Copper – Lead – Zinc

Pierre Perrot

Introduction

Zinc is known since 1850 as an element used to remove copper from lead, so the first extensive studies of the ternary system were carried out by [1914Par, 1922Nic, 1929Bau1, 1943Dan], then, more precisely by [1948Hen]. The measurements are in good agreement except for the results of [1922Nic]. The diagram given by [1914Par], accepted by [1929Bau2] is not fundamentally different from that of [1948Hen] which is used as a basis for recent thermodynamic assessments of [1998Jan, 2001Her]. Later investigations of [1955Sei] are in accordance with the previous experimental works. The Calphad assessment made by [1998Jan] using available information reproduces with a good accuracy the liquidus lines together with the invariant points experimentally obtained by [1948Hen], the isopleth at 2 mass% Pb drawn by [1929Bau1] and the isopleth at 10 mass% Cu given by [1955Sei]. A Calphad assessment made by [2001Her], unfortunately without publishing any optimized value, reproduces with a very good accuracy the liquidus lines and the isoplethic cut $x_{Zn} = 3x_{Pb}$ experimentally derived by [1948Hen]. An isoplethic section at 2 mass% Pb, which matches well the experimental work of [1929Bau1] has also been calculated by [2003Bor]. The existence of a large miscibility gap in the liquid phase which extends from the Cu-Pb to the Pb-Zn sides was recognized by [1914Par] and confirmed by [1922Nic, 1929Bau2]. The liquidus lines in the Pb rich corner of the diagram have been experimentally determined by [1948Jol]. The experimental works made on the Cu-Pb-Zn system are resumed in Table 1.

Binary Systems

The Pb-Zn systems is accepted from [Mas2]. It presents a miscibility gap in the liquid phase with a critical point at 798°C and 28 at.% Pb. The Cu-Pb system accepted from [2006Sch] presents a miscibility gap in the liquid phase with a critical point at 995°C and 35 at.% Pb. The Cu-Zn system is taken from [2006Leb].

Solid Phases

They are given in Table 2. [1929Wer] shows that Pb can be dissolved up to 1.7 mass% in β brass and moves the (α+β)/β border towards the zinc corner of the binary Cu-Zn diagram, result which is not accepted in a following discussion by [1929Phi]. [1905Gui] gives a maximum solubility for Pb in α and β brass of 0.9%. However, a substantial solubility of Pb in Cu-Zn brasses, as reported by [1969Gue], is doubtful from today's point of view. A more precise investigation of [1972Leo] shows that, in α alloys, Pb is hardly soluble (less than 0.08 mass% in the α alloy with 30 mass% Zn) whereas in β alloys, at high temperatures, Pb is soluble up to a maximum of 0.35 mass%.

Invariant Equilibria

They are given in Table 3, mainly from the experimental investigations of [1948Hen, 1955Sei] accepted by [1979Cha]. The data given in mass% have been converted in at.% and the invariant reaction U_5, wrongly given as a transformation of the E type in [1979Cha] has been corrected.

Liquidus Surface

The liquidus surface, mainly from experimental investigations of [1948Hen, 1955Sei], accepted by [1979Cha, 1979Dri, 1998Jan] is given in Fig. 1. The Pb rich corner, from [1948Jol, 1979Cha] is shown in Fig. 2. It is worth to note that the compositions of the liquid L_2 given by [1979Cha] match perfectly the accepted monotectic invariant at 94 at.% Pb and 417.8°C in the binary Pb-Zn system. The reaction scheme is shown in Fig. 3.

Isothermal Sections

The partial isothermal sections at 700, 800 and 850°C, given respectively in Figs. 4a, 4b and 4c [1979Cha], show that Pb has the effect to move the (α+β)/β border towards the Zn corner of the diagram [1929Wer]. However, the solubility of Pb in α and β phases is much lower than that given in [1929Wer] and the slopes of some lines given by [1979Cha] have been modified for the sake of thermodynamic coherency. The phase equilibria calculated at 835°C [2003Bor], shown in Fig. 5 demonstrate how a Pb rich liquid can form even at very low Pb content.

Temperature – Composition Sections

Figure 6 shows the isoplethic cut $x_{Zn} = 3x_{Pb}$. It is mainly taken from [2001Her], however temperatures of the invariant reactions U_1, U_2, U_3 have been moved up to the values accepted from [1948Hen, 1955Sei, 1979Cha], therefore some lines in this region are shown dashed. The calculated section by [2001Her] is in excellent agreement with the experimental result of [1948Hen]. The thermodynamic mistake in the liquidus slopes drawn by [1948Hen] is corrected by the model. The isoplethic section at 2 mass% Pb measured by [1929Bau1] and calculated by [1998Jan, 2003Bor], shown in Fig. 7, confirms the formation of a Pb rich liquid alloy even at very low Pb contents.

Thermodynamics

The zinc isoactivity lines in liquid alloys have been experimentally measured at 802°C by [1994Sur] from an isothermal-isopiestic method, and showed a good agreement with the tie-lines of the miscibility gap which are given in Fig. 8. The authors propose to describe the excess Gibbs energy of the liquid phase at 802°C by a Redlich-Kister development:

$$\Delta G^{xs}/J\cdot mol^{-1} = X_{Cu} X_{Zn} [-21\,480 - 30 (X_{Cu} - X_{Zn})] + X_{Pb} X_{Zn} [17\,500 - 2\,940 (X_{Pb} - X_{Zn})]$$
$$+ X_{Cu} X_{Pb} [20\,680 + 1\,660 (X_{Cu} - X_{Pb})] + X_{Cu} X_{Pb} X_{Zn} [-59\,420 + 57\,730 (X_{Cu} - X_{Zn})$$
$$- 147\,680 (X_{Pb} - X_{Zn}) - 95\,970 (X_{Cu} - X_{Pb})].$$

This development which does not include any term function of T, must be used with caution at other temperatures. Figure 9 shows the zinc partial pressures calculated above the monophased liquid at 1150°C.

