Copper – Antimony – Zinc

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Introduction

Phase equilibria data on the Cu-Sb-Zn system are very sparse. Mainly physical and mechanical properties have been investigated by [1906Gui, 1912Car]. They suggested a solubility of Sb in α and β brasses of about 0.5 at.%. This solubility was later investigated by [1946McL] by thermal analysis, metallographic observations and mechanical properties measurements on the alloys. Samples have been prepared from electrolytic Cu, Zn of comparably high purity and Sb containing Pb, Fe and S as impurities. The charges, melted under a glass cover were water quenched or slowly cooled from 450 to 200°C in 6 h. The solubility of Sb in α brass ($Cu_{0.7}Zn_{0.3}$) was found to decrease from 0.6 at.% at 550°C to 0.01 at.% at 200°C. The solubility of Sb in (Cu) at 200°C is thus reduced from 2 at.% to 0.01 at.% when the Zn content of the alloy goes from 0 to 30 at.%. This agrees with the results of [1906Gui, 1912Car] but disagrees with the statement of [1956Gla] which reports without giving any experimental details a solubility of 1 at.% Sb in α brass at 400°C, which may increases up to 2 at.% at 550°C.
[1936Kee] gave some indications about the phase equilibria at room temperature. He found seven pseudobinary sections for the triangulation of the ternary system by the clear-cross method: CuZn-Cu_3Sb, CuZn-Cu_2Sb, CuZn-Sb, Cu_2Zn_3-Sb, Cu_2Zn_3-ZnSb, Cu_2Sb_3-Zn_4Sb_3 and Cu_2Zn_3-Zn_3Sb_2. Unfortunately, only metallographic methods have been applied and the binary phases described in this work are no more in agreement with the widely accepted binary phase diagrams. The binary compound Cu_2Zn does not exists and the Zn_3Sb_2 phase does not crystallize at room temperature. The results have thus to be considered as doubtful and are not reported here.
The thermodynamic properties of the liquid Cu-Sb-Zn alloys were measured with an electromotive force method at four cross sections characterized by a Cu:Sb ratio of 2, 1, 0.5 and 0.33 [1995Pen] and integral quantities were derived by Gibbs-Duhem integration. The set of data obtained have then been compared with the result of calculation using four different models [1996Pen, 1996Qia].

Binary Systems

The Cu-Sb and Cu-Zn and Sb-Zn binary systems are respectively accepted from [2006Rok], [2006Leb] and [Mas2]. These systems are thermodynamically well known. The most complete Calphad assessments are from [2000Liu] for the Cu-Sb and Sb-Zn systems, and [2003Dav] for the Cu-Zn system.

Solid Phases

Unary and binary phases are presented in Table 1. No ternary compound is known.

Temperature – Composition Sections

Figure 1 presents the partial vertical section at 30 at.% Zn as suggested by [1946McL]. The liquidus was determined by thermal analysis and the solids mainly by micrography. The results illustrate the low solubility of Sb in the Cu-Zn phases. For a final judgment on the correctness of the figure, further experiments including annealing and X-ray analysis are necessary.

Thermodynamics

The partial Gibbs energy of mixing of zinc in the ternary liquid alloy has been determined at 600 and 700°C by means of a galvanic cell: Zn(l)/LiCl – KCl + 0.5 % $ZnCl_2$(l)/alloy(l). The integral Gibbs energy of mixture and the integral enthalpy of mixture in the liquid phase at 700°C are respectively shown in Figs. 2 and 3. The diagrams show clearly that the chemical short range order observed in Sb-Zn liquid alloys is

suppressed by addition of copper. Since the thermodynamic properties of the three binary systems are well known, four different models were used to calculate the Gibbs energy of mixing and the enthalpy of mixing of the ternary alloys from the three binary systems [1996Pen]. The asymmetric models of Toop and Hillert with Cu as the asymmetric component gave an almost perfect agreement with experimental results. [1996Qia] pointed out the importance of the choice of the asymmetric component in asymmetric models of solutions.

