

Cu-Fe-Si (Copper-Iron-Silicon)

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The early experimental results of this ternary system were reviewed by [1979Cha] and [1992Rag]. More recent publications on the experimental results of [1997Oht] (isothermal sections at 1300, 1200 and 1100 °C), [1999Hin] (isothermal sections at 1450, 1350 and 1250 °C) and [2002Wan] (isothermal sections at 1450, 1300 and 900 °C) were reviewed in an update by [2002Rag]. A thermodynamic assessment applicable to Si-lean alloys was done by [2003Mie] and reviewed by [2009Rag]. An updated evaluation of the system was carried out by [2005Leb]. Very recently, [2009Zha] carried out a detailed thermodynamic assessment of the system, including new experimental results in the optimization. This work will be reviewed briefly in this update.

Binary Systems

There are no intermediate phases in the Cu-Fe system. A metastable liquid miscibility gap is known in this system. The Cu-Si phase diagram [Massalski2, 2009Ria] has the following intermediate phases: Cu₃Si (rhombohedral, denoted η , other ordered low-temperature forms η' and η''), Cu₁₅Si₄ (impurity stabilized; cubic, denoted ε), Cu₄Si (hexagonal, denoted δ), Cu₅Si (β Mn-type cubic, denoted γ), β (14-17 at.% Si, stable between 852-785 °C; bcc), and Cu₇Si (cph, denoted κ). In the Fe-Si system [Massalski2],

the Fe-based face-centered cubic phase γ is enclosed by a loop. The bcc phase α exists in the ordered forms: α_2 (B2, CsCl-type cubic) and α_1 (D0₃, BiF₃-type cubic). The other intermediate phases are: Fe₂Si (stable between 1212 and 1040 °C; hexagonal), Fe₅Si₃ (D8₈, Mn₅Si₃-type hexagonal), FeSi (B20-type cubic), β FeSi₂ (tetragonal) and α FeSi₂ (orthorhombic). Computed diagrams of the above binary systems were given by [2009Zha].

Ternary Phase Equilibria

With starting metals of 99.8% Cu, 99.6% Fe and 99.9% Si, [2009Zha] arc-melted under Ar atm 17 ternary alloys. The alloys were annealed at 750 °C for 19 days and quenched in water. The phase equilibria were studied with scanning electron microscope, energy dispersive x-ray analysis, electron probe microanalysis and x-ray powder diffraction. Differential thermal analysis (DTA) was carried out between 1450 and 750 °C at a heating/cooling rate of 5 °C per min. The measured compositions of the identified phases and the thermal arrests in the DTA tests were listed. The isothermal section at 750 °C constructed by [2009Zha] is shown in Fig. 1. The compound FeSi forms tie-lines with all the Cu-Si binary compounds. No third-component solubility was observed. No ternary phases were found.

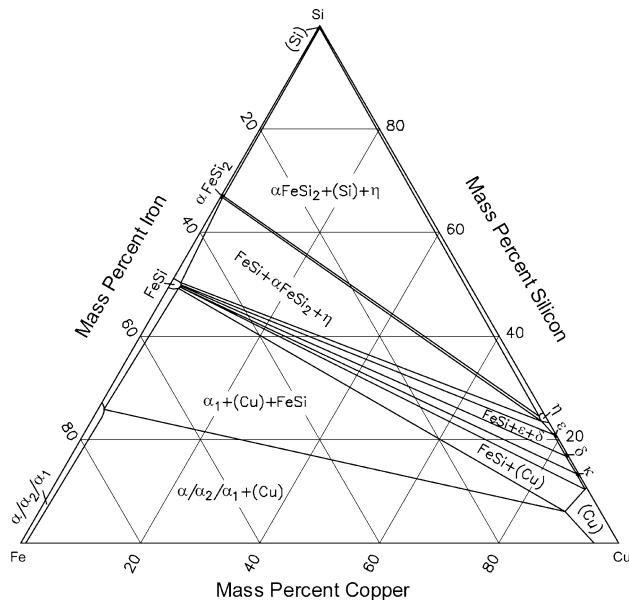


Fig. 1 Cu-Fe-Si experimental isothermal section at 750 °C [2009Zha]. Narrow two-phase regions are omitted

