Copper – Silicon – Zinc

Nataliya Bochvar, Tatyana Dobatkina

Introduction

[1906Gui, 1912Car, 1930Gou, 1930Vad1, 1930Vad2, 1931Vad1, 1931Vad2, 1942Mas, 1945Smi, 1974Smi] investigated the Cu rich part of the Cu-Si-Zn system containing up to 40 mass% Zn and 6 mass% Si. The boundaries of the (Cu) field have been determined at 800°C by [1930Gou], at 750°C by [1930Vad1, 1930Vad2] and at 400, 600, 800°C by [1945Smi]. [1974Smi] shows the variation of the limiting solubility of the (Cu) region as a function of the composition at 0, 5, 10, 15, 20, 25, 30 (mass%) Zn and up to 5 mass% Si and temperature from 1050 to 300°C. At 800°C, the boundaries of the α + β and β phase fields have also been determined [1930Gou]. These authors report lower solubility of Si in the Cu-Zn alloys than in later investigations [1957Mim, 1962Pop, 1964Pop1]. A part of the Cu-Si-Zn diagram, up to 30 at.% Si and 90 at.% Zn, has been investigated in detail by [1956Mim, 1957Mim, 1960Mim1, 1960Mim2, 1964Mim1, 1964Mim2]; another part, up to 20 at.% Si and 50 at.% Zn, has been studied by [1962Pop, 1964Pop1]. The projection of the liquidus surface has been constructed by [1956Mim]. The range near η solid solution has been investigated by [1960Mim1, 1960Mim2] in detail. Isothermal sections at 700, 600, 400°C were constructed by [1957Mim, 1960Mim1, 1960Mim2] and by [1962Pop, 1964Pop1] at 847, 760, 600 and 482°C. [1985Far] quotes a ternary eutectic between "Cu_4Si and two unidentified ternary phases" at 19 mass% Zn, 7 mass% Si and 765°C. This is very near to the quasibinary peritectic minimum L + β ⇌ γ found by [1957Mim] at 21.5 mass% Zn, 6.9 mass% Si and 775°C, which contains only two solid solution phases β and γ. [1969Gue, 1979Dri, 1979Cha] give the review of the Cu-Si-Zn system. [2003Bor] used the thermodynamic calculation for construction of isothermal sections at 670, 720, and 760°C in the composition range up to 60 mass% Zn and 10 mass% Si and vertical section at 1 mass% Si. Phase diagram information from [1964Pop1] and the personal experimental data were used by [2003Bor] in optimization. Experimental methods used in different works are summarized in Table 1.

Binary Systems

The binary systems Cu-Zn, Cu-Si and Si-Zn are accepted from [2006Leb], [2002Leb] and [1996Jac] respectively. The δ, γ, and ε phases of the Cu-Si binary system [2002Leb] are designated here as δ_1, γ_1, and ε_1, respectively.

Solid Phases

Ternary phases do not form. The β phase of the binary Cu-Si and Cu-Zn systems forms continuous series of solid solutions at high temperatures [1956Mim, 1957Mim, 1962Pop, 1964Pop1]. Reported by [1956Mim, 1957Mim, 1964Pop1] the formation of the continuous solid solution between γ phase of Cu-Zn system and high temperature δ_1 phase of Cu-Si system is not accepted, because they have different crystal structure. The γ phase has very wide homogeneity range towards Cu-Si system up to alloy with the composition of 1.7 at.% Zn and 17.3 at.% Si in equilibrium with δ_1 phase at 760°C. The solubility of Zn in the κ phase is significant; it reaches ~16 at.% Zn at 700°C. The solubility of Zn in the η phase is 2.9 at.% at the eutectic temperature, 530°C. In the ε_1 and γ_1 phases it is about 2 at.% Zn. The data on the solid phases are summarized in Table 2.

Quasibinary Systems

Based on metallographic and thermal analyses, [1956Mim] established that along the γ - Si section at 721°C, 58 mass% Zn and 3.7 mass% Si, a eutectic L ⇌ γ + (Si) occurs. However this section can not considered as quasibinary because γ phase forms by peritectic reaction.

Invariant Equilibria

Four four-phase and one three-phase invariant equilibria (E_2, U_6, U_{10}, U_{14}, e_4) with the participation of liquid have been found by [1956Mim]. The quasibinary peritectic minimum $L + \beta \rightleftharpoons \gamma$ at 775°C determined by [1956Mim] is doubtful, because the γ and δ_1 phases do not form a continuous solid solution. One can suppose that there is the transaction reaction $L + \beta \rightleftharpoons \gamma + \delta_1(U_1)$ at 775°C instead of the peritectic minimum. According to [1985Far] in this point exist three phases: Cu_4Si and two unidentified ternary phases. The composition of Cu_4Si phase is close to δ_1 phase. One of the ternary phases can be β ternary solid solution and another - γ phase with dissolved Si. Moreover five hypothetical invariant equilibria with the participation of the δ_1 phase (U_2, U_3, U_4, U_5, E_1) were given by us supplementary. In solid state seven invariant equilibria have been established by [1957Mim]. However, two of them contradict with the isothermal sections [1964Pop1]. A four-phase reaction $\kappa + \beta \rightleftharpoons$ (Cu) + γ after [1957Mim] occurs at 625°C, whereas after [1962Pop, 1964Pop1] this reaction is below the isothermal section given for 600°C. To obtain the three-phase equilibria [1962Pop, 1964Pop1] at 482°C three four-phase reactions are necessary between 600 and 482°C, whereas the section given by [1957Mim] for 400°C, showing the three-phase equilibria (Cu) + γ_1 + γ and ε_1 + γ_1 + γ, implies only one four-phase equilibrium in this range. Invariant reactions in points U_7, U_9, U_4 and E_5 are given according to the phase equilibria after [1964Pop1] at the temperatures 600°C and below. The reaction scheme is given in Fig. 1. The hypothetical invariant equilibria are shown by dashes lines. Determined by [1956Mim] eutectic (E_4) and transition (U_6, U_{10}) reaction temperatures as 559, 667, 598°C, were corrected according to accepted binary Cu-Zn system [2002Leb] as ~548, ~665 and ~574°C. The compositions of the phases are given in Table 3. The compositions of the liquid phase in the invariant equilibria at 597 and 424°C have been corrected to a non-zero Si content, which was neglected by [1956Mim]. At 600, 500, and 480°C [1960Mim1, 1960Mim2] reported identical compositions for η and η' or η' and η''. This contradicts the rules of heterogeneous equilibria and therefore it is tentatively corrected in Table 3.

Liquidus Surface

The projection of the liquidus surface presented in Fig. 2 is based on [1956Mim] and on the assumption of the existence of the primary crystallization field of the δ_1 phase. Nine fields of primary crystallization, of the (Cu), β, γ, δ_1, δ, ε, η, (Si) and (Zn) phases, are separated from each other by the lines of monovariant equilibria. The hypothetical monovariant equilibria are shown by dashed lines.

Isothermal Sections

The isothermal sections constructed by [1957Mim] at 600°C and below disagree with those of [1962Pop, 1964Pop1]. [1962Pop, 1964Pop1] identified the phases by micrography and X-ray diffraction, whereas [1957Mim] used only micrography, which is less secure for the identification of phases than X-ray diffraction. Therefore, the results by [1962Pop, 1964Pop1] are preferential. Five isothermal sections constructed at 847, 760°C by [1964Pop1], at 700 by [1957Mim] and 600, 482°C by [1964Pop1] are displayed in Figs. 3 to 7. They are corrected to satisfy the accepted binary systems [2002Leb, 2006Leb]. Some details, not given by [1957Mim] or [1964Pop1] but following from the reaction scheme and the liquidus surface, are given by dashed lines.

