is made up of binaries of definitely different character. Judged by the enthalpy of mixing Au-Sn and Au-Zn are exothermic compound-forming systems [15, 16], whereas Sn-Zn is endothermic and tends to demixing [17]. In this paper the behaviour of the ternary system will be analyzed in terms of the

concentration-concentration fluctuations in the long-wavelength limit $S_{cc}^{ij}(0)$ which are a measure of the mean square concentration fluctuations in the liquid. It was of interest to find out how the concentration fluctuations correlate with the variation of the surface tension in the ternary system.

2. Method

The concentration-concentration fluctuations $S_{cc}^{ij}(0)$ in the long wavelength limit were evaluated in terms of the second derivatives of the Gibbs free energy G^m of mixing with respect to the alloy compositions c_i, c_j :

$$G_{ij} = \left(\frac{\partial^2 G^m}{\partial c_i \partial c_j} \right)_{P,T,c'} \quad (1)$$

The subscript c' implies that the compositions not involved in the differentiation are held constant. This paper was concerned with the concentration-concentration fluctuations of like species ($i = j$) which according to the expression of Bhatia and Ratti [18] are given as

$$S_{cc}^{ii}(0) = \frac{Nk_B T G_{jj}}{G_{ii} \cdot G_{jj} - G_{ij} \cdot G_{ij}} \quad (2)$$

More details on the theoretical background and formalism are given in their original article. The evaluation was based on the experimental values of G^m reported by Karlhuber *et al.* [12]. For practical use throughout the paper the excess free energy of mixing G^{xs} was represented by the multi-parameter model of Lee *et al.* [19]:

$$\begin{aligned} \frac{G^{xs}}{RT} = & \sum_{i=1}^3 \sum_{j>1}^3 c_i c_j \{ a_1^{ij} c_i + a_2^{ij} c_j + c_i c_j (a_3^{ij} c_i + a_4^{ij} c_j) \} \\ & + c_1 c_2 c_3 \sum_{k=1}^3 a_k^{123} c_k \end{aligned} \quad (3)$$

Starting from the basic assumption that the chemical potential of each individual component in the surface layer is equal to its chemical potential in the bulk plus the surface energy, Butler [14] derived the equation

$$\sigma = \sigma_i + \frac{RT}{s_i} \ln \frac{c_i^m}{c_i} + \frac{RT}{s_i} \ln \frac{\gamma_i^m}{\gamma_i} \quad (4)$$

where σ is the surface tension of the alloy, σ_i that of the i -th component, c_i and c_i^m are the atomic fractions of the i -th component in the bulk and the surface monolayer, respectively; γ_i and γ_i^m are the corresponding thermodynamic activity coefficients. Based on the argumentation that the free energy of the alloy is due to pair-wise interactions between the atoms, γ_i and γ_i^m can be related to the ratio of the respective coordination numbers [20]:

$$\ln \gamma_i^m / \ln \gamma_i = z^m / z \quad (5)$$

Considering a close packed structure as reference for dense liquids the coordination number is assumed to be $z \approx 12$ for the bulk and $z^m \approx 9$ for the surface layer which gives an estimate of $z^m/z \approx 0.75$. The activity coefficients are related to the derivative of the Gibbs free energy in the usual manner via

$$\ln \gamma_i = \frac{1}{RT} \cdot \left(\frac{\partial G^m}{\partial c_i} \right)_{P,T,c} - \ln c_i \quad (6)$$

The analytical expressions of $\ln \gamma_i$ obtained from Equation 3 are lengthy and are given in [19]. A graphical method of differentiating G^m was also applied to control the values of γ_i .

The molar surface area s_i of the pure components were computed from the molar volumes V_i of the pure liquids according to [21]

$$s_i = b \cdot N_A^{1/3} \cdot V_i^{2/3} \quad (7)$$

The geometric factor b was given the value of 1.091 which is assumed to be representative of close packed structures [22]. The input data for the molar volumes were taken from the compilation of Crawley [23]. The reference temperature throughout the paper was 973 K. The surface tensions of the elements at their melting points and the respective temperature coefficients for the conversion to the reference temperature were those given by Iida and Guthrie [24]. If not stated otherwise the compositions are given as atomic fractions or atomic percent.

Equation 4 holds for each constituent of the system, therefore the solution of the problem is to find the set of surface concentrations (c_1^m, c_2^m, c_3^m) which satisfies all three equations simultaneously.

