Copper – Silicon – Zirconium

Suray Bhan, Nataliya Bochvar, Boris Kasper, Ortrud Kubaschewski,
Hari Kumar, Peter Rogl, Svitlana Ilyenko

Introduction

Information on the ternary system is rather limited. [1965Smi] showed three isothermal sections of the copper corner at 700, 1000 and 1050°C investigated by metallography. Also shown is a vertical section from Cu to "Zr_6Si_5" including a eutectic maximum at 1045°C and 97.28 at.% Cu, 1.36 at.% Zr and 1.36 at.% Si obtained by thermal analysis and metallographic methods. [1970Nic] reported this eutectic reaction at a temperature of 1055°C and at the composition 95.6 at.% Cu and 2.2 at.% Si using metallography and DTA. An isothermal section at 800°C was presented by [1974Spr1] based on 168 alloys revealing seven ternary compounds. The experimental techniques used were X-ray powder diffraction, electron microprobe analysis and chemical analysis. A projection of the liquidus surface for the Cu corner is due to [1974Spr1, 1974Spr2].
[1979Dri] reviewed the ternary system citing the work of [1965Smi] and [1974Spr1]. Crystal structures of the ternary compounds have been examined by [1967Gan, 1967Nic, 1972Spr, 1974Spr1, 1975And, 1983Thi]. The majority of the alloys were prepared by argon arc melting metal ingots of 99.5% min. purity [1972Spr, 1974Spr2]. A floating zone technique has been employed for some alloys in the region of the pseudobinary eutectic [1970Nic, 1974Spr1]. Some of the ternary compounds have been synthesized by reaction sintering of powder compacts [1967Gan, 1983Thi]. [1965Smi] used a Tamann induction furnace in graphite or alumina crucible and a protective melt of equal proportions of NaF, CaF_2 and SiO_2. After casting in metallic moulds the samples were annealed (800°C), cold worked (50%) and homogenized up to 240 h.

Binary Systems

The binary system Si-Zr have been accepted in the version of [Mas2]. The binary systems Cu-Si and Cu-Zr are taken from the MSIT Binary Evaluation Program [2002Leb], [2006Sem].

Solid Phases

Seven ternary compounds are established. All unary, binary and ternary solid phases are summarized in Table 1.

Quasibinary Systems

[1965Smi] investigated the copper rich part of the vertical section Cu-Zr_6Si_5. [1974Spr2] confirmed the quasibinary eutectic behavior and corrected the diagram replacing Zr_6Si_5 with the phase ZrCuSi established by [1967Nic, 1974Spr1]. Figure 1 shows the vertical section from [1974Spr2] with the inclusion of the homogeneity range (Cu) from [1965Smi]. The temperature for the eutectic reaction e_1(max) was given by [1965Smi] at 1045°C in agreement with that of [1970Nic] 1055°C and [1974Spr2] 1045°C. The composition of the eutectic reaction suggested by [1974Spr2] 95.1 at.% Cu, 2.45 at.% Zr and 2.45 at.% Si is in good agreement with [1970Nic] given at of 95.6 at.% Cu, 2.2 at.% Zr and 2.2 at.% Si. With respect to the much larger solid solubility of Si in (Cu) than that of Zr in (Cu), a reinvestigation of the precise location of the e_1(max) is recommended.

Invariant Equilibria

In the copper corner there are two invariant reactions, one three-phase reaction e_1(max) (see above) and one four-phase reaction E. The partial reaction scheme is given in Fig. 2.
The temperature and the composition of the ternary eutectic E has not been established yet.
ZrCuSi is reported by [1974Spr2] to form peritectically at a temperature of 1610 ± 50°C.

Liquidus Surface

Figure 3 shows the copper corner of the liquidus projection accepted from [1974Spr2]. The regions of primary crystallization of (Cu), $ZrCu_5$ and ZrCuSi are added to the diagram. The isotherms of the liquidus projection given by [1974Spr2] were omitted since these were rough estimates without experimental measurements.

