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Enthalpies of solution of vanadium and chromium in liquid copper by high temperature calorimetry

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Abstract

Standard enthalpies of solution of vanadium and chromium in liquid copper measured directly by high temperature calorimetry at 1873 K are reported. Solution of the solid metals was accompanied with endothermic effects approaching the values 87.1 ± 6.0 kJ mol^{-1} for vanadium, and 112.0 ± 6.3 kJ mol^{-1} for chromium at infinite dilution.

Concentration dependence of the partial molar enthalpies of solution was represented by the following equations:

$$\overline{\Delta H}_{\langle \mathrm{V} \rangle}/\mathrm{kJ\ mol^{-1}} = (1 - x_{\mathrm{V}})^2(87.13 - 575.94x_{\mathrm{V}}) \quad 0 \leq x_{\mathrm{V}} \leq 0.09$$

$$\overline{\Delta H}_{\langle \mathrm{Cr} \rangle}/\mathrm{kJ\ mol^{-1}} = (1 - x_{\mathrm{Cr}})^2(111.99 - 494.42x_{\mathrm{Cr}}) \quad 0 \leq x_{\mathrm{Cr}} \leq 0.14$$

Considerable positive enthalpies of mixing of vanadium and chromium with copper are consistent with the existence of immiscibility ranges of liquid alloys in these systems.

Keywords: Enthalpies of solution; Liquid alloys; Cu–V; Cu–Cr; Thermochemistry

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1. Introduction

Thermodynamic properties of Cu–V and Cu–Cr liquid alloys are among the least studied for copper alloys with 3d-transition metals. The evident reason for this delay lies with the necessity to conduct experiments at very high temperatures, well above 1500°C, to provide both noticeable solubility of the above mentioned metals in liquid copper, and high enough rates of their dissolution. The latter requirement is crucial for successful direct calorimetric measurements.

The results of our recent study of the solution enthalpies of solid vanadium and chromium in molten copper at 1873 K are reported in this paper in comparison with earlier data [1]. This research is a part of systematic revision of the thermochemical properties of liquid binary copper alloys with the elements of the fourth period.

2. Experimental details

The measurements were carried out in a self-made high temperature heat flux calorimeter, basically similar to the instrument described elsewhere [2]. Major modifications introduced refer to the replacement of some components of electronic equipment that improved temperature stabilization of the calorimeter core and made the data acquisition system more versatile.

As the particulars of our high-temperature instrument have not been disclosed in English language publications before, we shall briefly discuss here the general principles adopted at the design stage and highlight a few distinctive features. The instrument is build on the chassis of a high-temperature vacuum resistance furnace and comprises (a) the vacuum and gas filling system, (b) the calorimeter, (c) the tempera-

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ture stabilization system, and (d) the data acquisition system.

A scheme of the central part of instrument is shown in Fig. 1. The calorimeter basically consists of a core, the molybdenum–niobium cell (1) with a W–Re 5/20 thermopile mounted on it and a crucible with liquid metal (2) placed inside, and an isothermal enclosure, a massive (about 2.5 kg) molybdenum–niobium block (3), located in the isothermal zone of a tungsten resistance heater (4).

Pursuing an objective to standardise the conditions of heat exchange between the calorimetric cell and isothermal enclosure, it was decided to eliminate direct contact of all thermoconducting bodies, like thermocouple, stirrer, calibration heater, etc., with the melt. As, from the very beginning, the instrument was intended for use at temperatures above 1200°C, and mostly for 1500–1700°C range, this would not simply improve sensitivity and reproducibility of the results but also add to the long-term reliability of the calorimeter (no moving parts in the high-temperature zone) and reduce contamination of liquid bath.

To decrease heat losses, the heater is surrounded with a number of reflecting shields made of molybdenum foil (5). Crucible, internal and external blocks are placed on insulating beds of boron–aluminium-nitride (6) that improve thermostabilization of separate parts of the core and assist the major part of heat flux to flow through the walls of the calorimetric cell. Fulfilment of the latter requirement, in conjunction with a specific design of thermoelectric detector [3], allowed an increase in the sensitivity of the instrument by an order of magnitude compared with our previous model [4].

