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**CALCULATION OF THE LIQUIDUS SURFACE
IN TERNARY Co-Cu-Si SYSTEM****OBLICZENIE POWIERZCHNI LIKWIDUS W UKŁADZIE
TRÓJSKŁADNIKOWYM Co-Cu-Si**

Constituent binary subsystems Co-Cu, Co-Si and Cu-Si were described briefly, and their calculated phase diagrams were presented and invariant reactions of the liquid phase, as well.

Thermodynamic parameters for Co-Si and Cu-Si systems were taken from the former own assessments and coefficients for binary system Co-Cu were accepted from the one of the most recent literature evaluations. Tdb file was then set up by means of binary formalism. Equilibrium calculations resulted in the parameters of all invariant reactions with liquid phase involved, and the Scheil reaction scheme was constructed as well. Graphical representation of the calculated liquidus surface was shown as the projection onto the Gibbs triangle plane.

Podano zwięzłe charakterystyki składowych układów podwójnych Co-Cu, Co-Si i Cu-Si oraz zaprezentowano ich obliczone wykresy fazowe i parametry równowag niezmienniczych fazy ciekłej. Parametry termodynamiczne dla układów Co-Si i Cu-Si zaczerpnięto z wcześniejszych opracowań własnych a dla układu Co-Cu zaakceptowano wyniki jednego z najnowszych opracowań z literatury. Termodynamiczną bazę danych dla rozpatrywanego układu potrójnego zestawiono za pomocą tzw. formalizmu dwójkowego. W wyniku obliczeń równowagowych uzyskano parametry równowag niezmienniczych z udziałem fazy ciekłej; obliczoną powierzchnię likwidus przedstawiono w postaci projekcji politermicznej na płaszczyznę trójkąta Gibbsa oraz skonstruowano schemat reakcji Scheila dla tego układu trójskładnikowego.

1. Introduction

The raw product of extraction of some copper ores is the metal alloy consisting mainly of copper with considerable additions of cobalt and silicon.

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The knowledge of phase relations in such an alloy is substantial for its further treatment, and determination of the liquidus surface in this ternary system is one of the stages of the study. The knowledge of the thermodynamics and constitution of the ternary system Co-Cu-Si is almost nil. The only constitutional study of Gronostajski [1] employed DTA, metalography, XRD and dilatometry and was limited to copper-rich corner with up to 1.2 at.% Co and up to 13.6 at.% Si, and thermodynamics was represented by six compositions of the liquid phase measured calorimetrically by Fitzner [2]. Having so scarce information, attempts to determine ternary interaction parameters failed, and in this situation it was decided to base calculations on the binary formalism.

2. Cobalt — Copper system

Four critical assessments of this system were made so far by: Kaufman [3], Hasebe and Nishizawa [4], Kumar and Wollants [5] and most recently by Kubista and Vrestal [6]. In the last paper the (Co-hcp) phase was not considered, therefore the parameters derived by [5] were accepted for the purpose of the current calculations. Co-Cu system is topologically relatively simple, although some of its features like retrograde solidus, metastable miscibility gap in the fcc phase and magnetic transition in the cobalt-rich fcc phase make it difficult for CALPHAD method application.

The following phases were distinguished in this system: liquid, Co-rich fcc solid solution, Cu-rich fcc solid solution and Co-rich hcp solid solution. The phase boundaries were determined precisely except of Co-rich solidus line, and thermodynamic properties of both liquid and solid alloys were derived by various experimental techniques like calorimetry, emf and mass spectrometry. Liquid phase was modeled by substitutional solution model with Redlich-Kister excess term and two-sublattice model was applied to solid phases; magnetic contribution to the Gibbs energy of the (Co-fcc) phase was taken into account as well.

To unify the notation in further considerations the (Co-fcc), (Cu-fcc) and (Co-hcp) phases were marked as fcc, fcc2 and hcp, respectively. The only invariant reaction with liquid phase involved exists in the system and its parameters are listed in the table 1, and calculated phase diagram is presented in figure 1.

The maximal solid solubility on the Co-rich side is 20.48 at.% Cu at 1617 K. Curie temperature for pure cobalt is 1396 K, and decreases linearly crossing solvus line at 1323 K and 8.47 at.% Cu.

TABLE I
Calculated invariant reaction with liquid phase involved in the system Co-Cu

No	Reaction	Phase composition % at.Cu	Temperature K	Reaction symbol
1	L + fcc = fcc2 peritectic	95.13 11.74 92.28	1380.3	p3