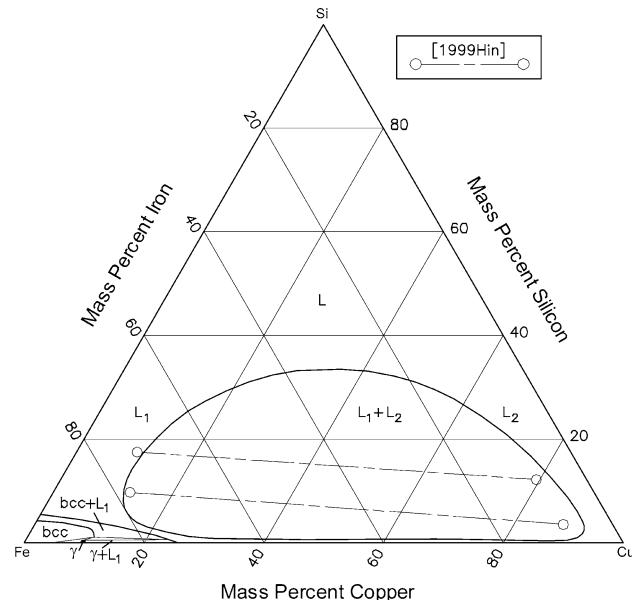


Fig. 2 Cu-Fe-Si computed isothermal section at 1450 °C [2009Zha]

Section II: Phase Diagram Evaluations

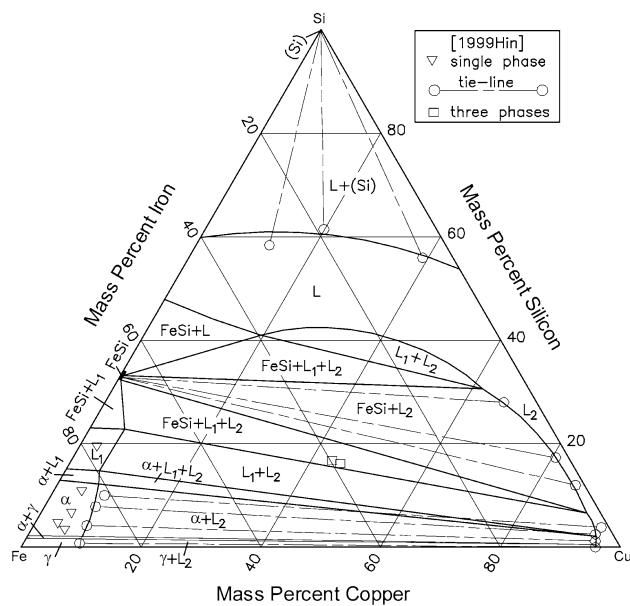


Fig. 3 Cu-Fe-Si computed isothermal section at 1250 °C
[2009Zha]

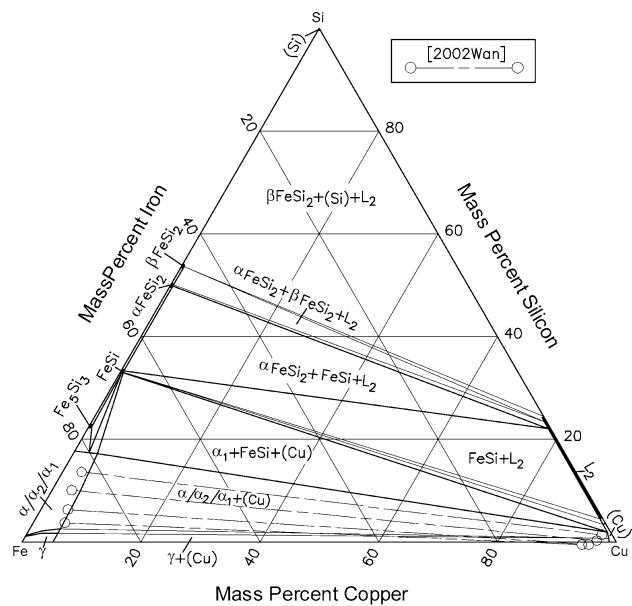


Fig. 4 Cu-Fe-Si computed isothermal section at 1000 °C
[2009Zha]

