

PHASE EQUILIBRIA AND THERMODYNAMICS OF BINARY COPPER SYSTEMS WITH 3d-METALS. II. THE COPPER – VANADIUM SYSTEM

M. A. Turchanin

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Thermodynamic assessment of the Cu – V system was carried out using the CALPHAD method. The excess heat capacity of the liquid phase was taken into account in the model of its excess Gibbs free energy. Excess thermodynamic properties of limiting solid solutions were represented by regular solution models. A self-consistent set of thermodynamic parameters was obtained using data on the mixing enthalpy and information on the phase equilibria. The thermodynamic properties of the phases and the phase diagram along with its metastable extension were calculated using this set of parameters. The thermodynamic model of the system was used in order to predict the composition limits of formation of supersaturated solid solutions prepared by highly nonequilibrium methods of synthesis.

Keywords: *phase diagram, thermodynamics, thermodynamic modelling, metastable transformation, copper alloy, supersaturated solid solution.*

Vanadium is a modifying agent to copper alloys [1]. The high chemical affinity of vanadium to oxygen along with low chemical affinity to copper makes it possible to expect an effective deoxidizing action for this addition. Introduction of vanadium leads to hardening and increase of heat resistance of copper alloys [1]. As has been shown in [2], reinforcement of this effect is possible due to extension of the vanadium solubility limits in copper during synthesis of alloys by quenching from a liquid state. Vanadium dissolves up to several atomic percentages of copper, that as result of this may be considered as an effective alloying addition for solution hardening of vanadium based alloys. Therefore a thermodynamic modelling of the copper – vanadium system is of interest not only from a theoretical point of view but also practically.

PHASE TRANSFORMATIONS AND THERMODYNAMIC PROPERTIES OF PHASES

Modern ideas on the nature of phase relations in the copper – vanadium system are based on the results of works [3-6]. According to these data, two regions of primary solidification are observed in the system: solid solution based on the copper, (Cu)-phase, and solid solution based on the vanadium, (V)-phase. The (Cu)-phase forms according to peritectic reaction $L + (V) \rightleftharpoons (Cu)$ at a temperature insignificantly exceeding the melting temperature of copper, and is characterized by low limiting solubility of vanadium. The (V)-phase forms according to monotectic reaction $L_2 \rightleftharpoons L_1 + (V)$ and it dissolves up to several atomic percents of copper at the temperature of nonvariant transformation. The temperature of this transformation remains a main point at issue of the phase equilibria in this system.

In [4] phase equilibria in the system were studied by thermal and x-ray analyses, optical microscopy, microhardness measurement and electrical resistance methods. Miscibility gap was detected in the system for components in the liquid state, and the occurrence of monotectic ($T = 1803 \pm 15$ K) and peritectic ($T = 1393 \pm 5$ K) reactions was established. In [5] the miscibility gap in the liquid state was studied on the basis of the chemical analysis of specimens quenched from the temperature region of immiscibility and at the monotectic temperature. Results of these studies are presented in Fig. 1.

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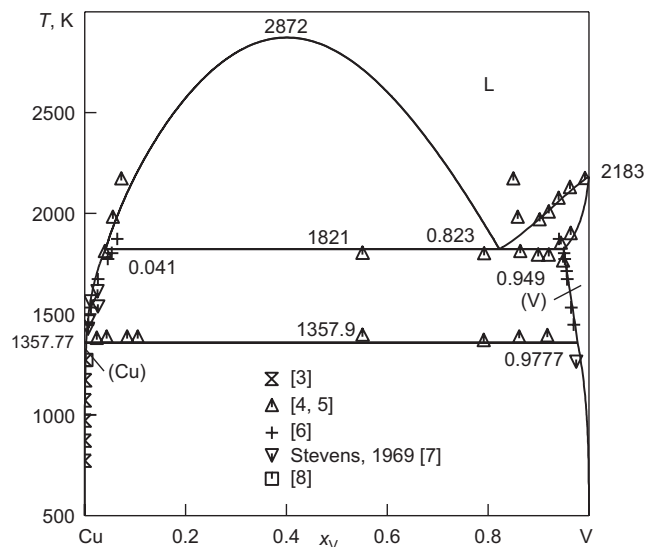


Fig. 1. Phase diagram of the copper – vanadium system calculated within the framework of the thermodynamic evaluation, and the position of the phase boundaries established experimentally: here and further the results of experiments are indicated by symbols and the lines show the results of calculations

