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Experimental determination of phase equilibria and reassessment of Ag–Pd system

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ABSTRACT

The existing assessment of thermodynamic and phase equilibrium data in the Ag–Pd system was revised on the basis of calorimetric data for liquid Ag–Pd alloys published recently in the literature and on new determination of liquidus and solidus temperatures and activity data for Ag in liquid phase, using differential scanning calorimetry (DSC) coupled with Knudsen cell mass spectrometry (KC/MS). A substantially narrower liquid/fcc two-phase field in phase diagram as well as new non-ideal activity data were revealed.

1. Introduction

In lead-free soldering, silver is usually used as a solder component and palladium often constitutes the substrate component. It follows that the Ag–Pd system is of interest in terms of possible interference between components in solder joints. The importance of this interference to the degradation of solder joints rises with increasing temperatures of operation in electronic packages containing solders (e.g. in the automotive industry).

The Ag–Pd phase diagram is characterized by complete miscibility in the liquid and solid states. The first assessment of the Ag–Pd system was published by Ghosh et al. [1], where the experimental phase equilibrium data were taken from Karakaya and Thompson [2]. Ruer [3] and Savitskij and Pravoverov [4] also determined solidus and liquidus boundaries by thermal analysis.

The thermodynamic properties of Ag–Pd liquid solutions were studied by Vatolin et al. using the Knudsen effusion method at 1873 K [5]. These results show nearly ideal behaviour within the system. The thermodynamic properties of Ag–Pd solid solutions have been studied extensively in [6–15]. The enthalpy of mixing of solid alloys has been measured calorimetrically at 915 K [8] and at 1200 K [12]. These two data sets agree fairly well.

The activities of Ag have been measured at a temperature range of 1000–1273 K by electrochemical [7,13], vapour pressure [9,10], and spectroscopic [14,15] techniques. The activities of Pd have been measured at a temperature range of 923–1023 K by a gas equilibrium technique [6,11].

Assessment of thermodynamic data performed in [1] yields good agreement in terms of the calculated enthalpy of mixing of fcc Ag–Pd alloys with experimental data [7–9,12–14] and the activities of Ag and Pd in fcc Ag–Pd alloys are also in reasonable mutual agreement with calculated data. The calculated activities of Ag in liquid Ag–Pd alloys differ from those determined experimentally, but only one set of four measurements is available [5] revealing nearly ideal behaviour. Phase equilibrium data from [3,4] are in good agreement with those calculated.

Recently, Luef et al. [16] performed calorimetric measurement of the enthalpy of mixing of liquid Ag–Pd alloys up to ca. 55 at.% Pd at 1400 °C. Comparison of the enthalpy of mixing of liquid Ag–Pd alloys determined in [16] with that calculated in [1] reveals a substantial discrepancy (see Fig. 1), in the light of which reassessment appears to be necessary.

In the work reported here, phase equilibrium data on solidus and liquidus lines and activities of Ag were redetermined by differential scanning calorimetry (DSC) coupled with Knudsen cell mass spectrometry (KC/MS) representing, together with the data from [16], a new basis for thermodynamic reassessment. The new thermodynamic description of the Ag–Pd system is of great importance not only from the point of view of lead-free soldering but

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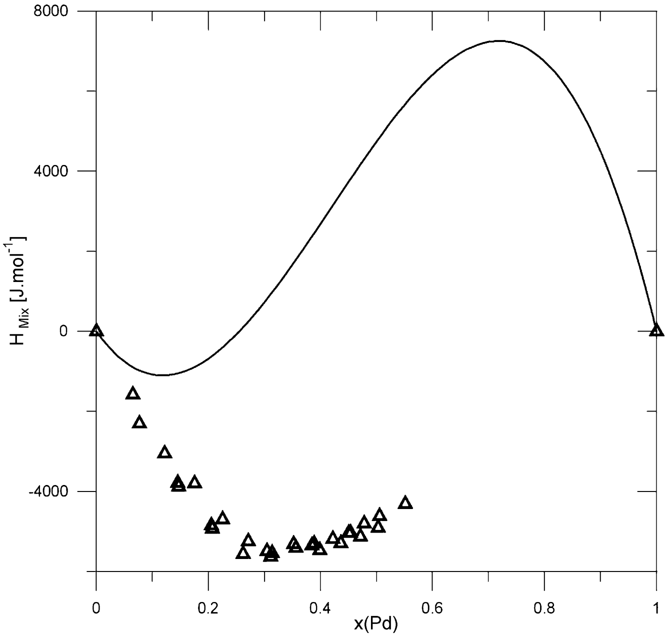

Fig. 1. Comparison of enthalpy of mixing of liquid Ag–Pd alloys at 1673 K predicted by [1] (solid line) with experimental determination in [16] (triangles).

also because of the use of this material as a hydrogen storage alloy system [17–19].

