Silver – Copper – Zinc

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Introduction

After early investigations by Ueno [1929Uen], Keinert [1932Kei] and Weigert [1954Wei], Gebhardt *et al.* [1962Geb] reexamined the phase relations in the ternary system thoroughly and published a set of very consistent diagrams on the constitution of the system Ag-Cu-Zn. Investigations were carried out by means of differential thermal analysis (DTA) and metallographic and dilatometric techniques. In order to prepare 130 different alloys 99.97% Ag, 99.99% Zn and electrolytic copper were melted together under a suitable slag or in an atmosphere of Ar inert gas. Heat treatments were carried out in sealed evacuated glass tubes at 600, 500 and 350°C with subsequent water quenching. Few alloys were annealed also at 550 or 400°C. From the results the following diagrams were drawn: a liquidus projection, isotherms at 600, 500 and 350°C, isopleths at 20, 40 and 60 mass% Ag (12.84-13.16 at.% Ag, 28.20-28.78 at.% Ag, or 46.92-47.62 at.% Ag, respectively), 40 and 60 mass% Cu (53.08-40.68 at.% Cu or 71.80-60.68 at.% Cu, respectively) and 20 mass% Zn (29.20-19.55 at.% Zn) and a projection of the three- and four-phase equilibria containing liquid onto the concentration triangle.
Several reviews of the Ag-Cu-Zn phase diagram were published [1949Jae, 1967McD, 1969Gue, 1973Sis, 1977Cha, 1978Cha, 1979Dri], except two early ones [1949Jae, 1969Gue] mainly based on [1962Geb].
The order-disorder transformation $\beta \rightleftharpoons \beta'$ and the transformation of quenched metastable β to ζ were studied in detail by several authors [1967Nak, 1967Yon, 1971Mur1, 1971Mur2, 1980Mat, 1982Gra, 1983Mur, 1984Mur, 1985Nak, 1987Mat].
Moeller [1943Moe] measured lattice parameters of the hexagonal close packed ε solid solution phase at different compositions and confirmed the continuous range of solid solutions between the Ag-Zn and Cu-Zn ε phases.
[1997Roe] measured diffusion paths between (Ag) and (Cu) solid solutions, one of them containing up to 25 at.% Zn, the other one without Zn. They determined the compositions of coexisting (Ag) and (Cu) phases after long time (700-850 h) annealing at 550, 650, 670 and 700°C.
The Zn vapor pressure of Ag-Cu-Zn alloys was measured by [1965Arg] at 727°C and by [1990Sir] at 1000°C. By means of a high temperature isoperibolic calorimeter [2002Wit] measured partial enthalpies of mixing of the three components in liquid Ag-Cu-Zn alloys at 795 and 840°C and calculated integral enthalpies of mixing from the results.

Binary Systems

The binary phase diagrams are accepted: Ag-Cu from the MSIT evaluation [2002Rom], Ag-Zn from [Mas2] and Cu-Zn from [1994Mio]. Additional information on metastable Ag-Cu alloys was reviewed by Giessen [1980Gie].
Thermodynamic datasets were assessed for all three binary systems: Ag-Cu by [1986Hay, 1988Jon], Ag-Zn by [1998Gom, 1999Oht], Cu-Zn by [1993Kow]. [1988Jon] seems to contain typing errors for the unary Ag and Cu terms of the liquid description. If, however, the reported excess terms are used and the unary terms of all phases are replaced by the newer ones of [1991Din], the resulting calculated phase diagram reproduces very well the accepted one. [1999Oht] contains a typing error: instead of the excess terms of the ζ phase those of the β phase are repeated, thus the description of ζ is incomplete.