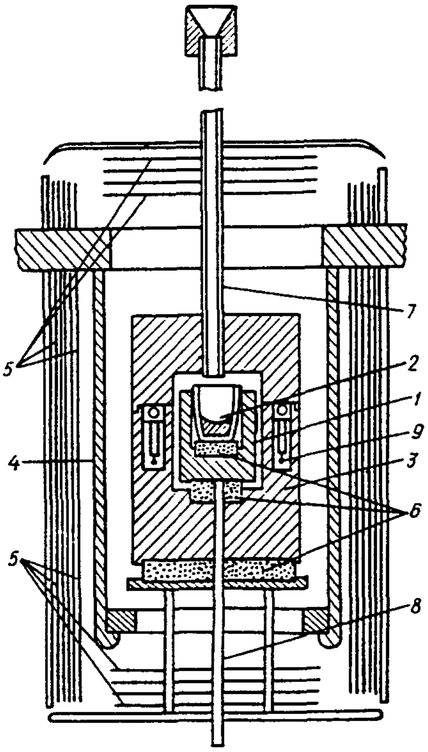

Fig. 1. A scheme of the central part of the calorimeter. See text for details.

The temperature inside the heater is maintained constant at a level of ± 0.4 K by means of an analogue PID-regulator that governs the voltage supply to the lowering transformer through a bridge of electronic valves. A thermocouple located in the immediate vicinity of the heater surface, in its uniform temperature zone, serves as a feedback detector of temperature.

Operation of the instrument is based on the successive introduction of thermostatted solid samples, stored outside the calorimeter, into the bath of liquid metal via the directing ceramic tube (7), followed by the evaluation of heat fluxes between the bath and isothermal enclosure. In practice, time integration of heat flux is attained by means of a differential thermoelectric pile [3] encapsulating the calorimetric cell, so that the output e.m.f. of the thermopile duly reflects thermogenesis inside the cell. Connecting wires of the thermopile (8) are led out of the core through the bottom of furnace. The output of the thermopile is compensated by a high precision potentiometer and the part corresponding to the thermal perturbation caused by the drop of a sample, as well as the electronically integrated signal, are amplified, recorded, and stored in digital form for further treatment. Sensitivity of the thermopile constitutes about 4 mV W^{-1} at 1800 K, with typical values of 0.5 mV voltage amplitude, and 2–4 min peak registration time for many systems.

The temperature of an experiment is measured by the thermopile (9) assembled in the massive molybdenum block. The variation of the readings of this thermopile in the course of experiment, when converted into temperature, usually does not exceed ± 0.2 K. All thermocouples employed in the calorimeter core were of W–Re 5/20 type, and were made from the same consignment of thermocouple wire that had previously been calibrated by comparison with the exemplary Pt–PtRh/10 thermocouple.

Problems of both (i) equalisation of the concentration within the melt without stirring and (ii) varying spatial thermogenesis, due to random location of the sites of dropping samples, are successfully addressed by using the thermoelectric pile which efficiently integrates the heat flux passing through the surface of the cell. Moreover, the small size of the crucibles used (about 6 cm^3), and the small quantities of material required, diminish the influence of the above-mentioned factors and considerably reduce the cost of research.

The calorimeter was extensively tested with a number of liquid metallic systems, in particular with a thorough study of the Cu–Ge system [2]; it proved to be free from systematic errors, reliable, and highly efficient.

Recorded heat exchange curves, together with the knowledge of the masses of samples and temperature of the experiment, constitute the bulk of raw data. Calculation of the enthalpy of solution of samples is based on the equation of heat balance and was meticulously discussed elsewhere [4]. In particular, partial molar enthalpy of solution of component M is given by

$$\overline{\Delta H}_{\mathrm{M}} = -\Delta H^{T}_{T_0,m}(\mathrm{M}) - \frac{k}{n_{\mathrm{M}}} A\,, \qquad (1)$$

where $\Delta H^{T}_{T_0,m}(\mathrm{M})$ is molar enthalpy content of component M when heated from room temperature T_0 to the temperature of experiment T (usually found from the reference data); k is heat exchange coefficient for the instrument; $A = \int \Delta E(t)\mathrm{d}t$ is the area of heat exchange peak; n_{M} is the number of moles of a sample. The above approximation is acceptable if a drop of a single sample does not shift the composition of the alloy by more than about 1–2 at.%, which is easily attainable in our experiments. The value of $\overline{\Delta H}_{\mathrm{M}}$ is commonly assigned to the middle point of the composition range before and after addition.

