Influence of Tin on Lead Activity in Cu–Pb–Sn Dilute Solutions

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The Cu–Pb–Sn ternary system has been studied by the method of equilibrium saturation with lead vapour (improved isopiestic method) at low tin and lead concentrations. The Cu–Pb solution has been chosen as a reference system. The values of interaction parameter \( \xi_{\text{SnPb}} \) have been determined to be equal to 4.93, 4.72, 4.49 at temperatures 1373, 1423 and 1473 K respectively. Results of this study are compared with the literature data. \( \xi_{\text{SnPb}} \) interaction parameters in Cu–Pb–X solutions have been interpreted with the concept of the relative difference of ionic volumes.

Keywords: activity, copper-lead-tin dilute solutions, interaction parameter \( \xi_{\text{SnPb}} \), improved isopiestic study

I. Introduction

Some divergent results concerning lead activity in Cu–Pb–Sn dilute solutions are presented in the literature. The aim of this study was to obtain the lead activity values by a different method. The range of composition was 0.02 ≤ \( N_{\text{Sn}} \) ≤ 0.1 and 0.02 ≤ \( N_{\text{Pb}} \) ≤ 0.1, while the temperature range was 1373–1473 K.

II. The Method of Investigations

Investigations have been carried out by the method of equilibrium saturation with metal vapours (improved isopiestic method)\(^{(1)}\). It is a relative method of activity determination. The method consists in holding the investigated solution and the reference one in the closed crucible until the thermodynamic equilibrium between gas and liquid phases is reached. Both the investigated solution and the reference one contain lead.

The vapour pressure of copper (0.13 Pa) and of tin (0.19 Pa) are negligible if compared with vapour pressure of lead (910 Pa)\(^{(2)}\). In the case of the most diluted lead solution (i.e. \( N_{\text{Pb}} = 0.02 \)), its vapour pressure calculated according to Raoult Law is approx. 18 Pa, i.e. 2 orders of magnitude bigger than that of copper. The condensate of metal vapours which has been found on the asbestos isolation has been analysed. 0.02% Cu and 0.007% Sn have been determined by chemical analysis (ASA). On the basis of these facts it has been assumed, that lead is the only evaporating metal at conditions applied. The equilibrium between the solutions has been reached, when the vapour pressure of lead over solutions has the same value. The activity coefficient of lead in the investigated solution can be calculated when the equilibrium compositions of both solutions and the activity of lead in the reference solution are known.

The Cu–Pb binary solution has been chosen as the reference system. It has been studied by different methods. Wypartowicz, Zabdry and Fitzner have carried out the critical analysis of literature data\(^{(3)}\). They have determined the most probable dependence of the lead activity coefficient on temperature and composition, that is,

\[
\ln \gamma_{\text{Pb}} = \left( \frac{3360}{T} - 0.6 \right) \times (1 - N_{\text{Pb}})^{2.1}.
\]

III. Materials Applied in This Study

Copper applied in this study was oxygen-free of MOOB grade (99.99% Cu), refined tin (99.999% Sn) and refined lead (99.999% Pb) which have been manufactured by Z.D. Skawina (Poland). The graphite crucibles have
been made of high quality graphite of EK 412 type supplied by Ringsdorf (FRG).

IV. Experiments

The scheme of isopiestic apparatus for equilibrium saturation with lead vapour is presented in Fig. 1. The apparatus has been placed inside the coil of the induction vacuum furnace VSG 02 type (Balzers). The Cu–Pb–Sn and Cu–Pb alloy specimens have been placed in the graphite crucible inside the alundum crucible, which has not been hermetically sealed. A small gap has been left in sealing between the crucible (2) and its cover (5) for the air evacuation from and for argon introduction into the crucible.

It has been proved in preliminary tests that the lead activity equilibration in both systems with the lead vapour transport is much quicker than the lead vapour escape out of the crucible. The optimal parameters values (argon pressure and exposition time) of the investigations have been established in preliminary tests as well.

