

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

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Thermodynamic assessment of the Cu – Sc system was carried out using the CALPHAD method. A set of self-consistent model parameters was obtained with the usage of the information about phases equilibria and thermodynamic. Gibbs energy for the liquid phase was assessed within the framework of the model of ideal associated solution. Optimized model parameters make it possible to reproduce satisfactorily the phase diagram and thermodynamic values. Analysis of the relative thermodynamic stability of supercooled melts and competing crystalline phases let us to predict their glass forming ability by rapid quenching from the liquid state.

Keywords: phase diagram, thermodynamics, thermodynamic modeling, copper alloy, amorphous alloy.

INTRODUCTION

Two-component alloys of copper with 3d-transition metals demonstrate unique spectrum of thermophysical, electric, and magnetic properties. Therefore today they exemplify the large-tonnage production of single-alloyed composites (systems Cu – Cr, Cu – Mn, Cu – Fe, Cu – Co, Cu – Ni). Even more chances of using these materials occur in different spheres of techniques as a result of developing new methods for metallurgical synthesis, which permit to prepare such metallic materials as supersaturated solid solutions, amorphous, and nanocrystalline alloys. The development of theoretical and technological bases for their preparing requires the specification of information about the thermodynamic properties of phases, and also parameters for equilibrium and metastable transformations with their participation. Nevertheless there remain many unexplained questions and contradictory opinions in this sphere.

Thermodynamic evaluation of the systems may contribute to the solving of many arguable questions concerning the properties of phases and their transformations. As things now stand the approach, which allows to generalize and make the information about phase equilibria and phases thermodynamics more precise within the context of a self-consistent model, has become one more powerful means of theoretical study and ascertainment of the most reliable information. The application of this method to such objects as alloys of copper with transition metals is of a great interest. These objects demonstrate a broad spectrum of components interaction: short chemical order in melts and formation of intermetallic compounds in solid alloys (Cu – Sc and Cu – Ti systems); complete miscibility in solid and liquid states (Cu – Mn and Cu – Ni systems), limited miscibility of components in solid and liquid states (Cu – V, Cu – Cr, Cu – Fe, Cu – Co systems). This series of articles proposed by us exemplifies the usage of common approach to describe a large number of systems, and thereby is really valuable for understanding the fundamental modelling aspects of metals interaction.

This series of articles started in fact in [1, 2], where we opened the questions touched mentioned above were considered for the copper – iron and copper – titanium systems. The copper – scandium system became the object of thermodynamic study and modelling in this work.

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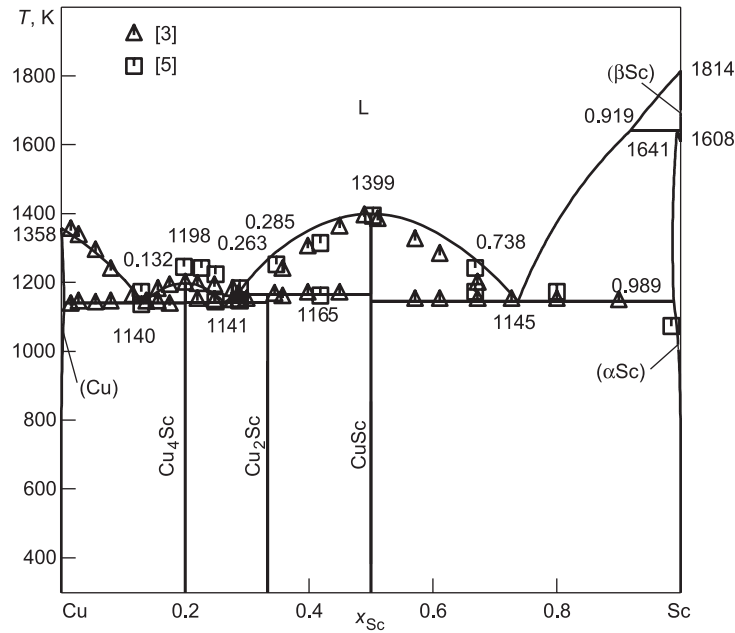