Temperature – Composition Sections

A vertical section from Cu + 20 mass% Zn to Cu + 10 mass% Si has been constructed by [1942Mas]. However, this section disagrees with the binary Cu-Zn [2006Leb] and ternary systems [1957Mim, 1962Pop, 1964Pop1]. Several vertical sections at constant content of Si (2 and 4 mass%) and constant content of Zn (5 and 20 mass%) were constructed by [1957Mim]. Only one section with 2 mass% Si agrees with phase equilibria obtained by [1962Pop, 1964Pop1]. This section constructed in at.% is shown on Fig. 8. Some correction was made in solid state according to the isothermal sections [1964Pop1]. Also, the temperatures of invariant reactions on this section were corrected according to the reaction scheme (Fig. 1). Other vertical sections contradicted isothermal sections at temperatures 600°C and below obtained in [1962Pop,

1964Pop1] and are not shown in the present assessment. The vertical section at 1 mass% Si calculated by [2003Bor] is not accepted here. It shows the increase the temperature of peritectic reaction from Cu-Zn system when Si is added, whereas this temperature must be lower according to the liquidus surface.

Notes on Materials Properties and Applications

[1930Gou] studied the effect of Si on the hardness of ternary Cu-Si-Zn alloys in the composition range from ~13 to ~15 mass% Zn and 3.9; 5.1 mass% Si and in the composition range from ~37 to 40 mass% Zn and 0.8 mass% Si. The hardness of alloys was measured after casting and after quenching at 850°C followed by annealing at 750, 600, 550, 500, 450, 350 and 250°C.
[1956Fre] made review of copper-base alloys most commonly used for making castings in UK. The constitution and the effect of composition and structure on properties are discussed.
Mechanical properties for sand-casting, chill-casting, extruded into rods and annealed at different temperatures of Cu-Si-Zn alloys were studied in many works [1930Vad1, 1930Vad2, 1931Vad1, 1931Vad2, 1942Mas, 1974Smi, 2003Ois]. These alloys with high silicon content, especially when it is all retained in solid solution, have valuable properties. They can be worked hot as well as cold.
[1972Wie, 1974Sol, 1977Wie, 1984Mur] investigated the shape memory behavior in the β phase region of ternary Cu-Si-Zn alloys containing from 33.4 to 35.9 at.% Zn and from 0.1 to 2.2 at.% Si.

Miscellaneous

[1964Mim1, 1964Mim2] using thermal analysis, microscopic examination and also partially X-ray diffraction and resistivity measurements studied the influence of Si on the $\beta \rightleftharpoons \beta'$ and $\gamma \rightleftharpoons \gamma_1$ transformations. The $\beta \rightleftharpoons \beta'$ transformation temperature depends only slightly on the additions of Si. The $\gamma \rightleftharpoons \gamma_1$ transformation temperature is lowered by Si or Cu additions. This transformation proceeds by a diffusionless martensitic mechanism. The twin-like figure which appears in the γ_1 phase of the slowly cooled specimens is attributed to the transformation from γ to γ_1.
[1970Mim] investigated the phase transformation in high strength brass containing 35-40 mass% Zn, 1-5 mass% Si and about 2 mass% Mn by DTA, electron probe X-ray micro-analysis, microscopic examination. Four phases were observed in the specimens slowly cooled from 850 to 550°C and quenched into ice water, that is (Cu), β, (Mn, Si)-intermetallic compound and Si-bearing Cu-Zn solid solution.
The morphology and the structure of martensite phases have been examined by [1967Pop, 1968Pop, 1974Cor, 1976Gil, 1980Fuk, 1982Gar]. The investigations were carried out on alloys with 33 to 36 at.% Zn and from 0.6 to 2.2 at.% Si. The martensitic phases are composed of a lamellar mixture of two close-packed structures (orthorhombic and cubic) with different stacking sequence. The martensitic transformation temperature depends on the composition and the temperature of quenching. The mechanism of stabilization of Cu-Si-Zn martensite has been studied by [1991Dut, 1993Dut]. Cu-Si-Zn alloys show a significant tendency to martensite stabilization after ageing at room temperature. After continuous heating (20 $K \cdot min^{-1}$) of stabilized Cu-Si-Zn martensite to 300°C no significant structural changes were found.
[1991Udo] investigated structure of diffusion layer which is formed during thermochemical treatment of Cu-39 mass% Zn alloy at 800 - 860°C for 4 h in powder mixture containing Si. [1991Udo] shown that wear rate and friction coefficient are depended from structure of surface layer. Porous layer has better properties.
[2002Yos] investigated season cracking susceptibility of Cu-1Si-30Zn (mass%) alloy after exposure in ammonical environment using optical micrographs, SEM and tensile testing methods.
[2003Ois] determined the grain size of specimens Cu-10 mass% Zn-(0.3 to 2.07) mass% Si using the intercept method with optical micrographs and showed that the grain size of these specimens becomes smaller with increasing silicon concentration.

References

[1906Gui] Guillet, L., "General Investigations of Brasses" (in French), *Rev. Metall.*, **3**, 159-204 (1906) (Review, 1)

[1912Car] Carpenter, H.C.H., "The Effect of other Metals on the Structure of the β Constituent in Copper - Zinc Alloys", *J. Inst. Met.*, **8**, 59-73 (1912) (Experimental, Morphology, 2)

[1930Gou] Gould, H.W., Ray, K.W., "Effects of Silicon on the Properties of Brass", *Metals and Alloys*, **1**(10), 455-457 (1930) (Phase Diagram, Phase Relations, Experimental, Mechan. Prop., 4)

[1930Vad1] Vaders, E., "A New Silicon - Zinc - Copper Alloy", *J. Inst. Met.*, **44**, 363-383 (1930) (Experimental, Phase Diagram, Phase Relations, Mechan. Prop., Morphology, Phys. Prop., 6)

[1930Vad2] Vaders, E., "A New Silicon-Zinc- Copper Alloy", *Met. Ind. London,* **37,** 278, 315-318, 365-368 (1930) (Phase Diagram, Phase Relations, Experimental, Mechan. Prop., Morphology, Phys. Prop., 6)

[1931Vad1] Vaders, E., "A New Silicon-Zinc- Copper Alloy", *Met. Ind.*, **29**(3), 108-110 (1931) (Phase Diagram, Mechan. Prop., Phys. Prop., 5)

[1931Vad2] Vaders, E., "A New Silicon-Zinc-Copper Alloy", *Met. Ind.*, **29**(4), 155-156 (1931) (Experimental, Mechan. Prop., Phys. Prop.)