Notes on Materials Properties and Applications

Microstructure, microhardness, density, line broadening, electrical and thermoelectric properties have been investigated by [1962Yur]. According to his conclusion, the alloys between: $CuZn_3$?, Cu_5Zn_8, CuZn and Zn_3Sb_2 (actually $Zn_{58}Sb_{42}$ at low temperatures) are mechanical mixtures of pure binary phases. Zn_3Sb_2 (h_1 and h_2) are high temperature modifications of $Zn_{58}Sb_{42}$ and cannot remain stable at low temperatures after the slow cooling applied by [1962Yur]. The electrical and thermoelectric properties of the alloys were non linear functions of composition. A short review of the published data is given in [1979Dri].

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, (Cu) < 1084.62	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 361.46	Dissolves up to 5.8 at.% Sb at 645°C and 38.27 at.% Zn at 454°C [Mas2]
(Sb) < 630.755	*hR*6 *R*$\bar{3}$*m* αAs	*a* = 450.67 α = 57°11′	[Mas2]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	*a* = 266.50 *c* = 494.70	Dissolves up to 2.83 at.% Cu at 425°C [Mas2]
β, CuZn 902 - 454	*cI*2 *Im*$\bar{3}$*m* W	*a* = 295.39	36.1 to 55.8 at.% Zn [Mas2] at 47.5 at.% Zn [V-C2]
β', CuZn < 468	*cP*2 *Pm*$\bar{3}$*m* CsCl	*a* = 295.9	44.8 to 48.2 at.% Zn [Mas2] at 49.5 at.% Zn [V-C2]
γ, Cu_5Zn_8 < 834	*cI*52 *I*$\bar{4}$3*m* Cu_5Zn_8	*a* = 887.8	57 to 70 at.% Zn [Mas2] lattice parameter from [V-C2]
δ, $CuZn_3$ 700 - 560	*hP*3 *P*$\bar{6}$ $CuZn_3$	*a* = 427.5 *c* = 259.0	72.45 to 76 at.% Zn [Mas2] lattice parameters from [V-C2]
ε, $CuZn_4$ < 598	*hP*2 $P6_3/mmc$ Mg	*a* = 274.18 *c* = 429.39	78 to 88 at.% Zn [Mas2] lattice parameters from [V-C2]
$CuSb_5$ 488 - 400	*hP*2 $P6_3/mmc$ Mg	-	15.5 to 16 at.% Sb [Mas2]
$CuSb_4$ < 462	*hP** $P6_3/mmc$ Mg	-	18.5 to 20 at.% Sb [Mas2]
$Cu_3Sb(h_3)$ 683 - 440	*oF*16 *Fm*$\bar{3}$*m* BiF_3	*a* = 601	19.4 to 30.8 at.% Sb [Mas2] From high temperature X-ray diffraction [1994Sub]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$Cu_3Sb(h_2)$ 445 - 360	*oP*8 *Pmmn* βCu_3Ti	*a* = 550.4 *b* = 435.3 *c* = 476.8	22.8 to 25.3 at.% Sb at 24 at.% Sb, annealed 8 d at 425°C [1994Sub]
$Cu_3Sb(h_1)$ 390 - 260	*hP*26 $P\bar{3}$ $Cu_{10}Sb_3$	*a* = 992.0 *c* = 432.0	21.3 to 21.6 at.% Sb at 24 at.% Sb, annealed 8 d at 425°C [1994Sub]
Cu_2Sb < 586	*tP*6 *P*4/*nmm* Cu_2Sb	*a* = 403.7 *c* = 615.2	32.0 to 33.3 at.% Sb [Mas2] at 33.3 at.% Sb [1994Sub]
ZnSb < 546	*oP*16 *Pbca* CdSb	-	50 to 53 at.% Zn [Mas2]
$Zn_{11}Sb_9$ 527 - 493	-	-	54 to 56 at.% Zn [Mas2]
$Zn_4Sb_3(h)$ 564 - 492	-	-	57 to 58.5 at.% Zn [Mas2]
$Zn_4Sb_3(r)$ < 494	-	-	57 to 58 at.% Zn [Mas2]
$Zn_3Sb_2(h_2)$ 566 - 440	*oI**	*a* = 1516 *b* = 2442 *c* = 721	60 to 61 at.% Zn [Mas2]
$Zn_3Sb_2(h_1)$ 455 - 409	*oP*30 *Pmmn* ?	*a* = 803.2 *b* = 732.2 *c* = 1134	60 to 61 at.% Zn [Mas2]