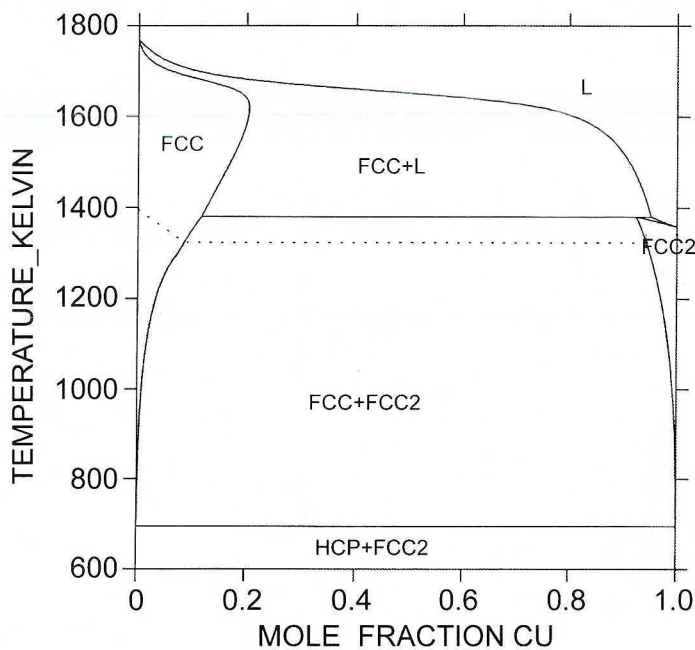


Fig. 1. Co-Cu phase diagram calculated by [5]

3. Cobalt-Silicon system

First of four assessments of this system was made by Kaufman [7], but for a number of simplified assumptions the system required further evaluations. Ishida et al. [8] prepared a new version of the Co-Si phase diagram as a contribution to Massalski's monograph, pointing out some uncertainties of the existing experimental informations on this system. Choi [9] made the next assessment of the system using Lukas software, but his published coefficients were burdened by some errors. In meantime new experimental data on thermodynamic properties of cobalt siccides appeared and on lattice stabilities, as well, therefore Zabyr et al. [10] re-assessed the Co-Si system again. According to [10] the system consists of eight phases: liquid, fcc and hcp Co-rich solid solutions, four intermetallic compounds: ϕ -Co₃Si, λ -Co₂Si, κ -CoSi, ω -CoSi₂, and (Si) which is assumed to have no solid solubility. The solution phases were modeled as substitutional with R-K excess term, compounds were treated as stoichiometric and lattice stabilities for Co and Si were taken from Dinsdale's compilation [11]; all thermodynamic quantities were referred to Standard Element Reference — SER.

The optimisation was carried out by PARROT module of ThermoCalc package and appropriate thermodynamic parameters were derived. Then equilibrium calculations

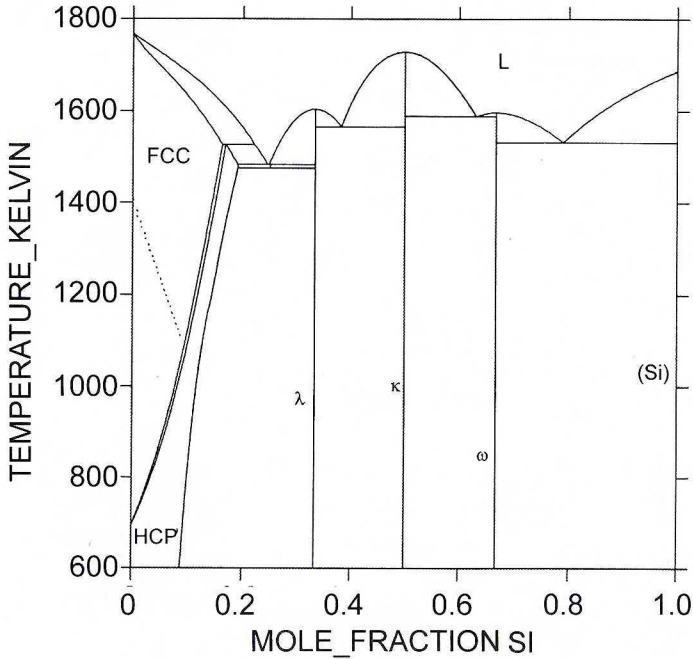


Fig. 2. Cobalt — silicon phase diagram calculated by [10]

TABLE 2
Calculated invariant reactions with liquid phase involved in Co-Si system

No	Reaction	Phase composition at. % Si	Temperature K	Reaction symbol
1	$L + \text{fcc} = \text{hcp}$ peritectic	22.13 16.29 16.9	1526.2	p1
2	$L = \text{hcp} + \phi\text{-Co}_3\text{Si}$ eutectic	24.53 19.07 25	1482.2	e4
3	$L + \lambda\text{-Co}_2\text{Si} = \phi\text{-Co}_3\text{Si}$ peritectic	24.8 33.3 25	1482.7	p2
4	$L = \lambda\text{-Co}_2\text{Si}$ congruent p.	33.3	1603.7	
5	$L = \lambda\text{-Co}_2\text{Si} + \kappa\text{-CoSi}$ eutectic	38.15 33.3 50	1564.8	e2
6	$L = \kappa\text{-CoSi}$ congruent p.	50	1728.1	
7	$L = \kappa\text{-CoSi} + \omega\text{-CoSi}_2$ eutectic	63 50 66.7	1588.9	e1
8	$L = \omega\text{-CoSi}_2$ congruent p.	66.7	1597	
9	$L = \omega\text{-CoSi}_2 + (\text{Si})$ eutectic	78.9 66.7 100	1530.8	e3

were performed resulting in phase diagram and invariant reaction's parameters, as well. As in case of the Co-Cu system, the magnetic contribution to Gibbs energy of fcc Co-rich solid solution was taken into account. For the purpose of current study only invariant reactions with liquid phase involved are of interest and their parameters are listed in table 2.