2. Experimental methods

The samples were prepared from pure elements, Ag (purity: 99.999%) and Pd (99.98%), producer AlfaAesar Co. Proper amounts of the elements were weighed out to a total sample weight of 1–1.5 g per one prepared alloy. Alloying was carried out in an arc furnace. No weight loss of samples during arc-melting was recorded. After alloying, the samples were ground and polished and the structure was developed using a commercial OP–S suspension, in which the polishing with silica is combined with fine etching (pH 8.9). The homogeneity of the samples was tested with a JEOL JSM-6460 scanning electron microscope using an EDAX analyzer. The microstructure of the samples was, in all cases, found to be homogeneous throughout the whole sample volume. The samples were then investigated by DSC and KC/MS (STA 409 CD/3/403/5/G, Netzsch). After both DSC and KC/MS measurements, the samples were investigated by scanning electron microscope in order to check their overall composition. Composition changes were not greater than 2 at.%.

3. Results and discussion

3.1. DSC curve determination

The thermal analysis was carried out by means of a Netzsch STA 409 CD/3/403/5/G apparatus. This instrument enables us to do the detections of the differential scanning calorimetry signal (DSC, heat flow) and allows measurements at a temperature range of 25–1400 °C. The thermal effect upon heating and cooling was measured at a rate of 10 K/min. The experiments were carried out in an inert gas atmosphere (high-purity argon) using a constant gas flow (70 ml/min).

The experimental DSC signal was compared with a simulated DSC signal. This evaluation was based on previous work [20], but several simplifications [21] were accepted. The CALPHAD method was applied for prediction of thermodynamic description of the liquid and solid phases. The thermodynamic parameters of the phases were taken from the COST531 thermodynamic database [22]. The CALPHAD approach allowed a predicted temperature-dependent enthalpy function (ΔH) to be obtained for each alloy studied and the values of temperature enthalpy derivatives $\partial \Delta H/\partial T$ were subsequently used for comparison with DSC experimental signals. The use of the enthalpy data by Ghosh et al. [1] and/or those by Luef et al. [16], respectively, in the COST531 thermodynamic database resulted in a ca. 10% difference in $\partial \Delta H/\partial T$ values only (the size of DSC signal). It had no negative influence on the liquidus and solidus temperature evaluation from DSC measurements, but led to a better understanding of the experimental DSC signals and to a correct evaluation of liquidus and solidus temperatures with high accuracy. The experimental solidus and liquidus temperatures are given in Table 1. Because the composition uncertainty of the Ag–6.62Pd sample (see Table 1 and Fig. 2) could not be evaluated due to a lack of independent overall composition measurements, we assume the uncertainty for this alloy is similar to that of the other samples, i.e. ±2 at.% of Pd. This also explains why the Ag-rich data are below the assessed curve.

Table 1
Chemical composition of alloys together with determined solidus and liquidus temperatures.

Pd content (at.%)	Temperature (K)	
	Solidus	Liquidus
6.62	1247.9	1277.5
12.86	1291.6	1325.0
18.06	1328.0	1372.0
23.27	1375.6	1418.4
25.92	1398.2	1441.1

3.2. KC/MS activity determination

Knudsen cell mass spectrometry (KC/MS) was performed with Netzsch STA 409 CD/3/403/5/G apparatus, a specially-adapted type of the commercial STA 409 CD – QMS 403/5 Skimmer Coupling Instrument. The DSC carrier in this instrument can be replaced by one with a Knudsen cell from alumina. The diameter and height of the Knudsen cell were 15 and 8 mm, respectively, and the diameter of the effusion orifice in the middle of the alumina lid was 1 mm. The Knudsen cell was heated by resistance furnace and the temperature measured with a Pt–PtRh thermocouple. The thermocouple was calibrated against the melting point of several pure metal samples, including pure silver. Ions were formed by means of 70 eV electron beam and separated by a quadrupole mass spectrometer (Balzers, QMH 400-5). Ion currents of characteristic isotopes ^{107}Ag and ^{109}Ag of the corresponding gaseous species were detected. The