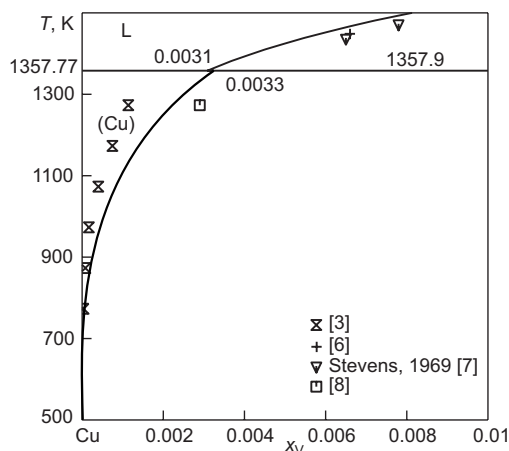


Fig. 2. Solubility of vanadium in (Cu)-phase in the case of peritectic transformation $L + (V) \rightleftharpoons (Cu)$

The position of the low-temperature part of the liquidus line and solidus line of the (V)-phase (Fig. 1) were studied by electromagnetic separation method in [6]; the obtained results do not contradict fundamentally with the phase diagram proposed by [4, 5].

The solubility of vanadium in copper was studied in [3] on the base of the relationship between the electrical resistance of specimens and their quenching temperature (Fig. 2). The most complete review of experimental works devoted to studying of phase equilibria in the copper – vanadium system was given in [7]. The authors of this review cite data of yet two more works. In one of them (unpublished work of R. E. Stevens, 1969) the position of the liquidus and solidus lines for the (V)-phase was established, and in another [8] the solubility of vanadium in copper was studied at 1273 K. Results of the both works are shown in Figs. 1 and 2.

Currently known literature data on the coordinates of nonvariant transformations are presented in Table 1.

The results of calorimetric study of the formation enthalpy of liquid enriched by copper alloys at 1873 K [9] are the single information on the thermodynamic properties of phases of the system. It was established in [9] that melts of the system form with considerable endothermic thermal effects reaching for the first mixing enthalpy of vanadium

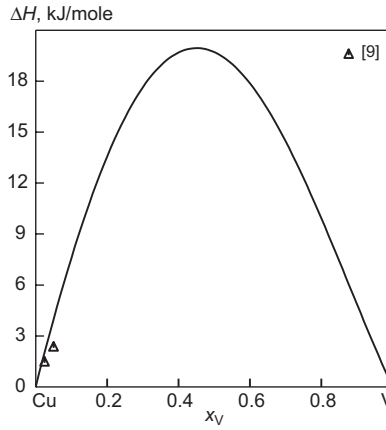


Fig. 3. Mixing enthalpy of liquid copper and vanadium at 1873 K

$\Delta\bar{H}_V^\infty = 69.7 \pm 6.8$ kJ/mole. The concentration dependence of the integral mixing enthalpy of liquid copper and supercooled vanadium in the composition range $0 \leq x_V \leq 0.09$ was described by the equation

$$\Delta H = x_V(1 - x_V)(69.71 - 504.75x_V - 1554.68x_V^2) \text{ kJ/mole.}$$

The results of work [9] are presented in Fig. 3. They do not contradict to the approximate value of the first enthalpy of dissolution of vanadium in copper at 1373 K ($\Delta\bar{H}_{<V>}^\infty = 80 \pm 25$ kJ/mole) obtained in [10], that in the opinion of the authors was understated.

TABLE 1. Experimentally Determined and Computed Parameters of Nonvariant Transformations in the Cu – V System

$L_2 \Leftrightarrow L_1 + (V)$				
T, K	$x_V^{L_1}$	$x_V^{L_2}$	$x_V^{(V)}$	Source
Experimental data				
1803 ± 15	0.04	0.864	0.92	[4, 5]
>1873	>0.065		<0.941	[6]
Results of calculations				
2051				[6, 7]
2052.7	0.22	0.81	0.95	[11]
1821	0.041	0.823	0.949	P. w.*
$L + (V) \Leftrightarrow (Cu)$				
T, K	x_V^L	$x_V^{(Cu)}$	$x_V^{(V)}$	Source
Experimental data				
1393 ± 5	0.004	0.008	>0.96	[4, 5]
		>0.001		[3]
1358		<0.003		[8]
1361 ± 3			$<0.97-0.98$	[7]
Results of calculations				
1358		0.0017		[7]
1358.4	0.0016	0.0019	0.9696	[11]
1357.9	0.0031	0.0033	0.9777	P. w.
* Present work.				