Every experiment has begun by evacuation of air from the furnace. Next argon has been introduced and the apparatus has been heated. Argon has been evacuated up to the pressure which has been determined in the preliminary experiments after reaching the desired temperature by the system. This value of pressure and temperature has been maintained until the same lead activity in both solutions has been reached. Then argon has been introduced to stop the evaporation process and the apparatus has been cooled. The equilibrium state has been “frozen” in such a way. The alloys have been weighed before and after the exposition with the assumption that lead is the only evaporating metal.

V. Results

The results of investigations are shown in Figs. 2, 3 and 4 at temperatures 1373, 1423 and 1473 K, respectively. Every figure consists of five straight lines, which represent the $\ln \gamma_{Pb}$ as a function of lead concentration $N_{Pb}$ at constant tin concentration $N_{Sn}$. The fifth line represents the activity coefficient of lead in Cu–Pb solution (i.e. $N_{Sn}=0$). The lines have been extrapolated to $N_{Pb}=0$ to determine the $(\ln \gamma_{Pb})_{N_{Pb}=0}$ values at different tin concentrations. These values are presented as a function of tin concentration in Figs. 5, 6 and 7. The slopes of the straight lines determine the value of interaction parameter $\varepsilon^P_{Sn}$. It equals $4.93 \pm 0.82$ at 1373 K, $4.72 \pm 0.80$ at 1423 K and $4.49 \pm 0.74$ at 1473 K.

Some additional calculations have been carried out to assure that the linear dependence of $\ln \gamma_{Pb}(N_{Pb})$ exists in all the concentration range 0–0.1 $N_{Pb}$ and 0–0.1 $N_{Sn}$. The line obtained by calculations in the concentration range 0–0.06 $N_{Pb}$ and 0–0.06 $N_{Sn}$ lies inside the confidence interval of the graph obtained for the concentration range 0–0.1 $N_{Pb}$ and 0–0.1 $N_{Sn}$ (see Figs.
5-7). Therefore it is thought that the straight line determines with good accuracy the ln $\gamma_{Pb}$ change with composition in all the concentration range studied.

The interaction parameter versus reciprocal of temperature is presented in Fig. 8. The temperature dependence of $\varepsilon_{Pb}^{Sn}$ is as follows:

$$\varepsilon_{Pb}^{Sn} = \frac{8720}{T} - 1.42. \quad (2)$$

It is valid in the temperature range 1373-1473 K. This relation is consistent with the general rule stating that solution becomes ideal at $T=\infty$.

VI. Comparison of Results with Literature Data

Two papers only concerning activity measurements in Cu–Pb–Sn solution have been found in the available literature. The results obtained in this study differ slightly from the literature data. Azakami(4) has measured the activity of lead in Cu–Pb–Sn solution at temperature 1373 K by a transportation method. He has found that $\varepsilon_{Pb}^{Sn} = 3.3$. The graphs which are presented in this paper show that the experiments have been carried out correctly. However one should remember that the transportation method belongs to the group of dynamic, non-equilibrium methods. Therefore the results obtained by this method sometimes can not be very precise, especially in the case of diluted solutions.

Hayashi et al.(5) have studied dilute solutions of Cu–Ag–Pb, Cu–Sn–Pb, Cu–Au–Pb, Cu–Ga–Pb and Cu–In–Pb systems at 1403 K by the Knudsen effusion method. The figures presented in this paper make possible to carry out the more detailed analysis of results.
dependencies of $\ln \gamma_{Pb}$ versus $N_{Pb}$ calculated on the basis of the figures mentioned are shown in Fig. 9. The non-linear dependence of $\ln \gamma_{Pb}$ on lead concentration can be noticed. Some discrepancy between the character of $\ln \gamma_{Pb}$ in Cu–Pb solution and in Cu–Pb–Sn one is observed. Therefore it is supposed that the values of interaction parameters, which have been calculated on the basis of the results presented are not very precise.

The method of equilibrium saturation with metal vapour (improved isopiestic method), which has been applied in this study has a general advantage if compared with the method of Knudsen effusion or with the transportation method. This is the equilibrium method. This feature is very important,
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especially at high temperature studies and in the case of dilute solutions. One should remember on the other hand, that this method is a relative one and some error is introduced by thermodynamical data of the reference solution as well. However, taking into account the above discussion, the authors are of opinion that the total error made in this study is probably smaller than the experimental errors of studies presented in the literature.