Notes on Materials Properties and Applications

A direct application of the Cu-Pb-Zn phase diagram is the use of zinc to remove copper from lead according to the Parkes' process [1948Hen, 1949Jol]. Lead is known to improve the workability of brasses [1905Gui]. However, above 1.5 mass% in brasses, it is no more soluble, is visible under the form of black dots scattered throughout the crystals [1912Joh, 1972Leo] and has a deleterious effect on the yield strength, the resistance to impact and the ductility of brasses, while affecting slightly the hardness [1906Gui, 1912Car, 1972Leo]. A copper alloy Cu-36Zn-3Pb (in mass%) prepared by spray deposition shows a Young's modulus of 99 GPa and a yield stress of 480 MPa [1999Mor].

Small amounts of Cu added to Pb-Zn liquid alloys increase the value of the viscous flow measured above the binodal temperatures [2000Neu]. The viscosity η of the liquid alloys vary according to an Arrhenius' law: $\eta = \eta^\circ \exp(-E_a/RT)$, where η° is viscosity at the temperature of infinity, E_a - activation energy. The viscosity of the $Zn_{95}Pb_5$ alloy, measured at 3.2 mPa·s at 600°C with an activation energy of 10.7 kJ·mol^{-1} goes down to 2.2 mPa·s at the same temperature for the $Zn_{90}Pb_5Cu_5$ alloy with an activation energy of 14.8 kJ·mol^{-1}.

Miscellaneous

Two alloys, Cu-39Zn-3Pb and Cu-40Zn-2Pb (in mass%), produced by melting recycles scraps were shown to present a high tendency to the formation of hardspots due to the presence of many impurities, even at concentrations lower than 0.2 mass% [2000Las]. Very difficult to observe due to their small size, their presence may be recognized by the dimples of the fracture surface after tensile testing.

References

[1905Gui] Guillet, M.L., "Research on Copper Alloys, Special Brasses and Quenched Bronzes" (in French), *Rev. Metall.*, **2**, 97-120 (1905) (Mechan. Prop., Experimental, 0)

[1906Gui] Guillet, M.L., "General Investigations on Special Brasses" (in French), *Rev. Metall.*, **3**, 159-204 (1906) (Mechan. Prop., Experimental, 1)

[1912Car] Carpenter, H.C.H., "The Effect of other Metals on the Structure of the β-Constitutent in Copper-Zinc Alloys", *J. Inst. Met.*, **8**, 59-73 (1912) (Mechan. Prop., Morphology, 2)

[1912Joh] Johnson, F., "The Influence of Tin and Lead on Microstructure of Brass", *J. Inst. Met.*, **7**, 201-217 (1912) (Morphology, 4)

[1914Par] Parravano, N., Mazzetti, C., Moretti, R., *Gazz. Chim. Ital.*, **44**(11), 475-502 (1914) (in Italian) (Phase Relations, Experimental, 12)

[1922Nic] Niclassen, H., "The System Copper-Zinc-Lead" (in German), *Forschungsarb. Metallkd.*, **7**, 2-9 (1922) (Experimental, Morphology, Phase Diagram, Phase Relations, 5)

[1929Bau1] Bauer, O., Hansen, M., "Influence of a Third Element on the Constitution of Brasses" (in German), *Z. Metallkd.*, **21**(5), 145-151 (1929) (Experimental, Phase Diagram, 37)

[1929Bau2] Bauer, O., Hansen, M., "Influence of a Third Element on the Constitution of Brasses. I. Lead Influence" (in German), *Z. Metallkd.*, **21**(6), 190-196 (1929) (Experimental, Phase Diagram, Morphology, 49)

[1929Phi] Phillips, A.J., "A Discussion of L. R. van Wert`s Paper, "The Effect of Lead on the (α + β)/β Equilibrium in a 60/40 Brass (Muntz Metal) Published in the November Issue of Metals and Alloys, **1**, 200 (1929)", *Metals and Alloys*, **1**(6), 262 (1929) (Experimental)

[1929Wer] van Wert, L.R., "The Effect of Lead on the (α + β)/β Equilibrium in a 60/40 Brass (Muntz Metal)", *Metals and Alloys*, **1**(5), 200-205 (1929) (Experimental, Morphology, Phase Relations, 13)

[1943Dan] Dannenmuller, M., "Miscibility Gap at the Liquid State in the Alloys", *Rev. Metall. (Paris)*, **40**, 85-90 (1943) (Phase Relation, Experimental, 9)

[1948Hen] Henglein, E., Koester, W., "About the Application of the Parkes' Process on the Basis of Alloys Systems. The Pb-Zn and Bi-Zn Systems with Ag and Cu" (in German), *Z. Metallkd.*, **39**, 391-400 (1948) (Experimental, Phase Diagram, 11)

[1948Jol] Jollivet, L., "About Equilibrium of the Lead-Copper-Zinc System in the Lead Corner" (in French), *Compt. Rend. Acad. Sci. Paris*, **226**, 2076-2077 (1948) (Experimental, Phase Diagram, Phase Relations, 4)

[1949Jol] Jollivet, M.L., "On the Equilibrium of the Lead-Rich Complex Systems Containing Some Zinc and other Elements" (in French), *Compt. Rend. Acad. Sci. Paris*, **228**, 1128-1130 (1949) (Experimental, Phase Relations, 2)

[1955Sei] Seith, W., Johnen, H., Wagner, J., "Miscibility Gaps in Molten Binary and Ternary Metallic Systems" (in German), *Z. Metallkd.*, **46**(11), 773-779 (1955) (Experimental, Phase Diagram, 20)

[1969Gue] Guertler, W., Guertler, M., Anastasiadias, E., "Copper-Zinc-Lead", *A Comp. of Const. Ternary Diagr. Met. Systems, Isr. Pro. Sci. Tr., Jerusalem*, 611-613 (1969) (Phase Diagram, Review, 7)