Isothermal Sections

Figure 4 shows the isothermal section of the copper corner at 1000°C accepted from [1965Smi]. The solid solubility of Zr in (Cu) was adjusted to make it consistent with the accepted binary phase diagram. Figure 5 shows the modified version of the isothermal section for 800°C accepted mainly from [1974Spr1]. The authors showed small homogeneity ranges for the binary and ternary phases. However, all solid phases in the two binary sub-systems Cu-Zr and Si-Zr are shown as line compounds in the accepted binary phase diagrams. As no detailed information is available on the extension of the ternary compounds, these phases are considered without ranges of homogeneity. Thus the two-phase regions presented in the diagram [1974Spr1] are degenerated into single lines.
The two binary phases δ,Cu_5Si and $ZrCu_5$ were found later than the report by [1974Spr1] and are included in the present version.
The region of existence for Zr_3Si_2(Cu) was corrected assuming Cu-Si exchange at constant Zr content. The position of the compound τ_7 was reinterpreted keeping its location at a constant Zr-content of 50 at.% (as suggested in the text of [1974Spr1]) but accepting the higher Cu-content of ~3 at.% as shown in the original publication.
The location of the ternary compounds drawn in the isothermal section at 800°C by [1974Spr1] do not correspond to the chemical formulae. Assuming lattice vacancies, the positions for τ_1, τ_2 and τ_3 have been adjusted according to the experimentally determined compositions [1974Spr1].

Miscellaneous

[1955Rob] carried out investigations of reactions between molten copper and various disilicides including $ZrSi_2$ and observed the formation of complex phases of low melting points. [1986McR] investigated the electrical properties of the ternary compounds $ZrCu_xSi$ (x = 0, 0.5, 1.33) between 4.2 and 300 K.

References

[1955Rob] Robinson, D.A., Jenkins, I., "The Stability of Some Metal Silicides of Potential Value in High-Temperature Materials", *Plansee Proc., Reutte, Tyrol*, 187-198 (1955) (Experimental, 9)

[1965Smi] Smiryagin, A.P., Kvurt, O.S., "The Cu Corner of the Cu-Si-Zr System" (in Russian), *Trudy Gosudarst. Nauch. Issledovatel. i Proekt. Inst. po Obrabotke Tsvetn. Met*., **26**(24) (1965) (Phase Diagram, Experimental, *, 10)

[1967Gan] Ganglberger; E., Nowotny; H., Benesovsky; F., "Some New E-Phases" (in German), *Monatsh. Chem*., **98**, 95-99 (1967) (Crys. Structure, Experimental, 3)

[1967Nic] Nickl, J.J., Sprenger, H., "Single Crystals of the Ternary Compounds TiCuSi and ZrCuSi" (in German), *Naturwissenschaften*, **54**, 18 (1967) (Experimental, Crys. Structure, 1)

[1970Nic] Nickl, J.J., Sprenger, H., "Unidirectional Solidification in the System Cu-ZrCuSi" (in German), *Z. Metallkd.*, **61**, 229 (1970) (Experimental, 6)

[1972Spr] Sprenger, H., Nickl, J.J., "New Ternary Transition Metal Silicides and Germanides of the Fe_2P-Type" (in German), *J. Less-Common Met*., **27**, 163-168 (1972) (Experimental, Crys. Structure, 13)

[1974Spr1] Sprenger, H., "The Ternary Systems (Ti, Zr, Hf)-Cu-Si" (in German), *J. Less-Common Met*., **34**, 39-71 (1974) (Experimental, Crys. Structure, Phase Diagram, #, *, 79)

[1974Spr2] Sprenger, H., Nickl, J.J., "Unidirectional Solidification of the Cu/E-Phase Pseudobinary Eutectic" (in German*), J. Less-Common Met*., **34**, 73 (1974) (Experimental, Phase Diagram, #, *, 11)

[1975And] Andrukhiv, L.S., Lysenko, L.O., Yarmolyuk, Ya.P., Hladyshevsky, E.I., "On Structure of the Compounds $HfCuSi_2$, $HfCuGe_2$, $ZrCuSi_2$ and $ZrCuGe_2$" (in Ukrainian), *Dop. Akad. Nauk Ukrain. RSR, Ser. A, Fiz-Mat. Tekh. Nauki*, (7), 645-648 (1975) (Experimental, Crys. Structure, 6)