Solid Phases

The solid phases are listed in Table 1. Continuous solid solutions designated β, γ and ε connect the corresponding isostructural binary Ag-Zn and Cu-Zn phases. The β phase undergoes an order-disorder transformation. In the vicinity of the binary Ag-Zn system this transformation is in a metastable range slightly below the temperature of formation of the stable ζ phase. This range can be easily accessed by

quenching. [1967Yon, 1971Mur1, 1971Mur2, 1973Mur, 1980Mat, 1982Gra, 1983Mur, 1984Mur, 1985Nak, 1987Mat] studied this transformation in detail. [1983Mur, 1984Mur] found additionally spinodal phase separation in the β phase, leading to a modulated microstructure coarsening with annealing time. The mutual solubilities of the (Ag) and (Cu) phases increase somewhat with increasing Zn content [1962Geb, 1997Roe]. The ζ phase dissolves about 1.7 at.% Cu [1980Mat]. The Ag solubility in the δ phase was estimated by [1962Geb] as 25 mass% (16.7 at.%). Ternary phases were not found in this system.

Invariant Equilibria

Two invariant four-phase reactions were identified by [1962Geb]. Their temperatures and phase compositions are shown in Table 2. The complete reaction scheme is adopted from [1962Geb] and shown in Fig. 1. The temperatures of the two binary invariant reactions p_7 and p_8 are changed to the values assessed by [1994Mio], 600 to 598°C and 424 to 425°C, respectively.

Liquidus Surface

The liquidus surface after Gebhardt *et al.* [1962Geb], transformed to at.%, is shown in Fig. 2.

Isothermal Sections

Three isothermal sections at 600, 500 and 350°C are shown in Figs. 3a, 3b, 3c [1962Geb], converted to at.%. The Zn corner of the 600°C isotherm drawn by [1962Geb] corresponds to a slightly higher temperature, it disagrees with the 600°C isotherm of the liquidus surface and the temperature of 598°C for the binary L+δ+ε three-phase equilibrium. Therefore Fig. 3a was changed slightly compared with [1962Geb]. On the 350°C isotherm, the β and β′ (ordered) regions were labeled incorrectly as β′ and β, respectively, in the original paper [1962Geb].

Temperature – Composition Sections

Two vertical sections at 20 mass% Ag (12.84-13.16 at.% Ag) and 20 mass% Zn (29.20-19.55 at.% Zn) are shown in Figs. 4a, 4b, converted to at.%.
Figure 5 shows the section at constant Zn content of 45 at.%. The order-disorder temperature of the β/β′ transformation and the spinodal of the β phase, determined by [1984Mur] are included in Fig. 5. Some of the lines are measured only partially and drawn incompletely in the diagram.

Thermodynamics

The vapor pressure of Zn in the (Ag) and (Cu) phases was measured by [1965Arg] at 727°C. Replacing Ag by Cu in (Ag) decreases the activity coefficient of Zn, but replacing Cu by Ag in (Cu) within the accuracy of the measurements does not change the activity coefficient of Zn. Two tie lines between (Ag) and (Cu) were constructed from the results: (Ag +10.7 at.% Cu +9.8 at.% Zn) to (Cu +5.6 at.% Ag +13.5 at.% Zn) and (Ag +10.7 at.% Cu +14.6 at.% Zn) to (Cu +6.2 at.% Ag +18.6 at.% Zn) (digitized from a graph).
Witusiewicz *et al*. [2002Wit] determined partial enthalpies of all three elements in liquid at 795 or 840°C along the two lines with Ag:Cu ratios 2:3 and 3:2.
An assessment of a thermodynamic dataset was referenced by [1997Roe] as “to be published”. However, no publication could be found until now. The calculated isothermal section at 670°C, shown by 1997Roe], deviates by several at.% from the experimental results of [1962Geb].

Notes on Materials Properties and Applications

Alloys near the eutectic composition E_1 are proposed as Cd free brazing alloys to connect TiAl based alloys with Cr-steel [2002Hui]. Ag with 3% Zn, 1.75% Cu and 1.25% Sn (mass%) after internal oxidation is proposed to replace the toxic standard Ag-CdO material for electric contacts [1993Dev].