[1942Mas] Masing, G., Wallbaum, H.J., "On the Structure Transformations in a Silicon - Zinc - Copper Alloy" (in German), *Z. Metallkd.*, **34**, 87-89 (1942) (Experimental, Phase Diagram, Crys. Structure, Morphology, Mechan. Prop., *, 4)

[1945Smi] Smiryagin, A.P., "Phase Diagrams of Copper-Silicon, Copper-Silicon-Zinc and Copper-Silicon-Manganese" (in Russian), in "*Spesial Bronzes and Brasses*", Nemilov, V.A. (Ed.), Metallurgiya, Moscow, 5-20 (1945) (Phase Diagram, Phase Relations, Mechan. Prop., 30)

[1956Mim] Mima, G., Hasegawa, M., "The Diagram of Cu-Si-Zn Alloy (First Report)", *Technol. Repts. Osaka Univ.*, **6**, 313-321 (1956) (Experimental, Phase Diagram, Phase Relations, Morphology, #, *, 5)

[1956Fre] French, A.R., Member, F.I.M., "The Metallurgigal Control of Quality in the Production of Copper-Base Alloy Castings", *J. Inst. Met.*, **85**, 293-317 (1956) (Review, Phase Diagram, Mechan. Prop., Phys. Prop., Electr. Prop., 124)

[1957Mim] Mima, G., Hasegawa, M., "The Diagram of Cu-Si-Zn Alloy – II", *Technol. Repts. Osaka Univ.*, **7**, 385-397 (1957) (Experimental, Morphology, Phase Diagram, Phase Relations, #, *, 1)

[1960Mim1] Mima, G., Hasegava, M., "Phase Diagram of the System Cu-Si-Zn in the η Phase Region" (in Japanese), *Nippon Kinzoku Gakkai- Shi*, **23,** 585-587 (1959) (Experimental, Phase Diagram, Morphology, 14)

[1960Mim2] Mima, G., Hasegawa, M., "The Diagram of Cu-Si-Zn Alloy – III", *Technol. Repts. Osaka Univ.*, **10**, 157-168 (1960) (Experimental, Phase Diagram, Phase Relations, Morphology, #, *, 8)

[1962Pop] Pops, H., "The Contributuon of the Primary Solid Solubility Isothermal Limit and Some Intermediate Phase in Cu-Rich Cu-Si-Zn Alloys", *Dissertation Univ. Pittsburg*, 1-138 (1962) (Crys. Structure, Phase Diagram, Experimental, 30)

[1964Mim1] Mima, G., Hasegawa, M., "Study of the Diagram of Cu-Si-Zn Alloy in the Range Near γ Solid Solution" (in Japanese), *Nippon Kinzoku Gakkai-Shi.*, **27**, 370-376 (1963) (Crys. Structure, Experimental, Morphology, Electr. Prop., Phase Diagram, Phase Relations, 15)

[1964Mim2] Mima, G., Hasegawa, M., "The Diagram of Cu-Si-Zn Alloy - IV", *Technol. Repts. Osaka Univ.*, **14**, 623-633 (1964) (Experimental, Phase Diagram, Electr. Prop., Morphology, Phase Relations, #, *, 14)

[1964Pop1] Pops, H., "The Constitution of Copper-Rich Copper - Silicon - Zinc Alloys", *Trans. Met. Soc. AIME*, **230**, 813-820 (1964) (Experimental, Phase Diagram, Phase Relations, Morphology, #, *, 14)

[1964Pop2] Pops, H., "Lattice Parameters of α Phase in Copper - Silicon - Zinc Alloys", *Trans. Met. Soc. AIME*, **230**, 267-268 (1964) (Crys. Structure, Experimental, 5)

[1967Pop] Pops, H., Kittl, J.E., "Influence of Inhomogeneity on the Martensitic Transformation of a Cu-Zn-Si β-Phase Alloy", *Trans. Met. Soc. AIME*, **239**, 1668-1670 (1967) (Experimental, Phase Relations, Morphology, 7)

[1968Pop] Pops, H., Delaey, L., "Electron Microscopy of Cu-Zn-Si Martensitic", *Trans. Met. Soc. AIME*, **242**, 1849-1851 (1968) (Experimental, Phase Relations, Crys. Structure, Morphology, 11)

[1969Gue] Guertler, W., Guertler, M., Anastasiadias, E., "14-29-30", *A Comp. of Const. Ternary Diagr. Met. System, Isr. Pro. Sci. Tr., Jerusalem*, **19**(8), 555-561 (1969) (Review, Phase Diagram, Mechan. Prop., Morphology, Phase Relations, 6)

[1970Mim] Mima, G., Yamaguchi, M., Sato, J., On the Phase Transformation Observed in the High Strength Brass During Heat Treatment" (in Japanese), *Shindo Gijutsu Kenkyukai-Shi*, **9**, 182-184 (1970) (Phase Diagram, Experimental, Morphology, 4)

[1972Wie] Wield, D.V., Gillam, E., "Shape Memory Effect and Pseudoelasticity in Cu-Zn-Si", *Scr. Metall.*, **6**(12), 1157-1160 (1972), (Experimental, Phys. Prop., Mechan. Prop., Morphology, 15)

[1974Cor] Cornelis, I., Wayman, C.M., "Direct Observation of the 3R-Stacking Sequence in Cu-Zn-Si Martensite", *Mater. Res. Bull.*, **9**(8), 1057-1062 (1974) (Experimental, Crys. Structure, Morphology, 8)

[1974Smi] Smiryagin, A.P., Smiryagina, N.A., Belova, A.V., "Silicon Containing Brasses" (in Russian), in "*Industrial Non-Ferrous Metals and Alloys*", Metallurgiya, Moscow, 106-109 (1974) (Review, Phase Diagram, Mechan. Prop.)

[1974Sol] Solov'ev, L.A., Khachin, V.N., "Influence of Internal Stresses on the Process of Phase Transformation in Titanium-Nickel and Copper- Zinc-Silicon Alloys", *Phys. Met. Metallogr.*, **37**(5), 184-186 (1974), translated from *Fiz. Met. Metalloved.* **37**(5), 1095-1097 (1974) (Experimental, Phys. Prop., 12)

[1976Gil] Gillam, E., Wield, D.V., "Premartensitic Instability in beta-Cu-Zn-Si Alloys ", *Scr. Metall.,* **10**(11), 965-970 (1976) (Experimental, Crys. Structure, Morphology, Phase Relations, Phase Diagram, 22)

[1977Wie] Wield, D.V., Gillam, E., "Deformation Behavior of Cu-Zn-Si Allys Close to their Martensitic Transformation Temperature", *Acta Metall.*, **25**, 725-733 (1977) (Experimental, Mechan. Prop., Morphology, 18)

[1979Cha] Chang, Y.A., Neumann, J.P., Mikula, A., Goldberg, D., "Cu-Si-Zn", *INCRA Monograph Series. Phase Diagrams and Thermodynamic Properties of Ternary Copper-Metall Systems*, NSRD, Washington, **Vol. 6**, 669-675 (1979) (Review, Phase Diagram, Phase Relations, 16)

[1979Dri] Drits, M.E., Bochvar, N.R., Guzei, L.S., Padezhnova, E.M., Rokhlin, L.L., Turkina, N.I., "Ci-Si-Zn" (in Russian), *Binary and Multicomponent Copper-Base Systems*, Nauka, Moscow, 158-159 (1979) (Review, Phase Diagram, 11)

[1980Fuk] Fukamachi, M., Kajiwara, S., "Lattice Imaging Study of Boundaries in Martensite in Shape Memoruy Alloys", *Jpn. J. Phys.*, **19**(8), L479-L482 (1980) (Experimental, Phys. Prop., Morphology, 10)

[1982Gar] Garshina, M.N, Agapitova, N.V., Evsyukov, V.A., "Effect of Loading on the Crystal Structure of Cu-Zn-Si Alloy Martensite" (in Russian), *Phase Transformation in Solid State (Fazovye Prevrasheniya v Tverdykh Telakh),* Voronezh, 63-68 (1982) (Experimental, Crys. Structure, 2)

[1984Mur] Murakami, K., Murakami, Y., Mishima, K., Ikai, Y., "Degradation and Impruvement of Shape Memory Effect of Cu-Base Alloys" (in Japanese), *J. Jpn. Inst. Met*., **48**(2), 115-121 (1984) (Experimental, Mechan. Prop., Phys. Prop., 13)

[1985Far] Farkas, D. Birchenall, C.E., "New Eutectic Alloys and Their Heats of Transformation", *Metall. Trans*., **16A**, 323-328 (1985) (Experimental, Calculation, Morphology, Thermodyn., 18)