3. Results and discussion

In order to give a complete picture of the concentration fluctuations across the ternary field the individual values of $S_{cc}^{ii}(0)$ were evaluated for all three constituents. The values of $S_{cc}^{AuAu}(0)$, $S_{cc}^{SnSn}(0)$ and $S_{cc}^{ZnZn}(0)$ which are shown in Figs 1–3 refer to the difference to the ideal

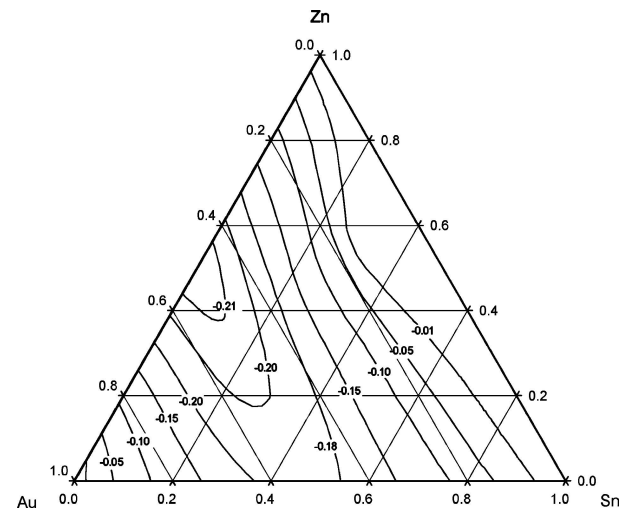


Figure 1 Concentration fluctuations $S_{cc}^{AuAu}(0) - S_{cc}^{AuAu}(0)_{id}$ in liquid Au-Sn-Zn in the long-wavelength limit at 973 K.

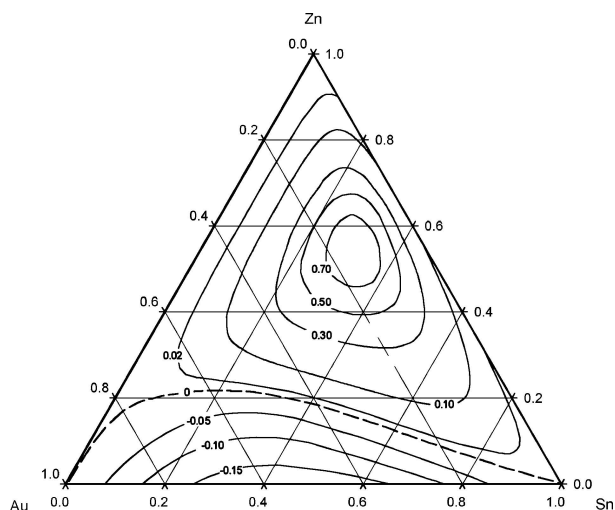


Figure 2 Concentration fluctuations $S_{cc}^{SnSn}(0) - S_{cc,id}^{SnSn}(0)$ in liquid Au-Sn-Zn in the long-wavelength limit at 973 K.

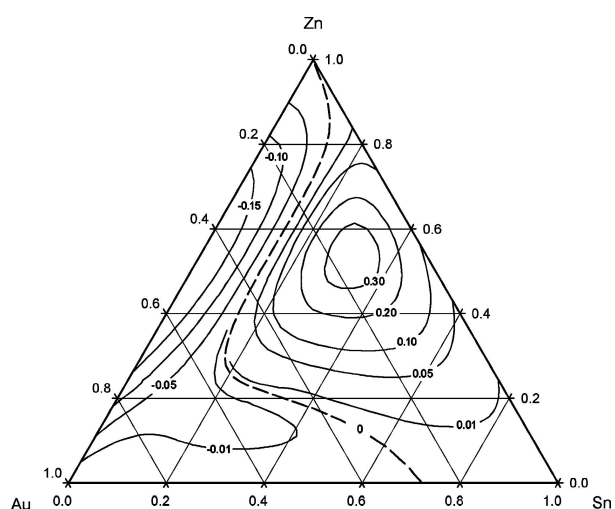


Figure 3 Concentration fluctuations $S_{cc}^{ZnZn}(0) - S_{cc,id}^{ZnZn}(0)$ in liquid Au-Sn-Zn in the long-wavelength limit at 973 K.

value so as to emphasize the deviations from the ideal behaviour ($S_{cc}^{ii}(0) = S_{cc}^{ii}(0) - S_{cc,id}^{ii}(0)$ and $S_{cc,id}^{ii}(0) = c_i(1 - c_i)$). The results obtained for $S_{cc}^{AuAu}(0)$ indicate reduced fluctuations in the section from $Au_{50}Zn_{50}$ to $Au_{55}Sn_{45}$ which are thermodynamically also the most stable compositions in the binaries [12]. Both $S_{cc}^{SnSn}(0)$ and $S_{cc}^{ZnZn}(0)$ signalize highly increased concentration fluctuations which are extremely pronounced around $Au_{15}Sn_{30}Zn_{55}$. The difference in the profile at $S_{cc}(0) = 0$ (i.e. those compositions where the fluctuations adopt the ideal values) is due to the obviously more attractive nature of the interactions in Au-Zn as compared to Au-Sn [15, 16].