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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
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	a = 408.62	pure element, 25°C [Mas2]
(Cu) < 1084.87	*cF*4 $Fm\bar{3}m$ Cu	a = 361.47 a = 369.74	pure element, 25°C [Mas2] $Cu_{65.44}Zn_{33.56}$ [P]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.49 c = 494.68	pure element, 25°C [Mas2]
β, (Ag,Cu)Zn (h)	*cI*2 $Im\bar{3}m$ W		
AgZn 710 - 258		a = 311.0	AgZn [V-C2]
CuZn 903 - 454		a = 299.67	CuZn, 871°C [P]
β′, (Ag,Cu)Zn (l) < 468	*cP*2 $Pm\bar{3}m$ CsCl	a = 315.58 a = 295.39	$Ag_{50.1}Zn_{49.9}$ quenched [P] $Cu_{52.34}Zn_{47.66}$ [P]
ζ, AgZn (l) < 274	*hP*9 $P\bar{3}$ AgZn(l)	a = 763.55 c = 282.00	$Ag_{50}Zn_{50}$ [P]
δ, $CuZn_3$ 700 - 560	*hP*3 $P\bar{6}$ $CuZn_3$	a = 427.5	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, $(Ag,Cu)_5Zn_8$	*cI*52		
Ag_5Zn_8	$I\bar{4}3m$	a = 934.07	[V-C2]
< 661	Cu_5Zn_8		
Cu_5Zn_8		a = 886.9	[V-C2]
< 834			
ε, $(Ag,Cu)Zn_4$	*hP*2	a = 276.0	$Ag_4Cu_{15}Zn_{81}$ [1943Moe]
	$P6_3/mmc$	c = 431.6	
	Mg		
		a = 277.7	$Ag_{10}Cu_{10}Zn_{80}$ [1943Moe]
		c = 434.5	
		a = 279.8	$Ag_{16}Cu_5Zn_{79}$ [1943Moe]
		c = 439.4	
ε (Ag-Zn)		a = 282.6	$Ag_{33}Zn_{67}$ [P]
< 631		c = 448.49	
		a = 281.16	$Ag_{12}Zn_{88}$ [P]
		c = 439.96	
$CuZn_4$		a = 273.83	$Cu_{21}Zn_{79}$ [P]
< 574		c = 429.37	
		a = 276.53	$Cu_{13}Zn_{87}$ [P]
		c = 429.78	

Table 2: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Ag	Cu	Zn
L ⇌ (Cu) + (Ag) + β	665	E_1	L	43.2	26.2	30.6
			(Cu)	5.5	66.0	28.5
			(Ag)	64.4	7.3	28.3
			β	37.4	29.2	33.4
L + γ ⇌ ε + δ	630	U_1	L	17.5	10.9	71.6
			γ	16.8	13.6	69.6
			ε	17.5	12.0	70.5
			δ	16.8	12.5	70.7