VII. Interpretation of Interaction Parameters in Cu-Pb-X Metallic Solutions

Several methods for prediction of activity coefficients or interaction parameters in liquid ternary solutions have been elaborated up to data. Alcock and Richardson(6)(7) and Wagner(8) have designed the prediction methods in the case of non-metal solutions in metallic solvents. While concepts of Wada and Saito(9) or Mukai(10) can be applied for metals and non-metals as well. The most universal solution of the problem has been proposed independently by Lupis(11) (central atom) and Mathieu et al.(12) (atom enrolled).

The methods mentioned are characterized by a narrow range of application. Good consistency of calculated values with experimental results is observed in general in cases of systems, basing on which methods have been developed, while in other cases large discrepancies occur very often. Besides most of the methods(6)-(8)(11) is based on binary systems forming the ternary one.

Another solution of this problem has been presented by Pomianek(13). It has been proposed, in the case of metallic solutions with predominating metallic bond, to apply the ionic radius (i.e. relative difference of ionic volume) as geometrical factor of a system, instead of atomic radii or mole volumes usually used. Based on this concept, two regularities occurring in seven analysed families of 1-Y-X ternary dilute metallic solutions (1-solvent and Y-component common of a family, X-component changing in a family) have been shown:

The distinct linear dependence of $\varepsilon_{XY}^2$ interaction parameter on the $d_i$ relative difference of ionic volumes of metals X and Y, if

$$d_i^{Y+X+\rho} = \frac{r_Y^{Y+\rho} - r_X^{X+\rho}}{0.5(r_Y^{Y+\rho} + r_X^{X+\rho})} \tag{3}$$

where

$r_Y^{Y+\rho}, r_X^{X+\rho}$ = ionic radii of Y and X metals respectively, and

$n, p$ = numbers of valence electrons transferred by metals Y and X respectively to the common electron cloud.

$\varepsilon_{XY}^2 > 0$ if $r_Y^{Y+\rho}$, the ionic radius of a solvent, is bigger than $r_X^{X+\rho}$ ionic radius of X metal. The opposite relation is valid as well: $\varepsilon_{XY}^2 < 0$ if $r_Y^{Y+\rho} < r_X^{X+\rho}$. Both regularities can be summarized by equation:

$$\varepsilon_{XY}^2 = A(d_i^{Y+X+\rho} - d_i^{Y+X-\rho}) \tag{4}$$

Interpretation of $\ln \gamma_{Pb}$ experimental values in
Cu-Pb-X solutions by the concept of relative difference of ionic volumes is presented in Fig. 10. The ionisation degree of the alloy components have been assumed to be equal to the main number of valence electrons and appropriate ionic radii are tabulated in Table 1. The both proposed regularities are fulfilled in the case of Cu-Pb-X family of solutions. Equation (4) takes form in this case according to the least squares method:

$$\varepsilon_{pb}^X = 10.3(d_{pb+2-X+p}^{X+p} - 0.65) - 2.31 \pm 1.40 \quad (5)$$

$\varepsilon_{pb}^X$ interaction parameters are directly proportional to $d_{pb+2-X+p}^{X+p}$ the relative difference of ionic volumes correlation coefficient $R=0.95$.

$$\varepsilon_{pb}^X = -2.31 \quad \text{at} \quad r_{Cu+1} = r_{X+p}. \quad \varepsilon_{pb}^X \text{ should be equal to zero. However, taking into account errors of } \varepsilon_{pb}^X \text{ and ionic radii in the experimental values, one can consider the results to be satisfactory.}

The above relations can be interpreted as follows: if X metal of $r_{X+p} < r_{Cu+1}$ is introduced to Cu-Pb solution, it results in closer packing of the structure and therefore the solubility of Pb big ions is decreased, while at $r_{X+p} > r_{Cu+1}$, the X metal makes the structure looser and the lead solubility is increasing. Equation (5) can be applied for description of $y_{pb}$ activity coefficient in any Cu-Pb-X liquid diluted solution. It takes form at 1403 K:

$$\ln y_{pb} = 1.79 - 3.77N_{pb} + [10.3(d_{pb+2-X+p}^{X+p} - 0.65) - 2.31]N_r. \quad (6)$$

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