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A CALORIMETRIC STUDY OF ALLOY FORMATION IN Au–Cu AND Au–In SYSTEMS

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Abstract

A calorimetric study of alloy formation in Au–Cu and Au–In systems was carried out. The heats of mixing, ΔH_{mix}, were measured at 1380, 1484 and 1604 K for Au–Cu and at 1387, 1449 and 1505 K for Au–In in the full concentration range. The results of experiments were described by approximating equations. Observed values of ΔH_{mix} were discussed using the phase diagrams of the systems. It was shown that the systems become closer to the ideal state with increasing temperature. From the experimental data, the dependencies of the enthalpies of the systems on the composition and temperature were estimated. The simultaneous effects of composition and temperature on enthalpy are represented in 3D diagrams. The specific heats of the alloys, in the temperature range of experiments, were derived from the slopes of enthalpy planes.

Keywords: calorimetry, enthalpy, heat of mixing, metal alloys, specific heat

Introduction

A constant interest in results of the experimental determination of thermodynamic functions of mixing of molten metals is generated by the never-ending development of calculational methods for the description of multicomponent systems on the basis of reliable binary data. In spite of numerous references to thermodynamic data for the same metal alloys, not all of these data are equivalent in reliability. In many cases heats of mixing ΔH_{mix} are evaluated indirectly from experimental data on thermodynamic activities of components with different model assumptions on entropy. So, for instance, the values of ΔH_{mix} available in publications, even on such a well-known system as Au–Cu [1–6], do not agree with each other and only in [1] was the heat of mixing measured just by calorimetry. It is obvious that direct calorimetry of alloy formation remains an irreplaceable facility for determination of heats of mixing of liquid metals. The information contained in calorimetric data greatly increases, if they reflect an influence of temperature T. Such an approach allows evaluation of not only a heat of mixing $\Delta H_{\mathrm{mix}}(T)$ by itself and a change of the system's total enthalpy $\Delta H(T)$, but some other properties as well, for instance specific heat c_{p}.

In this work the calorimetric determination of heats of mixing of metal alloys and their dependencies on the composition and temperature have been undertaken.

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We selected the Au–Cu system, as well as the lesser-known Au–In system, for study. Only fragmentary low-temperature information on the heat of solution at 723 K of the Au–In system [6, 7] was found. The two systems chosen give different types of phase diagram. In the first system there is a continuous series of solid solutions, but in the second system there is eutectic melting and formation of a series of chemical compounds [8]. All the alloys are of interest for the development of solders for electronic industry and new materials for jewelry.

Experimental

The heats of mixing of Au–Cu and Au–In alloys were measured by the drop-method, using a high-temperature thermal analyzer (Setaram) with a measuring calorimetric cell of differential type. Details of the use of this method and instrument for the determination of ΔH_{mix} were given earlier [9]. Experiments were carried out under the following conditions:

gas atmosphere in the cell – Ar,
mass of dropped samples – between 50 and 200 mg,
crucible material – alumina,
crucible capacity – 2 cm^3,
thermocouple and thermopile wire material – Pt–Rh6/Pt–Rh30 alloys, ř 0.3 mm.

The purities of initial metallic components in mass% were 99.99 for Au, 99.996 for Cu and 99.995 for In.

The calibration factor (in other words energy conversion factor) ε of the measuring cell, for each crucible in use and for each temperature of experiment T, and its dependence on the amount of substance m in the crucible, was found by one of the three possible ways described in [9]. Namely, the effects of adding drops of the first pure component into the cell was measured during the gradual accumulation of certain amount of this liquid metal in the crucible. Using reference data [10, 11] on the enthalpy change $\Delta H_{298}^{\mathrm{T}}=H(T)-H(298)$ of this first component, ε was calculated from the heat of each single drop, giving the $\varepsilon=f(m)$ dependency. Then, for the determination of ΔH_{mix} when adding drops of the second component with alloy formation, the value of ε was found by the extrapolation of the $\varepsilon=f(m)$ dependency up to the corresponding amount m of liquid alloy. The standard error of the experiments was calculated to be close to 5%, taking into account possible inaccuracies of measurements and reference data.