[1991Dut] Dutkiewicz, J., Kostorz, G., "High-Resolution Study of Stabilised Martensite in Cu-Zn-Si Alloys", *Phys. Status Solidi A*, **123**(1), 63-70 (1991) (Experimental, Crys. Structure, Morphology, 15)

[1991Udo] Udovitskii, I.V., Fedotov, I.A., "Intensification of Thermochemical Treatment in the Cu-Zn-Si System During Liquid Phase Formation" (in Russian), *Izv. Akad. Nauk SSSR, Met*., (1), 135-137 (1991) (Interface Phenomena, Experimental, Morphology, Mechan. Prop., 4)

[1993Dut] Dutkiewicz, J., Chandrasekaran, M., Cesari, E., "Stabilisation of Martensite in Cu-Zn-Si", *Scr. Metall. Mater.*, **29**(1), 19-24 (1993) (Experimental, Crys. Structure, Phase Relations, Morphology, 16)

[1996Jac] Jacobs, M.H.G., Spencer, P.J., "A Critical Thermodynamic Evolution of the Systems Si-Zn and Al-Si-Zn", *Calphad*, **20**(3), 307 (1996) (Phase Diagram, Phase Relations, Thermodyn., Calculation, 33)

[2002Yos] Yoshimura, Y., Kanai, K., Kita, K., Inoue, A., "Influence of Additional Elements on the Season Cracking Susceptibility of Cu-30 Mass%Zn Alloy", (in Japanese), *J. Jpn. Inst. Met*., **66**(9), 865-868 (2002) (Experimental, Mechan. Prop., Morphology, 11)

[2002Leb] Lebrun, N., Dobatkina, T.V., Kuznetsov, V.N., Li, Changrong, "Cu-Si (Copper-Silicon)", MSIT Binary Evoluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Service GmbH, Stuttgart, Dokument ID: 20.12505.1.20 (2002) (Phase Diagram, Crys. Structure, Thermodyn., Assessment, 23)

[2003Ois] Oishi, K., Sasaki, I., Otani, J., "Effect of Silicon Addition on Grain Refinement of Copper Alloys", *Mater. Lett*., **57**, 2280-2286 (2003) (Experimental, Morphology, Electr. Prop., Phys. Prop., 13)

[2003Bor] Borggren, U., Selleby, M., "A Thermodynamic Database for Special Brass", *J. Phase Equilib.,* **24**(2), 110-121 (2003) (Phase Diagram, Phase Relations, Thermodyn., 18)

[2006Leb] Lebrun, N., "Cu-Zn (Copper-Zinc)", MSIT Binary Evoluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Matrials Scince International Service GmbH, Stuttgart, to be published (2006) (Phase Diagram, Crys. Structure, Thermodyn., Assessment, 18)

Table 1: Investigations of the Cu-Si-Zn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1912Car]	Microscopic examination. Melting from copper-silicon, copper and zinc	51.05 mass% Cu, 47.70 mass% Zn, 1.19 mass% Si
[1930Gou]	Microscopic examination, hardness test. Melting in gas-fired crucible furnace, annealing at 725 to 825°C for 1 to 12 h and slowly cooling in the furnace	Alloys: 85 mass% Cu-15 mass% Zn up to 10 mass% Si and 60 mass% Cu-40 mass% Zn -up to 10 mass% Si. Annealing at 825°C and quenched in ice brine mixture. Phase boundaries (Cu)/(Cu) + β/β at 800°C. Hardness after annealing at 750, 650, 550, 450, 350 and 250°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1930Vad1] [1930Vad2] [1931Vad1] [1931Vad2]	Microscopic examination, tensile testing. Melting in a high frequency induction furnace, annealing at 750°C for 8 h and slowly cooling in the furnace	Alloys up to 70-90 mass% Cu, up to mass 5% Si, Zn to balance. Phase boundary of (Cu) at 750°C. Density, melting points. Tensile strength, elongation, Brinell hardness for sand-cast, chill-cast, extruded into rods and annealed at 600, 700, 750°C alloys.
[1942Mas]	Thermal, microscopic, X-ray analyses	The vertical section between alloys 80 mass% Cu-20 mass% Zn and 90 mass% Cu-10 mass% Si
[1945Smi] [1974Smi]	Thermal, microscopic analyses, hardness and electrical resistivity. Tensile testing, hardness. Heat treatment at 400 - 800°C for 12 to 240 h in atmosphere of nitrogen	Alloys up to 30 mass% Zn, up to 5 mass% Si, Cu to balance. Phase boundaries of (Cu) 400, 600 and 800°C. Region of (Cu) in Cu-Si-Zn as a function of the composition and temperature. Mechanical properties.
[1956Mim]	Thermal and microscopic analyses. Melting in electric furnace	Cu-Zn alloys with up to 20 mass% Si. Liquidus surface. Compositions and temperatures of invariant reactions
[1957Mim]	Thermal and microscopic analyses. Melting in electric furnace	Vertical sections at 5 and 20 mass% Zn. Isothermal sections at 400, 600, 700°C. Mono- and invariant reactions in liquid and solid states
[1960Mim1] [1960Mim2]	Thermal and microscopic analyses, measurement of electrical resistance. Melting in electric furnace	Alloys in the range near η phase. Projection of transformation of $\eta \rightleftharpoons \eta'$ and $\eta' \rightleftharpoons \eta''$
[1964Mim1] [1964Mim2]	Thermal and microscopic analyses, electrical resistance measurements. Melting in electric furnace. Homogenizing treatment at 650°C	Alloys in the range near γ phase. Annealing at 400°C for 12 h and 300°C for 24 h, air-cooling on water quenching. Transformation of γ phase and order-disorder transformation of β solid solution
[1962Pop] [1964Pop1]	X-ray diffraction and microscopic observations. Melting, homogenization in helium filled quartz tubes at 760°C for 10 days	Cu corner in the range up to 50 mass% Zn and 20 mass% Si Annealing at 847, 760, 600, 482°C for 1, 5, 10, 25 days, respectively. Then quenching in to an ice-brine solution. Isothermal sections at 847, 760, 600, 482°C and vertical section through the β phase field.
[1964Pop2]	X-ray method. Melting and casting under reduced pressures of helium in quartz capsules. Homogenization at 760°C for 10 days.	70 to 80 at.% Cu, 2 to 30 at.% Zn, 1,5 to 11 at.% Si. Lattice parameters values for (Cu) phase
[1985Far]	DTA, EMA, calculation. Melting in induction furnace	Measurement and calculation of eutectic composition, temperature, heat of fusion
[2003Bor]	X-ray spectroscopy analyses, thermodynamic calculation. Melting in high-frequency induction furnace, homogenization treatment at 760°C for 4 days	66 to 72 mass% Cu, 0.7 to 1.8 mass% Si, Zn to balance. Calculation of isothermal sections at 670, 720, 760°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu		Dissolves up to 11.25 at.% Si at 842°C [2002Leb] and up to 38.27 at.% Zn at 454°C [2002Leb],
		a = 361.46	pure Cu, 25°C [Mas2]
		a = 369.612	at 35.84 at.% Zn and 300°C [2006Leb]
		a = 365.49 to 365.90	at 17.5 at.% Zn and from 2 to 6.5 at.% Si [1964Pop2]
		a = 363.05 to 363.30	at 5 at.% Zn and from 6 to 11 at.% Si [1964Pop2]
		a = 364.06 to 364.21	at 10 at.%Zn and from 5 to 7 at.% Si [1964Pop2]
		a = 368.47	at 30 at.% Zn, 1.5 at.% Si, 68.5 at.% Cu [1964Pop2]
(Si) < 1414	*cF*8 $Fm\bar{3}m$ C (diamond)	a = 543.06	pure Si, 25°C [Mas2]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.50 c = 494.70	pure Zn, 25°C [Mas2]
β, $Cu_{10+7x}Zn_{10-10x}Si_{3x}$	*cI*2 $Im\bar{3}m$ W		$0 < x < 1$ 36.1 to 55.8 at.% Zn [2006Leb] 14.2 to 16.2 at.% Si [2002Leb]
CuZn(h) < 930 - 454		a = 259.39	at 47.5 at.% Zn [2006Leb]
~ Cu_6Si 853 - 787		a = 285.4	at 14.9 at.% Si [2002Leb]
β', CuZn(r) < 468	*cP*2 $Pm\bar{3}m$ CsCl	a = 295.9	at 49.5 at.% Zn [2006Leb]
γ, Cu_5Zn_8 < 835	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	a = 886.9	57 to 70 at.% Zn [2006Leb]
δ, $CuZn_3$ 700 - 560	*hP*3 - $CuZn_3$	a = 427.5 c = 259.0	72.45 to 76 at.% Zn [2006Leb] at 600°C, $Cu_{0.7}Zn_2$ [2006Leb]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ε, $CuZn_4$ < 574	*hP*2 $P6_3/mmc$ Mg	*a* = 274.18 *c* = 429.39	78 to 88 at.% Zn [2006Leb]
η, $Cu_3Si(h_2)$ 859 - 558	*hR** or *t*** $R\bar{3}m$	*a* = 247 α = 109.74° *a* = 726.7 *c* = 789.2	23.4 to 24.9 at.% Si [2002Leb]
η', $Cu_3Si(h_1)$ 620 - 467	*hR** $R\bar{3}$	*a* = 472 α = 95.72°	23.2 to 25.2 at.% Si [2002Leb]
η'', $CuSi_3$(r) < 570	*o***	*a* = 7676 *b* = 700 *c* = 2194	23.3 to 24.9 at.% Si [2002Leb]
ε_1, $Cu_{15}Si_4$ < 800	*cI*76 $I\bar{4}3d$ $Cu_{15}Si_4$	*a* = 961.5	at 21.2 at.% Si [2002Leb]
κ, Cu_7Si 842 - 552	*hP*2 $P6_3/mmc$ Mg	 *a* = 256.05 *c* = 418.46	11.05 to 14.5 at.% Si at 12.75 at.% Si [2002Leb]
δ_1, $Cu_5Si(h)$ 824 - 711	*t***	 *a* = 881.5 *c* = 790.3	17.6 to 19.6 at.% Si annealing at 700°C [2002Leb]
γ_1, Cu_5Si(r) < 729	*cP*20 $P4_132$ βMn	*a* = 619.8	17.15 to 17.6 at.% Si [2002Leb]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Cu	Si	Zn
L + β ⇌ γ + δ_1	775	U_1	L	66.2	14.5	19.3
L ⇌ γ + (Si)	721	e_4	L	37.2	8.1	54.7
			γ	39.4	2.7	57.9
			(Si)	0	100.0	0
L ⇌ γ + η + (Si)	683	E_2	L	41.0	18.4	20.6
			γ	60.5	14.8	24.7
			η	72.8	22.1	5.1
			(Si)	0	100.0	0