[1972Leo] Leoni, M., Fortina, G., "Investigation on the Solubility of Lead in Alpha and Duplex Brasses and on the Effects of Small Quaternary Additions on the Properties of these Alloys", *Final Report, INCRA Project 156b/194, Univ. of Missouri-Rolla*, **194**, 1-26 (1972) (Experimental, Mechanical Properties, Phase Relations, 8)

[1979Cha] Chang, Y.A., Neumann, J.P., Mikula, A., Goldberg, D., "Cu-Pb-Zn" in "*INCRA Monograph Series 6. Phase Diagrams and Thermodynamic Properties of Ternary Copper-Metal Systems*", NSRD, Washington, 643-651 (1979) (Phase Diagram, Review, 13)

[1979Dri] Drits, M.E., Bochvar, N.R., Guzei, L.S., Lysova, E.V., Padezhnova, Rokhlin, L.L., Turkina, N.I., "Cu-Pb-Te" (in Russian) in "*Binary and Multicomponent Copper-Base Systems*", Nauka, Moscow, 199 (1979) (Phase Diagram, Review, 3)

[1994Sur] Surapunt, S., Vasquez, R.R., Itagaki, K., "Activity Measurements in Liquid Cu-Zn-X (X = Pb, Ag, Au) Ternary Alloys" (in Japanese), *Shigen to Sozai,* **110**(8), 631-635 (1994) (Thermodyn., Experimental, 22)

[1998Jan] Jantzen, T., Spencer, P.J., "Thermodynamic Assessment of the Cu-Pb-Zn and Cu-Sn-Zn Systems", *Calphad*, **22**(3), 417-434 (1998) (Assessment, Phase Relations, Thermodyn., 33)

[1999Mor] Morris, D.G., "Recent Research on Advanced Copper Alloys: Possibilities for Osprey Spray Deposition?", *Powder Met.*, **42**(1), 20-26 (1999) (Electr. Prop., Experimental, Mechan. Prop., Phase Relations, Review, 35)

[2000Las] Lassman, S., "Hard-spots in Kupfer-Zinc Alloys" (in German), *Z. Metallkd.*, **91**(10), 868-873 (2000) (Morphology, Experimental, Mechan. Prop., 11)

[2000Neu] Neumann, H., Dong, C., Plevachuk, Yu., "The Viscosity of Liquid Immiscible Zn-Pb-Based Alloys", *Z. Metallkd.*, **91**(11), 933-936 (2000) (Experimental, Phys. Prop., Thermodyn., 9)

[2001Her] Hertz, J., "What will be done in the Future with O.J. Kleppa's Enthalpy Data Set?", *J. Alloys Compd.*, **321**(2), 201-222 (2001) (Phase Relations, Review, Thermodyn., 50)

[2003Bor] Borgrren, U., Selleby, M.,"A Thermodynamic Database for Special Brass", *J. Phase Equilib.,* **22**(2), 110-121 (2003) (Phase Relations, Thermodyn., 18)

[2006Leb] Lebrun, N., "Cu-Zn (Copper-Zinc)", MSIT Binary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), Materials Science International Services, GmbH, Stuttgart; to be published (2006) (Crys. Structure, Phase Diagram, Phase Realtaions, Assessment, 18)

[2006Sch] Schmid-Fetzer, R., Shcerban, O., Tomashik, V., Jialin, Y., "Cu-Pb (Copper-Lead)", MSIT Binary Evaluation Program, in *MSIT Workplace,* Effenberg, G. (Ed.), MSI, Materials Science International Services, GmbH, Stuttgart; to be published (2006) (Crys. Structure, Phase Diagram, Phase Relations, Assessment, 7)

Table 1: Investigations of the Cu-Pb-Zn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1914Par]	Thermal analysis	425-1043°C, the whole diagram, liquidus
[1922Nic]	Microscopic observations	599-968°C, the whole diagram, miscibility gap in the liquid phase
[1929Bau1]	Microscopic observations, thermal analysis	860-1000°C, > 52 mass% Cu, < 2.5 mass% Pb, isopleth diagram
[1929Bau2]	Microscopic observations	420-995°C, the whole diagram, miscibility gap in the liquid phase
[1943Dan]	Metallographic observations	400-900°C, < 2 mass% Pb, < 10 mass% Cu, miscibility gap in the liquid phase
[1948Hen]	Microscopic observations	327-1084°C, the whole diagram, liquidus
[1948Jol]	Microscopic observations	326-425°C, < 0.1 at.% Cu, < 0.1 at.% Zn, liquidus
[1955Sei]	Microscopic observations	500-1050°C, < 20 mass% Cu, isoplethic diagram, miscibility gap in the liquid phase
[1972Leo]	Microscopic observations	500-900°C, 30-42 mass% Cu, < 1 mass% Pb, solubility determination
[1994Sur]	Zinc activity measurements, isothermal isopiestic method	802°C, < 30 at.% Cu (measurement) 1150°C, the whole diagram (estimation)

