Copper – Manganese – Zinc

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Introduction

The results of phase diagram investigations, carried out in the early years of the last century, are not considered for the construction of the phase diagram [1905Gui, 1906Gui, 1912Car, 1924Hei, 1926Heu, 1928Heu], because manganese used contained significant amounts of impurities and therefore results are questionable. Copper rich sections of the ternary system were investigated by [1933Bau, 1934Bau, 1945Dea, 1949Gra]. [1933Bau, 1934Bau] used copper and zinc with 99.99% purity, respectively for mixing with a copper 67.7 mass%-manganese 30.92 mass% alloy containing 1.38 mass% impurities, to produce samples containing up to 7.5 mass% manganese. The temperature of the peritectic reaction α + melt ⇌ β, was determined for increasing amount of manganese employing thermal analysis and optical microscopy. The authors of [1945Dea, 1949Gra] prepared their samples from electrolytic metals with high purity and determined the solubility of manganese and zinc in α-brass for different temperatures employing X-ray and microscopic methods. [1949Gra] reports in addition the stability ranges of the beta phase in isothermal sections at 593°C and 648°C. The equilibrium between α and β phases was independently investigated by [1952Haw] on 56 samples, annealed at 672°C and investigated by optical microscopy. The results are similar to [1949Gra]. [1975Gon] and [1977Wat5] determined order-disorder transition temperatures for compositions of β-brass, containing 0.6-5.9 at.% manganese, by means of electrical resistivity and specific heat measurements. The transformation drops from 466°C in binary Cu-Zn to 402°C at the maximum solubility of manganese in β phase.
Reviews on the Cu-Mn-Zn system were presented by [1949Jae, 1979Cha, 1979Dri, 1980Bra].

Binary Systems

The binary Cu-Zn is accepted from [2006Leb], which is a compilation of [1994Mio], [1993Kow] and [2001Her]. Although [2006Leb] suggested the value of 665°C for the temperature of the p_4 reaction L + γ ⇌ δ, in this assessment we accepted the value of 700°C adopted from [1994Mio], which is now consistent with the ternary invariant reaction U_4.
The binary Cu-Mn was taken from [2005Tur], based on a critical assessment and thermodynamic calculation.
The Mn-Zn binary, presented in [Mas2, 1990Oka], tried to incorporate all information from older sources in respect to the various ε phases (ε, $ε_1$, $ε_2$). The ε phase adopts a simple close packed hexagonal structure and changes in lattice parameters are smoothly decreasing on the exchange of zinc with manganese. [Mas2] postulated different ε phases on the basis of speculations and investigations carried out before electrolytic manganese was available. The “peritectic” temperatures, corresponding to the formation of $ε_1$, $ε_2$ show a scattering range resulting obviously from impurities in the alloys. [1960Tez, 1964Nak] found a metastable ε phase with Ni_3Sn structure as a transition phase from ε phase to α' phase, but the changes of lattice parameters in the ε' phase measured by [1964Hen, 1970Far] show no anomalies. Therefore the existence of a thermodynamic stable $ε_1$ phase and $ε_2$ phase is doubtful. Superseding older data, it was clearly shown by [1971Rom], that there is only one field of a hcp ε phase extending from 42 to 88.6 at.% of Zn and no evidence for $ε_1$, $ε_2$. Throughout this assessment we therefore will adopt the ε phase region of [1971Rom] and assume the version of [Mas2] for the rest of the diagram. The low temperature region of the binary (δMn) phase field (called $β_2$ phase in this assessment) was in many reports addressed as an ordered CsCl type structure; authors, however, gave little justification for a phase transition (δMn) ⇌ $β_2$ at about 900°C.