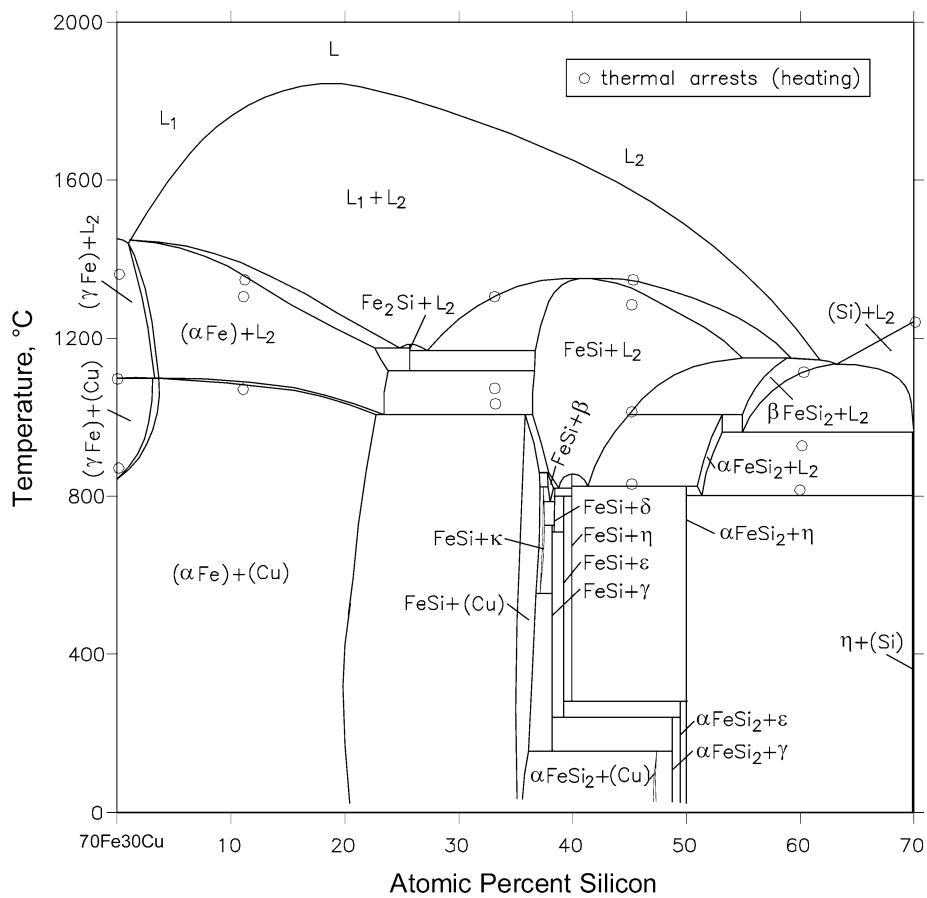


Fig. 5 Cu-Fe-Si computed vertical section at 30 at.% Cu [2009Zha]. For clarity, three-phase regions are not marked

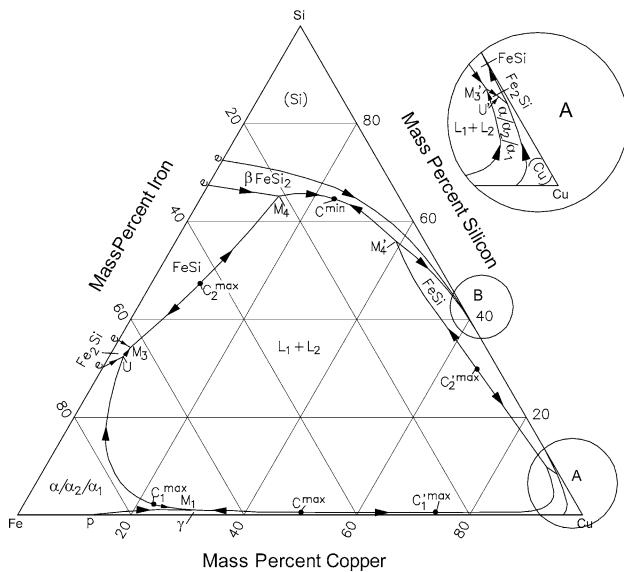


Fig. 6 Cu-Fe-Si computed liquidus projection [2009Zha]. For details in **B**, see [2009Zha]

In their thermodynamic modeling, [2009Zha] described the liquid, fcc and bcc phases as substitutional solutions. All binary phases were described as compounds with zero solubility for the third component. A single function was used to describe both bcc and *B*2 phases, by adding an ordering energy term to the expression for the disordered state. The optimized ternary interaction parameters for the liquid, fcc and bcc phases were listed. The parameters are fewer in number in the present optimization, as compared to those derived by [2003Mie] and [2002Wan].