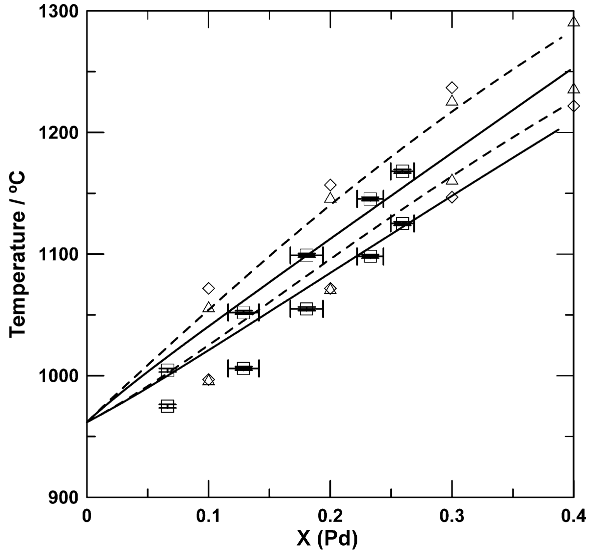

Fig. 2. Liquidus and solidus temperatures calculated in [1] – dashed lines, calculated in this work – full lines, measured in this work – squares, measured in [3] – triangles, measured in [4] – diamonds).

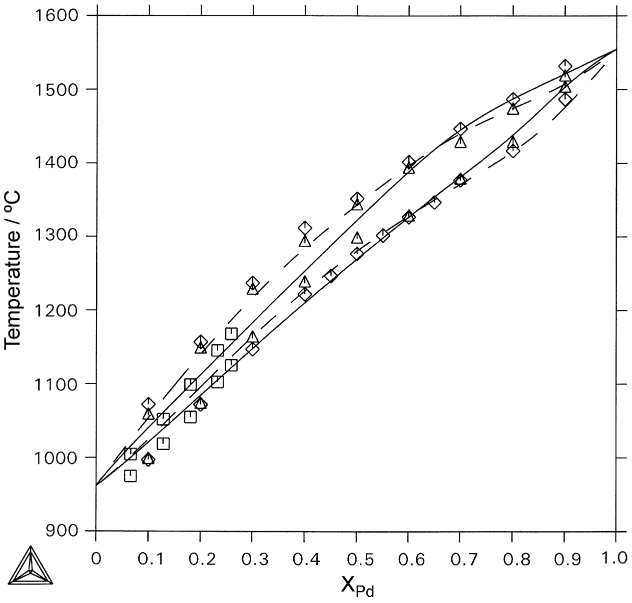

Fig. 3. Phase boundaries between solid fcc Ag–Pd and liquid Ag–Pd phases – full lines as the results of new assessment compared with original assessment in [1] – dashed lines and phase equilibrium data from this work – squares, measured in [3] – triangles, measured in [4] – diamonds.

activity of Ag in liquid alloys was obtained via measurement of ion currents of the isotopes from the samples versus ion currents of the isotopes from pure silver. The measurements were performed in 1 day. Measurements of pure metal were taken at the beginning as well as at the end of the experiment in order to check signal stability. The values of ion current intensities with respect to background were found to remain stable over the whole measurement period. The final temperature in the dynamic regime was selected at 1510 K in order to protect the ion source and the quadruple mass analyser against massive condensation of gaseous metal components. After final temperature had been achieved, a static regime was initiated and spectral data were collected for 10 min. The average value was used for determination of the activities of Ag. Only the alloys with contents of 18.06 and 25.92 at.% Pd were chosen for measurement.

3.3. *Thermodynamic data treatment*

Reassessment of thermodynamic parameters from [1] (parameters in Appendix) was performed by the assessment module in the ThermoCalc program [23] and addressed the parameters of the liquid phase only. Liquidus and solidus temperatures from the literature [3,4] and activity of Ag in liquid state [5], with the same weight equal one, were taken into account. Data on the enthalpy of mixing of the liquid phase determined calorimetrically [16] and the liquidus and solidus temperatures from DSC measurement, as well as the activities of Ag in liquid phase from KC/MS measurement – which were measured with higher accuracy in this work – were set to weight equal five. This procedure resulted in good agreement of solid–liquid phase boundaries with experimental data (Figs. 2 and 3) and in very good agreement of calculated enthalpy of mixing with that experimentally determined in [16] (Fig. 4). Comparison of calculated activities of Ag in liquid phase with newly obtained data from KC/MS measurement and with those from the work of Vatolin et al. [5] shows better agreement of the calculated values with the experimental information from this work (Fig. 5). As already stated, the thermodynamic parameters for the fcc phase of the Ag–Pd system were based on reliable experimental information [2–4,6–14]. For this reason, the values of the parameters for the solid fcc phase were not changed.