As regards the surface tension of the pure metals at the reference temperature Sn has the lowest surface tension (0.52 Nm^{-1}), followed by Zn (0.73 Nm^{-1}) and Au (1.26 Nm^{-1}). It is known that neither ideal nor real binary mixtures display a linear surface tension—composition relationship. According to the present calculations and the existing experimental results [25–27] this is also the case for Au-Sn, Au-Zn and Sn-Zn. The marked positive deviations from the ideal curve indicated for Au-Sn and Au-Zn are associated with the attractive interactions in the systems (Figs 4a–c).

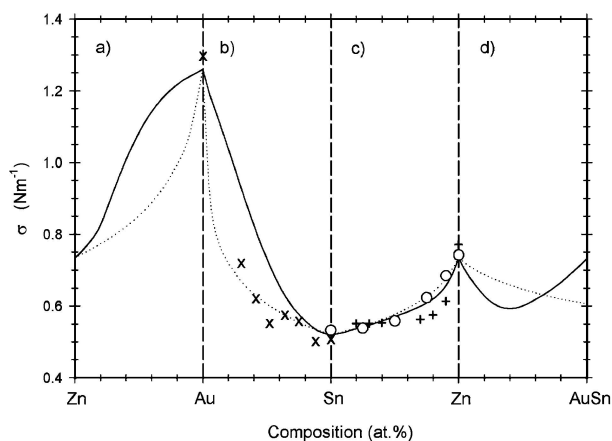


Figure 4 Calculated (—, 973 K) and experimental (x, o, +) surface tension in liquid alloys of (a) Au-Zn, (b) Au-Sn (x 1023 K [25]), (c) Sn-Zn (o 973 K [26], + 700 K [27]), (d) Zn - $Au_{50}Sn_{50}$ in comparison with the values obtained for ideal mixtures (.....).

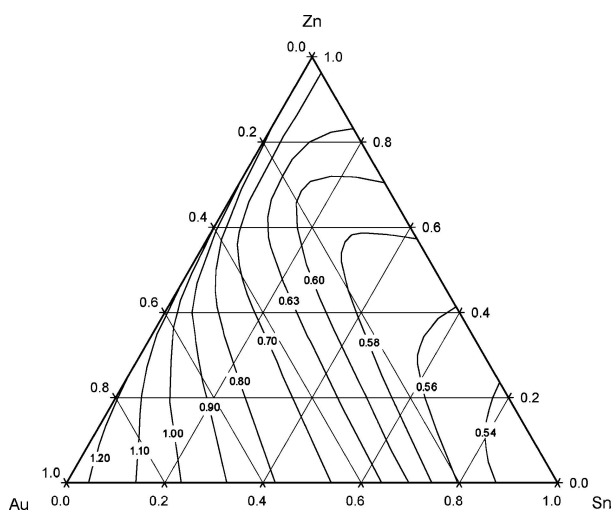


Figure 5 Surface tension in liquid Au-Sn-Zn at 973 K.

In contrast to the binaries, the ternary system shows a highly exceptional behaviour which could be of special interest from the application point of view (Fig. 5). It is evident that starting from pure Sn the addition of Au - and in particular that of Zn- has only a small effect on the surface tension. Along the section with a constant Au-content of $c_{Au} = 0.30$ the surface tension remains nearly constant ($\sigma \approx 0.6 \text{ Nm}^{-1}$) from $c_{Zn} \approx 0$ up to $c_{Zn} \approx 0.5$. In the section with $c_{Au}/c_{Sn} = 1$ (Fig. 4d) the surface tension passes even through a pronounced minimum at $Au_{20}Sn_{20}Zn_{60}$ with a surface tension of 0.59 Nm^{-1} which is not much higher than that of pure Sn at the melting point (0.56 Nm^{-1}). The findings imply that adding small amounts of Au to eutectic $Sn_{86}Zn_{14}$ or even large amounts of Zn to eutectic $Au_{06}Sn_{94}$ would not increase the surface tension to an appreciable extent. The very distinguished shape of the surface tension vs composition relationship near the Sn-Zn side of the system allows for large variations in composition without losing the benefit of a low surface tension.