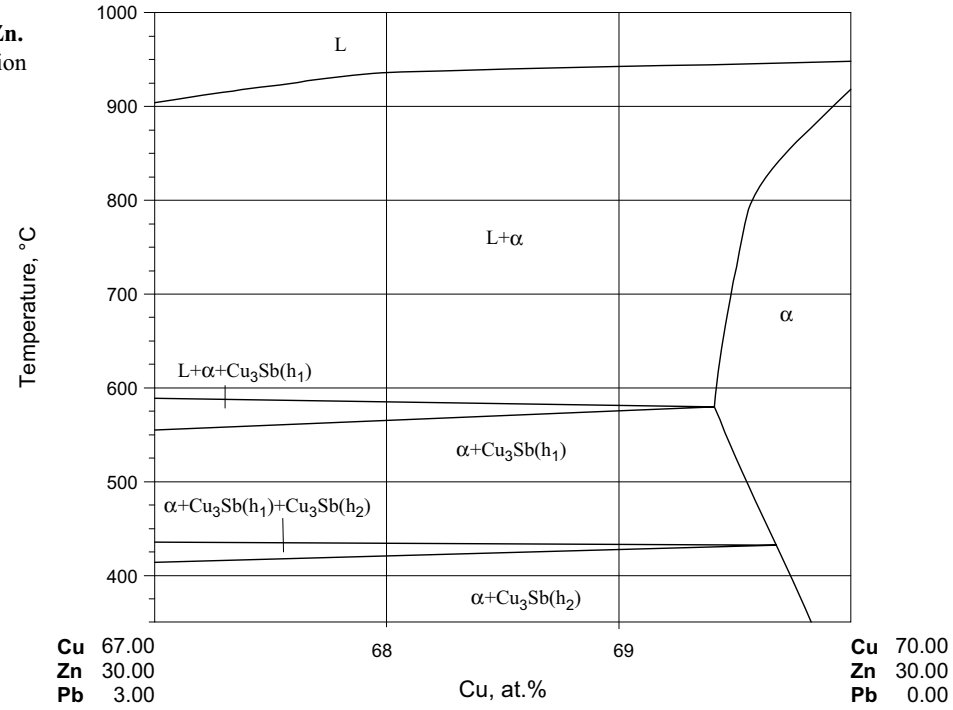

Fig. 1: Cu-Sb-Zn. Partial vertical section at 30 at.% Zn

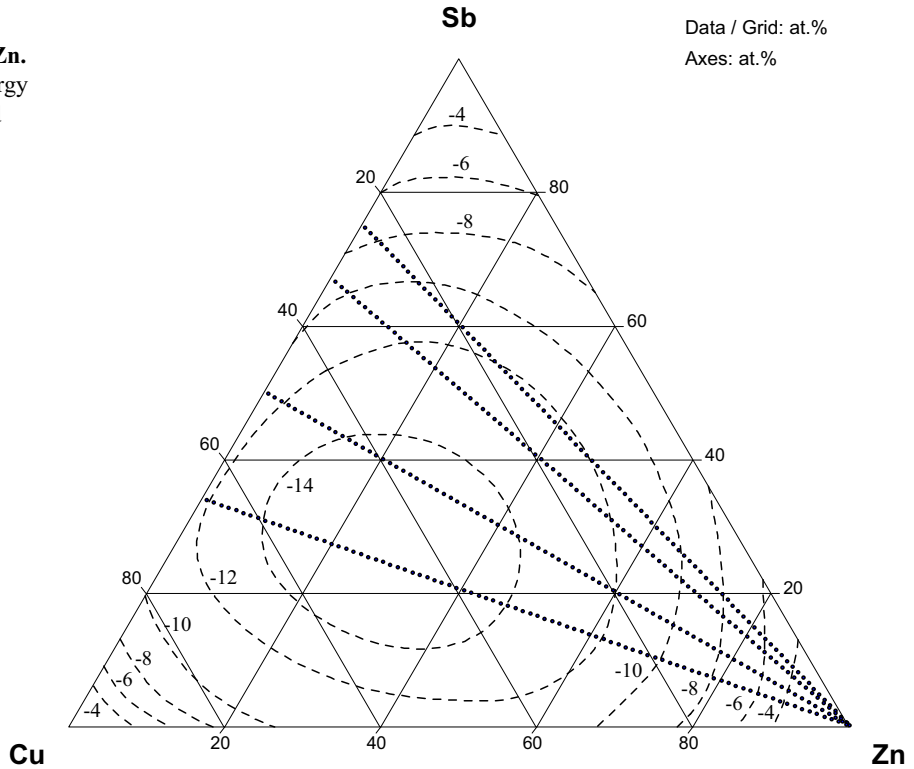

Fig. 2: Cu-Sb-Zn. Integral Gibbs energy of mixing