A revolving discharger for samples on the furnace lid allows up to 58 samples to be dropped in the course of one run. This will normally increase the volume and mass of the liquid bath from two to five times. Varying the amount of substance in the melt alters the heat capacity of the cell on one side, and on the other side the overall surface area of the liquid bath; both factors considerably affect the process of heat exchange between the cell and surroundings at high temperatures. The present instrument was designed with the clear intention to reduce the impact of the abovementioned effects on heat exchange coefficient k. Experiments with various pure liquid metals confirmed that this objective was successfully attained. For our calorimeter, the dependence of k on mass, volume, or height of the melt in a crucible within one run is insignificant if compared with rival instruments [5], and can be satisfactorily represented by a linear function of the form

$$k(m) = a + bm \qquad (2)$$

where m stands for mass of the liquid bath[2], with the slope b being considerably smaller than intercept a. Typical values of a and b for our instrument are 6.8 ± 0.2 kJ mV^{-1} s^{-1} and 0.05 ± 0.01 kJ mV^{-1} s^{-1} g^{-1} respectively. Nevertheless, occasional variations (in different runs) of the size of crucible and its position inside the cell affect numerical values of these coefficients. This makes preliminary calibration of the instrument impossible and hence requires control over the variation of k in each run. This task is accomplished by adding at the beginning of an experiment samples of solvent and/or indifferent substances to the melt; for many liquid metallic alloys, synthetic sapphire or tungsten proved to be suitable reference materials. As the enthalpy of solution for an indifferent species is zero, the numerical value of k can be deduced from Eq. (1). In the further course of experiment, additions of reference material are continued on a regular basis to establish the dependence of k on m and to use it for calculation of the enthalpies of solution.

Directly measured enthalpies of solution of solid B in liquid A are converted into partial molar enthalpies of mixing B by taking into account the reference data [6] on high temperature enthalpy contents and melting enthalpies of pure components. In some cases, as in the current experiments, the initial state of B may correspond to the overcooled liquid metal.

Several sets of $\overline{\Delta H}_{\mathrm{B}}$ data points from different runs are treated simultaneously by means of least squares regression. The linear model with orthonormal polynomials as basis functions is applied to the α_{B}-function $\alpha_B(x_B) = \{[\overline{\Delta H}_B(x_B)]/(1-x_B)^2\}$, where x_{B} stands for the molar fraction of B, to give the best fit curve. Orthonormal basis functions are generated according to the procedure of Forsythe [7], and the order of optimal model is chosen by means of the Fisher criterion. Such a scheme of data processing is computationally advantageous; it does not simply ensure primary smoothing of data, it also allows for the evaluation of their accuracy [8]. For the convenience of further usage, the coefficients of the orthonormal polynomial model are normally converted into coefficients $\{\theta_i\}$ of a simple polynomial model

$$\alpha_{\mathrm{B}}(x_{\mathrm{B}}) = \sum_{i=1}^{n} \theta_i x_B^{i-1} \qquad (3)$$

The integral and both partial enthalpies of mixing in a binary system are interrelated by the Gibbs–Duhem equation and are readily available if the function was continuously measured from the infinitely dilute solutions

$$\overline{\Delta H}_{\mathrm{B}}(x_{\mathrm{B}}) = (1-x_{\mathrm{B}})^2 \alpha_{\mathrm{B}}(x_{\mathrm{B}})$$

$$\Delta H(x_{\mathrm{B}}) = (1-x_{\mathrm{B}}) \int_{x_{\mathrm{B}}=0}^{x_{\mathrm{B}}} \alpha_{\mathrm{B}}(x_{\mathrm{B}})\mathrm{d}x_{\mathrm{B}}$$

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[2] As there is no significant difference in using m, v, or h as an independent variable, we will retain the most convenient form, mass, in all future considerations.