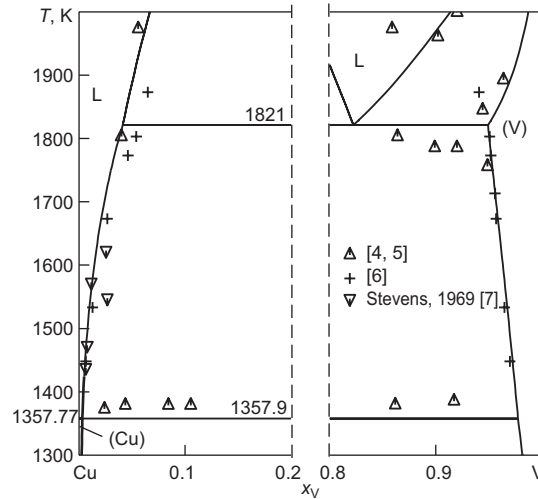


Fig. 4. Experimentally established and calculated phase boundaries for equilibria $L + (V) \leftrightarrow (Cu)$ and $L_2 \leftrightarrow L_1 + (V)$

The first attempt of theoretical calculation of the phase diagram or parts of it was carried out in [5]. In this work on the basis of calculations and reasoning that was empirical in nature a binodal of the liquid phase was constructed and the temperature of the critical point of immiscibility (2853 K) was established close to the equiatomic composition. In [6] on the basis of own experimental data on the solubility of vanadium in molten copper and solubility of copper in solid vanadium in the temperature range 1473-1873 K the parameters of regular solution models were evaluated for liquid and (V)-phase, and phase diagram of the system was calculated with a temperature of the monotectic reaction 2051 K and a temperature of the critical point 2220 K. Later, the results of this work were cited in [7]. In order to explain in [7] the considerable difference between the results of calculations [6] and primary experimental data on the monotectic temperature [4, 5] an argument about the insufficient purity of the vanadium used in [4, 5] (content of the main component 99.7 mass%) was adduced. A result similar in sense to [6] was obtained in [11]. In contrast to [6], in this work the thermodynamic models were presented for all three phases of the system.

Thus, with regard to the copper – vanadium system phase diagram the following situation had arisen currently. On the one hand the majority of reference books quote the results of calculations similar to [6, 11] ignoring the experimental information [4, 5] on the temperature of the monotectic reaction. At the same time any experimental information to the effect that the monotectic temperature may be so high and reach 2050 K [6, 11] is absent. On the other hand, none of the critics declining the results [4, 5] has estimated how there should be a thermodynamic interaction parameter of an impurity (with a limiting concentration of it less than 1 at.%) with copper-vanadium melts in order that the shift of temperature of the nonvariant transformation due to it reached $\Delta T \approx 250$ K.

THERMODYNAMIC DESCRIPTION OF THE SYSTEM AND MODELS

The aim of the present work is thermodynamic evaluation of the copper – vanadium system on the basis of generalizing the majority of known consistent data on its phase equilibria and data on the thermodynamic properties of melts. Consistent data on phase equilibria may be: information on the existence of miscibility gap, on the peritectic transformation in the system (Fig. 1), on the position of the low-temperature part of the liquidus line [4-7], information on the solidus of the (V)-phase [4, 6] (the last two portions are shown in Fig. 4 on an enlarged scale) and on the boundary of the saturation region of the (Cu)-phase [3, 8] (Fig. 2).

Thermodynamic evaluation of the system was carried out within the CALPHAD-method. The dependence of Gibbs free energy of the phase (ϕ) on temperature and composition was described by the expression

$$G^{(\phi)} = (1 - x_V)({}^\circ G_{Cu}^{(\phi)} - H_{Cu}^{SER}) + x_V({}^\circ G_V^{(\phi)} - H_V^{SER}) + RT((1 - x_V)\ln(1 - x_V) + x_V \ln x_V) + \Delta G_{exc}^{(\phi)}(x_V, T),$$

where $(^{\circ}G_{\text{Cu}}^{(\phi)} - H_{\text{Cu}}^{\text{SER}})$ and $(^{\circ}G_{\text{V}}^{(\phi)} - H_{\text{V}}^{\text{SER}})$ are molar energies of pure copper and vanadium; $\Delta G_{\text{exc}}^{(\phi)}(x_{\text{V}}, T)$ is the excess component of Gibbs free energy. Data on the thermodynamic properties of copper and vanadium were taken from the SGTE data base [12]. In order to describe the excess term of Gibbs free energy of solid and liquid solutions the following expression was used

