Al-Cu-Si (Aluminum-Copper-Silicon)

V. Raghavan

The early experimental data on this system were compiled by [1995Vil], which included a liquidus projection and a number of isothermal and vertical sections. In a recent review of this system, [2005Luk] presented only a tentative isothermal section at 400 °C, ruling that much of the data in early literature lacked reliability. [2005Pan] assessed the thermodynamic data on Al-rich liquid alloys, computed a liquidus projection and vertical sections depicting the liquidsolid equilibria and compared the results with the experimental data. This work was reviewed briefly in the update by [2007Rag]. The Cu-rich region of the system was modeled by [2007Mie]. Very recently, [2009Ria] determined an isothermal section at 500 °C for the whole composition range, with special attention to Cu-rich alloys. Also, [2009He] presented a thermodynamic assessment of the system, supplemented by new experimental results.

Binary Systems

The Al-Cu phase diagram [2004Ria, 2009Ria] depicts the following intermediate phases: CuAl₂ (C16-type tetragonal, denoted θ), CuAl(HT) (η_1 , orthorhombic) CuAl(LT) (η_2 , monoclinic), Cu₅Al₄(HT) (ζ_1 , orthorhombic, space group *Fmm2*), Cu₅Al₄(LT) (ζ_2 , orthorhombic, space group *Imm2*), ε_1 (HT) (cubic?), ε_2 (LT) (*B*8₁, NiAs-type hexagonal), Cu₃Al₂ (rhombohedral), Cu₉Al₄(HT) (γ_0 , *D*8₂, Cu₅Zn₈-type cubic), Cu₉Al₄(LT) (γ_1 , *D*8₃,Cu₉Al₄-type cubic), and Cu₃Al (β , bcc). The Al-Si system is of the simple eutectic type with the eutectic at 577 °C and 12.2 at.% Si. The Cu-Si phase diagram [2009Ria] has the following intermediate phases: Cu₃Si (rhombohedral, denoted η , other ordered lowtemperature 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).

Ternary Isothermal Section at 500 °C

With starting metals of 99.999% Al, 99.999% Cu, and 99.99% Si, [2009Ria] arc-melted 54 Cu-rich ternary alloys and 9 binary Cu-Si alloys. The alloys were annealed at 500 °C for \sim 1 month and quenched in water. The phase equilibria were studied with optical and scanning electron metallography, x-ray powder diffraction and energy dispersive x-ray spectroscopy. The composition, crystal structure and lattice parameters of the observed phases were listed for all samples. The isothermal section at 500 °C constructed by [2009Ria] is shown in Fig. 1 and 2. The Al-Cu γ_1 phase dissolves 11.5 at.% Si and extends in a direction of constant valence-electron/atom ratio of 1.61. Cu₃Si dissolves appreciable Al. The (Cu) solid solution extends up to 20 at.% Al and 10 at.% Si. The Cu-Si k phase (cph) is stabilized by Al and is present in the ternary region. It may be noted that in the Cu-Si binary system, k decomposes eutectoidally at



Fig. 1 Al-Cu-Si Isothermal Section at 500 °C [2009Ria]



Fig. 2 Al-Cu-Si enlarged Cu-rich region of Fig. 1 [2009Ria]

Section II: Phase Diagram Evaluations

552 °C. A ternary compound labeled τ by [2009Ria] is present at the composition 1.5Al-21Si (at.%). It has the same cubic structure as the binary Cu₁₅Si₄ (ϵ), which is not stable at least in the temperature range of 500-780 °C. [2009Ria] showed that Cu₁₅Si₄ (ϵ) is present in binary samples made from Cu of 99.98% purity but not in samples made from Cu of 99.999% purity.

Thermodynamic Description

[2007Mie] employed literature assessments of the binary systems and optimized the interaction parameters of the ternary system. This description is applicable up to 18 mass% Al and 8 mass% Si. The Al-Cu intermediate phase γ_1 was modeled as a solution phase by [2009Mie], even though the compound formalism is expected to be used here.