Results

Results of the experimental determination of heats of mixing for the Au–Cu and Au–In systems, under different temperature conditions, are shown by the dark points on Figs 1 and 2, respectively. In the first system, the values [1] obtained by a similar method are given for comparison. The latter are shown by light points and the approximating dashed curve. The difference is seen as a slight shift of values along the

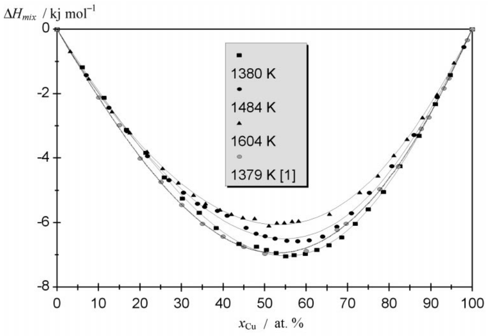

Fig. 1 Heat of mixing of Au–Cu alloys

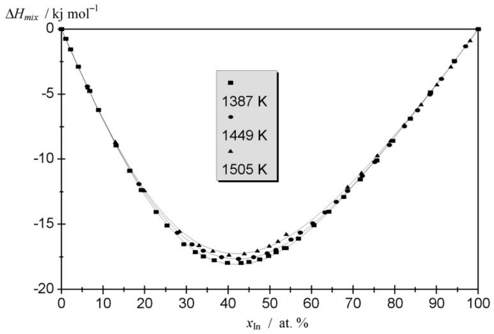

Fig. 2 Heat of mixing of Au–In alloys

concentration axis. Our results, in kJ mol^{-1}, for all the temperatures and compositions, can be described within an accuracy of not less than ±3.6% (for Au–Cu) and ±2.3% (for Au–In) by the following analytical expression:

$$\Delta H_{\text{mix}} = x_{\text{Au}} x_{\text{M}} (A + Bx_{\text{M}} + Cx_{\text{M}}^2 + Dx_{\text{M}}^3), \quad \text{kJ mol}^{-1} \tag{1}$$

where *M*=Cu, In; *x* is the amount of component in at.%. The factors *A, B, C, D* in Eq. (1) are provided in Table 1 for different systems and temperatures.

Table 1 The values of Eq. (1) factors

M	*T*/K	*A*	*B*	*C*	*D*
Cu	1380	$-1.990 \cdot 10^{-3}$	$-1.074 \cdot 10^{-5}$	$-2.325 \cdot 10^{-7}$	$2.644 \cdot 10^{-9}$
Cu	1484	$-2.190 \cdot 10^{-3}$	$5.786 \cdot 10^{-7}$	$-2.782 \cdot 10^{-7}$	$2.234 \cdot 10^{-9}$
Cu	1604	$-2.160 \cdot 10^{-3}$	$-8.761 \cdot 10^{-7}$	$-1.393 \cdot 10^{-7}$	$1.089 \cdot 10^{-9}$
In	1387	$-7.076 \cdot 10^{-3}$	$-8.739 \cdot 10^{-5}$	$2.434 \cdot 10^{-6}$	$-1.306 \cdot 10^{-9}$
In	1449	$-7.279 \cdot 10^{-3}$	$-6.205 \cdot 10^{-5}$	$1.926 \cdot 10^{-6}$	$-1.028 \cdot 10^{-9}$
In	1505	$-7.300 \cdot 10^{-3}$	$-5.454 \cdot 10^{-5}$	$1.862 \cdot 10^{-6}$	$-1.043 \cdot 10^{-9}$

Discussion

One can see from the results obtained that all the heats of mixing lie completely in a negative area. Minimum values of $\Delta H_{\mathrm{mix}}=f(x_{\mathrm{M}})$ dependencies were found at 55 at.% Cu and at 43 at.% In, respectively. Results were compared with the phase diagrams [8] of the systems under study. The extreme integral value of ΔH_{mix} for Au–Cu alloys corresponds to the minimum melting temperature of the solid solutions (56.55 at.% Cu). The minimum value of ΔH_{mix} for Au–In alloys is about halfway between the eutectic melting point (38.4 at.% In) and the stable chemical compound Au–In (50 at.%). Generally the heat evolution during mixing in a system with eutectic melting and chemical compound formation is noticeably more than when the formation of liquid alloys gives rise to a continuous series of solid solutions. In both cases, the system becomes closer to ideal behavior with increasing temperature.