[1979Dri] Drits, M.E., Bochvar, N.R., Guzei, L.S., Lysova, E.V., Padezhnova, E.M., Rokhlin, L.L., Turkina, N.I., "*Binary and Multicomponent Copper-Base Systems*" (in Russian), Nauka, Moscow, 158-161 (1979) (Review, Phase Diagram, Crys. Structure, 2)

[1983Thi] Thirion, F., Venturini, G., Malaman, B., Steinmetz, J., Roques, B., "Crystal Structures of $Zr_6Cu_8Si_{12}$ and Hf_2CuGe_4 and Characterisation of a Family of Semimetallic Pseudolamellar Compounds with the Formula $ZrCu_xSi_2$ for x = 0.5, 1 and 1.33" (in French), *J. Less-Common Met*., **95**(1), 47-54 (1983) (Exprimental, Crys. Structure, 11)

[1986McR] McRae, E., Mareche, J. F., Steinmetz, J., Francois, M., "Electrical Properties of Certain Pseudo-lamellar Phases of Formula $Zr(Hf)Cu_xSi(Ge)_2$ (x = 0, 0.5, 1.33) and ZrSiS", *J. Less-Common Met*., **115**(1), 9-15 (1986) (Experimental, 10)

[2000Kov] Koval, Yu.N., "High Temperature Shape Memory Effect in Some Alloys and Compounds", *Mater. Sci. Forum*, **327-328**, 271-278 (2000) (Experimental, Mechan. Prop., 19)

[2002Leb] Lebrun, N., Dobatkina T., Kuznetsov V., Li, C., "Cu-Si (Copper - Silicon)", MSIT Binary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 20.12505.1.20, (2002) (Crys. Structure, Phase Diagram, Assessment, 23)

[2006Sem] Semenova, E., Sidorko, V., "Cu-Zr (Copper-Zirconium)", 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, Assessment, 31)

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	at 25°C [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C-diamond	a = 543.06	[Mas2] 0 to 0.002 at.% Cu
(βZr) 1855 - 863	*cI*2 $Im\bar{3}m$ W	a = 356.8	dissolves up to 5.7 at.% Cu [2006Sem] pure βZr [V-C2]
(αZr) < 863	*hP*2 $P6_3/mmc$ Mg	a = 323.2 c = 514.7	dissolves up to ~0.2 at.% Cu [2006Sem] pure αZr at 25°C [V-C2]

Phase / Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$ZrCu_5$ < 1032	*cF*24 $F\bar{4}3m$ $AuBe_5$ or *t*** Zr_2Cu_9	*a* = 687.0	[2006Sem] long period superstructure derived from $AuBe_5$ type
$Zr_{14}Cu_{51}$ ≤ 1112	*hP*68 *P*6/*m* $Gd_{14}Ag_{51}$	*a* = 1124.44 *c* = 828.15	[2006Sem]
Zr_3Cu_8 ≤ 1028	*oP*44 *Pnma* Hf_3Cu_8	*a* = 786.93 *b* = 851.47 *c* = 646.0	[2006Sem]
$Zr_{24}Cu_{13}$ 960 - 915	*o**37	*a* = 1119.0 *b* = 791.2 *c* = 998.48	[2006Sem]
Zr_7Cu_{10} < 935	*oC*68 *C*2*ca* Zr_7Ni_{10}	*a* = 1267.29 *b* = 931.63 *c* = 934/66	[2006Sem]
ZrCu(h) 960 - 725	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 326.6	at 49.9 at.% and 25°C [2006Sem]
ZrCu(l) < 140	*mP*4 $P2_1/m$ TiNi *mC*16 *Cm*	*a* = 328.2 *b* = 414.8 *c* = 524.9 β = 103.7° *a* = 633.7 *b* = 856.3 *c* = 534.5 β = 105.6°	martensite, [2000Kov] martensite, [2000Kov]
Zr_2Cu(h) 1025 - 950	*tI*6 *I*4/*mmm* $MoSi_2$	*a* = 322.04 *c* = 1183.2	[2006Sem]
Zr_2Cu(r) < 950	*tP*150	*a* = 1592.4 *c* = 1132.8	[2006Sem]
κ, Cu_7Si 842 - 552	*hP*2 $P6_3/mmc$ Mg	 *a* = 256.06 *c* = 418.46	11.05 to 14.5 at.% Si at 12.75 at.% Si [2002Leb]
β, ~Cu_6Si 853 - 787	*cI*2 $Im\bar{3}m$ W	 *a* = 285.4	14.2 to 16.2 at.% Si at 14.9 at.% Si [2002Leb]
δ, Cu_5Si(h) 824 - 711	*t***	*a* = 881.5 *c* = 790.3	17.6 to 19.6 at.% Si Sample was annealed at 700°C [2002Leb]
γ, Cu_5Si(r) < 729	*cP*20 $P4_132$	*a* = 619.8	17.15 to 17.6 at.% Si [2002Leb]