Solid Phases

The Cu-Mn-Zn system includes a ternary Laves phase τ_1, designated as χ, λ, T or T_1 phase in literature, with the composition MnCuZn without any significant range of homogeneity at 400°C [1946Dea, 1962Tes, 1963Tes, 1969Tes]. The crystal structure of the τ_1 phase, was reexamined in detail from X-ray powder diffraction [1976Gon, 1977Wat4] revealing a random distribution of Cu,Zn atoms in the 16d-sites. The transformation temperature of the τ_1 phase to the high temperature β_2 phase, obtained by high temperature X-ray diffraction, is given as 502°C, in contradiction to [1946Dea] who gave a decomposition temperature at about 593°C without presenting any evidence.
On the basis of the X-ray results of [1977Wat5], showing β_2,MnZn and β,CuZn in a two-phase equilibrium, we assume that neither the phases β,CuZn, (δMn) nor the phases β',CuZn, β_2,MnZn form a continuous ternary solid solution. In both phase regions β,CuZn as well as (δMn) there is, however, a concentration and temperature dependent tendency towards ordering from the W type high temperature modification (β,CuZn, (δMn)) to a CsCl type low temperature modification (β',CuZn, β_2,MnZn). There is no evidence for a connection between phases β_2 and β_1. For details see Table 1.
Investigations of the crystal structure of the ε phase, a Hume-Rothery phase, was carried out by [1939Moe1, 1939Moe2, 1943Moe]. A ternary solid solution connecting the ε phase of the Cu-Zn and Cu-Mn systems at 400°C was reported after investigation of 5 compositions. Without specification of the temperature a continuous solid solution ε,(Cu,Mn,Zn) was also reported by [1954Agl].
A ternary solid solution corresponding to the binary ζ phase from the Mn-Zn system was observed by [1991Kam]. The work includes only investigations by microscopy and microprobe analysis. [1991Kam] observed also a phase of the composition $MnCuZn_{10}$, it could be understood as a solid solution from the binary δ_1 phase of the MnZn system or the δ phase of the CuZn system. The observed phase shows a decreasing gradient of copper and an increasing gradient of manganese from the centre to the grain surface. However, in the case of the δ_1 phase, the authors could not give evidence for an existing connection to the binary δ_1 phase. Lattice parameters for the α-brass solid solution are given in [1960Cha]. The author has investigated 23 samples, prepared from ultra pure starting materials and found, that zinc and manganese together expand the copper lattice on a greater extend than the sum of the expansions when each of the solutes was considered separately.
The solid phases pertinent to the ternary diagram are listed in Table 1.

Invariant Equilibria

A part of the liquidus surface with copper- and zinc rich compositions was investigated by [1972Wat], who prepared 76 samples from pure electrolytic metals. The author shows 7 invariant reactions by using inverse rate differential thermal analysis, thermal dilatation, electrical resistance measurements, X-ray diffraction and microscopic examination. [1977Wat5] added three invariant equilibria in the Zn rich area. A eutectoid decomposition of the β_2 phase to β and τ_1 at about 498°C, was observed [1977Wat3]. A transformation from the disordered β,CuZn phase to the ordered β' phase as a function of Mn concentration is reported, however, the shown temperature *vs* concentration section is in contradiction to phase rules and was not considered among the presented phase diagrams. The invariant reactions are given in Table 2, temperature and compositions of the phases are taken as reported by [1977Wat5]. A diagram for the partial reaction scheme comprising the reactions in the Zn corner and for the Mn poor side of the diagram is shown in Fig. 1. It is in agreement with the experimental phase distribution in the Zn corner at room temperature [1977Wat5].

Liquidus Surface

A liquidus surface and two isothermal sections for the ternary Cu-Mn-Zn have been constructed from literature data, including all relevant data from 1926 to 1976 [1979Cha]. However the result is partially in contradiction to the known binary of Mn-Zn. These data have not been considered here. The ternary liquidus data as collected by [1977Wat5] are accepted and with some modifications to adapt to the known binary systems are used to construct the liquidus surface as shown in Fig. 2 and for the Zn corner of the diagram in Fig. 3.

Isothermal Sections

Figures 4 and 5 show the phase relations for the Mn poor region of the diagram for alloys annealed at 600°C and cooled to room temperature (Fig. 4) and for 600°C (Fig. 5). Both sections are after [1977Wat5] with some adaptation to ensure agreement with the accepted binary systems and to remove violation of the Schreinmaker rule. The original Fig. 5 was labelled “qualitative” by [1977Wat5].

