Copper – Titanium – Zinc

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Introduction

Phase equilibria (liquidus surface, reaction scheme and isothermal section at room temperature) for alloys containing up to 25 mass% Ti were investigated in detail by [1962Hei1]. The alloys were prepared by melting under Ar or air pure Cu, pure Zn and a Zn-3mass% Ti alloy. Phase analysis were done by optical microscopy and XRD. This work was later reviewed by [1979Cha, 1979Dri]. A more recent study of the zinc rich corner of the system has been carried out by [1996Zer]. The interactions between Cu-Zn brasses and Ti has been investigated by [2001Soa].

Binary Systems

The Cu-Ti and Cu-Zn systems are respectively taken from [2002Ans, 2006Leb]. The Ti-Zn accepted by [Mas2] is taken from the review of [1984Mur]. Later investigation [1997Glo] showed that the phases $TiZn_5$ and $TiZn_{10}$ whose structure was unknown were probably the same phase $TiZn_7$ whose composition, according to [1995Che] would be close to Ti_3Zn_{22}. The existence of this phase was confirmed by [2004Vas] who does not exclude a non stoichiometry between the compositions $TiZn_7$ and $TiZn_8$. An indication about the presence of a formerly unknown phase Ti_2Zn_3 has been found by [2004Vas].

Solid Phases

Two ternary phases have been reported, namely τ_1,Cu_2TiZn [1962Hei2, 1967Hof] and τ_2,Cu_2TiZn_{22} [1996Zer]. Lattice parameters change indicates a Cu solubility in Ti_2Zn [1964Ram]. [1959Bis] determined metallographically a Ti solubility between 0.68 and 1.22 mass% in the binary compound $Cu_{70}Zn_{30}$. This result was confirmed by [1966Zwi], who reports that zinc content has little effect on the Ti solubility in copper base alloys containing up to 10 mass% Zn. It should be noted however that [1959Bis], as well as [1964Ram] encountered oxidation phenomena in their alloys. The solubility of Ti in Zn-0.6 mass% Cu is less than 0.06 mass% [1961Pel]. Crystal structure data for Cu_2TiZn are given in Table 1 together with the data on binary boundary phases.

Invariant Equilibria

The invariant reactions are given in Table 2 which come mainly from the experimental work of [1962Hei1] and the review of [1979Cha]. However, they have been modified because the reactions E_1, E_2, and E_3 presented as “E type” in Table 2 were wrongly labelled “U type” in [1979Cha]. These reactions can not be of the U type because the composition of the liquid is situated inside the triangle formed by the three solid phases.

Liquidus Surface

The liquidus surface, shown in Figs. 1a and 1b is mainly derived from the experimental works of [1962Hei1, 2001Soa]. However, the maxima e_2, e_3 and e_4 missed by [1962Hei] have been introduced according to the Alkemade’s rule which states that the border line separating two crystallization fields is crossed by the straight line linking the compositions of the two phases in a point which must be a maximum. As a consequence, the invariant equilibria are coherent with elemental geometric considerations reminded above. The domain labelled “Ti_2Cu_3” is actually crossed by a border between “Ti_2Cu_3” and “$TiCu_2$”. However, the exact shape of the $TiCu_2$ domain is unknown. It must be very small because $TiCu_2$ crystallizes from the liquid phase only between 870 and 875°C. The reaction scheme is shown in Fig. 2.

Isothermal Sections

The isothermal section at room temperature, shown in Fig. 3 for alloys containing up to 25 mass% Ti [1962Hei1], is dominated by equilibria surrounding the ternary phase τ_1,Cu_2TiZn. This compound presents a small homogeneity range. The solubility of the respective third element in either of the binary compounds is small, except for γCu_5Zn_8, which dissolves nearly 8 mass% Ti.

Notes on Materials Properties and Applications

Titanium additions in amount as low as 0.06 mass% have a marked effect on grain refining in Zn-0.6 mass% Cu alloys. The microstructure is stable in annealing 12 h at 350°C [1961Pel]. Improved recrystallization resistance is reported for the $Cu_{70}Zn_{30}$ alloy having dissolved Ti [1959Bis]. By transmission electron microscopy (TEM) observations on rapidly solidified Cu rich alloys, precipitation of orthorhombic Cu_4Ti was observed [1980Psh]. Cu-Ti-Zn alloys (15 mass% Ti) were used as a filler alloy in nitride ceramics [2004Zha] because Ti gives copper the same white color as nickel [2003Yos] without skin irritations resulting from the presence of Ni. The hardness of $Cu_{58}Zn_{10}Ti_5$ (at.%) alloy increases from 135 to 253 Vickers after ageing 30 min at 500°C. Zn-0.1% Cu-0.12% Ti alloys present an improved bendability [1984Weg] which depends on the ductile-brittle transition temperature.