Fig. 1. Phase diagram of the copper – scandium system: here and further the results of experiments are indicated by symbols and the lines show the results of calculations

PHASE TRANSFORMATIONS AND THERMODYNAMIC PROPERTIES OF PHASES

Phase transformations. Phase equilibria in the system were studied in [3-5]. The data of metallographic, thermal, dilatometric, and x-ray structural analyses were used in order to construct the phase diagram in [3]. In the experiments we used the scandium purified by vacuum distillation (99.8-99.9 mass%) Alloys were synthesized in an arc furnace on a copper water-cooled hearth in an atmosphere of purified helium, and subsequently their composition was checked by weight control and chemical analysis. Results of this work are presented in Fig. 1. The phase diagram is characterized by the appearance of three intermetallic compounds, two of which, Cu_4Sc and CuSc , melt congruently, and one, Cu_2Sc , is being formed by a peritectic reaction. It has been established [3] that the solubility of components is insignificant: $x_{\text{Sc}} = 0.005$ in (Cu)-phase and $x_{\text{Cu}} = 0.01$ in (αSc)-phase.

Scandium solubility in (Cu)-phase was studied more closely in [4] with help of microscopic, differential thermal, and x-ray phase analyses, and also by measuring the rupture characteristics, micro- and macrohardness of alloys. Distilled scandium with a purity of 99.6 mass% was used. Specimens were prepared on a copper water-cooled hearth of an arc furnace in an atmosphere of purified argon. Cast alloys were treated by forging, annealed in evacuated quartz ampoules at 873-1123 K and with the following quenching in water. The results of this study are presented in Fig. 2. The maximum solubility of scandium was $x_{\text{Sc}} = 0.0049$ at the eutectic temperature 1135 ± 5 K.

In [5] the state diagram of the system was constructed on the base of differential thermal, metallographic, x-ray and microprobe analyses data. Specimens were synthesized in an electric arc furnace in an atmosphere of purified argon. The congruent nature of melting was established for all of the intermetallic compounds. For the compound Cu_4Sc the area of homogeneity was determined in the range $x_{\text{Sc}} = 0.19-0.23$. The solubility of copper in (αSc)-phase was $x_{\text{Sc}} = 0.015$ at 1073 K.

Information about the possible existence of a homogeneity area of Cu_4Sc compound was not confirmed in [6] whose authors studied the structure and electric properties of this intermetallic compound within the cast and rapidly quenched bulk specimens and within thin films prepared by vapour codeposition and magnetron deposition. An assumption as to the melting temperature for Cu_4Sc may exceed the values obtained in [3, 5] by about 100 K was given in this work on the basis of indirect results. This assumption should be confirmed directly by the experiments in order to be taken into consideration.