Calculated phase diagram of the cobalt-silicon system is presented in figure 2, and magnetic transition line is also shown; details of the central part of the Co-Si phase diagram presented in figure 3 shows the stability range of the ϕ -Co₃Si intermediate phase.

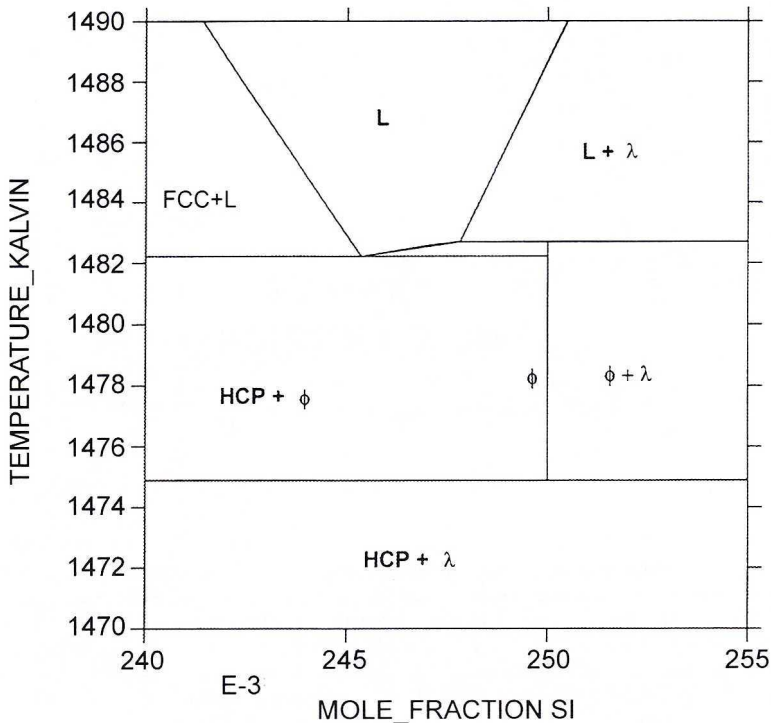


Fig. 3. Stability range of ϕ -Co₃Si phase

4. Copper — Silicon system

Cu-Si system was assessed critically many times to mention works of: Kaufman [7], Olesinski et al. [12], Luedecke [13], Jacobs [14], Jantzen et al. [15], Zabdyr et al. [16], and again Jantzen et al.[17]. Phase equilibria of the liquid phase in the last two works did not differ each other, but [17] did not present any of numerical values of thermodynamic coefficients, therefore parameters of [16] were accepted for the purpose of this work.

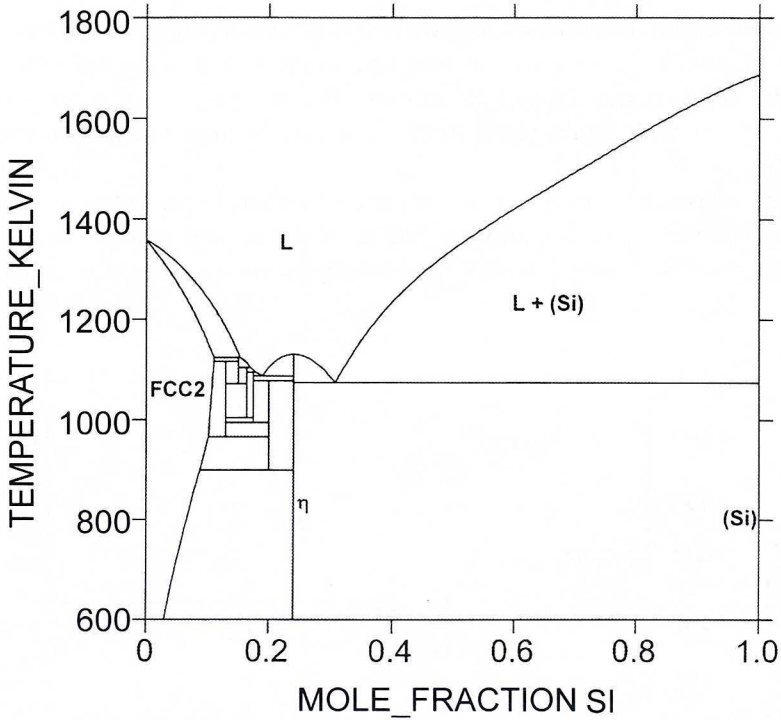


Fig. 4. Cu-Si phase diagram calculated by [16]