Table 2: 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 a = 361.61	(α brass) dissolves up to 37.28 at.% Zn at 454°C [Mas2] at 300°C, 35.84 at.% Zn
η, (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
(Pb) < 327.502	*cF*4 $Fm\bar{3}m$ Cu	a = 495.02	[Mas2]
β, CuZn 902 - 454	*cI*2 $Im\bar{3}m$ W	a = 295.39	from 36.1 to 55.8 at.% Zn (β brass) at 47.5 at.% Zn [V-C2]
β´, CuZn < 468	*cP*2 $Pm\bar{3}m$ CsCl	a = 295.9	from 44.8 to 48.2 at.% Zn (ordered form of β brass) at 47.5 at.% Zn [V-C2]
γ, Cu_5Zn_8 < 834	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	a = 886.9	from 57 to 70 at.% Zn [Mas2, V-C2]
δ, $CuZn_3$ 700 - 560	*hP*3 $P\bar{6}$	a = 427.5 c = 259.0	from 72.5 to 76 at.% Zn [Mas2, V-C2]
ε, $CuZn_4$ < 598	*hP*2 $P6_3/mmc$ Mg	a = 274.18 c = 429.39	from 78 to 88 at.% Zn [Mas2, V-C2]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Cu	Zn	Pb
L′ + (Cu) ⇌ L′′ + β	886	U_1	L′	57.0	36.2	6.8
			(Cu)	68.6	31.4	0
			L′′	6.4	3.3	90.3
			β	63.7	36.3	0
L′ + β ⇌ L′′ + γ	825	U_2	L′	35.3	62.4	2.3
			β	44.7	55.3	0
			L′′	4.9	3.9	91.2
			γ	39.7	60.3	0
L′ + γ ⇌ L′ + δ	690	U_3	L′	18.7	80.7	0.6
			γ	30.6	69.4	0
			L′′	2.8	4.5	92.7
			δ	27.6	72.4	0
L + δ ⇌ L_2 + ε	590	U_4	L	10.3	89.4	0.3
			δ	24.5	75.5	0
			L_2	1.56	5.14	93.30
			ε	21.5	78.5	0
L + δ ⇌ γ + ε	555	U_5	L	1.57	3.96	94.47
L′ + ε ⇌ L′′ + (Zn)	422	U_6	L′	1.25	98.5	0.25
			ε	13.3	86.7	0
			L′′	0.62	5.78	93.6
			(Zn)	2.78	97.22	0
L + (Cu) ⇌ β + (Pb)	324	U_7	L	0.23	0.19	99.58
L + β ⇌ γ + (Pb)	322	U_8	L	0.16	0.47	99.37
L + γ ⇌ ε + (Pb)	320	U_9	L	0.10	1.00	98.90
L ⇌ ε + (Zn) + (Pb)	320	E	L	0.06	1.26	98.68