Phase / Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ε, $Cu_{15}Si_4$ < 800	*cI*76 $I\bar{4}3d$ $Cu_{15}Si_4$	*a* = 961.5	21.2 at.% Si [2002Leb]
η, $Cu_3Si(h_2)$ 859 - 558	*hR** $R\bar{3}m$ or *t***	*a* = 247 α = 109.74° *a* = 726.7 *c* = 789.2	23.4 to 24.9 at.% Si [2002Leb] [V-C2]
η', $Cu_3Si(h_1)$ 620 - 647	*hR** $R\bar{3}$	*a* = 472 α = 95.72°	23.2 to 25.2 at.% Si [2002Leb]
η'', Cu_3Si(r) < 570	*o***	*a* = 7676 *b* = 700 *c* = 2194	23.3 to 24.9 at.% Si [2002Leb]
$ZrSi_2$ < 1620	*oC*12 *Cmcm* $ZrSi_2$	*a* = 373 *b* = 1472 *c* = 367	[V-C2]
ZrSi(r) ≤ 1460	*oP*8 *Pnma* FeB	*a* = 699.5 *b* = 378.6 *c* = 529.6	[V-C2]
Zr_5Si_4(r) < 1860	*tP*36 $P4_12_12$ Zr_5Si_4	*a* = 712.25 *c* = 1300.0	[V-C2]
Zr_3Si_2 ≤ 2215	*tP*10 *P*4/*mbm* U_3Si_2	*a* = 708.2 *c* = 371.5	[V-C2]
Zr_2Si < 1925	*tI*12 *I*4/*mcm* $CuAl_2$	*a* = 660.9 *c* = 529.8	[V-C2]
$ZrSi_{1-x}Cu_x$	*oC*8 *Cmcm* CrB	 *a* = 376.3 *b* = 994.4 *c* = 374.7	[Mas2] *x* = 0.06 [V-C2] stabilized to low temperature τ_7, [1974Spr1]
ZrSi(h) 2210 - 1460		*a* = 375.7 *b* = 991.5 *c* = 374.0	*x* = 0.0 [V-C2]
* τ_1, $Zr_3Cu_4Si_6$	*tI*26 *I*4/*mmm* $Zr_3Cu_4Si_6$	*a* = 373.8 *c* = 2822.3	[V-C2] "$Zr_2Cu_3Si_4$", [1974Spr1]
* τ_2, $ZrCuSi_2$	*tP*8 *P*4/*nmm* $ZrCuSi_2$	*a* = 372.4 *c* = 902.9	[V-C2]

Phase / Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_3, Zr_2CuSi_4	*oC*28 *Cmcm* Hf_2CuGe_4	*a* = 370.4 *b* = 3291.0 *c* = 368.1	[V-C2]
* τ_4, $Zr_3Cu_4Si_4$	*oI*22 *Immm* $Gd_3Cu_4Ge_4$	*a* = 1309.0 *b* = 639.3 *c* = 393.4	[V-C2]
* τ_5, ZrCuSi	*oP*12 *Pnma* Co_2Si (TiNiSi)	*a* = 650.6 *b* = 392.1 *c* = 727.8	[V-C2]
* τ_6, $Zr_3Cu_4Si_2$	*hP*9 $P\bar{6}2m$ Fe_2P	*a* = 637.2 *c* = 389.0	[V-C2]
* τ_7, ~$Zr_{50}Cu_3Si_{47}$	*oC*8 *Cmcm* CrB	*a* = 376.3 *b* = 994.4 *c* = 374.7	[V-C2], [1974Spr1]