References

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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
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	a = 361.46	Dissolves up to 38.27 at.% Zn at 454°C and up to 9 at.% Ti at 985°C.
(βTi) 1670 - 790	*cI*2 $Im\bar{3}m$ W	a = 330.65	Dissolves up to 10 at.% Cu at 1005°C [Mas2]
(αTi) < 882	*hP*2 $P6_3/mmc$ Mg	a = 295.06 c = 468.35	Dissolves up to 1.5 at.% Cu at 790°C [Mas2]
(Zn) < 419.6	*hP*2 $P6_3/mmc$ Mg	a = 266.50 c = 494.61	at 22°C [Mas2]
$\beta TiCu_4$ 885 - ~400	*oP*20 *Pnma* Au_4Zr	a = 452.5 b = 434.1 c = 1295.3	[2002Ans];78 - 80.9 at.% Cu

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αTiCu$_4$ ≲ 500	*tI*10 *I*4/*m* MoNi$_4$	-	[2002Ans]; 78 - 80.9 at.% Cu
TiCu$_2$ 890 - 870	*oC*12 *Amm*2 Au$_2$V	*a* = 436.3 *b* = 797.7 *c* = 447.8	[2002Ans]
Ti$_2$Cu$_3$ < 875	*tP*10 *P*4/*nmm* Cu$_3$Ti$_2$	*a* = 313 *c* = 1395	[2002Ans]
Ti$_3$Cu$_4$ < 925	*tI*14 *I*4/*mmm* Cu$_4$Ti$_3$	*a* = 313.0 *c* = 1994	[2002Ans]
TiCu < 982	*tP*4 *P*4/*nmm* CuTi	*a* = 310.8 to 311.8 *c* = 588.7 to 592.1	[2002Ans] Range from 48 to 52 at.% Cu
Ti$_2$Cu < 1005	*tI*6 *I*4/*mmm* MoSi$_2$	*a* = 295.3 *c* = 1073.4	[2002Ans]
β, CuZn(h) 902 - 454	*cI*2 *Im*$\bar{3}$*m* W	*a* = 295.39	at 47.5 at.% Zn [2006Leb] Range from 36.1 to 55.8 at.% Zn
β', CuZn(r) < 468	*cP*2 *Pm*$\bar{3}$*m* CsCl	*a* = 295.9	at 49.5 at.% Zn [2006Leb] Range from 44.8 to 50 at.% Zn
γ, Cu$_5$Zn$_8$ < 835	*cI*52 *I*$\bar{4}$3*m* Cu$_5$Zn$_8$	*a* = 885.9 to 888.7	[2006Leb] Range from 57 to 70 at.% Zn
δ, CuZn$_3$ 700 - 560	*hP*3 *P*$\bar{6}$ CuZn$_3$	*a* = 427.5 *c* = 259.0	[2006Leb] Range from 72.5 to 76.0 at.% Zn
ε, CuZn$_4$ < 574	*hP*2 *P*6$_3$/*mmc* Mg	*a* = 274.18 *c* = 429.39	[2006Leb] Range from 78.0 to 88.0 at.% Zn
TiZn$_{15}$ < 445	*oC*68 *Cmcm* TiZn$_{15}$	*a* = 769.8 *b* = 1141.4 *c* = 1180.0	93.75 to 94.1 at.% Zn [1995Che, 1996Zer, 2004Vas]
TiZn$_7$ < 468	*tP*100 *P*4$_2$/*mbc*	*a* = 1152.3 *c* = 1145.6	Exactly Zn$_{2.842}$Ti$_{22.160}$ [1995Che]
TiZn$_3$ < 650	*cP*4 *Pm*$\bar{3}$*m* AuCu$_3$	*a* = 393.22	[1984Mur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$TiZn_2$ < 950	*hP*12 $P6_3/mmc$ $MgZn_2$	*a* = 506.4 *c* = 821.0	[1962Hei1, 1984Mur]
TiZn < 1050	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 314.6	[1962Hei1, 1984Mur]
Ti_2Zn < 664.6	*tI*6 *I*4/*mmm* $MoSi_2$	*a* = 303.6 *c* = 1067.8	[1984Mur]
* τ_1, Cu_2TiZn < 950	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 296	[1962Hei2]
* τ_2, Cu_2TiZn_{22}	*cF** $Fd\bar{3}$ or $Fd\bar{3}m$ C (diamond)	*a* = 1386 ± 2	[1996Zer]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ti	Cu	Zn
L + $TiCu_4$ ⇌ (Cu) + Ti_2Cu_3	< 875	U_1	L	23.8	72.4	3.8
L ⇌ (Cu) + Ti_2Cu_3 + τ_1	< 875	E_1	L	20.2	69.6	10.2
L + (Cu) ⇌ β + τ_1	< 875	U_2	L	14.2	48.8	37.0
L + β ⇌ γ + τ_1	< 834	U_3	L	14.3	31.4	54.3
L + (Zn) ⇌ $TiZn_{15}$ + ε	< 425	U_4	L	0.7	0.5	98.8
L + $TiZn_{15}$ ⇌ $TiZn_7$ + ε	< 425	U_5	L	1.4	1.0	97.6
L + $TiZn_7$ ⇌ $TiZn_3$ + ε	< 425	U_6	L	2.8	6.4	90.8
L ⇌ $TiZn_3$ + δ + ε	< 425	E_2	L	4.0	11.2	84.8
L ⇌ $TiZn_3$ + γ + δ	< 425	E_3	L	5.4	18.2	76.4
L + $TiZn_3$ ⇌ $TiZn_2$ + γ	< 425	U_7	L	14.3	26.5	59.2
L ⇌ $TiZn_2$ + γ + τ_1	< 425	E_4	L	14.3	30.4	65.3

