

# Thermodynamic reassessment of the Cu–V system supported by key experiments

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## Abstract

The temperature of the degenerated invariant reaction in the Cu–V system was accurately determined by means of Differential Scanning Calorimetry (DSC) measurements. On the basis of the experimental data from the present work and those critically assessed from the literature, an optimal thermodynamic data set for the Cu–V system was obtained. Significant improvements have been made, compared with the previous assessments.

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**Keywords:** Phase diagram; Cu–V system; Thermodynamic calculation; Thermal analysis

## 1. Introduction

The addition of V in Cu alloys can improve mechanical properties and heat resistance of Cu alloys [1]. This effect can be reinforced by increasing the solubility of V in Cu during the synthesis of the alloys [2]. It is recognized that knowledge of phase equilibria and thermodynamic properties of the Cu–V system is of fundamental importance for technological applications of Cu–V-based alloys. In addition, the Cu–V system attracts basic scientific interest due to the existence of the degenerated phase equilibria in extreme Cu side, viz. the invariant reaction temperature is very close to the melting point of Cu. As shown in Table 1, the reaction temperatures reported in the studies [3–5] show noticeable discrepancies. For example, the temperature is reported to be 1085 °C by McHugh [3], which is only higher by 0.6 °C than the melting point of Cu. However, Savitskii et al. [4] reported a higher reaction temperature of 1120 °C.

The Cu–V system has been critically assessed by Hansen and Anderko [6], and updated by subsequent investigators [7–10]. Using the Lukas program, Härmäläinen et al. [11] first performed a complete thermodynamic calculation for the Cu–V system. However, the experimental data from Savitskii et al. [4] and Efimov [12] were

not considered by Härmäläinen et al. [11]. A most recent calculation was conducted by Turchanin [13] considering all the experimental data available in the literature. Although the calculated phase equilibria and thermodynamic properties agree well with the experimental ones, Turchanin [13] used too many parameters for the descriptions of the individual phases. For example, as many as 5 parameters are employed to describe the liquid phase. There is no experimental evidence for the introduction of so many parameters for the liquid phase.

The purposes of the present study are to (i) determine the degenerated invariant reaction temperature in the Cu–V system accurately using a novel experimental method proposed by Du et al. [14], and (ii) perform a thorough thermodynamic modeling for the Cu–V system based on the experimental data critically assessed from the literature, supplemented with the present work.

## 2. Evaluation of experimental phase diagram and thermodynamic data

By means of X-ray diffraction (XRD) analysis, optical microscopy, microhardness measurement and electrical resistance methods, Savitskii et al. [4] observed a wide range of miscibility gap in the liquid phase. The temperatures of a monotectic reaction ( $L_2 \leftrightarrow L_1 + (V)$ ) and a peritectic reaction ( $L + (V) \leftrightarrow (Cu)$ ) are determined to be  $1530 \pm 15$  °C and  $1120 \pm 5$  °C, respectively [4]. Subsequently, Efimov [12] investigated the

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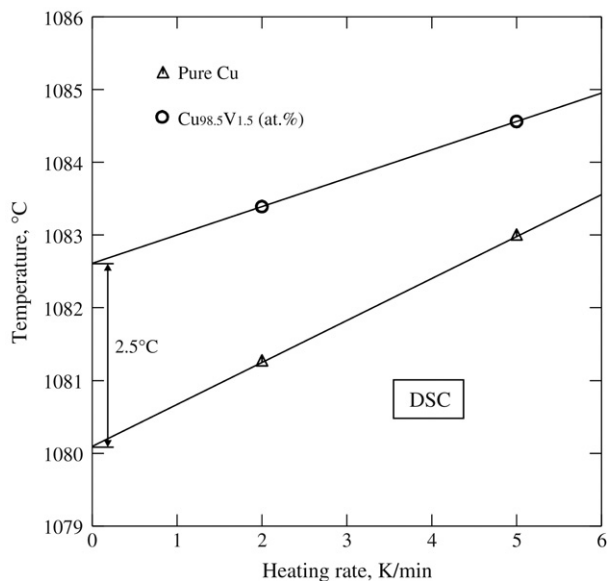