Basically, this is the consequence of the preferential segregation of Sn-atoms into the surface layer. Fig. 6 shows that over an extremely wide range of compositions the surface layer is primarily occupied by Sn

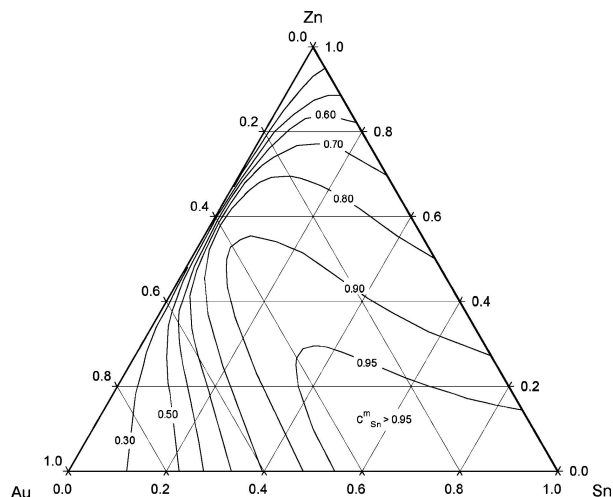


Figure 6 Surface concentration of Sn in liquid Au-Sn-Zn at 973 K.

atoms which, in turn, is responsible for a low surface tension and a reduced surface energy. The most striking feature is that the boundary of $c_{\text{Sn}}^m \geq 0.90$ extends far towards the Au-Zn side. In fact, it is a remarkable result that at the nominal composition of $\text{Au}_{40}\text{Sn}_{10}\text{Zn}_{50}$ still more than 90% of the surface atoms are Sn atoms. It seems that—excepting the very vicinity of Au or Zn—the surface tension of the ternary is mainly dominated by Sn-atoms.

The results on $S_{cc}^{ii}(0)$ hint at a close relationship between the concentration fluctuations and the segregation tendency: the larger the fluctuations in the concentration the more the individual constituent tends to segregate to the surface.

Due to $S_{cc}^{\text{SnSn}}(0) \geq S_{cc}^{\text{ZnZn}}(0) > S_{cc}^{\text{AuAu}}(0)$ it can be assumed that Sn-atoms have the strongest tendency to segregate to the surface. However, it is also clear that as the concentration of Sn decreases Zn-atoms tend to populate the surface layer which is in fact responsible for the decrease of c_{Sn}^m toward the Zn-rich corner of the system. Towards the Au-rich corner $S_{cc}^{\text{SnSn}}(0)$ itself tends to negative values—i.e. $S_{cc}^{\text{SnSn}}(0) < S_{cc,\text{id}}^{\text{SnSn}}(0)$ —and therefore c_{Sn}^m is expected to decrease. The minimum of $S_{cc}^{\text{ZnZn}}(0)$ around $\text{Au}_{50}\text{Zn}_{50}$ signals that in this particular direction (e.g. in the section from Sn to $\text{Au}_{50}\text{Zn}_{50}$) Zn-atoms are not in competition with Sn-atoms in segregating to the surface. This substantiates why the boundary $c_{\text{Sn}}^m \geq 0.90$ extends so far towards the Au-Zn side.

The most obvious correlation is that between the concentration fluctuations and the surface tension itself. It is apparent from Fig. 5 that the range of low surface tension ($\sigma < 0.60 \text{ Nm}^{-1}$) comprises definitely those compositions where $S_{cc}^{\text{SnSn}}(0)$ and $S_{cc}^{\text{ZnZn}}(0)$ have their distinguished maxima (Figs. 2 and 3). Based on a phenomenological theory Bhatia and March [28] have related the surface tension of a binary system to the concentration-concentration fluctuations $S_{cc}(0)$ via

$$\sigma \sim \frac{L}{\kappa_T} \cdot \frac{1}{1 + \delta^2 \cdot S_{cc}(0)/nk_B T} \kappa_T \quad (8)$$

L is the thickness of the surface layer, κ_T the isothermal compressibility, δ a size difference factor, and n is the

number density. Equation 8 makes plausible that large fluctuations in the concentration favour a small surface tension.