The computed isothermal section at 750 °C (not shown here) agrees with the experimental section in Fig. 1, except for the homogeneity range of (Cu). The other computed isothermal sections at 1450, 1250 and 1000 °C are compared in Fig. 2-4 with the experimental data of [1999Hin] and [2002Wan]. The agreement is satisfactory. The metastable liquid miscibility gap in the Fe-Cu system becomes stable even with very small additions of Si. Two vertical sections at 30 and 70 at.% Cu were computed by [2009Zha] and were compared with the DTA arrests. Figure 5 shows the vertical section at 30 at.% Cu. Even though the DTA data were not used in the optimization, the agreement is seen

to be good. The liquidus projection computed by [2009Zha] is shown in Fig. 6. The details near the Cu corner are shown enlarged. The reaction labeled M_2 by [2009Zha] is redesignated as U in Fig. 6. In the region marked **B**, a number of invariant reactions depicting the regions of primary crystallization of the Cu-Si compounds β , δ and η occur at extremely small concentrations of Fe. For details, see [2009Zha]. A reaction sequence corresponding to the computed liquid-solid reactions was given by [2009Zha].

References

- 1979Cha:** Y.A. Chang, Y.P. Neumann, A. Mikula, and D. Goldberg, Copper-Iron-Silicon, *Phase Diagrams and Thermodynamic Properties of Ternary Copper-Metal Systems*, International Copper Research Association, National Standard Reference Data System, National Bureau of Standards, Washington, DC, 1979, p 492-497
- 1992Rag:** V. Raghavan, The Cu-Fe-Si (Copper-Iron-Silicon) System, *Phase Diagrams of Ternary Iron Alloys, Part 6B*, Indian Institute of Metals, Calcutta, 1992, p 759-767
- 1997Oht:** H. Ohtani, H. Suda, and K. Ishida, Solid/Liquid Equilibria in Fe-Cu Based Ternary Systems, *ISIJ Int.*, 1997, **37**(3), p 207-216
- 1999Hin:** M. Hino, T. Nagasaka, and T. Washizu, Phase Diagram of Fe-Cu-Si Ternary System Above 1523 K, *J. Phase Equilib.*, 1999, **20**(3), p 179-186
- 2002Rag:** V. Raghavan, Cu-Fe-Si (Copper-Iron-Silicon), *J. Phase Equilib.*, 2002, **23**(3), p 267-270
- 2002Wan:** C.P. Wang, X.J. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, Phase Equilibria in Fe-Cu-X (X: Co, Cr, Si, V) Ternary Systems, *J. Phase Equilib.*, 2002, **23**(3), p 236-245
- 2003Mie:** J. Miettinen, Thermodynamic Description of the Cu-Fe-Si System at the Cu-Fe Side, *CALPHAD*, 2003, **27**, p 389-394
- 2005Leb:** N. Lebrun, P. Perrot, and M. Harmelin, Copper-Iron-Silicon, *Landolt-Bornstein Series IV*, Vol 11D4, Springer, Berlin, p 1-26
- 2009Rag:** V. Raghavan, Cu-Fe-Si (Copper-Iron-Silicon), *J. Phase Equilif. Diffus.*, 2009, **30**(1), p 96-97
- 2009Ria:** P. Riani, K. Sufryd, and G. Cacciamani, About the Al-Cu-Si Isothermal Section at 500 °C and the Stability of the ϵ -Cu₁₅Si₄ Phase, *Intermetallics*, 2009, **17**, p 154-164
- 2009Zha:** J. Zhao, L. Zhang, Y. Du, H. Xu, J. Liang, and B. Huang, Experimental Investigation and Thermodynamic Assessment of the Cu-Fe-Si System, *Metall. Mater. Trans. A*, 2009, **40**, p 1811-1825