Fig. 1. Measured phase transition temperatures as a function of the heating rate for pure Cu and Cu<sub>98.5</sub>V<sub>1.5</sub> (at.%) annealed at 1000 °C for 14 days.

liquid miscibility gap by using chemical analysis of specimens. Using electromagnetic separation technique, Allibert and Driole [15] measured liquidus and solidus lines of the (V) phase. Based on the relationship between the electrical resistance of specimens and the corresponding quenching temperatures, the solubility of V in Cu was determined by Eicke and Hahlbohm [16]. All the above experimental data [4,12,15,16] are utilized in the present work since they are consistent with each other. The liquidus and solidus lines of (V) phase determined by Stevens [5] and the solubility of V in Cu at 1000 °C measured by McHugh [3] are also used in the present optimization.

Using a high temperature reaction calorimetry, Watanabe and Kleppa [17] determined the enthalpy of mixing for Cu<sub>99.97</sub>V<sub>0.03</sub> (at.%) melt at 1100 °C. However, a high uncertainty as much as 20–30 kJ/mol was attached to this single experimental data. By means of a high temperature calorimetry, Turchanin and co-workers [18,19] measured standard enthalpies of V in liquid Cu with a high accuracy. Consequently, the experimental data from [18,19] are employed in the present optimization, while that from [17] is not.

### 3. Experimental process

In order to measure the degenerated equilibrium in extreme Cu side of the Cu–V system accurately, two decisive alloys, Cu<sub>98.5</sub>V<sub>1.5</sub> (at.%) and Cu<sub>50</sub>V<sub>50</sub> (at.%), were prepared by using 99.98 wt.% purity Cu pieces and 99.8 wt.% V rods in an arc-melting furnace (WKDHL-I, Opto-electronics Co. Ltd., Beijing, China) under high purity argon atmosphere using a nonconsumable W electrode. The buttons were remelted five times to improve their homogeneities. No chemical analysis for the alloys was conducted since the weight losses of alloys were all less than 0.5 wt.% during arc-melting. The two alloys as well as pure Cu were sealed in evacuated quartz tubes under vacuum of 10<sup>-4</sup> bar in an L4514-type diffusion furnace (Qingdao

Table 1

Summary of experimental data on the invariant equilibrium in extreme Cu side of the Cu–V system

Source	Method	Invariant equilibrium
[3]	TA on cooling	L + (V) ↔ (Cu) at 1085 °C
[4]	MSM, TA, HM, MHM, and ERM	L + (V) ↔ (Cu) at 1120 °C
[5]	TA	L + (V) ↔ (Cu) at 1088 ± 3 °C
This work	DSC on heating	L + (V) ↔ (Cu) at 1087 ± 2 °C

TA = Thermal analyses; MSM = Microstructural measurements; HM = Hardness measurements; MHM = Microhardness measurements; ERM = Electron resistivity measurements.

Instrument & Equipment Co. Ltd., China), and annealed at 1000 °C for 14 days, followed by water quenching. The phase identification was performed by means of XRD (Rigaku D/max2550VB, Japan).

Differential Scanning Calorimetry (DSC) (DSC404C, Netzsch, Germany) measurements were carried out in order to determine the degenerated equilibrium temperature accurately. Both the Cu and Cu<sub>98.5</sub>V<sub>1.5</sub> alloys were subjected to DSC measurements from room temperature to 1300 °C with heating rates of 2 and 5 K/min. The transition temperature is obtained by extrapolating the heating rates to 0 K/min as described by Du et al. [14]. Differential Thermal Analysis (DTA) (DSC404C, Netzsch, Germany) measurement was performed for the Cu<sub>50</sub>V<sub>50</sub> alloy from room temperature up to 1550 °C with a heating rate of 5 K/min.