Thermodynamics

Thermodynamic functions for zinc- and copper rich solutions with manganese were derived from measurements of vapor pressure of zinc by [1961Cha]. In addition, magnetic susceptibilities of these alloys were determined in the range of –78°C to 200°C by using a Sucksmith ring balance. [1986Tak] carried out interdiffusion experiments of the α solid solution at 800°C. The obtained interaction parameter was used for the calculation of the bond strengths, received by dilute solution approximation. The effect of manganese on the order-disorder transformation in the β phase was investigated by [1977Wat1]. It is shown that the transition temperature is decreasing linearly with increasing manganese content. The ordering parameter and activation energy are obtained from heat capacity and resistivity measurements.

Notes on Materials Properties and Applications

The interest in manganese addition for the production of brass alloys was the observation of an enhanced hardness of brass, without becoming brittle [1912Car]. The hardness, tensile and yield strengths and ductility of brass by adding manganese were discussed by [1926Sma, 1944Lon, 1946Dea, 1961Die, 1966Lah]. It was shown that with increasing amount of manganese the ductility increases and hardness and tensile- and yield-strengths decrease and the alloys possess good cold working proportions; they are more resistant to stress corrosion cracking than pure Cu-Zn alloys. The elongation of single phase alloys increases with zinc content. These alloys could be prepared in conventional furnaces [1966Lah]. The age hardening behavior of an Cu-25.2Zn-19.1Mn (mass%) alloy, aged at 200°C, is due to the eutectoid decomposition of β_2 phase [1977Wat2]. The dispersion-strengthening effect was investigated using scanning electron microscopy (SEM) with electron dispersion spectroscopy (EDS) techniques by [2004Sar].

Miscellaneous

[1985Kan] investigated the diffusion in the α phase at 775°C. A not explicitly described metastable phase was observed after decomposition of the β_2 phase. The effect of cold working procedures on lattice parameters and substructures of α solid solutions has been investigated by [1984Gho] using X-ray diffraction with calculation of peak shift, peak broadening and peak asymmetry analyses. It is reported, that a changing manganese content has no significant effect in deformed substructures. The variation of zinc indeed ends up in an enhanced faulting concentration.