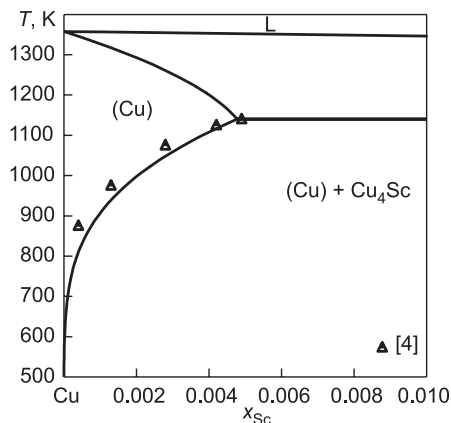


Fig. 2. Solubility of scandium in (Cu)-phase

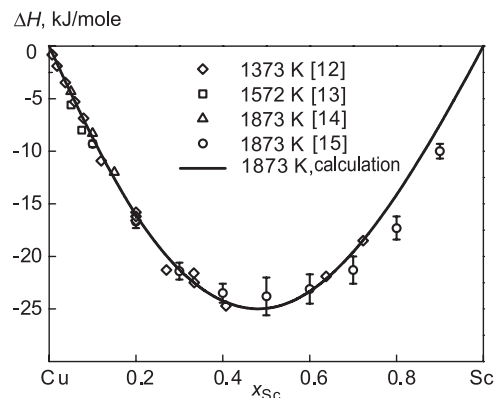


Fig. 3. Isotherms of integral mixing enthalpy of copper and scandium

By comparing the results in [3, 5] presented in Fig. 1 it is possible to note some difference for alloys with $x_{Sc} = 0.17-0.40$. According to [5] the melting temperature for the compound Cu_4Sc appears to be 50 K higher and the phase itself acquires the area of homogeneity. But the main difference may be seen in the nature of melting for the Cu_2Sc compound: not congruent according to [3] and congruent according to data in [5]. In [7] this contradiction was declined due to the analysis of change regularity of melting character for the compounds of the same type within the number of copper systems with rare-earth metals (REM) [8]. By considering scandium as a metal of the yttrium sub-group the authors of [7] suggested a version of the phase diagram for the system with congruently melting compound Cu_2Sc . This variant of the phase diagram is widely quoted in modern reference books, for example in [9]. At the same time, it can't be taken as certain. On the one hand, scandium differs greatly from other REM by the nature of reaction with elements [10], which may be concerned with the difference of the electronic structure, electronegativities, and atomic radii. Thus, a conclusion about the nature of melting of the Cu_2Sc intermetallic compound made in [7] on the basis of general features for a whole series of REM is not strict. On the other hand, the phase diagram suggested in [7] is mentioned in [11] as an example of incorrect combination of the liquidus line, that first of all may be related to coterminous parts of the liquidus lines of Cu_4Sc and Cu_2Sc .

Thus, there are some disagreements in experimental information about phase equilibria in the copper – scandium system, which may be surmounted within the framework of thermodynamic assessment of the system based on generalizing data about phase equilibria and thermodynamic properties of systems phases.

Thermodynamic properties of liquid alloys. The heat of liquid alloys formation for the copper – scandium system was studied by several groups of authors [12-16]. In [12] the integral enthalpy of dissolution of crystalline scandium in liquid copper was obtained by high-temperature calorimetry at 1373 K in the compositions range $x_{Sc} = 0-0.72$. Obtained values are presented in Fig. 3. The minimum value of integral mixing enthalpy of the components was $\Delta H_{min} = -24.66$ kJ/mole close to the equiatomic composition, and the first mixing enthalpy of scandium was $\Delta \bar{H}_{Sc}^{\infty} = -102$ kJ/mole. In [13] the partial enthalpy of dissolution of crystalline scandium was studied calorimetrically at 1572 K in the composition range $x_{Sc} = 0-0.08$. The calculated in this work values of integral enthalpy of mixing components are presented in Fig. 3. The authors derive a value of the first enthalpy of mixing for scandium $\Delta \bar{H}_{Sc}^{\infty} = -103$ kJ/mole.

The partial enthalpy of mixing for liquid scandium in the composition range $x_{Sc} = 0-0.16$ has been studied calorimetrically at the temperature of 1873 K [14]. The corresponding isotherm of integral mixing enthalpy is presented in Fig. 3. The first mixing enthalpy of scandium amounted to $\Delta \bar{H}_{Sc}^{\infty} = 88 \pm 3$ kJ/mole.

In [15] calorimetric study of the mixing enthalpy of copper and scandium in the whole composition range was undertaken for the first time. The temperature of the experiments was 1873 K. The partial mixing enthalpy of scandium

was studied in the composition range $x_{Sc} = 0-0.52$, the partial mixing enthalpy of copper was studied in the composition range $x_{Cu} = 0-0.51$. Combined processing of two corresponding branches of the integral mixing enthalpy made it possible to obtain an equation for the concentration dependence of the property over the whole composition range:

$$\Delta H = x_{Sc} (1 - x_{Sc}) (-100.49 - 11.53 x_{Sc} - 309.64 x_{Sc}^2 + 2098.33 x_{Sc}^3 - 4180.34 x_{Sc}^4 + 3185.94 x_{Sc}^5 - 785.80 x_{Sc}^6) \text{ kJ/mole.}$$