More recently, [2009He] carried out a thermodynamic modeling of this system, using new experimental results in the optimization. With starting metals of 99.9% Al, 99.99% Cu, and 99.9% Si, [2009He] arc-melted 16 ternary alloys. The samples were annealed at 600 or 500 °C for 21 d and quenched in water. The phase equilibria were studied with optical and scanning electron microscopy, energy dispersive x-ray spectroscopy, electron probe microanalysis, x-ray powder diffraction and differential thermal analysis at a heating/cooling rate of 5 °C per min. The composition, crystal structure and lattice parameters of the observed



Fig. 3 Al-Cu-Si computed vertical section at 4 mass% Cu [2009He]

phases were listed for all samples. In the thermodynamic modeling, liquid, fcc, bcc, and cph phases were treated as substitutional solutions. The binary compounds were described by appropriate sublattice models. The ternary solubility of Al in γ and η phases of the Cu-Si system was neglected by [2009He].

The computed results of [2009He] included a liquidus projection, three isothermal sections at 600, 500, and 400 °C and a number of vertical sections. The occurrence of the κ phase in the ternary region below its binary stability range was seen in the results, but the homogeneity range of (Cu) and the ternary solubility ranges of the binary phases could not be reproduced well. In particular, the ternary extension of the CuAl- γ_1 phase was computed to be at constant Cu content by [2009He], whereas their own results indicated an increase in its Cu content, as it extends into the ternary region. Further more, the influence of impurities in stabilizing $Cu_{15}Si_4(\varepsilon)$ as a binary phase was not considered. Two computed vertical sections at 1 mass% Si and 4 mass% Cu, respectively, are in the Al-rich region. The section at 1 mass% Si was earlier computed also by [2005Pan] (reviewed in [2007Rag]) and was shown to be in good agreement with experimental results. The vertical section at 4 mass% Cu computed by [2009He] is shown in Fig. 3. It shows good agreement with experimental data of [1953Phi].

References

- 1953Phi: H.W.L. Phillips, The Constitution of Aluminum-Copper-Silicon Alloys, J. Inst. Metals (London), 1953-1954, 82, p 9-15
- **1995Vil:** P. Villars, A. Prince, and H. Okamoto, Al-Cu-Si, *Handbook of Ternary Alloy Phase Diagrams*, ASM International, Materials Park, OH, 1995, **3**, p 3331-3351
- 2004Ria: P. Riani, L. Arrighi, R. Marazza, D. Mazzone, G. Zanicchi, and R. Ferro, Ternary Rare-Earth Aluminum Systems with Copper: A Review and a Contribution to their Assessment, J. Phase Equilib. Diffus., 2004, 25(1), p 22-52
- 2005Luk: H.L. Lukas and N. Lebrun, Aluminum-Copper-Silicon, Landolt-Bornstein New Series IV, G. Effenberg and S. Ilyenko, Ed., 2005, Vol 11A2, p 135-147
- 2005Pan: X.M. Pan, C. Lin, J.E. Morral, and H.D. Brody, An Assessment of Thermodynamic Data for the Liquid Phase in the Al-Rich Corner of the Al-Cu-Si System and Its Application to the Solidification of a 319 Alloy, *J. Phase Equilib. Diffus.*, 2005, 26(3), p 225-233
- 2007Mie: J. Miettinen, Thermodynamic Description of the Cu-Al-Si System in the Cu-Rich Corner, *CALPHAD*, 2007, 31(4), p 449-456
- 2007Rag: V. Raghavan, Aluminum-Copper-Silicon, J. Phase Equilib. Diffus., 2007, 28(2), p 180-182
- **2009He:** C.Y. He, Y. Du, H.L. Chen, and H. Xu, Experimental Investigation and Thermodynamic Modeling of the Al-Cu-Si System, *CALPHAD*, 2009, **33**(2), p 200-210
- **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