TABLE 3

Calculated liquid phase invariant reactions in Cu-Si system

No	Reaction	Phase composition at.% Si	Temperature K	Reaction Symbol
1	$L + \text{fcc2} = \beta\text{-Cu}_{85}\text{Si}_{15}$ peritectic	15.31 11.07 15	1124.6	p4
2	$L + \beta\text{-Cu}_{85}\text{Si}_{15} = \gamma\text{-Cu}_{56}\text{Si}_{11}$ peritectic	16.96 15 13	1104.3	p5
3	$L + \gamma\text{-Cu}_{56}\text{Si}_{11} = \delta\text{-Cu}_{33}\text{Si}_7$ peritectic	18 16.4 17.5	1095	p6
4	$L = \eta\text{-Cu}_{19}\text{Si}_6 + \delta\text{-Cu}_{33}\text{Si}_7$ eutectic	19 24 17.5	1088	e5
5	$L = \eta$ congruent point	24	1131	
6	$L = (\text{Si}) + \eta\text{-Cu}_{19}\text{Si}_6$ eutectic	30.7 100 24	1074.5	e6

There exist nine phases in the copper-silicon system: liquid, Cu-terminal solid solution — fcc2, (Si) with no solid solubility (like in the Co-Si) and six intermetallic compounds — α -Cu₈₇Si₁₃, β -Cu₈₅Si₁₅, γ -Cu₅₆Si₁₁, δ -Cu₃₃Si₇, ϵ -Cu₄Si, and η -Cu₁₉Si₆. Similarly to Co-Si system solution phases were treated as substitutional with R-K excess term and compounds were modeled as stoichiometric. As usually, the lattice stabilities of pure constituents were taken from [11] and all the thermodynamic quantities were referred to SER. Parameters of invariant reactions and phase diagram were obtained as a result of equilibrium calculations. Liquid phase invariant reactions are listed in table 3 and calculated phase diagram is shown in figure 4 and details of its central part are zoomed in figure 5.

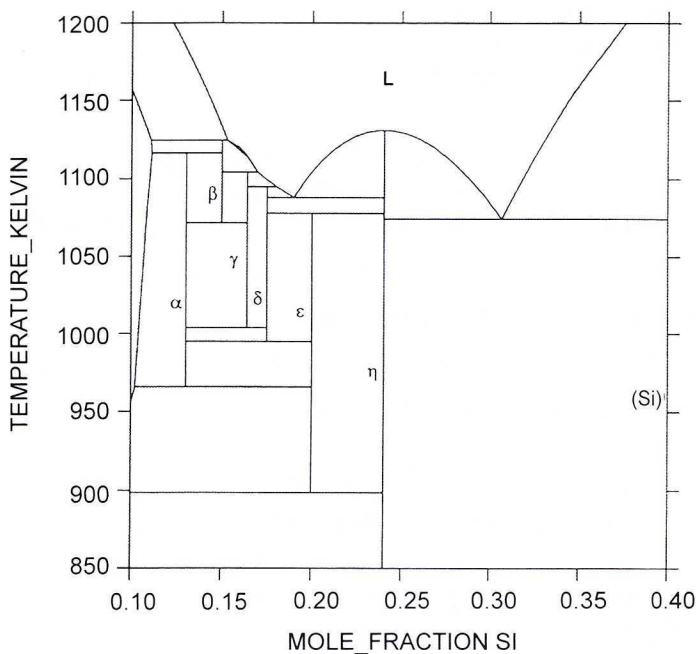


Fig. 5. Central part of Cu-Si phase diagram

5. Cobalt-Copper-Silicon thermodynamic database

On the basis of all the informations about binary subsystems described above one can distinguish the following phases in the ternary Co-Cu-Si system :

- ternary solution phases: liquid — L, high temperature Co-rich solid solution — fcc, low temperature Co-rich solid solution — hcp, Cu-rich solid solution — fcc2, and virtually pure (Si);
- binary intermetallics: ϕ -Co₃Si, λ -Co₂Si, κ -CoSi, ω -CoSi₂, α -Cu₈₇Si₁₃, β -Cu₈₅Si₁₅, γ -Cu₅₆Si₁₁, δ -Cu₃₃Si₇, ϵ -Cu₄Si, and η -Cu₁₉Si₆.

Solution phases were modeled as substitutional R-K, and intermetallics were treated as stoichiometric. The binary formalism was employed to set up thermodynamic database for the system under consideration and the following relations for Gibbs energy terms of all the phases of the system were derived on the basis of coefficients reported in [5], [10] and [16], respectively; quantities for pure elements were taken from [11]:

GHSECO =

$$298 - 1768 \text{ K: } 310.241 + 133.36601 \cdot T - 25.0861 \cdot T \cdot \ln T - 2.654739 \cdot 10^{-3} \cdot T^2 - 1.7348 \cdot 10^{-7} \cdot T^3 + 72527 \cdot T^{-1};$$

$$1768 - 6000 \text{ K: } -17197.666 + 253.28374 \cdot T - 40.5T \cdot \ln T + 9.3488 \cdot 10^{30} \cdot T^{-9};$$

GHSECU =

$$298 - 1358 \text{ K: } -7770.458 + 130.485235 \cdot T - 24.112392 \cdot T \cdot \ln T - 2.65684 \cdot 10^{-3} \cdot T^2 + 1.29223 \cdot 10^{-7} \cdot T^3 + 52487 \cdot T^{-1};$$

$$1358 - 3200 \text{ K: } -13542.026 + 183.803828 \cdot T - 31.38 \cdot T \cdot \ln T + 3.642 \cdot T^{-9};$$