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Cu	Si	Zn
L + γ ⇌ δ + (Si)	~665	U_6	L	19.6	0.7	79.7
			γ	31.2	0.7	68.1
			δ	27.6	0	72.4
			(Si)	0	100.0	0
ε_1 + η ⇌ γ + η'	600	U_9	ε_1	78.7	20.4	0.9
			η	76.3	22.4	1.3
			γ	68.3	15.2	16.5
			η'	76.7	22.0	1.3
L + δ ⇌ ε + (Si)	~574	U_{10}	L	~11.5	0.7	87.8
			δ	24.0	0	76.0
			ε	22.0	0	78.0
			(Si)	0	100.0	0
η ⇌ η' + γ + (Si)	530	E_4	η	73.5	23.6	2.9
			η'	73.9	23.6	2.5
			γ	84.8	12.4	2.8
			(Si)	0	100.0	0
γ_1 + η' ⇌ η'' + (Si)	480	U_{13}	γ_1	57.6	11.1	31.3
			η'	73.3	23.9	2.8
			η''	73.6	23.6	2.8
			(Si)	0	100.0	0
L + ε ⇌ (Zn) + (Si)	424	U_{14}	L	1.5	~0.7	97.8
			ε	12.8	~0	87.2
			(Zn)	2.8	~0	97.2
			(Si)	0	100.0	0