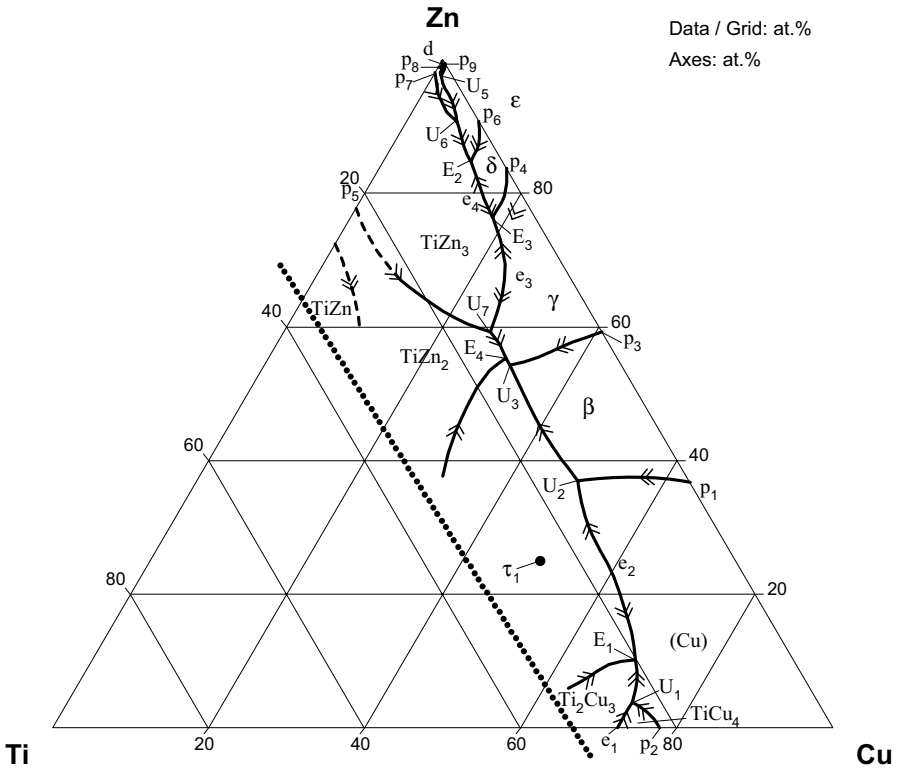

Fig. 1a: Cu-Ti-Zn. Partial liquidus projection up to 30 at.% Ti

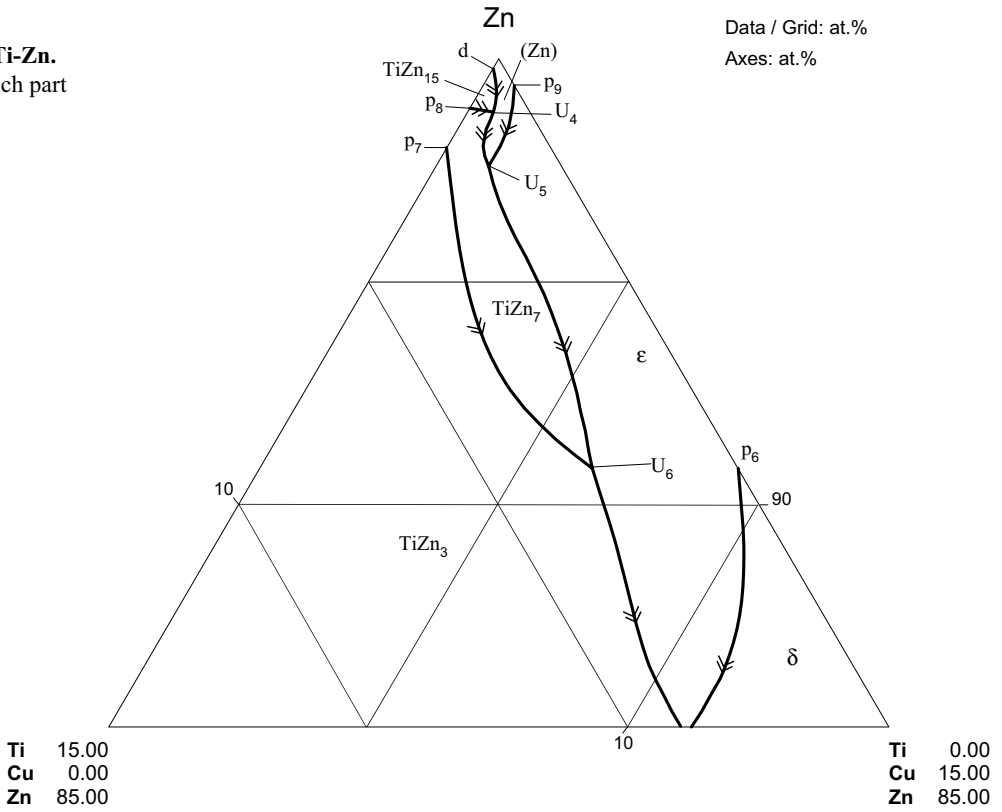

Fig. 1b: Cu-Ti-Zn. Enlarged Zn rich part of the liquidus projection (schematic)