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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, $Cu_{1-x-y}Mn_xZn_y$	*cF*4	*a* = 371.31	*x* = 0.116, *y* = 0.256 [1960Cha]
(Cu)	$Fm\bar{3}m$	*a* = 361.46	*x* = *y* = 0, at 25°C [Mas2]
< 1084.62	Cu		melting point [1994Sub]
			complete solid solution with (γMn) and dissolves 38.95 at.% Zn at 454°C [Mas2]
(γMn)		*a* = 386.0	*x* = 1, [Mas2] dissolves 34 at.% Zn
1138 - 1100			
(δMn)		*a* = 308.0	[Mas2] dissolves 50 at.% Zn
1246 - 1138			dissolves 12.5 at.% Cu
β_2, (MnZn)Cu[1)]	*cP*2		described as low temperature ordering variant of (δMn) [Mas2], at 39.8 at.% Zn [1990Oka]
	$Pm\bar{3}m$		
MnZn	CsCl		
ca. 900 - 620		*a* = 306.0	at 550°C [1977Wat4]
		a = 296.8	
(βMn)	*cP*20	*a* = 631.52	[Mas2]
1100 - 727	$P4_132$		dissolves 48 at.% Zn
	βMn	*a* = 649	at 46 at.% Zn [1990Oka]
(αMn)	*cI*58	*a* = 891.26	at 25°C [Mas2]
< 727	$I\bar{4}3m$		dissolves 1.7 at.% Zn
	αMn		
(Zn)	*hP*2	*a* = 267.73	[V-C2]
< 425°C	$P6_3/mmc$	*c* = 483.17	
	Mg		dissolves 2.8 at.% Cu at 425°C [Mas2]
			dissolves 1 at.% Mn at 417.25°C [Mas2]
β, (CuZn)Mn	*cI*2		dissolves 36.1 to 55.8 at.% Zn [Mas2]
CuZn(h)[1)]	$Im\bar{3}m$	*a* = 295.39	at 52.3 at.% Cu [V-C2]
902 - 454	W	*a* = 294.90	at 54.9 at.% Cu [V-C2]
			dissolves about 10 at.% Mn at 600°C and 19 at.% Mn at 799°C [1977Wat5]
β', CuZn(r)[1)]	*cP*2		dissolves 44.7 to 48.2 at.% Zn [Mas2]
< 468°C	$Pm\bar{3}m$	*a* = 294.9	at 44.7 at.% Cu [V-C2]
	CsCl	*a* = 295.9	at 50.5 at.% Cu [V-C2]
low temperature variant of β,CuZn(h)			dissolves about 8 at.% Mn at 25°C [1977Wat5]
γ, Cu_5Zn_8	*cI*52	*a* = 885.9 to 888.7	[2006Leb]
< 834°C	$I\bar{4}3m$		dissolves 57.0 to 70.0 at.% Zn
	Cu_5Zn_8		dissolves about 15 at.% Mn at 600°C and about 12 at.% Mn at 25°C [1977Wat5]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ, $CuZn_3$ 700 - 560	*hP*3 $P\bar{6}$ $CuZn_3$	*a* = 427.5 *c* = 259.0	dissolves 72.45 to 76 at.% Zn [2006Leb]
β_1, MnZn < 180	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 306.5	dissolves from ? to 50 at.% Zn [Mas2] at 43.5 at.% Zn [1990Oka]
ε, $Mn_xCu_{1-x-y}Zn_y$	*hP*2 $P6_3/mmc$ Mg		[1943Moe] described a complete solid solution from the Cu-Zn to the Mn-Zn system at 400°C
Mn_xZn_y [2)] 815 - 220			[1971Rom] reported a continuous solution from 42 to 88.6 at.% Zn
		a = 273.1 *c* = 445.5	at 45.7 at.% Zn [1990Oka]
		a = 276.60 *c* = 444.52	at 85.4 at.% Zn [1990Oka]
		a = 275.0 *c* = 442.4	33.8 at.% Cu and 66.2 at.% Zn
		a = 273.1 *c* = 428.4	18.9 at.% Cu and 81,1 at.% Zn
α'(h), $Mn_{7.5-x}Zn_{2.5+x}$ < 325	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 386	69 to 75 at.% Zn; $0 < x < 6$ [Mas2] [V-C2]
α_1'(r), $Mn_{7.5-x}Zn_{2.5+x}$ < –143	*tP*2 *P*4/*mmm* AuCu	*a* = 390 *c* = 372	70 to 75 at.% Zn; $0 < x < 5$ [Mas2] [V-C]
γ and γ_1, $MnZn_4$ < 420	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	*a* = 916.0	[Mas2] solves 77 to 84.4 at.% Zn [1990Oka] eventually shows ordering at lower temperatures (γ_1)
δ_2, $MnZn_{\sim 10}$ 462 - 380	*hP**	-	86.5 - 90.6 at.% Zn [Mas2] a solid solution to δ_1 is assumed by [1991Kam]
δ_1, $MnZn_{10}$ < 424	*hP**	*a* = 1283 *c* = 577	88.9 - 90.8 at.% Zn [Mas2] [1990Oka] a solid solution to δ is assumed by [1991Kam]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ζ, $MnZn_{13}$ < 428	*mC*28 *C*2/*m* $CoZn_{13}$	*a* = 1348.3 *b* = 766.26 *c* = 513.4 β = 127.78°	[V-C] solves 92.6 to 92.9 at.% Zn [Mas2]
* τ_1, MnCuZn < 502	c*F*24 $Fd\bar{3}m$ Cu_2Mg	*a* = 697.96 *a* = 696.6 *a* = 695.0	[1976Gon] [1962Tes] from multi-phase alloy $Cu_{1.5}MnZn_{0.5}$ [1963Tes] Designations used in different publications: T, T_1, λ, χ