in liquid alloys at 700°C, in $kJ \cdot mol^{-1}$

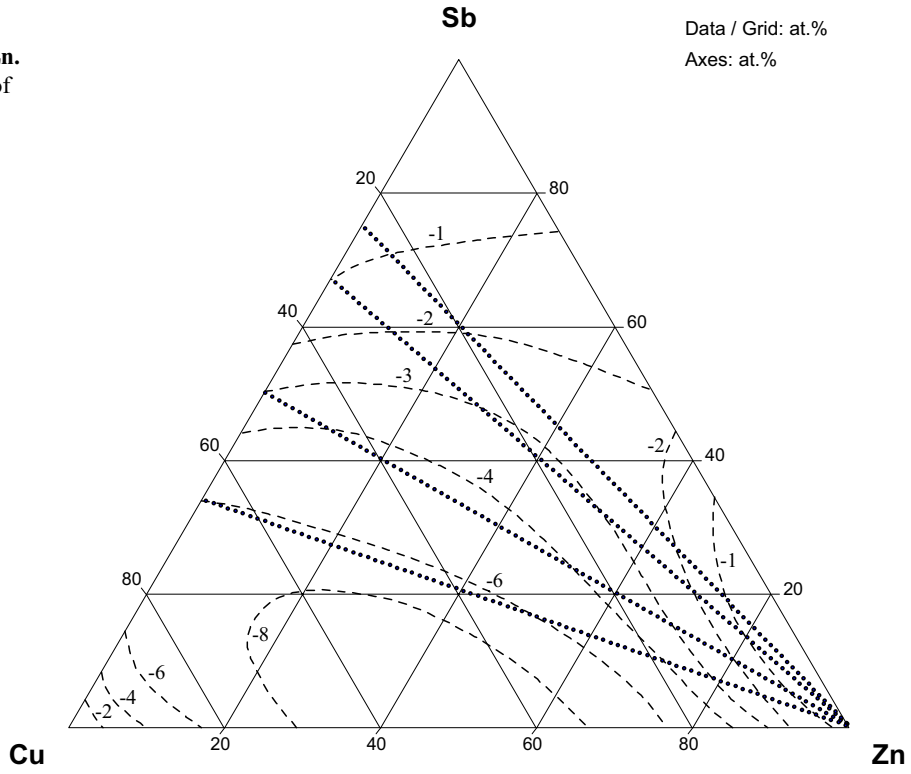

Fig. 3: Cu-Sb-Zn. Integral enthalpy of mixing in liquid alloys at 700°C, in $kJ \cdot mol^{-1}$