High degree of the polynomial is connected with the complex composition course of the function expressed by broad minimum nearby the equiatomic composition (Fig. 3). It was substantiated in [15] using the statistical Fisher criterion. The integral mixing enthalpy reveals almost symmetrical concentration course reaching a minimum value $\Delta H_{\min} = -23.9 \pm 1.8 \text{ kJ/mole}$ at $x_{Sc} = 0.48$. The first mixing enthalpies of the components came to $\Delta \bar{H}_{Sc}^{\infty} = -100.5 \pm 6.3 \text{ kJ/mole}$ and $\Delta \bar{H}_{Cu}^{\infty} = -103.5 \pm 6.5 \text{ kJ/mole}$.

Almost total agreement of results obtained by different authors is demonstrated in Fig. 3. This situation is interesting due to the showing on a background of experimental temperatures difference at 500 K that may figure it out, that there is no temperature dependence for the integral mixing enthalpy. To explain the nature of the temperature dependence of the mixing enthalpy in this system in [16] a calorimetric study was attempted at lower temperatures and it was established that the first mixing enthalpy of scandium equals $\Delta \bar{H}_{Sc}^{\infty} = -124 \pm 6 \text{ kJ/mole}$ at 1573 K. Comparison of values of the first mixing enthalpy of scandium obtained in [15, 16] indicates that within the range of 1573-1873 K for this property a temperature dependence is typical: with an increasing of temperature increases also the mixing enthalpy. The average partial value for excess heat capacity of scandium at infinite dilution in the temperature range may be evaluated as $\Delta C_P^{exc \infty} = -80 \pm 40 \text{ J/(mole} \cdot \text{K)}$. Apparently agreement of the ΔH isotherm mentioned above, which were obtained by different authors over a wide temperature range one may concern with the casual superposition of measurement errors.

There are no experimental data on the thermodynamic activities of components in melts of the copper – scandium system.

TABLE 1. Thermodynamic Parameters of Intermetallic Compounds Formation of Copper – Scandium System

$T, \text{ K}$	$\Delta_f G, \text{ J/mole}$	$\Delta_f H, \text{ J/mole}$	$\Delta_f S, \text{ J/(mole} \cdot \text{K)}$	Source
Cu₄Sc				
298	-	-14000 ± 430	-	[12]
650-1049	-	-23100 ± 800	-9.2 ± 1.0	[17]
900	-21980 ± 90	-22400 ± 2900	-0.47 ± 0.13	[18]
		-18267	-3.27	P. w.*
Cu₂Sc				
298	-	-17370 ± 1140	-	[12]
650-1049	-	-32800 ± 1000	-14.5 ± 1.2	[17]
900	-27950 ± 70	-35500 ± 1400	-8.4 ± 1.4	[18]
		-29833	-8.57	P. w.
CuSc				
298	-	-20850 ± 1280	-	[12]
650-1049	-	-35500 ± 1300	-13.5 ± 1.6	[17]
900	-33390 ± 120	-39300 ± 1800	-6.5 ± 1.8	[18]
		-43597	-15.2	P. w.

* Present work (here and in Table 2).

Thermodynamic properties of solid alloys. Thermodynamic properties of intermetallic phases have been studied in [12, 17, 18]. In [12] standard formation enthalpies $\Delta_f H$ of compounds were studied calorimetrically. The heats of dissolution of compounds in molten copper were studied for that at 1373 K. The authors of [17] studied the temperature dependence of the free energy of formation of intermetallic compounds $\Delta_f G$ in the range 650-1040 K using a chronopotentiometric version of the electromotive force (emf) method for a galvanic element with a salt electrolyte. In [18] the values of $\Delta_f G$ of intermetallic compounds of the system were determined by the emf method with salt electrolyte within the temperature range 870-970 K. The data obtained in these works are presented in Table 1.

THERMODYNAMIC DESCRIPTION OF THE SYSTEM AND MODELS

An attempt to carry out thermodynamic evaluation of the system was first undertaken by [19]. Models of the thermodynamic properties of phases presented in this work don't give an opportunity to reproduce the phase diagram in a form which the authors show in figures in [7, 19]. Inaccurate reproduction of the eutectic temperatures (average error ~35 K), the presence of a eutectoid decomposition of the Cu_2Sc phase at 1095 K, and the absence of description of terminal solid solutions are typical for phase diagram calculated according to the model [19]. All that shows that the copper – scandium system requires new thermodynamic evaluation.