[1)] On the basis of the X-ray results of [1977Wat5], showing β_2,MnZn and β,CuZn in a two-phase equilibrium, we assume that neither the phases β,CuZn, (δMn) nor the phases β',CuZn, β_2,MnZn form a continuous ternary solid solution. In both ternary phase regions starting from binary β,CuZn as well as (δMn) there is, however, a concentration and temperature dependent tendency towards ordering from the W type high temperature modification (β,CuZn, (δMn)) to a CsCl type low temperature modification (β',CuZn, β_2,MnZn). There is no evidence for a connection between phases β_2 and β_1.

[2)] According to [1971Rom] a continuous solution with hexagonally closed packed Mg type structure extends from 42 to 88.6 at.% Zn comprising the ε phases, which in several reports are listed as ε (Mg type), ε_1 (Ni_3Sn type), ε_2 (hexagonal, *hp**) of which ε_1, ε_2 likely are metastable.

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Cu	Mn	Zn
$L + \alpha \rightleftharpoons \beta + \beta_2$	799	U_1	L	35.9	28.2	35.9
$L + \beta \rightleftharpoons \beta_2 + \gamma$	786	U_2	L	32.3	21.5	46.2
$L + \beta_2 \rightleftharpoons \varepsilon + \gamma$	743	U_3	L	26.6	18.6	54.9
$L + \gamma \rightleftharpoons \varepsilon + \delta$	682	U_4	L	21.1	7.0	71.9
$\beta_2 \rightleftharpoons \alpha + \beta + \tau_1$	490	D_1	-	-	-	-
$\beta_2 \rightleftharpoons \gamma + \varepsilon + \tau_1$	477	D_2	-	-	-	-
$\beta_2 \rightleftharpoons \beta + \gamma + \tau_1$	473	D_3	-	-	-	-
$L + \varepsilon \rightleftharpoons \delta_2 + (Zn)$	422	U_5	-	-	-	-
$L + \delta_2 \rightleftharpoons (Zn) + \zeta$	419.5	U_6	-	-	-	-
$\delta_2 \rightleftharpoons (Zn) + \zeta + \delta_1$	341	D_4	-	-	-	-