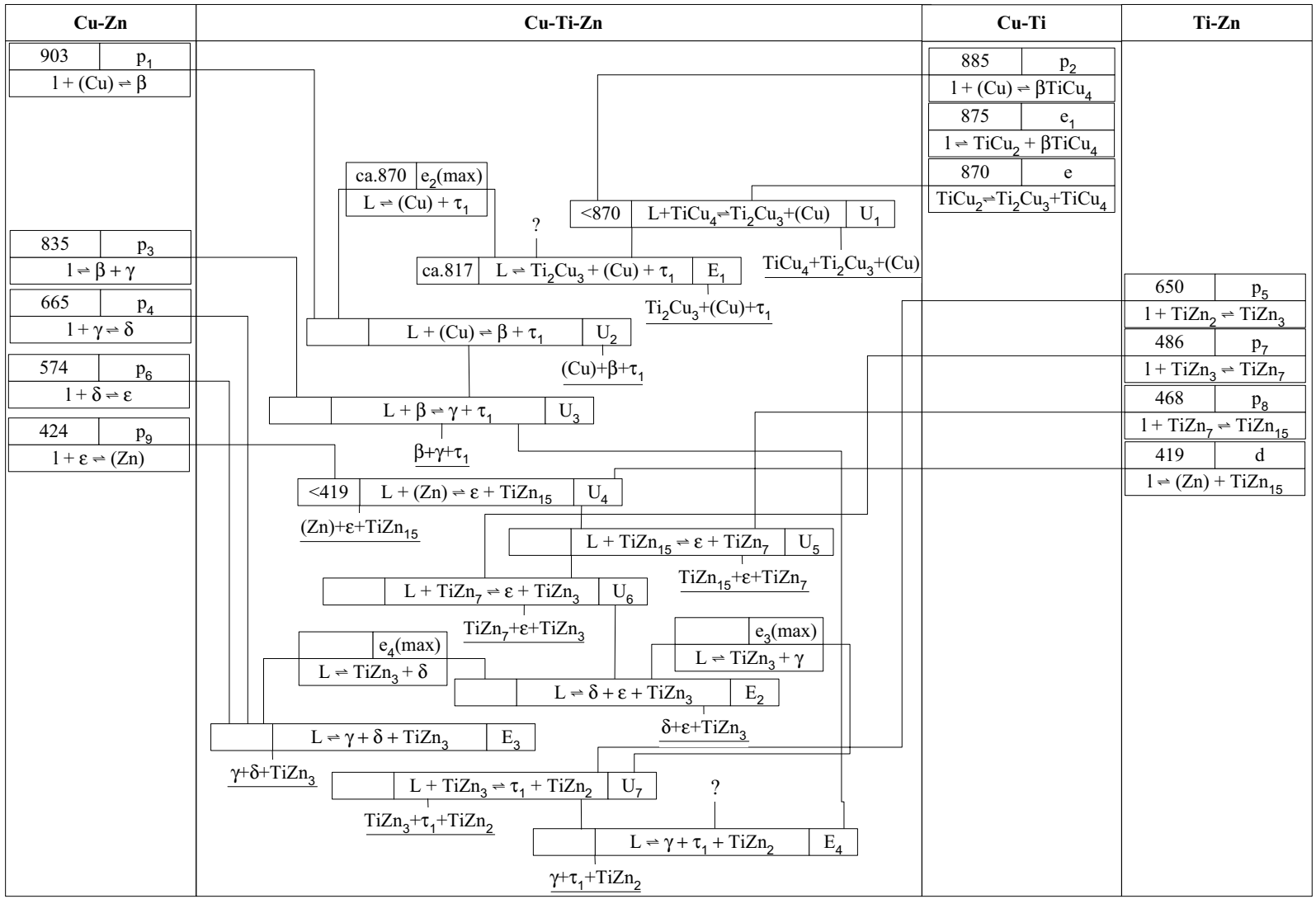

Fig. 2: Cu-Ti-Zn. Partial reaction scheme