In this work thermodynamic description of the system is carried out within the framework of the CALPHAD-method. In order to describe the temperature and concentration dependences of Gibbs free energy of the phases the following models were adopted.

Solid solutions. The temperature-composition dependence of Gibbs free energy for the solid solution (ϕ) on temperature is described by the expression

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

where $(^\circ G_{\text{Cu}}^{(\phi)} - H_{\text{Cu}}^{\text{SER}})$ and $(^\circ G_{\text{Sc}}^{(\phi)} - H_{\text{Sc}}^{\text{SER}})$ are molar energies for pure copper and scandium with a crystal structure corresponding to the phase (ϕ) counted off from the standard state for these elements; $\Delta G_{\text{exc}}^{(\phi)}(x_{\text{Sc}}, T)$ is the excess term of Gibbs free energy for the solid solution (ϕ). In order to describe the last term the following expression was used

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

where i is the power of the Redlich-Kister polynomial; A_i, B_i are coefficients of the model. It was suggested that the (βSc)-phase does not possess a homogeneity area.

Liquid phase. The temperature-concentration dependence of Gibbs free energy for melts of the system was presented as

$$G^{\text{L}} = (1 - x_{\text{Sc}})(^\circ G_{\text{Cu}}^{\text{L}} - H_{\text{Cu}}^{\text{SER}}) + x_{\text{Sc}}(^\circ G_{\text{Sc}}^{\text{L}} - H_{\text{Sc}}^{\text{SER}}) + RT((1 - x_{\text{Sc}})\ln(1 - x_{\text{Sc}}) + x_{\text{Sc}}\ln x_{\text{Sc}}) + \Delta G_{\text{exc}}^{\text{L}}(x_{\text{Sc}}, T).$$

As it was shown in [20] before, the temperature-composition dependence of the excess Gibbs free energy $\Delta G_{\text{exc}}^{\text{L}}$ for liquid alloys with a strong interaction of components may be described successfully within the context of the model of an perfect associated solution (IAS). Different aspects of using the IAS model for describing thermodynamic properties of liquid alloys with negative deviations from ideality have been described carefully in [21]. In this case excess mixing thermodynamic functions of solution are determined by the parameters of the model, i.e. the number of associates, their composition, enthalpy, and enthalpy of formation:

$$\Delta G_{\text{exc}}^{\text{L}}(x_{\text{Sc}}, T) = f(\Delta H_i, \Delta S_i),$$

where ΔH_i and ΔS_i are enthalpy and entropy of formation of associates of the i -th type. Relatively symmetrical to the equiatomic composition concentration course of integral mixing enthalpy of the system Cu – Sc made it possible to suggest formation in the melt of associates of equiatomic composition or formation a set of associates of the Cu_xSc , CuSc , and CuSc_x type. According to [20], the concentration dependence of the mixing enthalpy of molten Cu – Sc may be satisfactorily described by a model with three associates.

TABLE 2. Experimentally Determined and Computed Parameters of Phase Transformations

L \leftrightarrow (Cu) + Cu₄Sc

T, K	x_{Sc}^L	$x_{Sc}^{(Cu)}$	$x_{Sc}^{Cu_4Sc}$	Source
1138	~0.13	~0.005	0.2	[3]
1138 ± 5	-	~0.0049	0.2	[4]
1133	~0.11	-	0.19-0.23	[5]
1140	0.1322	0.0048	0.2	P. w.

L \leftrightarrow Cu₄Sc

T, K	$x_{Sc}^{Cu_4Sc}$	Source
1198	0.2	[3]
1248	0.2	[5]*
1198	0.2	P. w.