GHSESI =

$$298 - 1687 \text{ K: } -8162.609 + 137.236859 \cdot T - 22.8317533 \cdot T \cdot \ln T + 1.912904 \cdot 10^{-3} \cdot T^2 - 3.552 \cdot 10^{-9} \cdot T^3 + 176667 \cdot T^{-1};$$

$$1687 - 6000 \text{ K: } -9457.642 + 167.281367 \cdot T - 27.196 \cdot T \cdot \ln T - 4.2037 \cdot 10^{30} \cdot T^{-9};$$

$$\text{GFCCO} - \text{GHSECO} = 427.59 - 0.61525 \cdot T; \quad 298 - 6000 \text{ K}$$

$$\text{GHPCU} - \text{GHSECU} = 600 + 0.2 \cdot T; \quad 298 - 6000 \text{ K}$$

$$\text{GFCSI} - \text{GHSESI} = 51000 + 21.8 \cdot T; \quad 298 - 6000 \text{ K}$$

$$\text{GHPSI} - \text{GHSESI} = 49200 - 20.8 \cdot T; \quad 298 - 6000 \text{ K}$$

GLIQCO - GHSECO =

$$298 - 1768 \text{ K: } 15085.037 - 8.931932 \cdot T - 2.19801 \cdot 10^{-21} \cdot T^7;$$

$$1768 - 6000 \text{ K: } 16351.056 - 9.683796 \cdot T - 9.3488 \cdot 10^{30} \cdot T^{-9};$$

GLIQU - GHSECU =

$$298 - 1358 \text{ K: } 12964.736 - 9.511904 \cdot T - 5.849 \cdot 10^{-21} \cdot T^7;$$

$$1358 - 3200 \text{ K: } 13495.481 - 9.922344 \cdot T - 3.642 \cdot 10^{29} \cdot T^{-9};$$

GLIQSI - GHSESI =

$$298 - 1687 \text{ K: } 50696.36 - 30.099439 \cdot T + 2.0931 \cdot 10^{-21} \cdot T;$$

$$1687 - 3600 \text{ K: } 49828.165 - 29.559068 \cdot T + 4.2037 \cdot 10^{30} \cdot T^{-9};$$

LIQUID:

$$L^0 (\text{LIQ, Co, Cu: Va}) = + 38923 - 6.384 \cdot T; \quad 298 - 3200 \text{ K}$$

$$L^1 (\text{LIQ, Co, Cu: Va}) = - 1389;$$

$$L^2 (\text{LIQ, Co, Cu: Va}) = + 8232 - 3.854 \cdot T;$$

$$L^3 (\text{LIQ, Co, Cu: Va}) = - 1185;$$

$$L^0 (\text{LIQ, Co, Si: Va}) = - 200104 + 47.13668 \cdot T; \quad 298 - 3600 \text{ K}$$

$$L^1 (\text{LIQ, Co, Si: Va}) = - 40783.1 + 3.371 \cdot T$$

$$L^2 (\text{LIQ, Co, Si: Va}) = 108723.5 - 50.43157 \cdot T$$

$$L^3 (\text{LIQ, Co, Si: Va}) = 143143.5 - 73.6364 \cdot T$$

$$L^0(\text{LIQ,Cu,Si:Va}) = -39688.86 + 14.27467 \cdot T; 298 - 6000 \text{ K}$$

$$L^1(\text{LIQ,Cu,Si:Va}) = -49937.13 + 29.7896 \cdot T$$

$$L^2(\text{LIQ,Cu,Si:Va}) = -31810.16 + 18.00804 \cdot T$$

FCC:

$$G(\text{FCC,Co:Va}) = \text{GFCCCO}; 298 - 6000 \text{ K}$$

$$TC(\text{FCC,Co:Va}) = 1396;$$

$$BM(\text{FCC,Co:Va}) = 1.35;$$

$$G(\text{FCC,Cu:Va}) = \text{GHSERCU}; 298 - 3200 \text{ K}$$

$$G(\text{FCC,Si:Va}) = \text{GFCCSI}; 298 - 6000 \text{ K}$$

$$L^0(\text{FCC,Co,Cu:Va}) = 39143 - 6.828 \cdot T; 298 - 3200 \text{ K}$$

$$TC^0(\text{FCC,Co,Cu:Va}) = 693.5$$

$$L^1(\text{FCC,Co,Cu:Va}) = -2432;$$

$$L^2(\text{FCC,Co,Cu:Va}) = 2422;$$

$$L^0(\text{FCC,Co,Si:Va}) = -148550 + 3.41324 \cdot T; 298 - 3600 \text{ K}$$

$$L^1(\text{FCC,Co,Si:Va}) = -46243.5 + 37.58562 \cdot T;$$

$$L^0(\text{FCC,Cu,Si:Va}) = -23785 - 10.99965 \cdot T; 298 - 6000 \text{ K}$$

HCP:

$$G(\text{HCP,Co:Va}) = \text{GHSERCO}; 298 = 6000 \text{ K}$$

$$TC(\text{HCP,Co:Va}) = 1396;$$

$$BM(\text{HCP,Co:Va}) = 1.35;$$

$$G(\text{HCP,Cu:Va}) = \text{GHCPCU}; 298 - 3200 \text{ K}$$

$$G(\text{HCP,Si:Va}) = \text{GHCPPI}; 298 - 6000 \text{ K}$$

$$L^0(\text{HCP,Co,Cu:Va}) = 29561; 298 - 3200 \text{ K}$$

$$L^0(\text{HCP,Co,Si:Va}) = -147438 + 1.78253 \cdot T; 298 - 3600 \text{ K}$$

$$L^1(\text{HCP,Co,Si:Va}) = -45650.9 + 35.84748 \cdot T;$$

(Si):

$$G(\text{DIA,Si}) = \text{GHSERSI}; 298 - 6000 \text{ K}$$

Co₃Si:

$$G(\text{Co}_3\text{Si,Co:Si}) = -3 \cdot \text{GHSERCO} - \text{GHSERSI} = -78452 - 26.512 \cdot T; 298 - 3600 \text{ K}$$

Co₂Si:

$$G(\text{Co}_2\text{Si,Co:Si}) - 2 \cdot \text{GHSERCO} - \text{GHSERSI} = -123120 - 36.35265 \cdot T + 8.27265 \cdot T \cdot \ln T$$

$$-10.7865 \cdot 10^{-3} \cdot T^2 + 3.5052 \cdot 10^{-7} \cdot T^3 + 44730 \cdot T^{-1}; 298 - 3600 \text{ K}$$

CoSi:

$$G(\text{CoSi,Co:Si}) - \text{GHSERCO} - \text{GHSERSI} = -100248.4 + 22.43696 \cdot T - 1.24215 \cdot T \cdot \ln T$$

$$-1.4823 \cdot 10^{-3} \cdot T^2 + 127806 \cdot T^{-1} + 1.7704 \cdot 10^{-7} \cdot T^3; 298 - 3600 \text{ K}$$

CoSi₂:

$$G(\text{CoSi}_2\text{,Co:Si}) - \text{GHSERCO} - 2 \cdot \text{GHSERSI} = -103227.9 + 11.2104 \cdot T - 0.1104 \cdot T \cdot \ln T$$

$$-2.84925 \cdot 10^{-3} \cdot T^2 + 70641 \cdot T^{-1} + 1.806 \cdot 10^{-7} \cdot T^3; 298 - 3600 \text{ K}$$

Cu₈₇Si₁₃:

$$G(\text{Cu}_{87}\text{Si}_{13}\text{,Cu:Si}) - 0.87 \cdot \text{GHSERCU} - 0.13 \cdot \text{GHSERSI} = -4125.71 + 124.26486 \cdot T - 23.945909 \cdot T \cdot \ln T - 2.56013 \cdot 10^{-3} \cdot T^2 + 1.1196 \cdot 10^{-7} \cdot T^3 + 68623 \cdot T^{-1}; 298 - 6000 \text{ K}$$

Cu₈₅Si₁₅:

$$G(\text{Cu}_{85}\text{Si}_{15}, \text{Cu}; \text{Si}) - 0.85 \cdot \text{GHSERCU} - 0.15 \cdot \text{GHSERSI} = -2978.98 + 122.99484 \cdot T - 23.920296 \cdot T \cdot \ln T - 2.54525 \cdot 10^{-3} \cdot T^2 + 1.0931 \cdot 10^{-7} \cdot T^3 + 71106 \cdot T^{-1}; 298 - 6000 \text{ K}$$

Cu₅₆Si₁₁:

$$G(\text{Cu}_{56}\text{Si}_{11}, \text{Cu}; \text{Si}) - 0.83582 \cdot \text{GHSERCU} - 0.16418 \cdot \text{GHSERSI} = -3484.01 + 123.32409 \cdot T - 23.902111 \cdot T \cdot \ln T - 2.53469 \cdot 10^{-3} \cdot T^2 + 1.0742 \cdot 10^{-7} \cdot T^3 + 72870 \cdot T^{-1}; 298 - 6000 \text{ K}$$

Cu₃₃Si₇:

$$G(\text{Cu}_{33}\text{Si}_{7}, \text{Cu}; \text{Si}) - 0.825 \cdot \text{GHSERCU} - 0.175 \cdot \text{GHSERSI} = -3730.72 + 123.47457 \cdot T - 23.88828 \cdot T \cdot \ln T - 2.52665 \cdot 10^{-3} \cdot T^2 + 1.0599 \cdot 10^{-7} \cdot T^3 + 74211 \cdot T^{-1}; 298 - 6000 \text{ K}$$

Cu₄Si:

$$G(\text{Cu}_4\text{Si}, \text{Cu}; \text{Si}) - 0.8 \cdot \text{GHSERCU} - 0.2 \cdot \text{GHSERSI} = -4864.25 + 124.39509 \cdot T - 23.856264 \cdot T \cdot \ln T - 2.50805 \cdot 10^{-3} \cdot T^2 + 1.0267 \cdot 10^{-7} \cdot T^3 + 77316 \cdot T^{-1}; 298 - 6000 \text{ K}$$