$$\Delta G_{\text{exc}}^{(\phi)}(x_{\text{V}}, T) = (1 - x_{\text{V}})x_{\text{V}} \sum_{i=0}^n (1 - 2x_{\text{V}})^i (A_i + B_i T + C_i T \ln(T)),$$

where i is the power of the Redlich-Kister polynomial, A_i , B_i , C_i are coefficients of the model. Model coefficients were optimized using the Thermo-Calc program. In the first stage of thermodynamic optimization the data on the thermodynamic properties of the liquid phase [9] and information on the parameters of monotectic and peritectic transformations [4, 5] were used. Here in order to describe the thermodynamic properties of each of the phases a set of coefficients A_0 and B_0 was used. In the next stage of optimization the experimental data on the location of the liquidus line of the (V)-phase [6, 7] in the region of alloys rich in copper, and in the region rich in vanadium [4], and also data on the location of the solidus line of the (V)-phase [4, 6, 7] and on the saturation limits of the (Cu)-phase [4, 8] were included. Simultaneous description of the low- and high-temperature portions of the liquidus line of the (V)-phase along with the mixing enthalpy isotherm of components required a complication of the structure of the model of the thermodynamic properties of the liquid phase. A coefficient A_1 was added for this purpose. In this stage the structure of the models of the thermodynamic properties of the (V)- and (Cu)-phases was simplified due to rounding to zero the corresponding coefficients B_0 . Then, in order to clarify the position of the monotectic and the binodal connected with it, the coefficients A_2 and C_0 were successively added in the thermodynamic model of the liquid phase. It appeared that introduction of the coefficient C_0 , taking into account the temperature dependence of the mixing enthalpy, had a greater effect on the results of calculation than further complication of the model due to the addition of coefficient A_i . The results of calculation of phase equilibria in the system are presented in Figs. 1-4 and in Table 1. Calculated model coefficients of the thermodynamic properties are listed in Table 2.

RESULTS OF CALCULATIONS AND DISCUSSION

As follows from Figs. 1-4, within the framework of the present thermodynamic evaluation of the system a simultaneous description may be obtained for the majority of known experimental data. For this purpose seven coefficients of the models describing the thermodynamic properties of three phases are required. It should be noted that in [11] a similar number of coefficients was used but there less correct description of the high-temperature part of the phase diagram was achieved. Therefore the current model of the liquid phase taking into account the excess specific heat appears to be entirely valid. At 1873 K the integral mixing enthalpy of melts reaches a maximum value of 19.9 kJ/mole at $x_{\text{V}} = 0.45$ (Fig. 3). The excess specific heat reaches a maximum value of 5.7 J/(mole · K) at the equiatomic composition.

The temperature of the monotectic reaction calculated by us was 1821 K, which is 18 K higher than the value obtained in [4, 5]. Coordinates of the critical point of immiscibility of the liquid phase were $T_{\text{cr}} = 2872$ K and $x_{\text{V}} = 0.4$, which agrees satisfactorily with the value of $T_{\text{cr}} = \sim 2853$ K and $x_{\text{V}} = 0.5$ calculated in [5]. According to the calculation [11] the corresponding temperature does not exceed ~ 2150 K. If this value is accepted, it becomes incomprehensible why the immiscibility cupola has not been studied in its central part by experiment.

According to calculation the peritectic transformation temperature exceeds insignificantly the melting temperature of pure copper and it is 1357.9 K, which corresponds to the maximum solubility of vanadium not exceeding several tenths of a percent (Table 1). Thereby the results obtained in [8] and in the work of Stephens from thermal analysis data are confirmed for the peritectic temperature according to which it exceeds by several degrees Kelvin the melting temperature of copper at comparable measurement error. The value of the vanadium solubility obtained by us at the peritectic temperature (Fig. 2) corresponds to a greater extent to the result [8] than [3]. Attempts to improve the conformity of results of the calculation and data [3] lead to a change in the type of reaction to eutectic $L \Leftrightarrow (\text{Cu}) + (\text{V})$ ($x_{\text{V}}^{(\text{Cu})} = 0.0019$, $x_{\text{V}}^{\text{L}} = 0.0031$, $x_{\text{V}}^{(\text{V})} = 0.9778$, $T = 1356.4$ K). The corresponding part of the phase diagram is presented