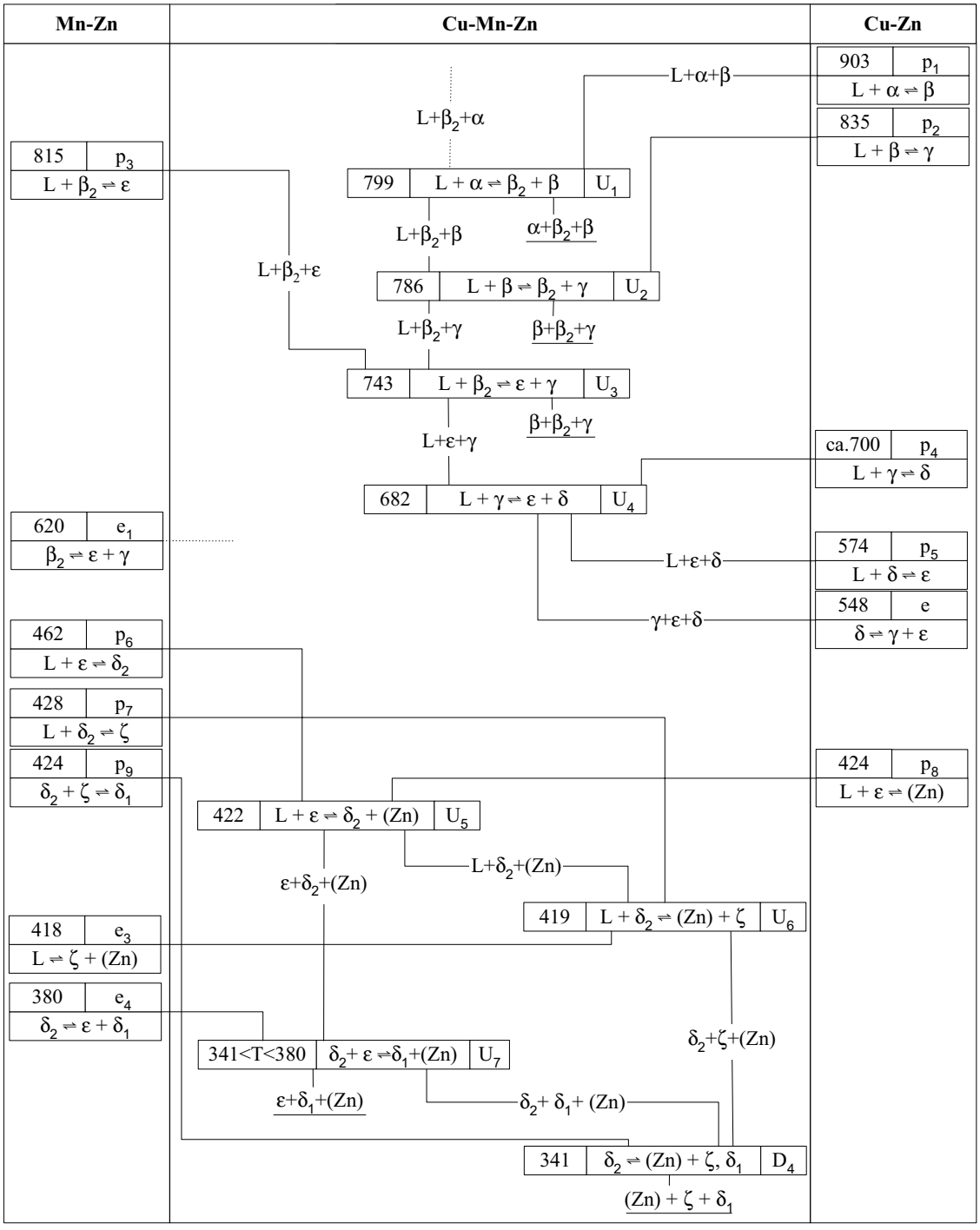

Fig. 1: Cu-Mn-Zn. A partial reaction scheme

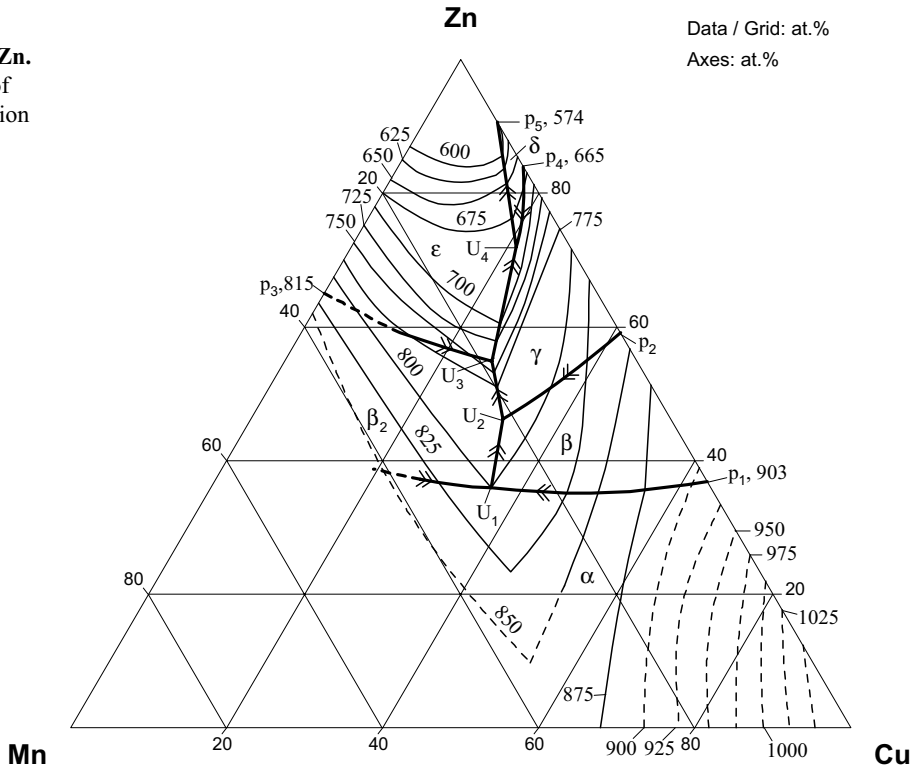

Fig. 2: Cu-Mn-Zn. Liquidus surface of the Cu-Zn rich region