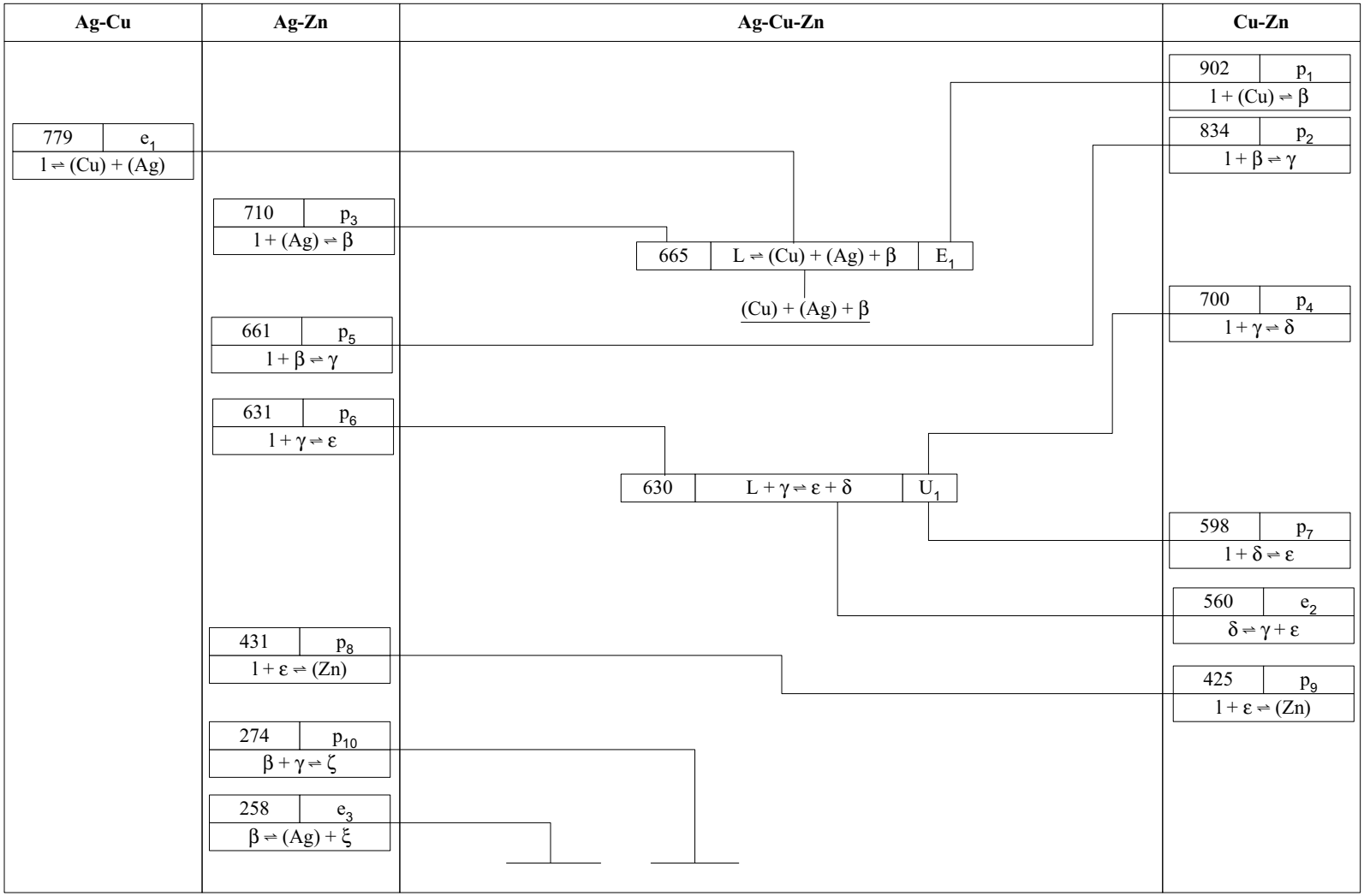

Fig. 1: Ag-Cu-Zn. Reaction scheme

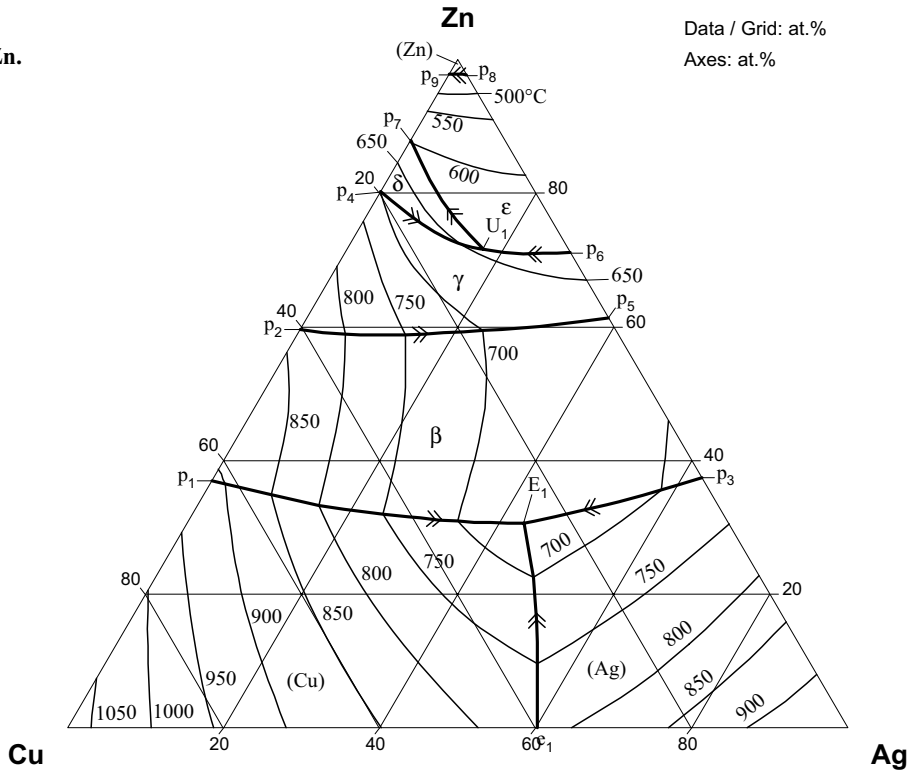

Fig. 2: Ag-Cu-Zn. Liquidus surface projection