Table 2 lists the results of phase identifications by XRD as well as the phase transition temperatures resulting from DSC and DTA measurements. Fig. 1 presents the phase transition temperatures measured by DSC against the heating rate for both pure Cu and the alloy Cu<sub>98.5</sub>V<sub>1.5</sub>. It clearly indicates that the degenerated temperature was higher by 2.5 °C than the melting point of Cu, showing a peritectic reaction among (Cu), liquid and (V) phases. The degenerated equilibrium temperature was placed at 1087 ± 2 °C by calibrating to the melting point of Cu assessed by Dinsdale [20]. The nonexistence of a thermal effect between the degenerated equilibrium temperature and 1550 °C in the DTA curve of the alloy Cu<sub>50</sub>V<sub>50</sub> indicates that the monotectic reaction (L<sub>2</sub> ↔ L<sub>1</sub> + V) should occur above 1550 °C.

### 4. Thermodynamic model

On the basis of the experimental data from the present work and the literature, a thorough thermodynamic optimization of the Cu–V system was then conducted. The thermodynamic properties of Cu and V are taken from the SGTE compilation [20]. Three phases, (Cu), (V) and liquid, in the Cu–V system are all treated as solution phases and their Gibbs energies are described by the Redlich–Kister polynomials [21]:

$$G_m^\phi - H_m^{\text{SER}} = (1-x)G_{\text{Cu}}^{0,\phi} + xG_{\text{V}}^{0,\phi} + RT[x \ln x + (1-x) \ln(1-x)] + x(1-x)[a_0 + b_0T + c_0T \ln(T) + (1-2x)(a_1 + b_1T + c_1T \ln(T)) + \dots] \quad (1)$$

in which  $H_m^{\text{SER}}$  is the abbreviation of  $(1-x)H_{\text{Cu}}^{\text{SER}} + xH_{\text{V}}^{\text{SER}}$ ,  $R$  is the gas constant, and  $x$  is the mole fraction

Table 2  
Summary of the phase and phase transition temperatures for the samples in the Cu–V system

No	Nominal composition (at.%)	Phase	Experimental method	Heating rate and transition temperature (°C)
1	Pure Cu	Cu	DSC on heating	2 K/min: 1081.3 5 K/min: 1083.0
2	Cu <sub>98.5</sub> V <sub>1.5</sub>	(Cu), (V)	DSC on heating	2 K/min: 1083.4 5 K/min: 1084.6
3	Cu <sub>50</sub> V <sub>50</sub>	(Cu), (V)	DTA on heating	5 K/min: 1087.1

The samples were annealed at 1000 °C for 14 days.

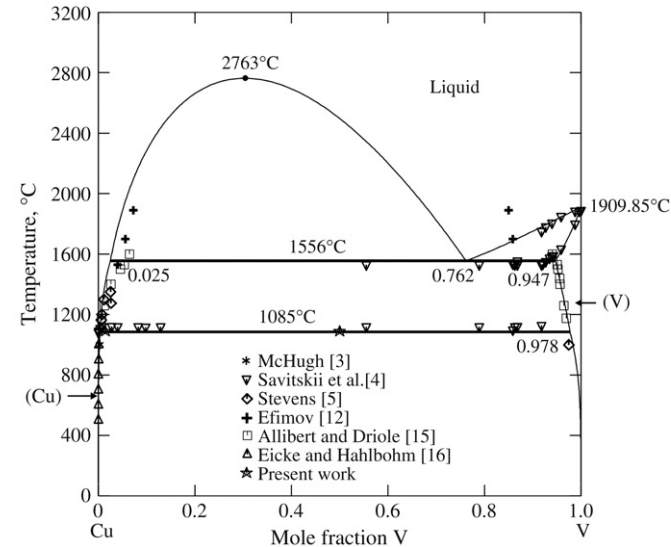


Fig. 2. Calculated Cu–V phase diagram along with the experimental data from the present work and the literature [3–5,12,15,16].

of V. The interaction parameters  $a_0$ ,  $b_0$ ,  $c_0$ ,  $a_1$ ,  $b_1$  and  $c_1$  could be optimized from the experimental phase diagram and thermodynamic data.