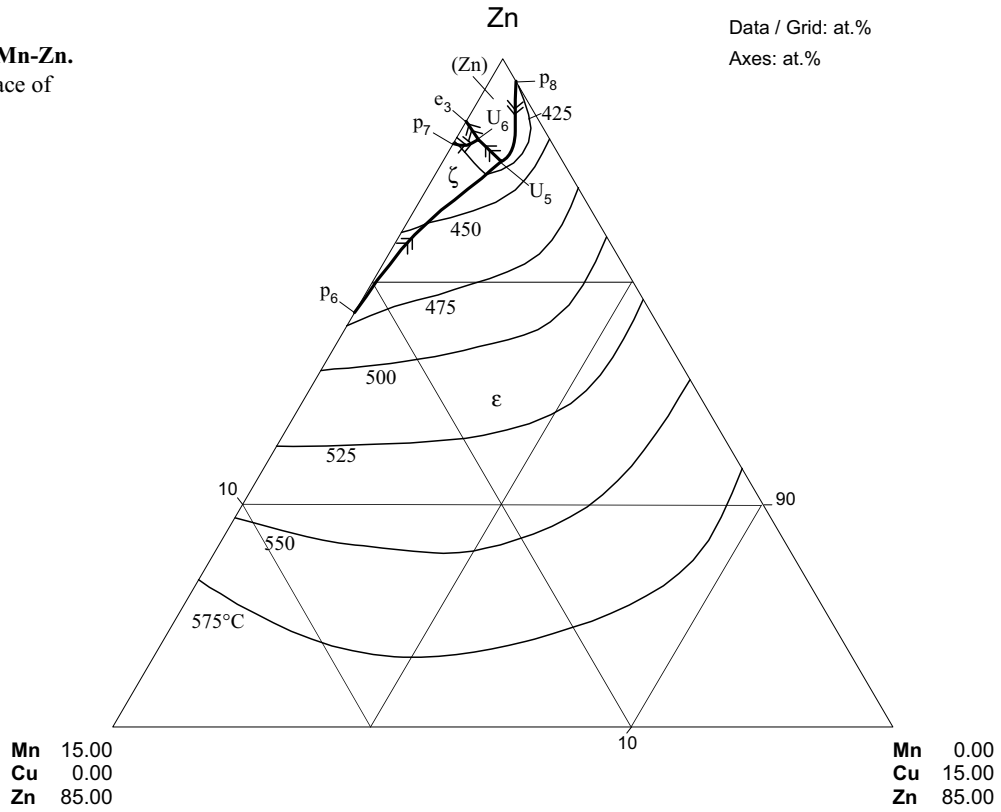

Fig. 3: Cu-Mn-Zn. Liquidus surface of the Zn corner

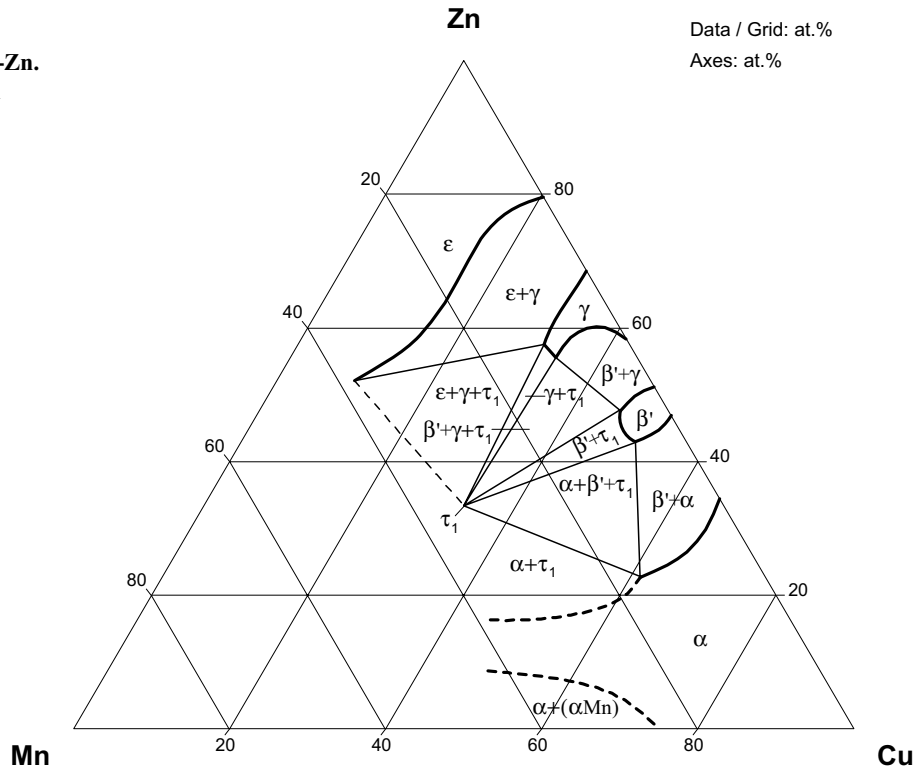