$$\overline{\Delta H}_{A}(x_B) = -x_B(1-x_B)\alpha_B(x_B) + \int_{x_B=0}^{x_B} \alpha_B(x_B)\mathrm{d}x_B \qquad (4)$$

High purity copper (99.997 wt.% plates, OC4-4-11), electrolytic vanadium (99.9 wt.%), electrolytic chromium (99.95 wt.%), and tungsten (99.96 wt.% rods, A-2) as inert reference material were employed in this study. All metals were of the former USSR origin. Enthalpy contents of added components were taken from the Hultgren et al. [6] reference book. The alloying process was performed in alumina crucibles of about 3 cm height, 2 cm external diameter and 6 cm^3 capacity. Before starting a series of measurements, the crucible was charged with about 4 to 10 g Cu. Masses of additions ranged from 0.15 to 0.25 g for copper, 0.02 to 0.08 g for vanadium or chromium samples, and 0.4 to 0.7 g for tungsten. Samples had a cylindrical shape with about 2 mm diameter and 1 cm height.

Enthalpies of solution were measured in three independent runs for each system at 1873 K. Experiments were carried out under a small excess pressure of high purity argon (99.997 vol.%).

3. Results and discussion

Solution of vanadium and chromium in liquid copper was accompanied with considerable endothermic effects. Fig. 2 illustrates the scattering of $\overline{\Delta H}_{\langle M\rangle}$ points in both systems along with the best fit smoothing functions. Statistical treatment of data allowed evaluation of random errors, which are subsequently reported as two population standard deviations.

The first enthalpy of solution of vanadium in copper (partial molar enthalpy of solution of solid vanadium in liquid copper at infinite dilution) was found to be $\overline{\Delta H}^0_{\langle V\rangle} = 87.1 \pm 6.0$ kJ mol^{-1}, while the first enthalpy of mixing of vanadium with copper (partial molar enthalpy of mixing of the overcooled liquid vanadium with liquid copper to produce infinitely dilute alloy) constituted $\overline{\Delta H}^0_{(V)} = 66.3 \pm 6.1$kJmol^{-1}. Respective values for chromium were found to be $\overline{\Delta H}^0_{\langle Cr\rangle} = 112.0 \pm 6.3$ kJ mol^{-1} and $\overline{\Delta H}^0_{(Cr)} = 95.3 \pm 6.4$ kJ mol^{-1}.

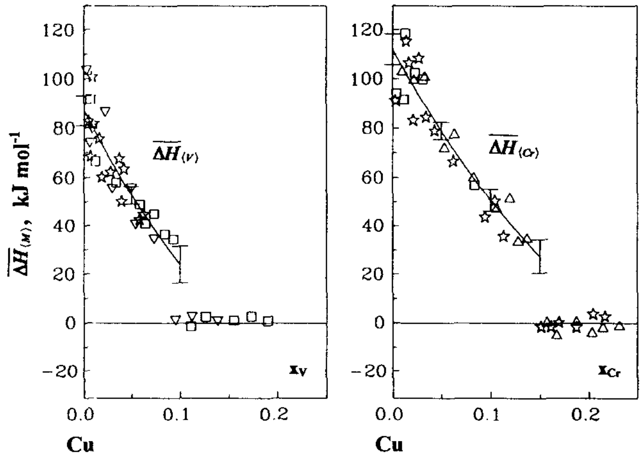

Fig. 2. Partial molar enthalpies of solution of solid vanadium and chromium in liquid Cu–V and Cu–Cr alloys at 1873 K. Confidence range corresponds to two population standard deviations.

As can be seen from Fig. 2, the solution of vanadium samples was observed to molar fraction $x_V = 0.09$, while chromium samples were dissolved to $x_{Cr} = 0.14$. This conclusion is based on the stepwise changes of partial molar enthalpies at the respective compositions. Such discontinuity of the concentration dependence of thermodynamic properties can be caused either by entering a heterogeneous region (in our case, presumably the region Liquid + (V)- or (Cr)-solid solution), or by decreasing the solution rate to such an extent that the power of the generated heat flux drops below the detection threshold of the instrument.