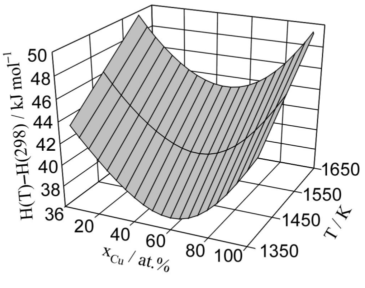

Fig. 3 Enthalpy of Au–Cu system

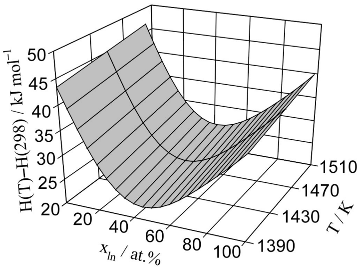

Fig. 4 Enthalpy of Au–In system

Since the heat of mixing is defined as the excess enthalpy of the real system with respect to the enthalpy of the hypothetical ideal system formed from the same components, one can easily pass from the heat of mixing to the general enthalpy of the system using the following expression:

$$\Delta H(T)=H(T)-H(298)=\Delta H_{\mathrm{id}}(T)+\Delta H_{\mathrm{mix}}(T) \qquad (2)$$

in which ΔH_{id} is an additive amount of enthalpy changes of pure components taken from the reference literature [10, 11] for the corresponding temperature range, and ΔH_{mix} is replaced by Eq. (1).

Unlike many usual experimental studies of heat of mixing of metal alloys, we tried in this work to consider not only a compositional effect on ΔH_{mix}, but also a temperature effect. Such an approach has increased the information value of the experimental data. Information on the simultaneous influence of composition and temperature on the enthalpy of the systems under study enabled us to represent ΔH in the form of 3D planes (Figs 3 and 4). Each plane on these figures is formed by three isothermal curves $\Delta H(T)=H(T)-H(298)$, calculated using Eq. (2), which are connected with each other by transverse lines, drawn through the points of equal composition (stepping in this instance by 5 at.%). These enthalpy planes demonstrate how the enthalpy of any alloy composition increases with increasing temperature.

There appeared to be the possibility of evaluating the specific heat of an alloy of given composition by the analysis of the slope of the corresponding iso-concentrational section of the ΔH plane, with respect to the temperature axis. We tried to find out the values of specific heats by linear fitting of slopes of ΔH planes, assuming invariability of c_p in the limited temperature interval of experiments. This assumption seems to be quite reasonable because the difference between the equicompositional points of the isotherms and corresponding fitting lines never exceeds 0.5%. The results of this estimation are given in Figs 5 and 6 as dotted curves for the whole concentration range, stepping by 1 at.% of *M*. The solid lines are the calculated additive specific heats drawn for comparison. One can see that our results do not confirm the Neumann–Kopp rule.

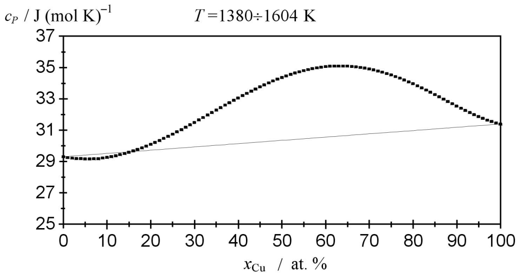

Fig. 5 Specific heat of Au–Cu alloys

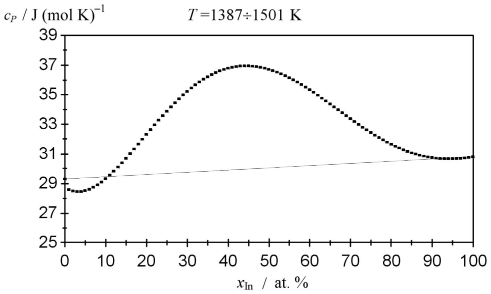

Fig. 6 Specific heat of Au–In alloys

Conclusions

The heats of mixing of Au–Cu and Au–In liquid alloys and their dependencies on composition and temperature have been measured by drop-calorimetry. Only negative values of ΔH_{mix} were observed. Dependencies of ΔH_{mix} on concentration correlate with the phase diagrams. Increasing the temperature decreases the heat evolution when mixing. The enthalpies of the systems were calculated from the experimental results. Specific heats of the alloys were estimated in the temperature range of the experiments. It was shown that the generally accepted idea about the additive nature of the specific heats of binary and multicomponent alloys is not confirmed by our experiments.

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