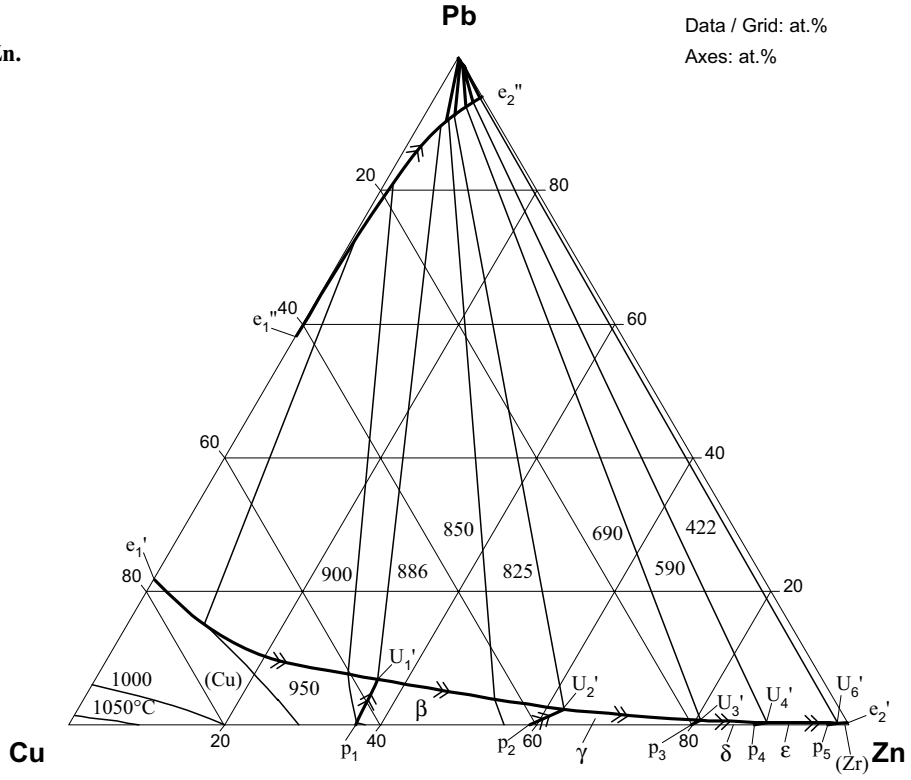

Fig. 1: Cu-Pb-Zn. Liquidus surface projection

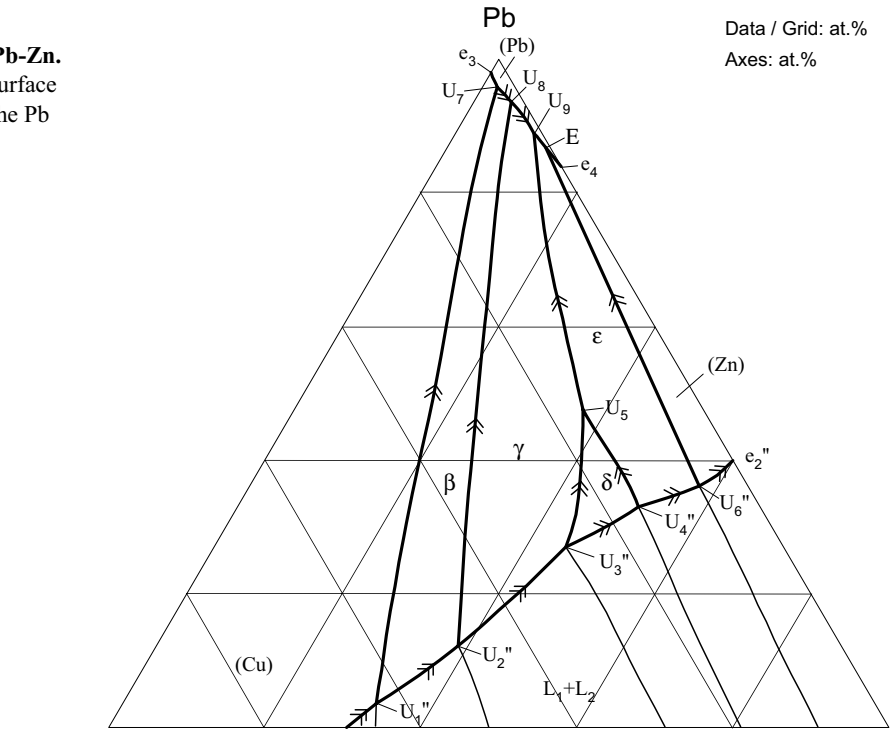

Fig. 2: Cu-Pb-Zn. The liquidus surface projection in the Pb rich corner

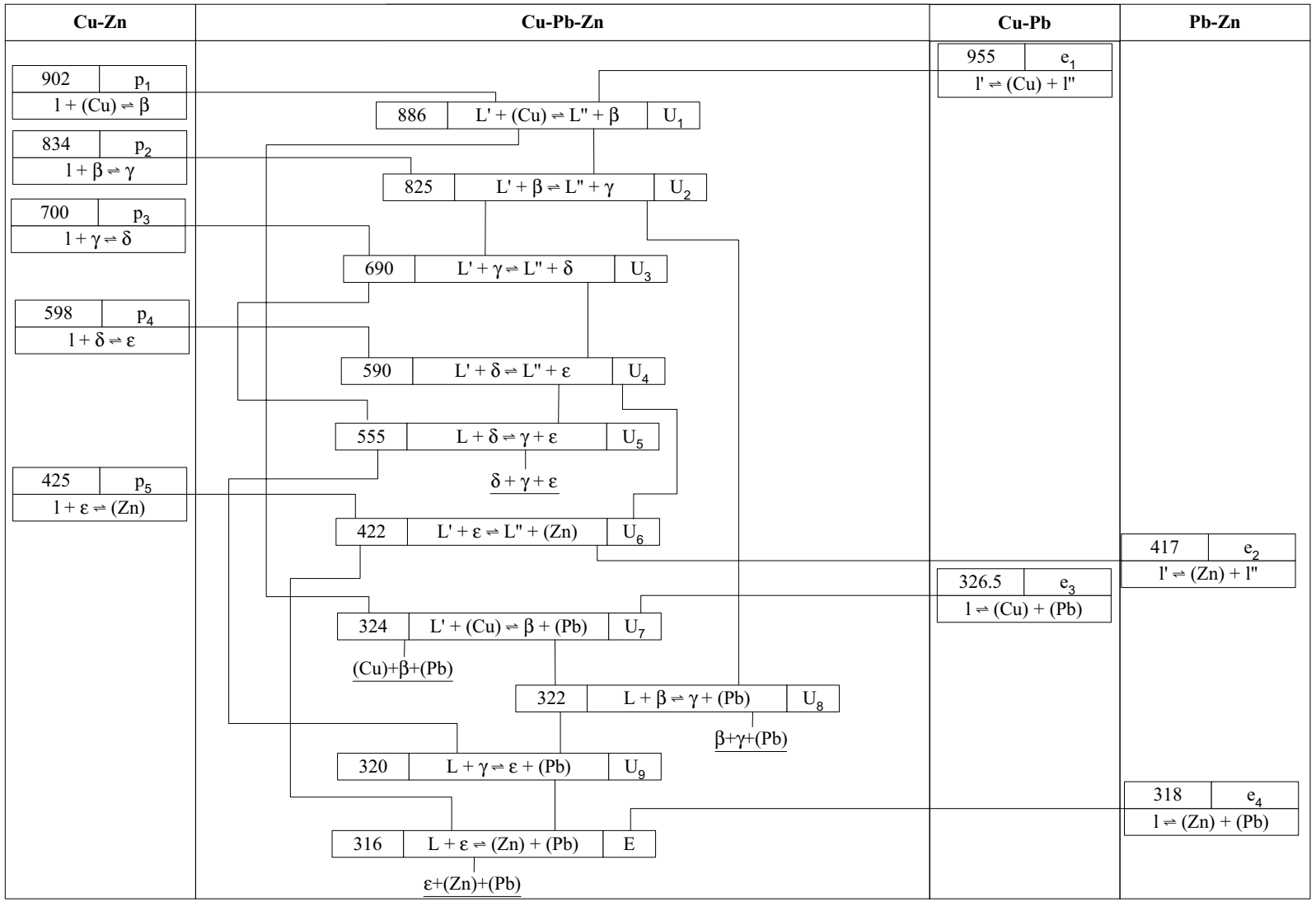

Fig. 3: Cu-Pb-Zn. Reaction scheme