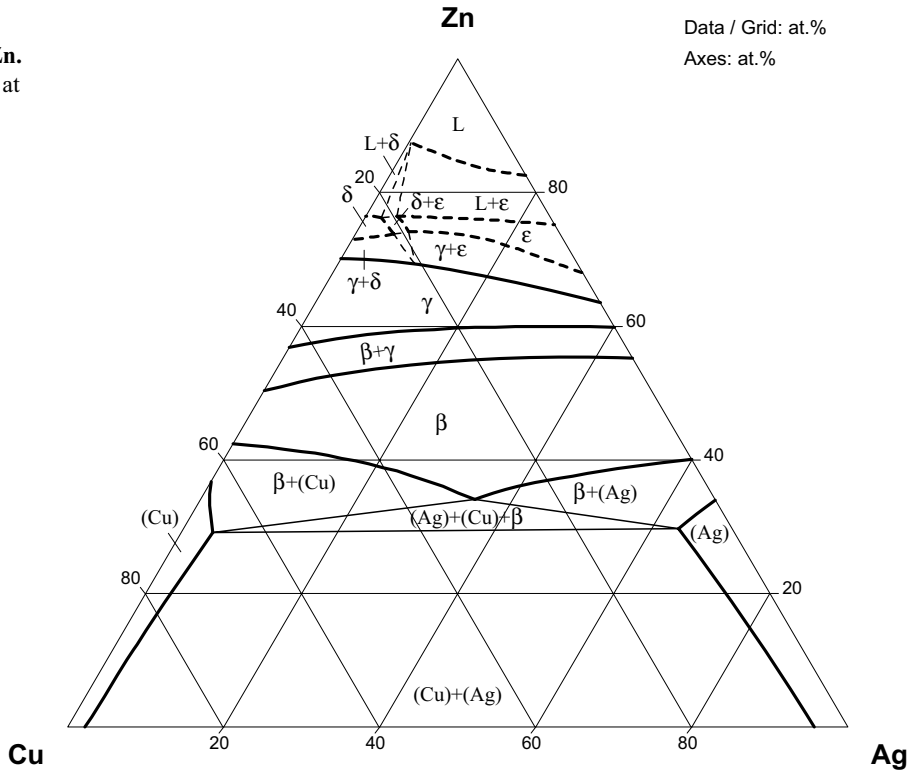

Fig. 3a: Ag-Cu-Zn. Isothermal section at 600°C

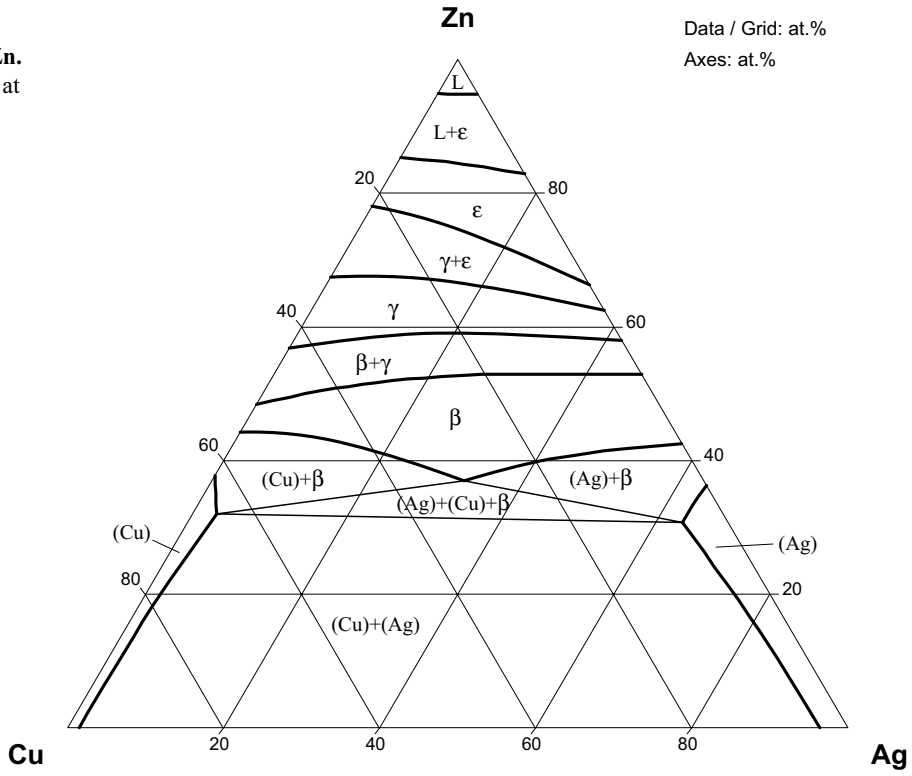

Fig. 3b: Ag-Cu-Zn. Isothermal section at 500°C