4. Conclusion

While Cu and Ag are potential additives in multi-component Sn-based solders such as Ag-Cu-Sn or Ag-Sn-Zn, the use of Au has not been taken into consideration. The parameters discussed in this paper are only a small contribution to the subject, however, they may serve as valuable information for optimizing the performance of lead-free solder materials. The advantages of a eutectic $\text{Au}_{06}\text{Sn}_{94}$ solder with additions of Zn, for one example, are that (a) due to the Sn-rich eutectics of both Au-Sn and Sn-Zn [29] the liquidus temperatures are not very different from the melting temperature of pure Sn, (b) even larger changes in the concentration of Zn or Au would not appreciably increase the surface tension, (c) Au should be much more effective than Cu or Ag in improving the corrosion resistance of Zn.

The semi-empirical treatment applied in the paper does not give precise results, however, the findings can be used as a guideline for further improvements. The variation of the surface tension deviates strongly from the ideal behaviour which is reflected in particular by the pronounced minimum in the section $c_{\text{Au}}/c_{\text{Sn}} = 1$. Apart from a few exceptions, such minima of the surface tension do not occur in binary metal systems, therefore it would be of special interest to verify the calculation by experiment.

Acknowledgments

The author thanks his colleague Adolf Mikula for drawing the department's attention to this highly interesting subject.

References

1. ABTEW and G. SELVADURAY, *Mater. Sci. Eng.* **27** (2000) 97.
2. S. VAYNMAN and M. E. FINE, *Scr. Mater.* **41** (1999) 1269.
3. M. MACCORMACK and S. JIN, *J. Electron. Mat.* **23** (1994) 635.
4. K. SAGANUMA, K. NIIHARA, T. SHOUTOKU and Y. NAKAMURA, *J. Mater. Res.* **13** (1998) 2859.
5. C. MELTON, *JOM* **45** (1993) 33.
6. W. J. TOMLINSON and A. FULLYLOVE, *J. Mater. Sci.* **27** (1992) 5777.
7. M. MCCORMACK and S. JIN, *J. Electron. Mater.* **23** (1994) 715.
8. T. C. CHANG, M. C. WANG and M. H. HON, *J. Cryst. Growth* **250** (2003) 236.
9. T. TAKEMOTO and T. FUNAKI, *Mater. Trans.* **43** (2003) 1784.
10. K. KAMEDA, *Trans. Japan Inst. Met.* **28** (1987) 41.
11. M. PENG and A. MIKULA, *J. Alloys Comp.* **247** (1997) 185.
12. S. KARLHUBER, K. L. KOMAREK and A. MIKULA, *Z. Metallk.* **85** (1994) 307.
13. S. KARLHUBER, A. MIKULA and F. SOMMER, *Mater. Trans.* **B27** (1966) 921.
14. J. A. V. BUTLER, *Proc. Roy. Soc.* **A135** (1935) 348.
15. E. HAYER, K. L. KOMAREK, J. P. BROS and M. GAUNE-ESCARD, *Z. Metallk.* **72** (1981) 109.
16. E. HAYER, *Z. Phys. Chem.* **156** (1988) 611.
17. E. SCHEIL and D. MÜLLER, *Z. Metallk.* **53** (1962) 389.
18. A. B. BHATIA and V. K. RATTI, *Phys. Chem. Liq.* **6** (1977) 201.

19. H. K. LEE, J. P. HAJRA and M. G. FROHBERG, *Z. Metallk.* **83** (1992) 638.
20. T. TANAKA and T. IIDA, *Steel Research* **65** (1994) 29.
21. T. D. TURKDOGAN, "Physical Chemistry of High Temperature Technology," (Academic Press, New York 1980).
22. T. P. HOAR and D. A. MELFORD, *Trans. Faraday Soc.* **53** (1957) 315.
23. A. F. CRAWLEY, *Int. Met. Rev.* **19** (1974) 32.
24. T. IIDA and R. I. L. GUTHRIE, "The Physical Properties of Liquid Metals" (Clarendon Press, Oxford 1988).
25. S. M. KAUFMAN and T. J. WHALEN, *Acta Met.* **13** (1965) 797.
26. E. Pelzl and BERG HÜTTENMÄNN, *Monatsh.* **4** (1949) 10.
27. M. KUCHARSKI, *Metalurgia i Odlewnictwo* (1977) 329.
28. A. B. BHATIA and N. H. MARCH, *J. Chem. Phys.* **68** (1978) 4651.
29. T. B. MASSALSKI, "Binary Alloy Phase Diagrams" (American Society of Metals, Metals Park, OH, 1986).

*Received 25 February 2004
and accepted 13 April 2005*