Fig. 4: Cu-Mn-Zn. Partial isothermal section at room temperature

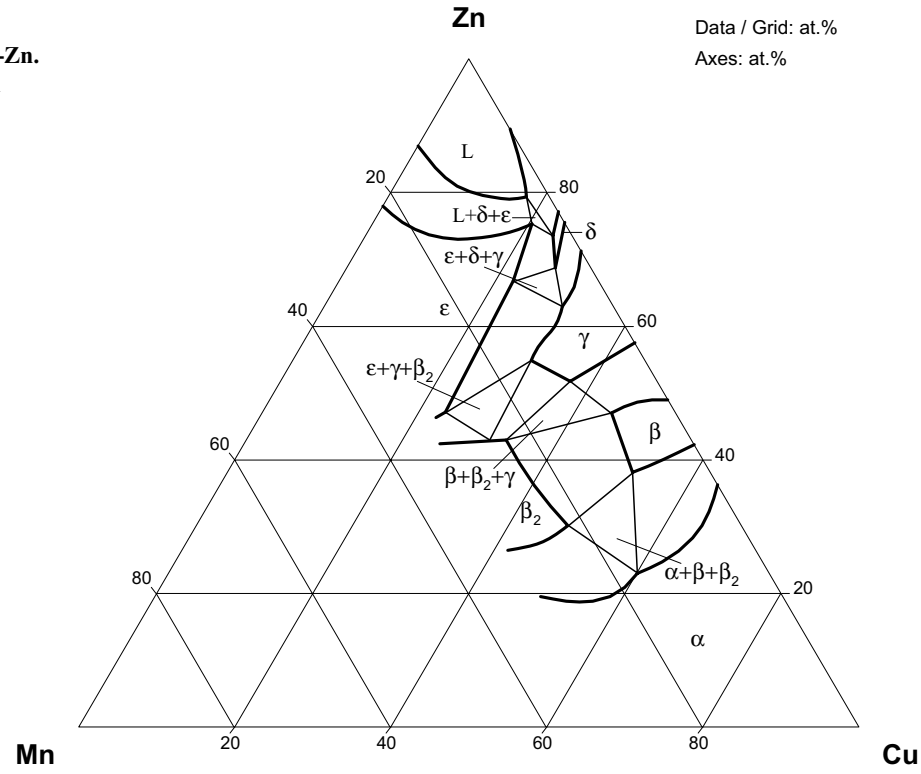

Fig. 5: Cu-Mn-Zn. Partial isothermal section at 600°C (“qualitative”)