L \leftrightarrow Cu₄Sc + Cu₂Sc

T, K	x_{Sc}^L	$x_{Sc}^{Cu_4Sc}$	$x_{Sc}^{Cu_2Sc}$	Source
1148	~0.30	0.2	0.333	[3]
1143	~0.32	0.19-0.23	0.333	[5]
1141	0.263	0.2	0.333	P. w.

L \leftrightarrow Cu₂Sc

T, K	$x_{Sc}^{Cu_2Sc}$	Source
1263	0.333	[5]*

L \leftrightarrow Cu₂Sc + CuSc

T, K	x_{Sc}^L	x_{Sc}^{CuSc}	$x_{Sc}^{Cu_2Sc}$	Source
1163	~0.39	0.5	0.333	[5]*

L + CuSc \leftrightarrow Cu₂Sc

T, K	x_{Sc}^L	x_{Sc}^{CuSc}	$x_{Sc}^{Cu_2Sc}$	Source
1163	-	0.5	0.333	[3]
1165	0.285	0.5	0.333	P. w.

L \leftrightarrow CuSc

T, K	x_{Sc}^{CuSc}	Source
1398	0.5	[3]
1398	0.5	[5]
1399	0.5	P. w.

L \leftrightarrow CuSc + (α Sc)

T, K	x_{Sc}^L	x_{Sc}^{CuSc}	$x_{Sc}^{(\alpha Sc)}$	Source
1148	~0.71	0.5	~0.99	[3]
1173	~0.71	0.5	<0.985	[5]
1145	0.738	0.5	0.989	P. w.

L + (α Sc) \leftrightarrow (β Sc)

T, K	x_{Sc}^L	$x_{Sc}^{(\alpha Sc)}$	$x_{Sc}^{(\beta Sc)}$	Source
1641	0.919	0.994	1.00	P. w.

* The data were not accounted in the present thermodynamic assessment.

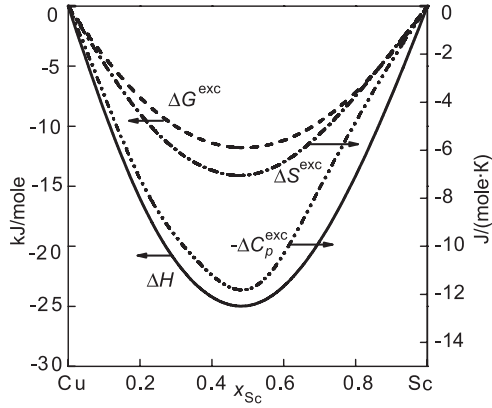


Fig. 4

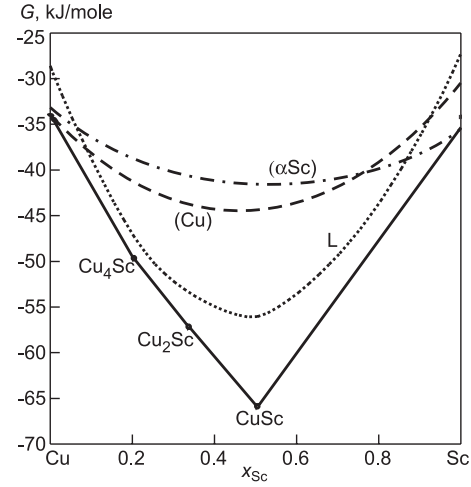


Fig. 5

Fig. 4. Excess thermodynamic properties of copper – scandium alloys at 1873 K: ΔH is integral mixing enthalpy; ΔG^{exc} excess mixing free energy; ΔS^{exc} is excess mixing entropy; ΔC_p^{exc} is excess heat capacity of melts

Fig. 5. Gibbs free energy of competing phases during solidification of alloys supercooled to $T = 800$ K