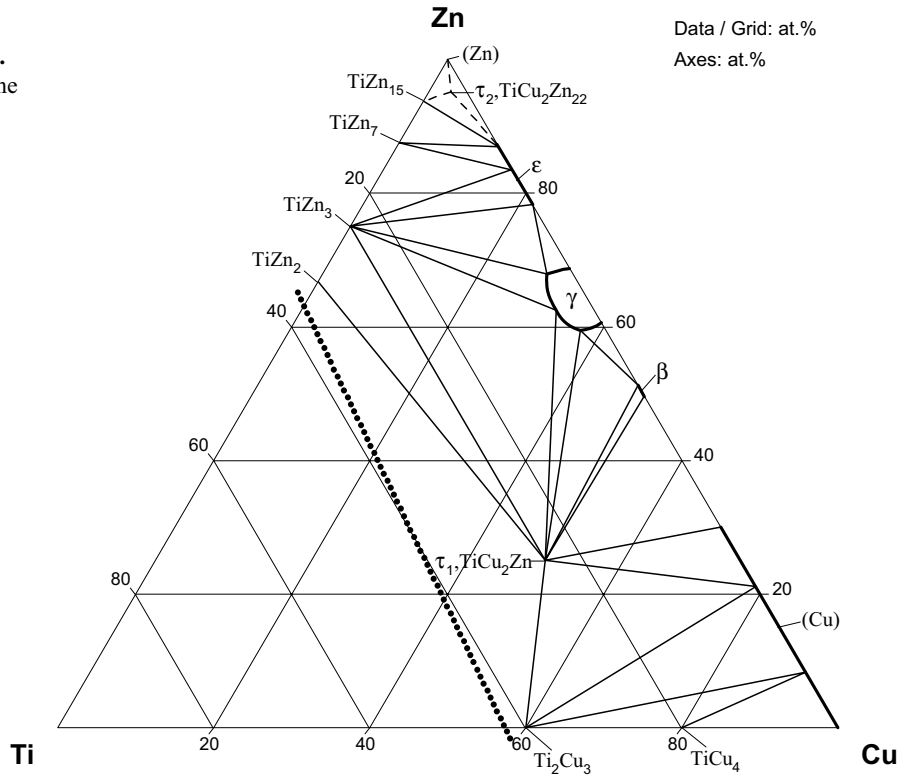

Fig. 3: Cu-Ti-Zn. Phase equilibria in the solid state