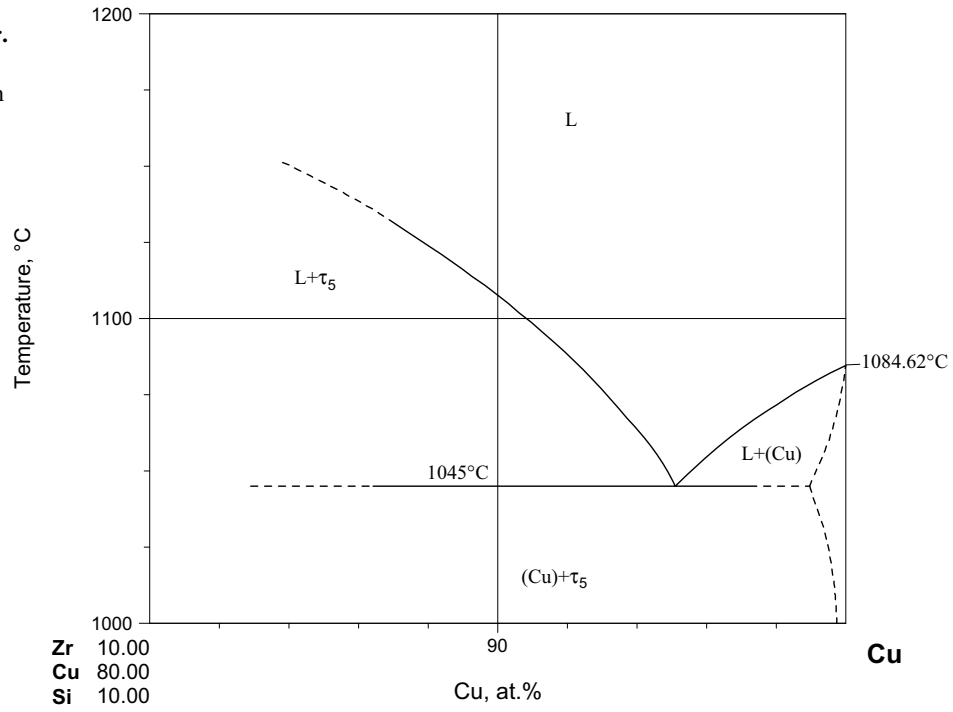

Fig. 1: Cu-Si-Zr. Part of the quasibinary section τ_5 - Cu

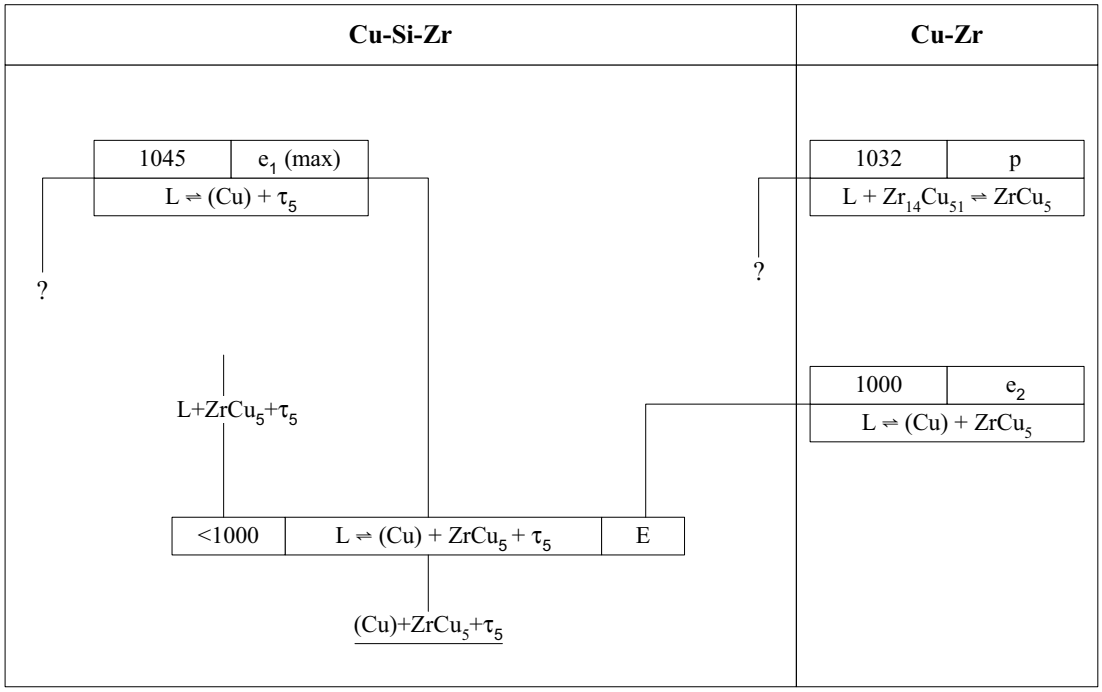