Intermetallic compounds. In the present calculations it was assumed that all intermediate phases of the system do not have a homogeneity range. In this case the expression for free energy of an intermetallic compound of the composition Cu_kSc in the calculation per one mole of atoms looked like that:

$$G^{\text{Cu}_k\text{Sc}}(T) = \Delta_f H^{\text{Cu}_k\text{Sc}} - T\Delta_f S^{\text{Cu}_k\text{Sc}} + \frac{1}{k+1} ({}^\circ G_{\text{Cu}}^{(\varphi)} - H_{\text{Cu}}^{\text{SER}}) + \frac{1}{k+1} ({}^\circ G_{\text{Sc}}^{(\varphi)} - H_{\text{Sc}}^{\text{SER}}),$$

where $\Delta_f H^{\text{Cu}_k\text{Sc}}$ and $\Delta_f S^{\text{Cu}_k\text{Sc}}$ are the enthalpy and entropy of formation for a compound. In this expression the standard reference states (FCC for copper and HCP for scandium) are taken for pure elements. All the data on thermodynamic properties of pure copper and scandium were taken from the SGTE data base [22].

TABLE 3. Model Parameters of the Gibbs Free Energy of Phases in the Copper – Scandium System (J/mole)

L					
$\Delta H_{\text{Cu}_3\text{Sc}}$	$\Delta S_{\text{Cu}_3\text{Sc}}$	ΔH_{CuSc}	ΔS_{CuSc}	ΔH_{CuSc_3}	ΔS_{CuSc_3}
-121488.72	-47.01	-72598.42	-20.57	-102875.24	-42.07
i	A_i		B_i		
(Cu)					
0	-38527		10.02		
(αSc)					
0	-10613.75		-		
$\Delta_f H^{\text{Cu}_k\text{Sc}}$			$\Delta_f S^{\text{Cu}_k\text{Sc}}$		
Cu_4Sc					
-18267.25			-3.27		
Cu_2Sc					
-29833.32			-8.574		
CuSc					
-43596.72			-15.2		

Model parameters were optimized using the “Thermo-Calc” program. Optimization was carried out in two stages. In the first stage, the data [3, 5] on the temperatures and compositions of nonvariant transformations and data in [12-18] on the thermodynamic properties of phases were used. In this stage it was established that not all of the data coordinate with each other. For example, an attempt to improve conformity of calculated values of the formation enthalpy of intermetallic compounds with given in [12] led to an unavoidable reduction of their thermal stability; an attempt to increase the melting temperature of Cu_4Sc in order to achieve the value presented in [5] led to the rise of temperature of adjoin eutectic transformations; an attempt to construct a phase diagram with congruent type of melting of the Cu_2Sc compound unavoidably led to its eutectoid decomposition. Therefore the results listed above were excluded from the optimization. In this stage the final set of associates of IAS model for the liquid phase, i.e., Cu_3Sc , CuSc , and CuSc_3 , were established and fixed.

In the next stage the data about the location of liquidus line [3, 5] and the composition limits of (Cu)- and (αSc)-phase [4, 5] were added to the optimization. The structure of the model of the thermodynamic properties of solid solutions was improved. A_0 and B_0 coefficients were used to describe the (Cu)-phase properties. For the (αSc)-phase the use of A_0 appeared to be enough.

Calculated coordinates of nonvariant transformations are given in Table 2, and calculated parameters of the model are given in Table 3.

RESULTS OF CALCULATION AND DISCUSSION

Results of calculations of phase boundaries are presented in Figs. 1 and 2. As it can be seen, satisfactory description was achieved for the majority of experimental data. The best agreement is observed for data [3, 4]. Calculations confirm the peritectic nature of the transformation with participation of Cu_2Sc established in [3]. Peritectic transformations with participation of (αSc) and (βSc) may be predicted at 1641 K. The calculated coordinates of the retrograde point of the solidus of the (αSc)-phase was $x_{\text{Sc}} = 0.987$ at $T = 1317$ K. The error in description of nonvariant transformations does not exceed 7 K in temperature and 2 at.% in composition. The only exception is the accuracy of description of the composition of the eutectic transformation $\text{L} \leftrightarrow \text{Cu}_4\text{Sc} + \text{Cu}_2\text{Sc}$. Possibly an effective means of improving the description of this transformation is to take into account the existence of a homogeneity area of the Cu_4Sc compound established in [5].

Satisfactory agreement was also achieved when describing the thermodynamic properties of intermetallic phases. Calculated values of thermodynamic parameters of intermetallic compounds formation appeared to be closer to those obtained in electrochemical studies [17, 18] than to the results of calorimetric studies [12].