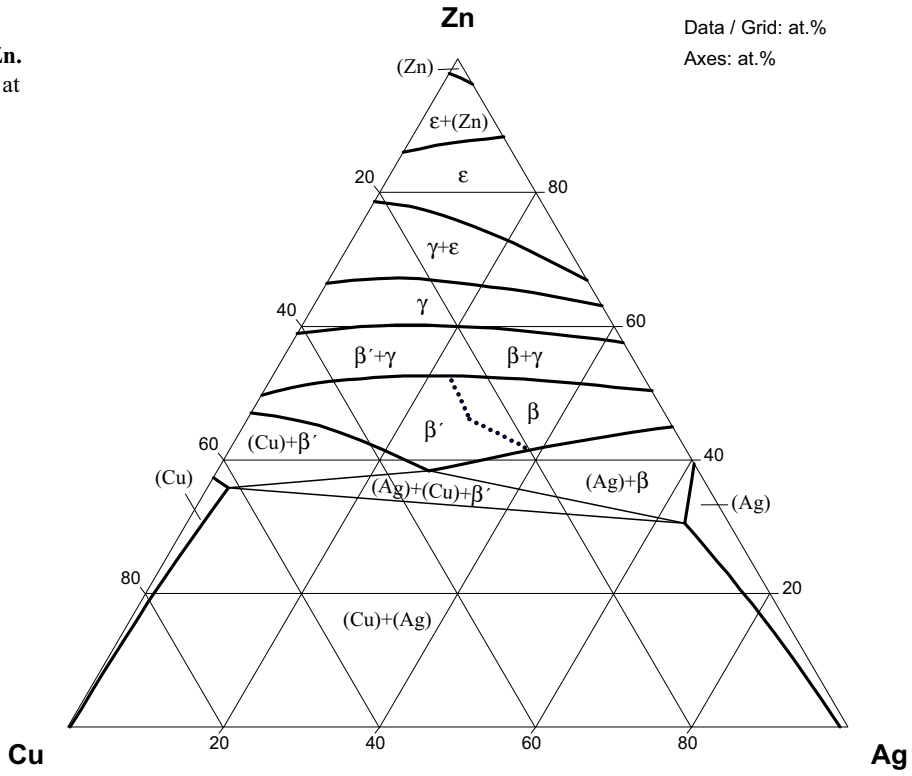

Fig. 3c: Ag-Cu-Zn. Isothermal section at 350°C

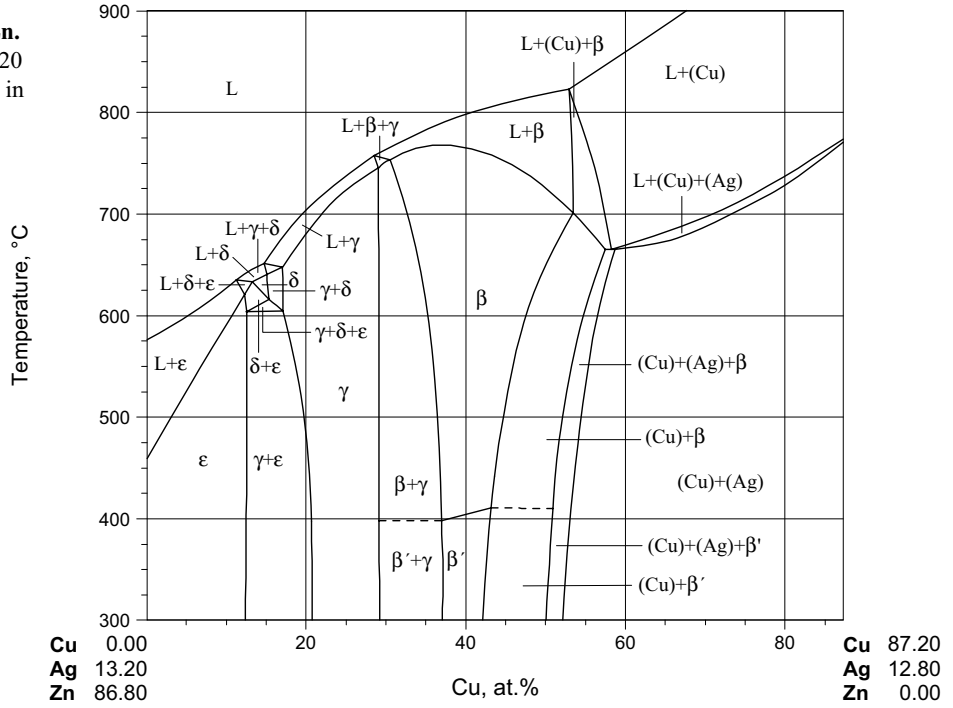

Fig. 4a: Ag-Cu-Zn. Vertical section at 20 mass% Ag, plotted in at.%