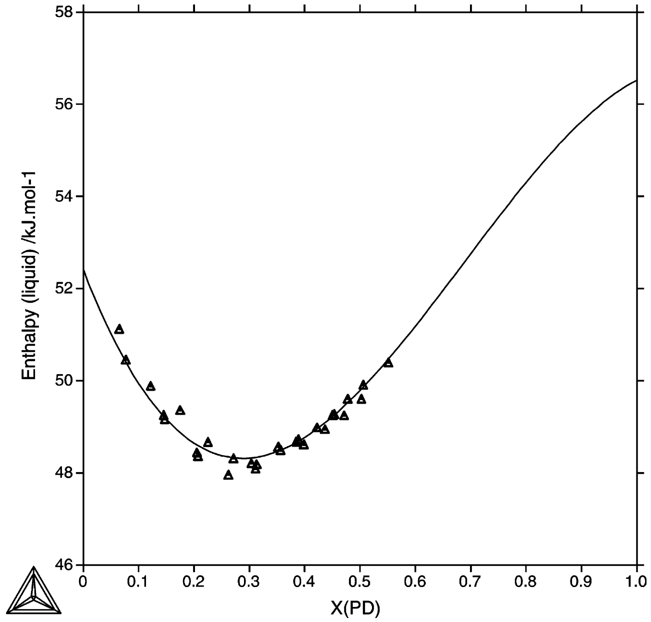

Fig. 4. Enthalpy of liquid phase at 1673 K calculated in this work (Appendix) compared with experimental data in [16] – triangles.

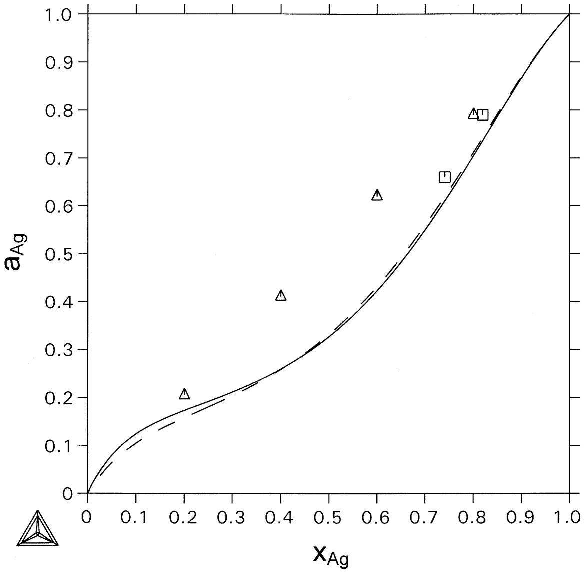

Fig. 5. Activity of Ag in liquid Ag–Pd system calculated at 1510 K in this work (Appendix) – full line and calculated at 1873 K in [1] – dashed line. Experimental activity data at 1873 K from [5] – triangles and at 1510 K from this work – squares.

The thermodynamic parameters of the new reassessment are given in Appendix and may be used for more exact thermodynamic studies of the Ag–Pd alloys used for hydrogen storage material. The new Ag–Pd thermodynamic parameters may be also useful for the hydrogen diffusion study in these alloys [17,24,25] and for a better understanding of solder joints.

4. Conclusions

Determination of liquidus and solidus curves and of Ag activities in the liquid phase in this work, with a contribution of data on the enthalpy of mixing of liquid Ag–Pd solution [16] and of all previously published data in the literature [1–15] produced a reliable basis for the reassessment of the thermodynamic parameters of the Ag–Pd system. The values of enthalpy of mixing for the solid fcc Ag–Pd phase as well as for the liquid Ag–Pd phase are crucial to thermodynamic assessment. It is shown that the determination of temperatures of phase transformations by DSC is more reliable than that obtained by simple DTA. A substantially narrower liquid/fcc two-phase field in phase diagram was confirmed. Furthermore, determination of the thermodynamic activities of Ag in liquid solution by means of KC/MS technique performed with Netzsch STA 409 CD/3/403/5/G apparatus proved very precise and reproducible.

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Appendix A. Appendix

Thermodynamic parameters describing phase equilibria in Ag–Pd system

Accepted from [1]:

- PARAMETER G(FCC_A1,AG,PD:VA;0) 298.15 – 19062.1913 + 7.7262 * T; 6000 N !
- PARAMETER G(FCC_A1,AG,PD:VA;1) 298.15 – 16944.4417 + 0.9988 * T; 6000 N !

This work:

- PARAMETER G(LIQUID,AG,PD;0) 298.15 – 19085 + 8.7604 * T; 3000 N !
- PARAMETER G(LIQUID,AG,PD;1) 298.15 – 15605 + 0.1213 * T; 3000 N !

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