As follows from Fig. 3, the IAR model obtained within the framework of thermodynamic assessment describes satisfactorily the mixing enthalpy of liquid alloys of the system. In addition, this model makes it possible to calculate the full set of excess thermodynamic properties of melts within a broad temperature range. Figure 4 demonstrates the results of calculation of enthalpy, excess Gibbs free energy and the entropy of mixing, and also excess heat capacity of melts at 1873 K.

In our previous works we demonstrated [23, 24] the effectiveness of calculations within the framework of the CALPHAD-method for modelling and predicting metastable phase transformations in systems. One of the possibilities is the prediction of transformations with the assistance of supercooled melts, in particular the evaluation of the composition ranges for their amorphization by quenching from liquid. Solution of this problem is possible on the basis of comparing thermodynamic stability of competing phases: supercooled liquid, terminal solid solutions, and intermetallic compounds. The most complicated task in conducting calculations like that is the evaluation of thermodynamic properties of supercooled melts over a broad temperature range. According to [23], it is possible to use the IAS models that permits to describe the complex temperature-composition dependence of thermodynamic mixing functions of melts strongly reacting metals. Gibbs free energies of all phases of the system calculated within the framework of this thermodynamic evaluation are presented at Fig. 5 at 800 K commensurable with amorphisation temperature of Cu – REM melts [25]. From Fig. 5 it follows that under given conditions the thermodynamic stability of intermetallic phases is greater than for supercooled liquid. At the same time, there is a broad composition range within

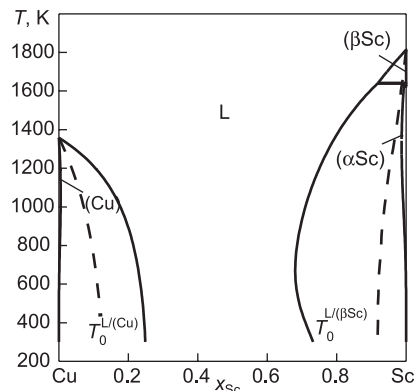


Fig. 6. Metastable phase diagram of the copper – scandium system with the assistance of supercooled liquid and terminal solid solutions obtained in the present work using the IAS model for the liquid phase: dashed lines show the free energy equality lines for solid solutions and the melt $T_0^{L/(\varphi)}$

which the melts appear to be more thermodynamically stable than the terminal solid solutions. If during high-speed quenching of these melts the formation of intermetallic phases is suppressed kinetically, their amorphous solidification is possible. For a row of two-component systems whose melts have a high glass forming ability, the possibility of evaluating of the concentration ranges of amorphization on the basis of analyzing the metastable phase diagram between supercooled melts and terminal solid solutions was demonstrated. From the direction of each of the components the boundary of this range lies between the metastable liquidus line and the line of equality of free energies of the solid solution and melt $T_0^{L/(\varphi)}$ [24]. The metastable phase diagram calculated by us for the Cu – Sc system with participation of supercooled liquid alloys and terminal solid solutions is presented in Fig. 6. It follows that in this system it is possible to expect the formation of amorphous alloys in the composition range $x_{Sc} = 0.2-0.8$. Another interesting feature of the system is the fact that quenching of its melts should not expect formation of supersaturated terminal solid solutions. This is indicated by the similar position of lines of the solidus for (Cu)- and (α Sc)-phases in the equilibrium and metastable phase diagrams.

Thus, in the present work the thermodynamic assessment of the system is carried out due to what it became possible to reproduce reliable experimental information about the equilibrium and thermodynamics of its phases with high accuracy. The proposed phase diagram of the system is characterized by congruent melting of Cu_4Sc and $CuSc$ compounds. The Cu_2Sc compound is formed by a peritectic reaction. For pure metals insignificant mutual solubility is typical. The possibility of amorphization of liquid alloys by rapid quenching is suggested and the concentration range of glass formation is evaluated theoretically on the base of analysis of the obtained thermodynamic models.

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