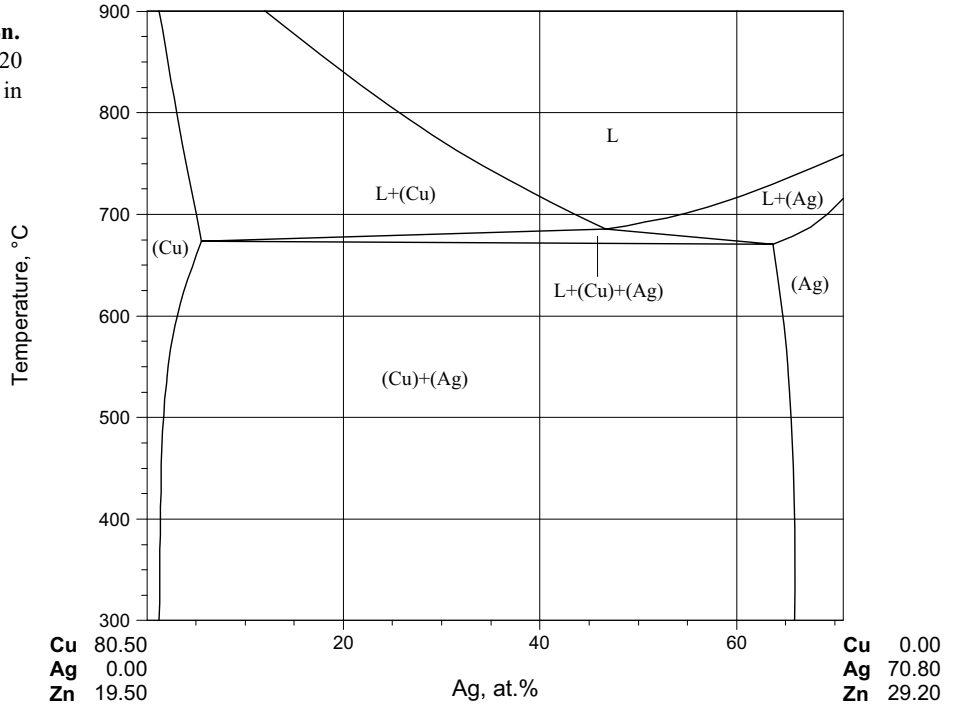

Fig. 4b: Ag-Cu-Zn. Vertical section at 20 mass% Zn, plotted in at.%

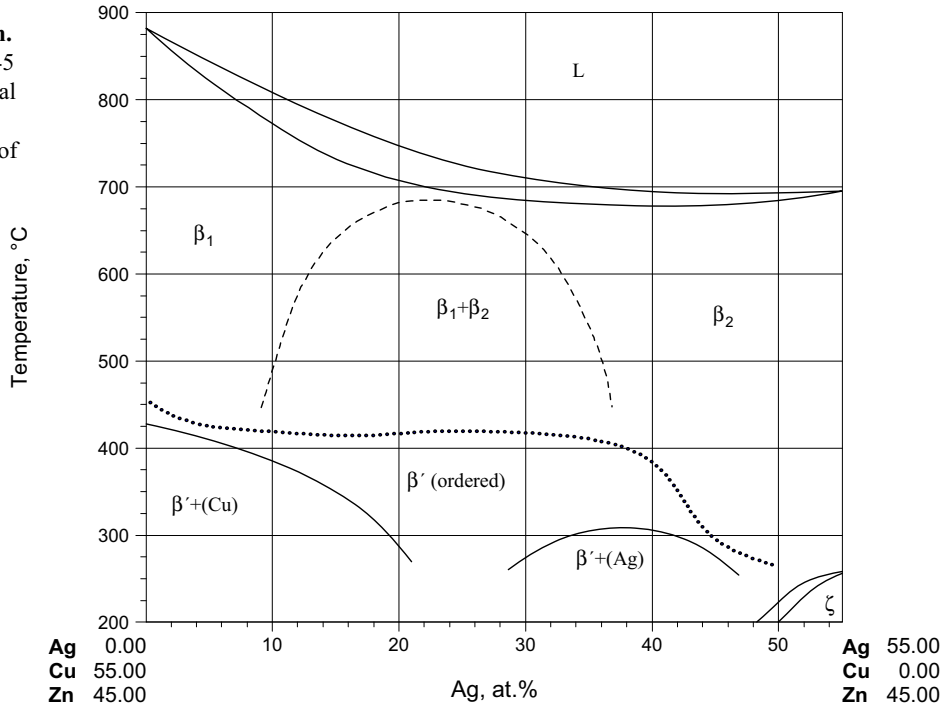

Fig. 5: Ag-Cu-Zn. Vertical section at 45 at.% Zn with spinodal of the β phase and critical temperature of the β/β´-ordering. Some lines are not completely determined and not drawn outside the investigated ranges