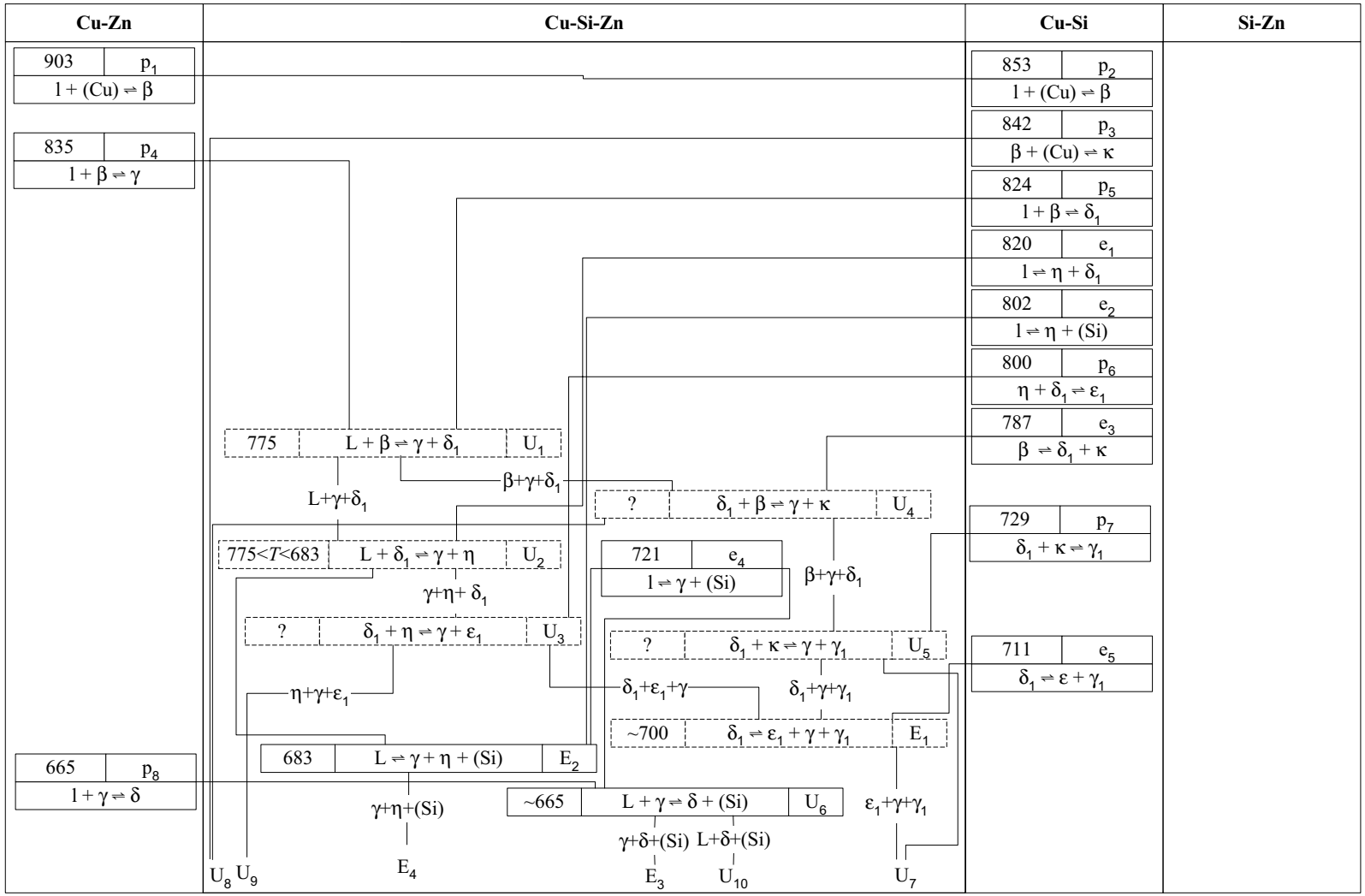

Fig. 1a: Cu-Si-Zn. Reaction scheme, part 1

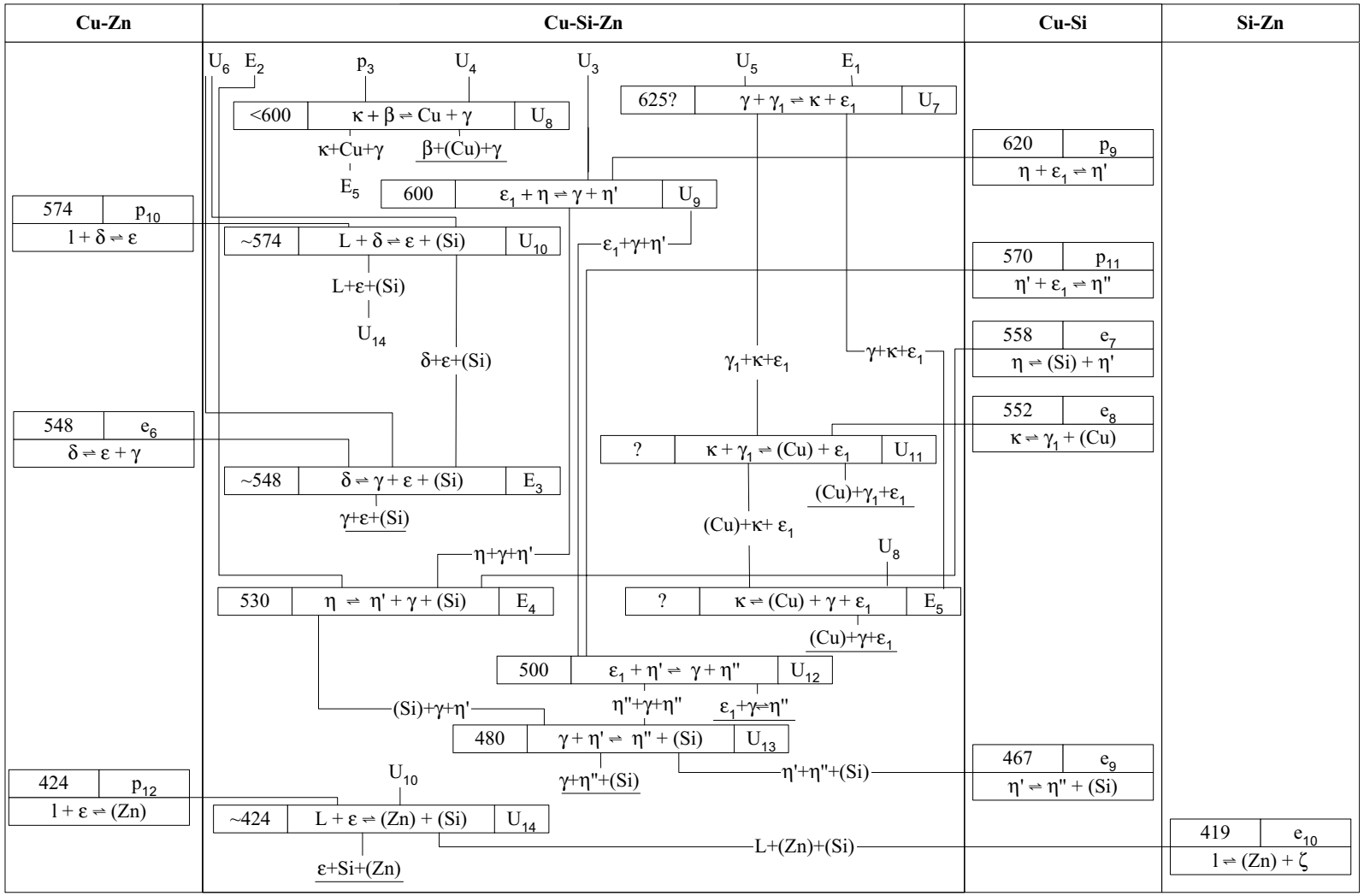

Fig. 1b: Cu-Si-Zn. Reaction scheme, part 2

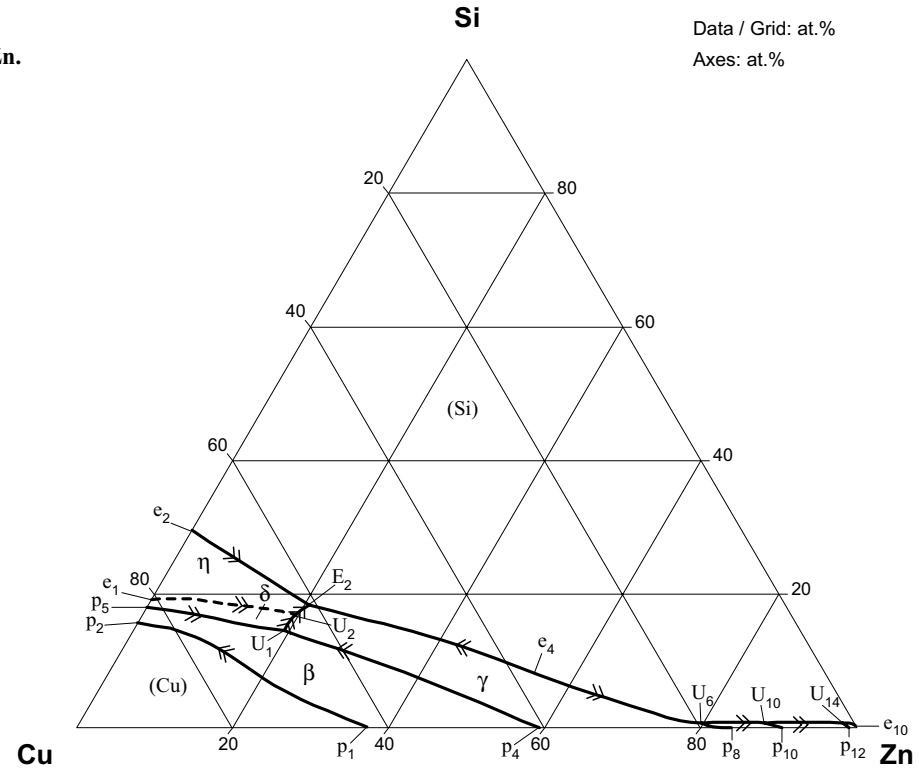

Fig. 2: Cu-Si-Zn. Liquidus surface projection

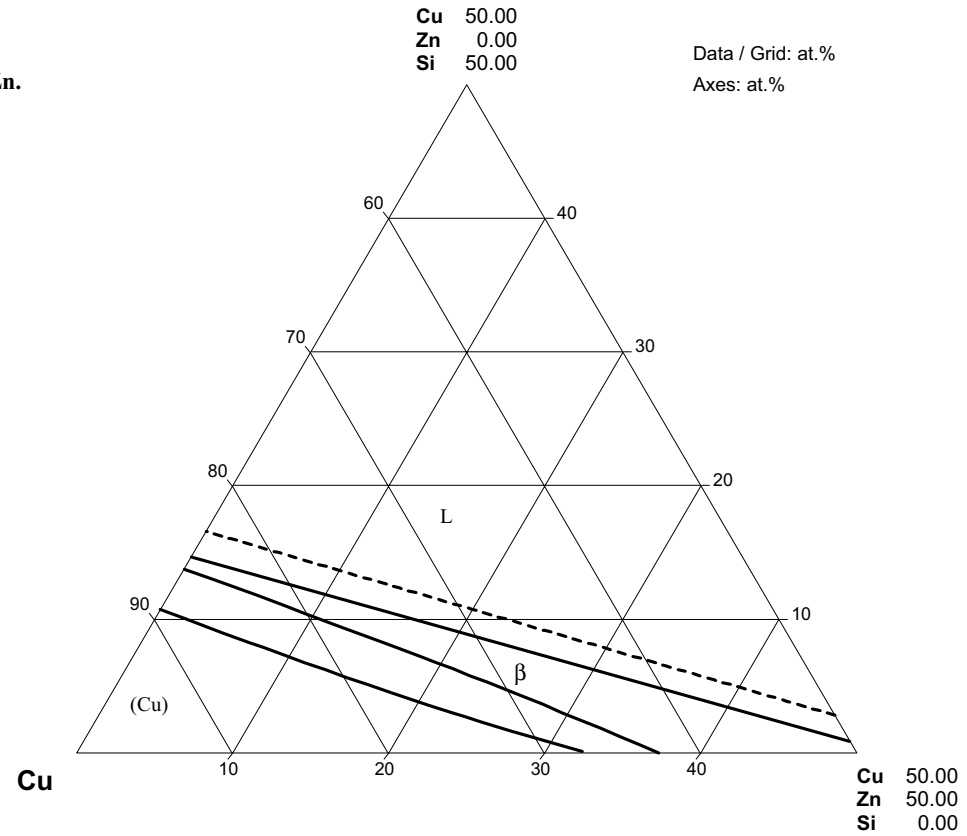