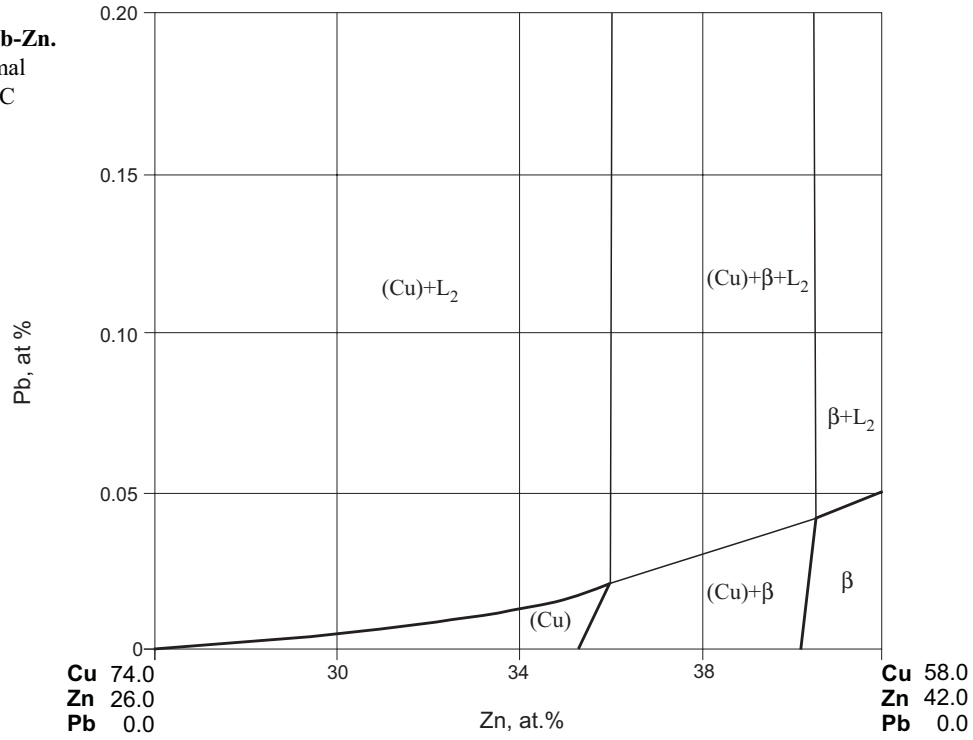

Fig. 4a: Cu-Pb-Zn. Partial isothermal section at 700°C

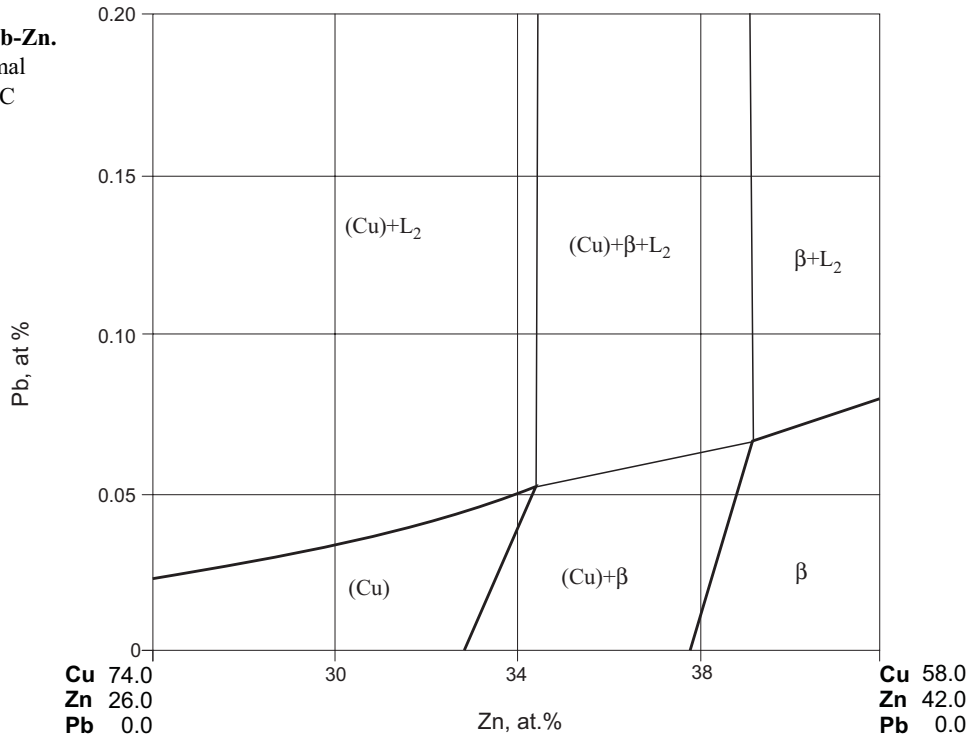

Fig. 4b: Cu-Pb-Zn. Partial isothermal section at 800°C

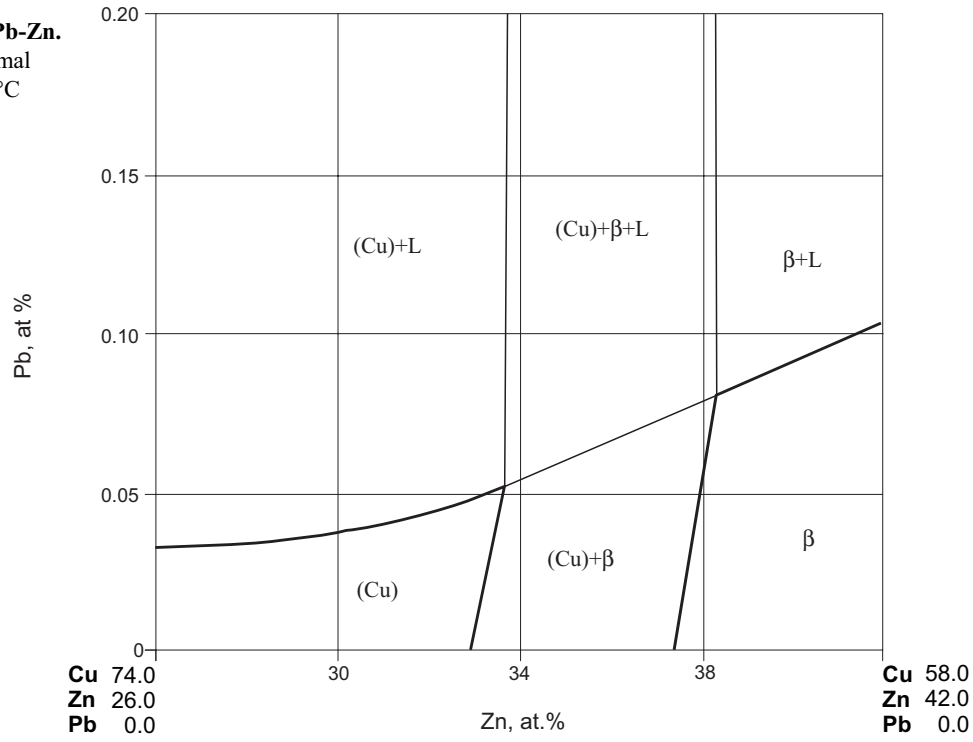

Fig. 4c: Cu-Pb-Zn. Partial isothermal section at 850°C