Cu₁₉Si₆:

$$G(\text{Cu}_{19}\text{Si}_6, \text{Cu}; \text{Si}) - 0.76 \cdot \text{GHSERCU} - 0.24 \cdot \text{GHSERSI} = -5669.1 + 124.93213 \cdot T - 23.805039 \cdot T \cdot \ln T - 2.4783 \cdot 10^{-3} \cdot T^2 + 9.736 \cdot 10^{-8} \cdot T^3 + 82283 \cdot T^{-1}; 298 - 6000 \text{ K}$$

6. Equilibrium calculations

Equilibrium calculations were performed by means of Poly-3 module of ThermoCalc package with liquid phase status set "fixed". All the invariant and univariant equilibria of the liquid phase were calculated in this way, enabling to establish invariant reaction's parameters, liquidus surface projection and Scheil reaction scheme, as well. Sixteen invariant reactions of the liquid phase were found in Co-Cu-Si system: one ternary eutectic and fifteen of U-type; their parameters are listed in table 4. Polythermal projection of the liquidus surface on the plane of Gibbs triangle is presented on figure 6, and its details are shown on figures 7 and 8. On the basis of informations from tables 1, 2, 3 and 4 and of figures 6, 7 and 8 Scheil reaction scheme was constructed, and it is presented on figure 9.

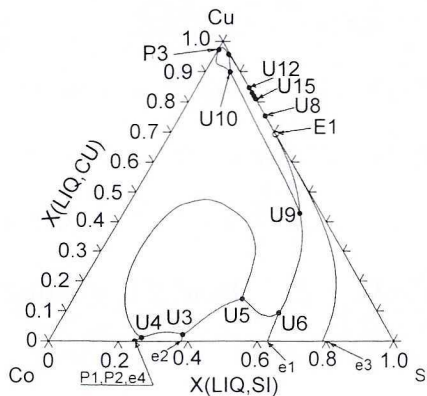


Fig. 6. Polythermal projekction of the calculated Co-Cu-Si liquidus surface

TABLE 4

Invariant reactions of the liquid in the Co-Cu-Si system

No	Reaction	Liquid composition		Temperature K	Reaction symbol
		% at.Cu	% at.Si		
1	$L + fcc = hcp + \phi$	7e-2	24.59	1481	U1
2	$L + \lambda = \phi + fcc$	0.105	24.72	1481	U2
3	$L + \kappa = \lambda + fcc2$	2.24	37.42	1546	U3
4	$L + fcc = \lambda + fcc2$	1.27	26.10	1514	U4
5	$L + k = fcc + fcc2$	14.04	48.67	1654	U5
6	$L + \omega = \kappa + fcc$	9.4	61.6	1549	U6
7	$L = \omega + \eta + (Si)$	69.3	30.67	1074	E1
8	$L + \kappa = \omega + \eta$	75.4	24.6	1130	U8
9	$L + \kappa = \omega + fcc$	42.74	50.96	1546	U9
10	$L + \kappa = \lambda + fcc$	89.9	7.2	1636	U10
11	$L + \kappa = \beta + fcc2$	95.67	3.8	1328	U11
12	$L + \kappa = \beta + fcc2$	84.6	15.35	1124	U12
13	$L + \kappa = \gamma + \beta$	83.03	16.96	1104	U13
14	$L + \kappa = \delta + \gamma$	82	18	1095	U14
15	$L + \kappa = \eta + \delta$	81	19	1088	U15
16	$L + \lambda = fcc + fcc2$	97.2	0.3	1367	U16