Fig. 3: Cu-Si-Zn. Partial isothermal section at 847°C

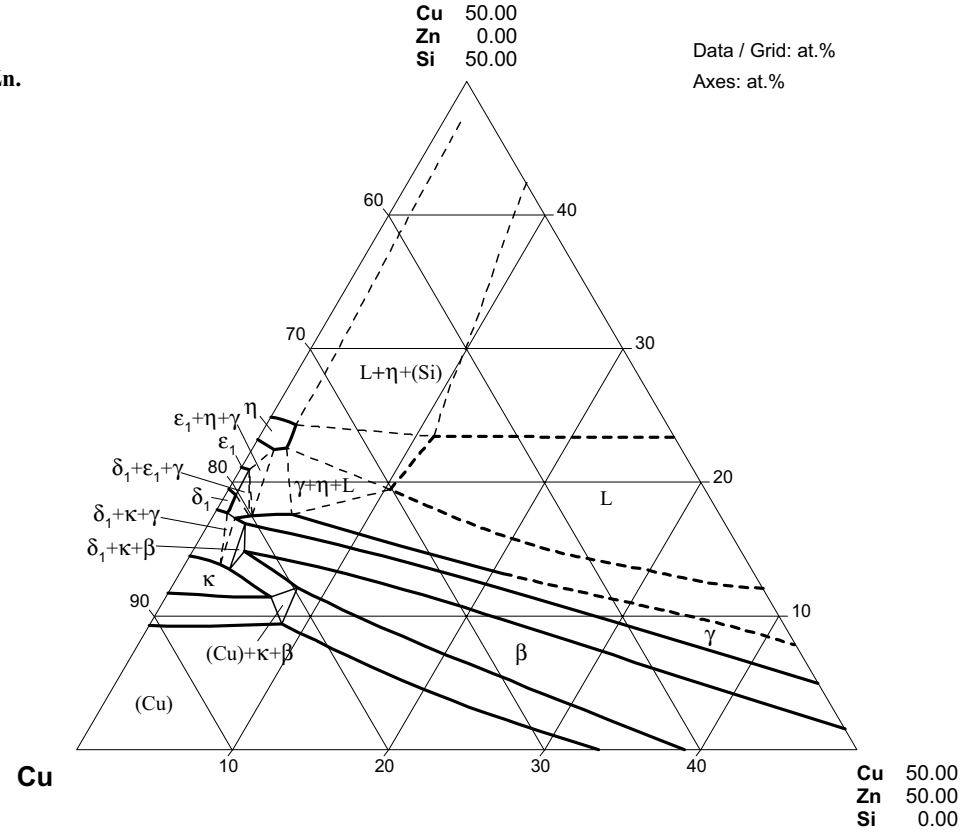

Fig. 4: Cu-Si-Zn. Partial isothermal section at 760°C

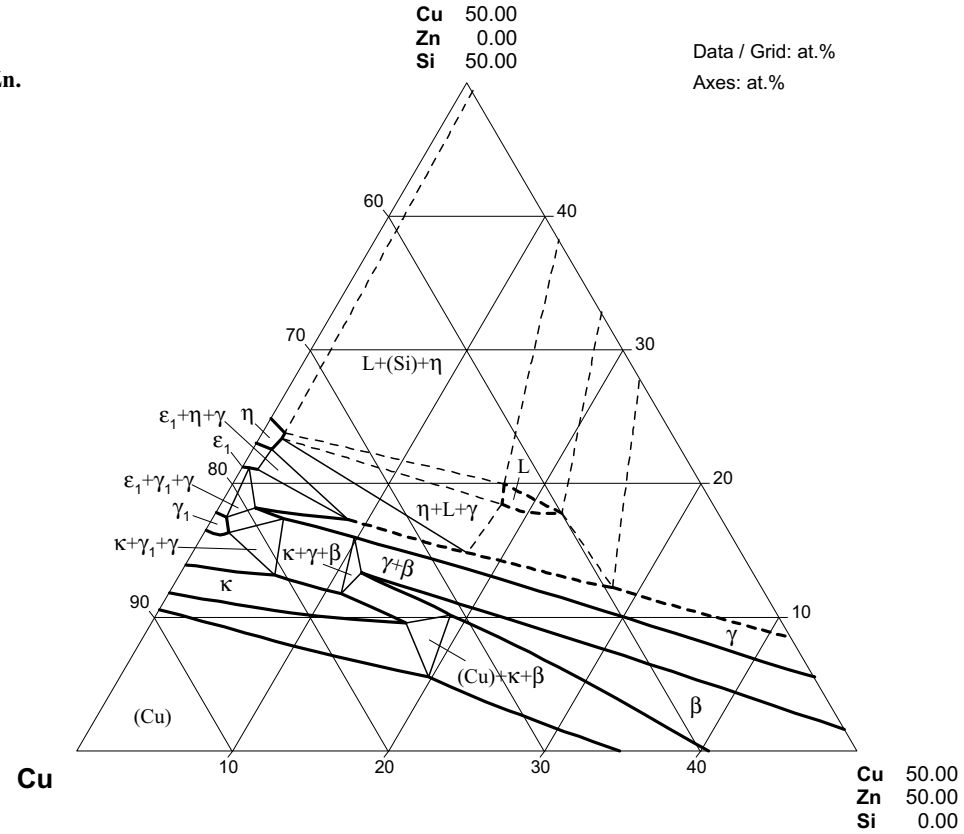

Fig. 5: Cu-Si-Zn. Partial isothermal section at 700°C