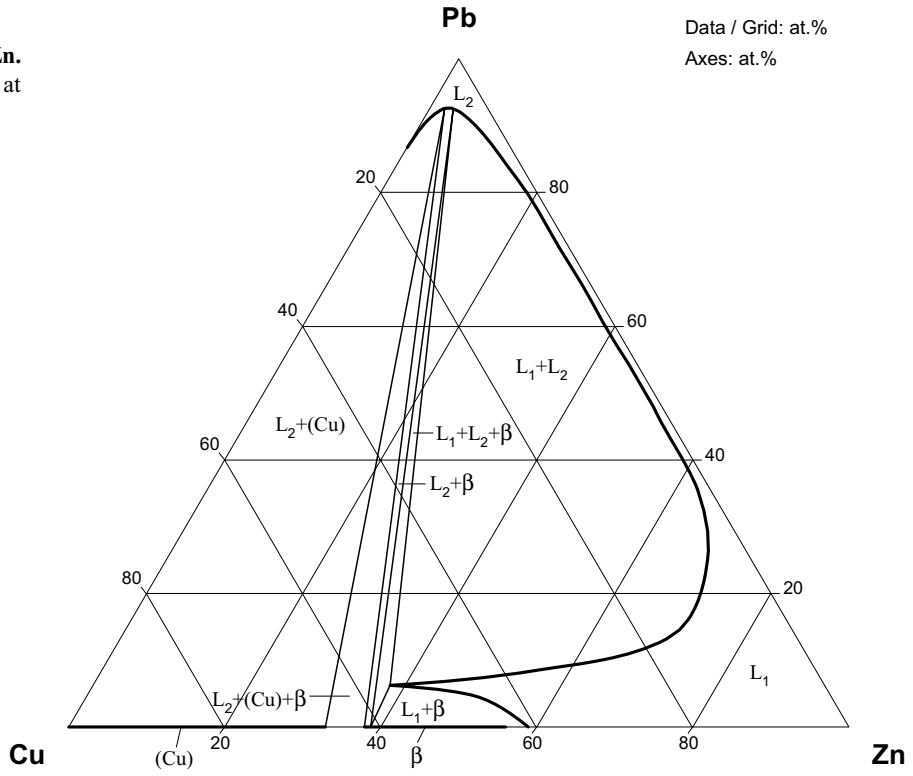

Fig. 5: Cu-Pb-Zn. Isothermal section at 835°C

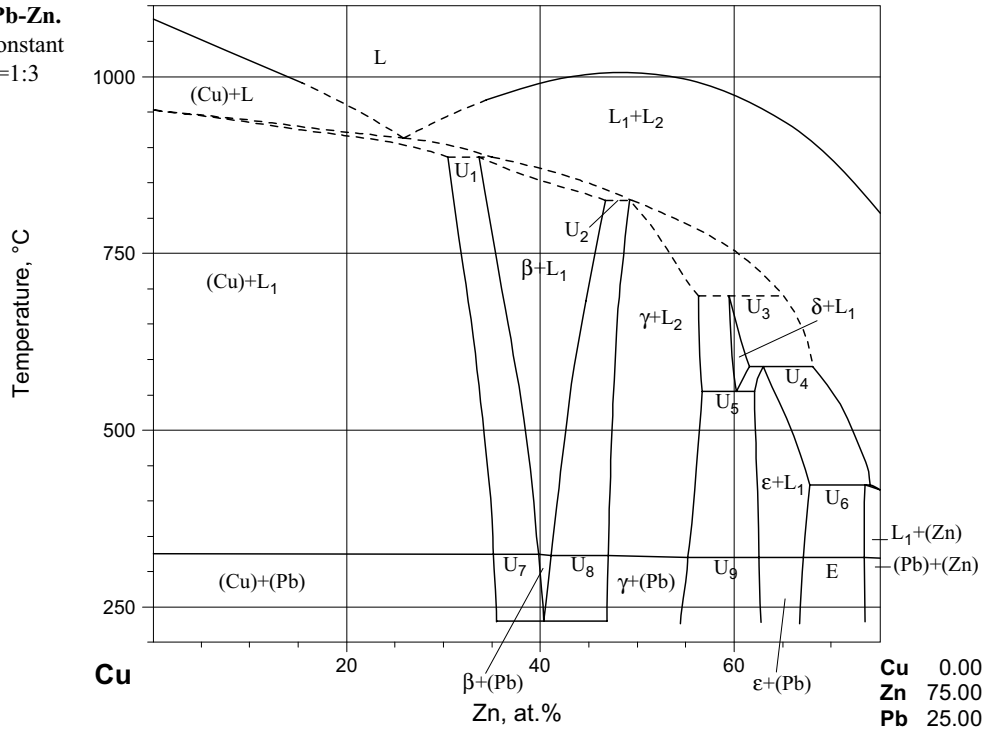

Fig. 6: Cu-Pb-Zn. Isopleth at a constant ratio of Pb:Zn=1:3

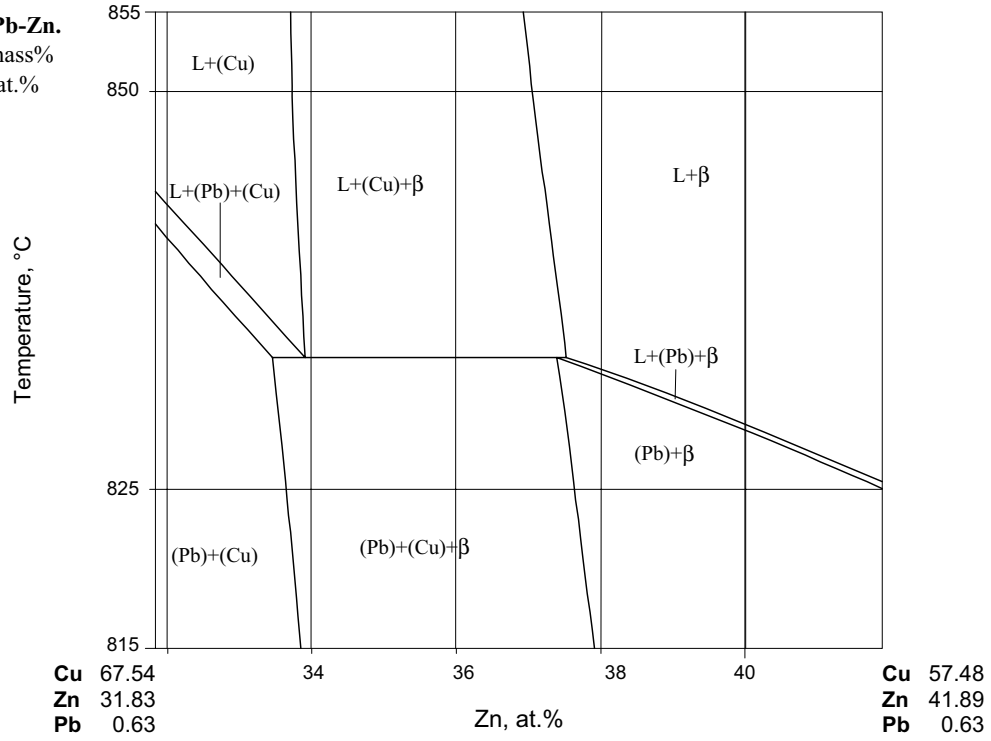

Fig. 7: Cu-Pb-Zn. Isopleth at 2 mass% Pb, plotted in at.%