The evaluation of the model parameters is attained by recurrent runs of the PARROT program [22], which works by minimizing the square sum of the differences between experimental values and computed ones. The step-by-step optimization procedure described by Du et al. [23] was utilized in the present assessment.

### 5. Results and discussion

The thermodynamic parameters finally obtained in the present work, as well as those from Hämmäläinen et al. [11] and

Table 3  
Optimized thermodynamic parameters in the Cu–V system from various sources

Redlich–Kister formalism:  ${}^{\text{ex}}G_m^\phi = x(1-x)[a_0 + b_0T + c_0T \ln(T) + (1-2x)(a_1 + b_1T + c_1T \ln(T)) + \dots]$  ( ${}^{\text{ex}}G_m^\phi$  is excess Gibbs energy;  $\phi = (\text{Cu})$  or  $(\text{V})$  or Liquid)

Phase	$i$	$a_i$ (J/(mol-atoms))			$b_i$ (J/(mol-atoms K))			$c_i$ (J/(mol-atoms K))		
		This work	[11]	[13]	This work	[11]	[13]	This work	[11]	[13]
(Cu)	0	53 650	56 136.78	55 000	–	3.51936	–	–	–	–
(V)	0	42 377.8	30 509.5	42 475.1	–	6.59362	–	–	–	–
Liquid	0	37 900	118 298.0	121 287.3	–	–38.4905	–213.21	–	–	22.65
	1	18 500	–1137.4	18 829.2	–	–	–	–	–	–
	2	–	–	–15 156.6	–	–	–	–	–	–

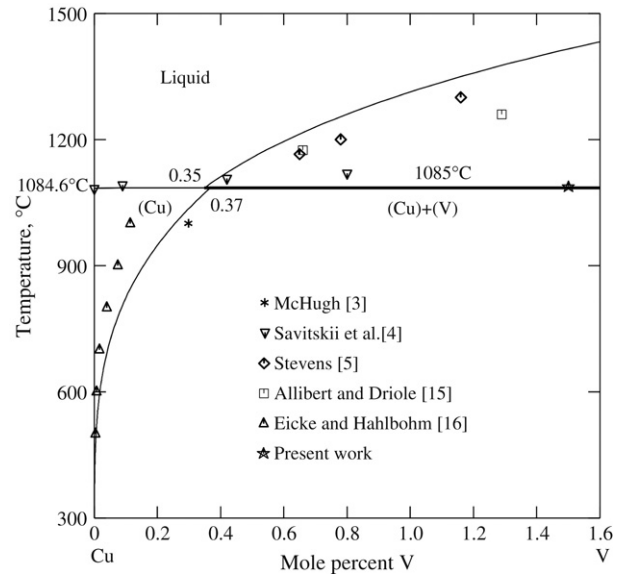


Fig. 3. Enlarged Cu-rich region indicating the detail of the degenerated equilibrium,  $L+(V) \leftrightarrow (\text{Cu})$ , along with the experimental data from the present work and the literature [3–5,15,16].

Turchanin [13], are listed in Table 3. As can be seen from the table, only 4 parameters are used in the present work while in the previous two assessments [11,13] as many as 7 parameters are used to describe this system. Fig. 2 shows the calculated Cu–V phase diagram along with the experimental data from the present work and the literature [3–5,12,15,16]. An enlarged Cu-rich region showing the detail of the degenerated equilibrium is presented in Fig. 3. The presently calculated solid solubility of V in Cu is slightly larger than the experimental one from Eicke and Hahlbohm [16]. It was found thermodynamically that the solubility data of Eicke and Hahlbohm [16] are not consistent with the presently measured degenerated equilibria among Liquid, (Cu) and (V). As shown in the two figures, the present calculations agree reasonably with the experimental data except for a slight deviation in the Cu-rich side. This deviation may be due to the inaccuracy of the experimental data in such a dilute solution region. The calculated phase diagrams from both the present work and Turchanin [13] are illustrated in Fig. 4. In spite of the less number of the adjustable parameters, a better agreement with the experimental data is obtained in the present work in comparison with the previous evaluations. The calculated enthalpies of mixing for liquid at 1600 °C along with the experimental data from Turchanin and Nikolaenko [18]