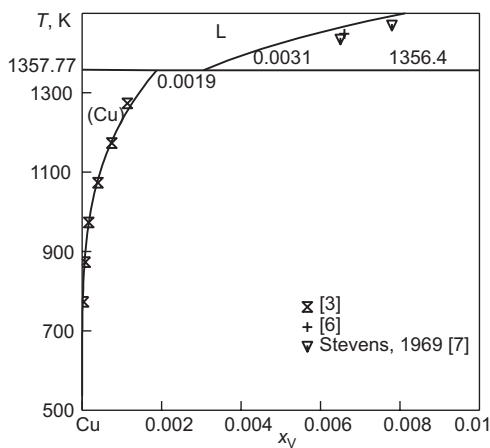


Fig. 5

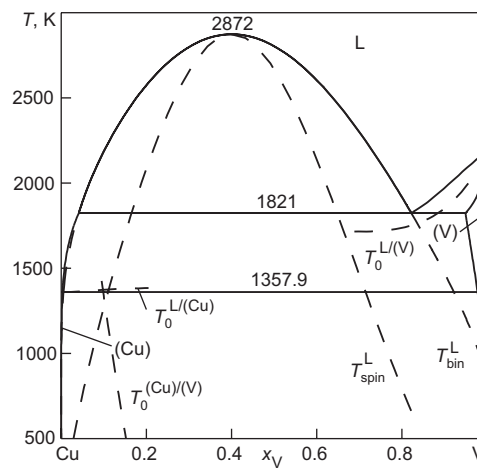


Fig. 6

Fig. 5. Solubility of vanadium in (Cu)-phase in the case of eutectic transformation $L \Leftrightarrow (Cu) + (V)$
 Fig. 6. Phase diagram of the copper-vanadium system, $T_0^{L/(Cu)}$, $T_0^{L/(V)}$, and $T_0^{(Cu)/(V)}$ lines, binodal T_{bin}^L and spinodal T_{spin}^L of the liquid phase

in Fig. 5. Such result may be obtained with a small change in coefficient A_0 for the (Cu)-phase to 61 kJ/mole. Such insignificant changes in temperature and composition of phases for this low-temperature nonvariant transformation do not make it possible to arrive at a final conclusion about its nature. For an unambiguous answer to this question more precise experimental definition of three values is required: transformation temperature, compositions of the liquid and (Cu)-phase at the transformation temperature. Currently, in accordance with the point of view adopted in publications, we present this transformation as peritectic.

Obtained thermodynamic models of phases give additional possibilities for evaluation of the concentration limits for occurrence in the system of some metastable transformations. One of these transformations is formation of supersaturated solid solutions with participation of supercooled melts. The phase diagram of the system is given in Fig. 6 together with a calculated spinodal for the liquid phase and $T_0^{L/(Cu)}$, $T_0^{L/(V)}$, and $T_0^{(Cu)/(V)}$ lines. From considerations of thermodynamics [13], the point of intersection of the $T_0^{L/(φ)}$ line with the spinodal of the liquid phase determines the theoretical limit of its supersaturation during quenching from a liquid. As follows from Fig. 6, the compositions at which the spinodal for melts intersects with $T_0^{L/(Cu)}$ and $T_0^{L/(V)}$ lines are equal respectively $x_V=0.107$ and $x_V=0.663$.

TABLE 2. Model Coefficients of the Thermodynamic Properties of Phases of the Copper – Vanadium System

$\Delta G_{exc}^{(\phi)} = (1 - x_V)x_V \sum_{i=0}^n (1 - 2x_V)^i (A_i + B_i T + C_i T \ln(T))$				
i	A_i		B_i	C_i
		L		
0	121287.28		-213.21	22.65
1	18829.2		-	-
2	-15156.6		-	-
		(Cu)		
0	55000		-	-
		(V)		
0	42475.08		-	-

At the same time, in [2] it was established that the solubility of vanadium in supersaturated solid solution prepared by melts spinning does not exceed 0.5 at.%. This value is satisfactory fit with the concentration of vanadium $x_V = 0.006$ at which the $T_0^{L/(Cu)}$ line intersects the binodal for the liquid phase. Apparently the moving force of decomposition of melts of the system is so great that cooling rates during melts spinning are not big enough to achieve that are required for reaching the theoretical saturation limit for the phases. By estimating the position of the $T_0^{(Cu)/(V)}$ line it is possible to suggest that with synthesis of supersaturated solid solution of the system by methods by-passing the liquid state (coprecipitation of elements on cooled substrates, grinding of powder metals in ball mills), the formation of a more extended composition region of BCC-solutions should be expected. This conclusion may be made on the basis of the fact that the $T_0^{(Cu)/(V)}$ line is shifted considerably in the direction of copper.

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