Concentration dependence of partial molar enthalpies of solution of vanadium and chromium in copper was represented for the respective ranges of liquid solutions by the equations

$$\overline{\Delta H}_{\langle V\rangle}\ /\mathrm{kJ\ mol^{-1}} = (1-x_V)^2(87.13 - 575.94x_V) \quad 0 \leq x_V \leq 0.09$$

$$\overline{\Delta H}_{\langle Cr\rangle}\ /\mathrm{kJ\ mol^{-1}} = (1-x_{Cr})^2(111.99 - 494.42x_{Cr}) \quad 0 \leq x_{Cr} \leq 0.14 \qquad (5)$$

Smoothed values of integral and partial enthalpies of mixing are reported in Table 1 along with the precision estimates.

Our results for the enthalpies of solution of vanadium and chromium are in good agreement with the values reported in Ref. [1]. In this earlier work, the authors studied the enthalpies of solution of the above metals in liquid copper at 1373 K. At such a low temperature the solubility of vanadium did not exceed 0.4 at.% and the first enthalpy was estimated as

Table 1
Integral and partial molar enthalpies of mixing in Cu–V and Cu–Cr systems at 1873 K, in kJ mol^{-1}; the accuracy of functions is reported as two population standard deviations

x_M	ΔH	$\overline{\Delta H}_{(M)}$	$\overline{\Delta H}_{(Cu)}$
Cu–V			
0.00	0	66.3 ± 6.1	0
0.05	2.41 ± 0.19	31.7 ± 3.7	0.87 ± 0.01
0.10	3.16 ± 0.85	3.2 ± 7.6	3.16 ± 0.09
Cu–Cr			
0.00	0	95.3 ± 6.4	0
0.05	3.89 ± 0.19	61.9 ± 3.5	0.84 ± 0.01
0.10	6.17 ± 0.52	33.8 ± 4.7	3.10 ± 0.06
0.15	7.0 ± 1.2	10.8 ± 7.0	6.37 ± 0.22

$\overline{\Delta H}^0_{\langle V\rangle} = 80 \pm 25$ kJ mol^{-1}. Chromium solubility did not exceed 1.5 at.% and the limiting partial enthalpy of solution totalled $\overline{\Delta H}^0_{\langle Cr\rangle} = 90 \pm 17$ kJ mol^{-1}. According to Ref. [1], the rate of solution of samples was low, which hampered establishing the exact moment of the end of dissolution. This might have resulted in certain underestimation of $\overline{\Delta H}^0_{\langle M\rangle}$ values. In light of the fact that our experiments were carried out at a 500 K higher temperature, which is generally known to reduce both exothermic and endothermic effects, underestimation of $\overline{\Delta H}^0_{\langle M\rangle}$ values in Ref. [1] becomes even more probable.

The value $\overline{\Delta H}^0_{(Cr)} = 33$ kJ mol^{-1} at 1823 K, reported in Ref. [9], is nearly three times less than measured directly in this work and more than twice less than found in Ref. [1]. Once again this proves that the enthalpies of mixing derived from the temperature dependence of the Gibbs function at high temperatures are unreliable for liquid alloys.

Limiting values of the partial molar enthalpies of liquid alloys predicted by Miedema's theory, $\overline{\Delta H}^0_{(V)} =$ 21 kJ mol^{-1} and $\overline{\Delta H}^0_{(Cr)} = 51$ kJ mol^{-1} [10], lay rather far from the experimental results. Indeed, the first estimate constitutes less than one third, while the second hardly one half of the values measured by calorimetry.

Large positive values of solution enthalpies of vanadium and chromium in liquid copper indicate strong positive deviations of the alloys from ideal behaviour, and, consequently, preferable interactions of similar atoms in the melt. This conclusion is supported by vapour pressure [9] and e.m.f. [11] activity measurements in dilute liquid alloys, as well as by the shapes of Cu–V and Cu–Cr phase diagrams [12,13]. Both systems exhibit ranges of immiscibility of liquid alloys in the vicinity of equiatomic concentration (in Ref. [12] the liquidus curve is drawn by dashed line and has a range of nearly flat liquidus). The wider range of liquid solutions detected calorimetrically in the Cu–Cr system, is fully in accord with the less extended (along both composition and temperature axes) range of immiscibility in it, reported in Ref. [13].

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