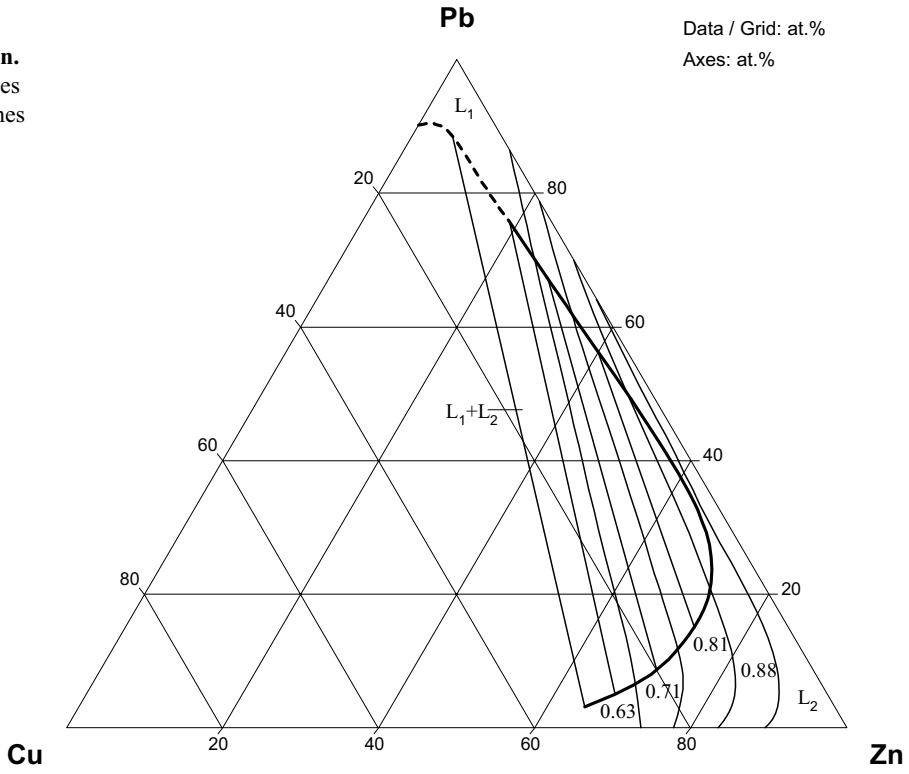

Fig. 8: Cu-Pb-Zn. Zinc isoactivity lines at 802°C and tie lines in the two liquidus domain

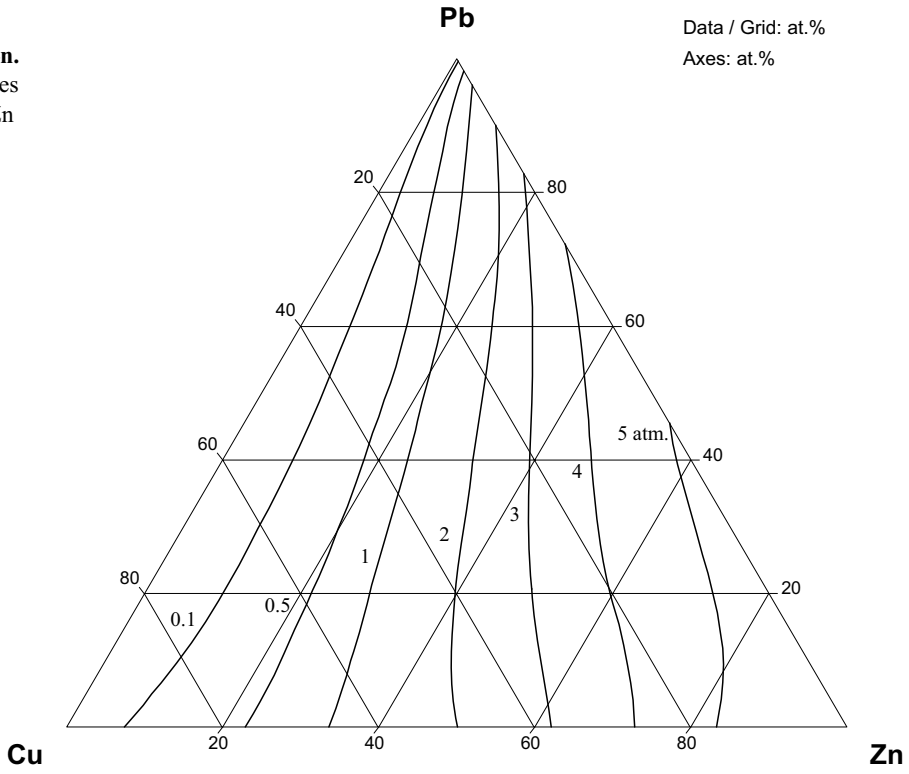

Fig. 9: Cu-Pb-Zn. Zinc vapor pressures above the Cu-Pb-Zn liquid alloys at 1150°C