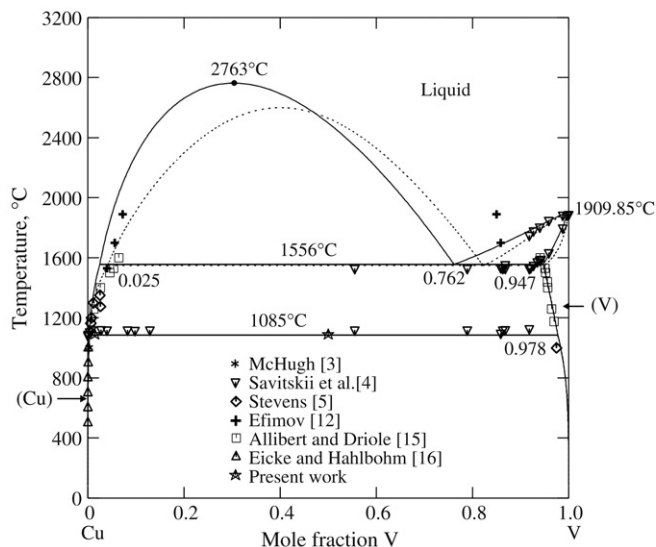


Fig. 4. Calculated Cu–V phase diagram from the present work (solid lines), compared with that from Turchanin [13] (dashed line).

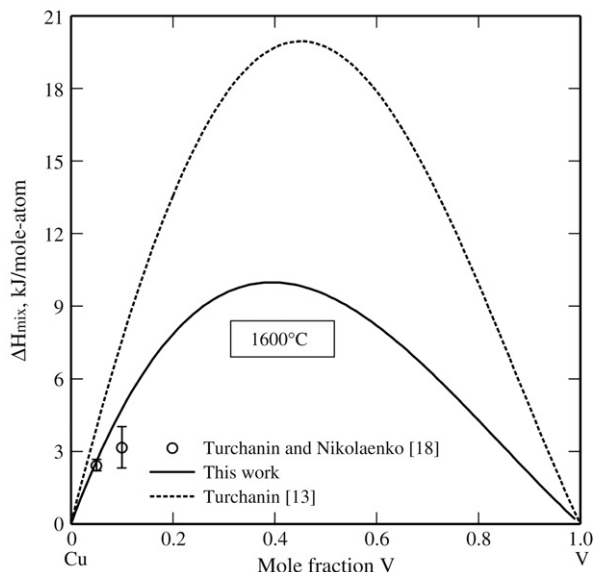


Fig. 5. Calculated enthalpies of mixing for the liquid at 1600 °C by means of the parameters obtained in the present work (solid line) and Turchanin [13] (dashed line), compared with the experimental data from Turchanin and Nikolaenko [18]. The reference states are liquid Cu and liquid V.

are shown in Fig. 5. As indicated in this figure, the present optimization yields a better fit to the experimental data than the previous assessment of Turchanin [13]. Additionally, the presently calculated value for enthalpy of mixing of the  $\text{Cu}_{99.97}\text{V}_{0.03}$  melt at 1100 °C is 56.34 kJ/mol. This computed datum agrees reasonably with the experimental one of 80 ± 25 kJ/mol from Watanabe and Kleppa [17].

## 6. Conclusions

The temperature associated with the degenerated reaction ( $\text{L} + (\text{V}) \leftrightarrow (\text{Cu})$ ) is accurately determined by means of

DSC measurements. On the basis of the experimental data from the present work and those critically assessed from the literature, an optimal thermodynamic data set for the Cu–V system was obtained. In the present modeling, the introduction of each parameter is justified by corresponding experimental evidence. The calculated phase diagram and thermodynamic properties agree reasonably with the experimental data. Significant improvements have been made, compared with the previous assessments. The presently obtained thermodynamic parameters in the Cu–V system are expected to be incorporated into thermodynamic databases of multi-component systems containing both Cu and V.

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