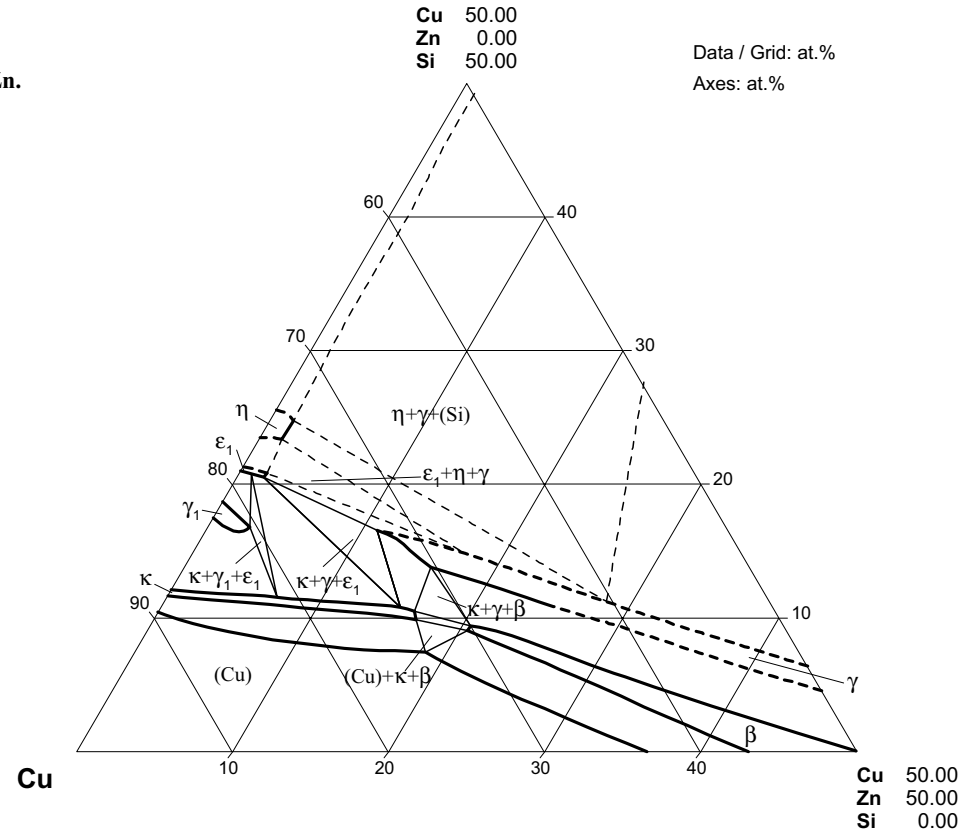

Fig. 6: Cu-Si-Zn. Partial isothermal section at 600°C

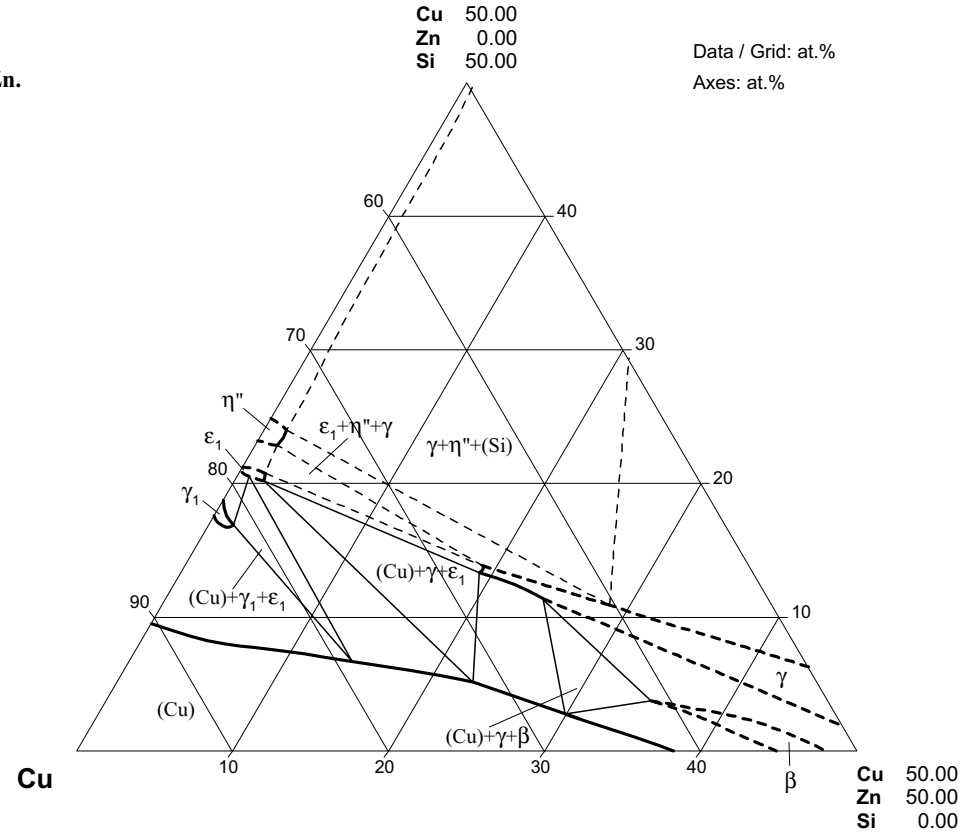

Fig. 7: Cu-Si-Zn. Partial isothermal section at 482°C

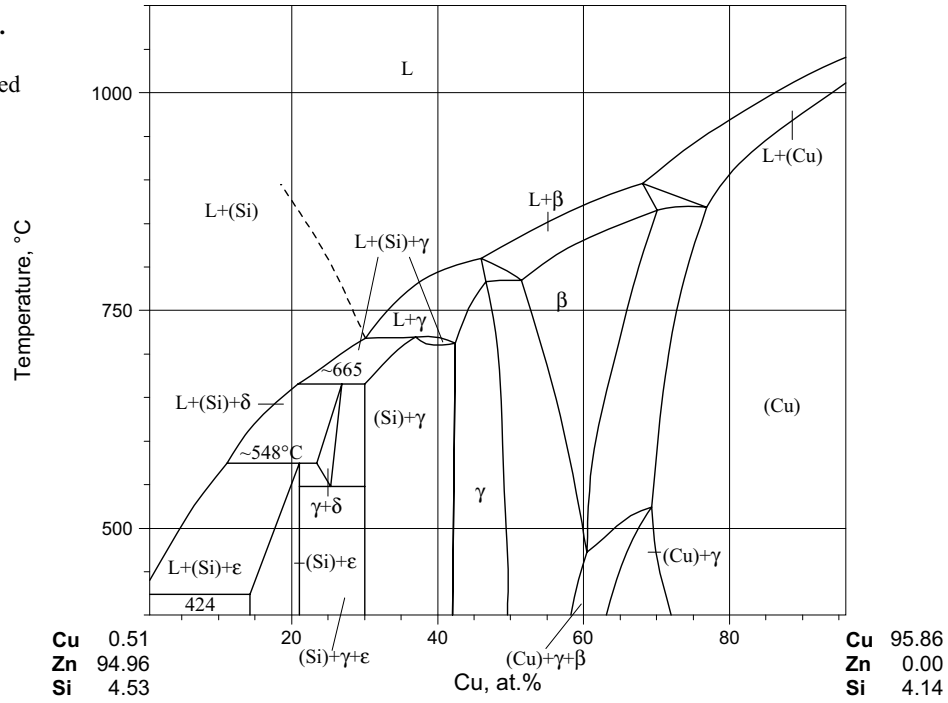

Fig. 8: Cu-Si-Zn. Vertical section at 2 mass% Si, plotted in at.%