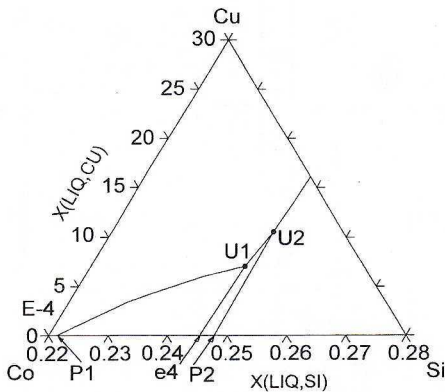


Fig. 7. Co-rich corner of the Co-Cu-Si liquidus surface

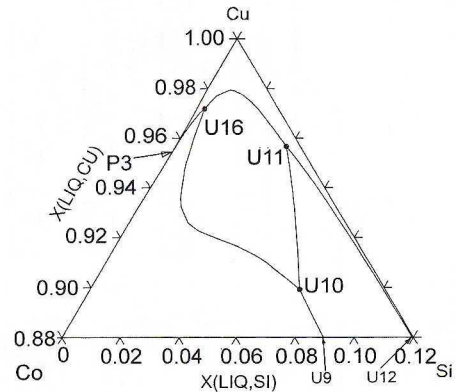


Fig. 8. Cu-rich corner of the Co-Cu-Si liquidus surface

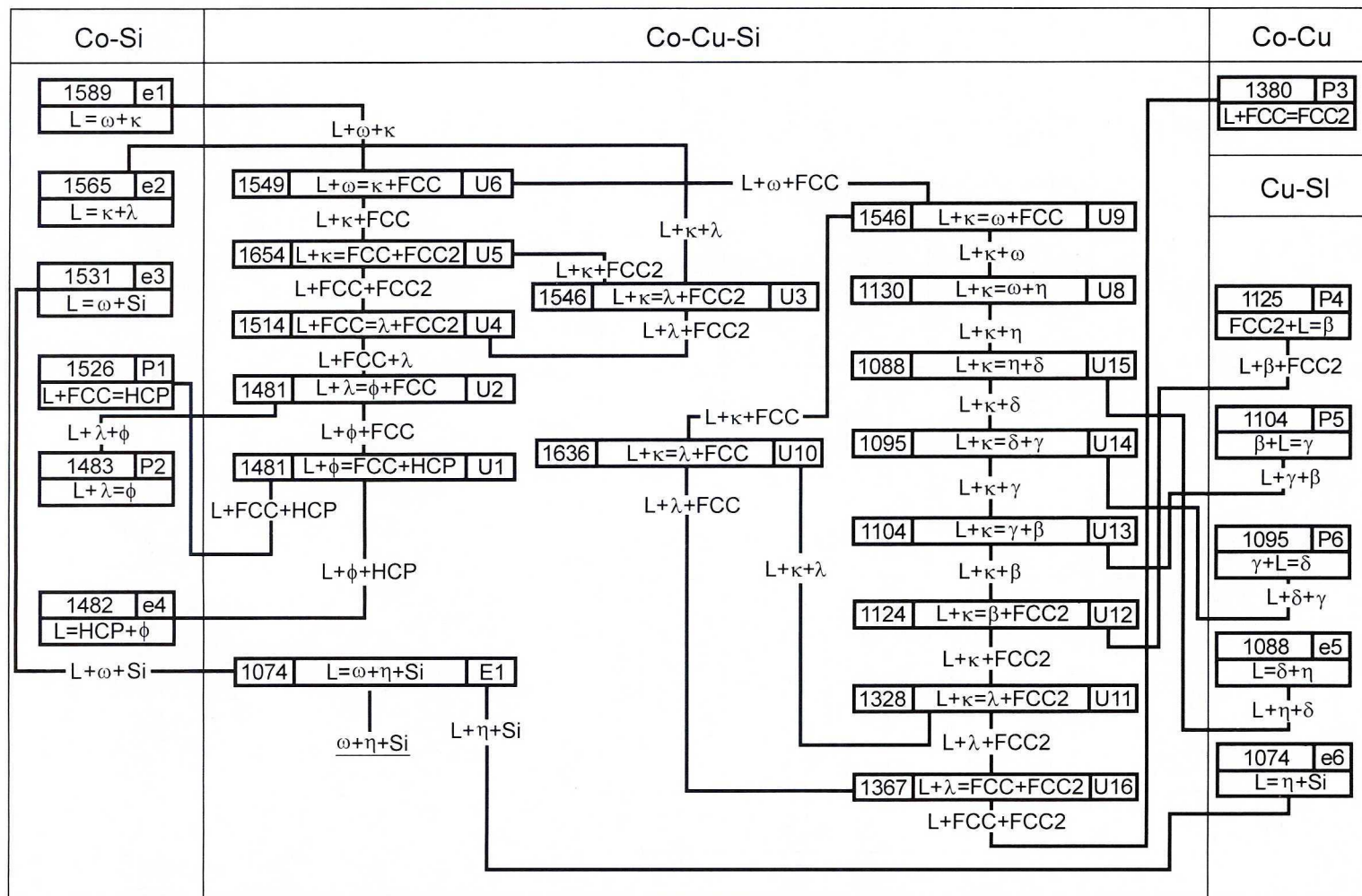


Fig. 9. Scheil reaction scheme for Co-Cu-Si system

7. Summary

Ternary Co-Cu-Si system is the hard objective for both theoretical considerations and for experimental examination. The considerable part of the liquidus surface is situated above or about 1500 K falling steeply down when approaching Cu-Si binary subsystem. Univariant loop-like line between U4 and U5 invariant reactions reflects the existence of the metastable miscibility gap of the fcc phase in the Co-Cu subsystem, and shape of the whole liquidus surface is dominated by very stable intermetallic compounds of the Co-Si subbinary system. Differences also exist considering chemical interactions in the liquid phase of the subbinaries: from strong negative in the Co-Si (-50 kJ/mole), through moderately negative in Cu-Si (-14) to slightly positive in Co-Cu ($+9$); numbers in parentheses refer to extremal value of the heat of mixing in the liquid phase (kJ/mole). Overlapping those complex characters of the binary subsystems makes calculations of even single initial equilibrium difficult and time consuming. This explains the fact that, although all three subbinaries were assessed several times, no attempts were made so far to calculate ternary system even by means of binary formalism.

The attempt to derive ternary interaction parameters failed because of very scarce experimental informations. With six experimental points of the heat of mixing in the liquid phase, combination of one and two adjustable ternary coefficients were tried, but numbers obtained did not changed significantly resulting Gibbs energy values falling within the experimental error. Usual optimisation procedure in such a case requires to fit all the adjustable parameters for a certain phase, and in this specific case twenty coefficients would be fitted to six experimental points, what is obvious mathematical absurd. In general, the reasonable number of the experimental data necessary for ternary system optimisation should be three times of that required for binary one.

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