Fig. 2: Cu-Si-Zr. Partial reaction scheme

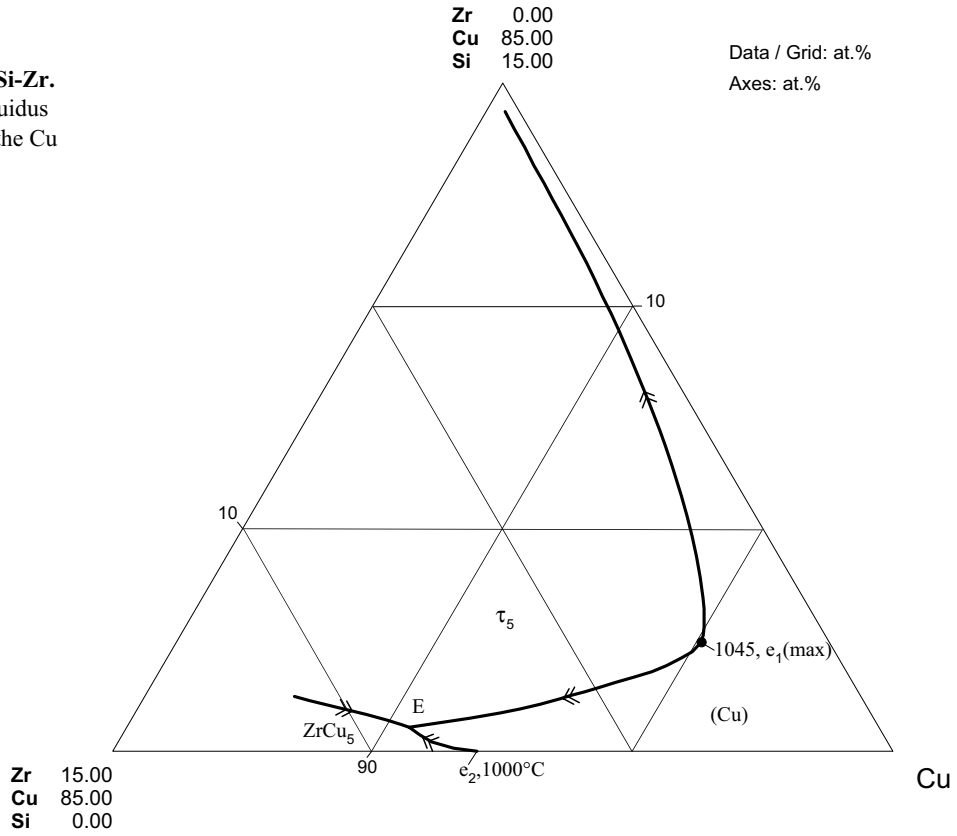

Fig. 3: Cu-Si-Zr. Schematic liquidus projection of the Cu corner

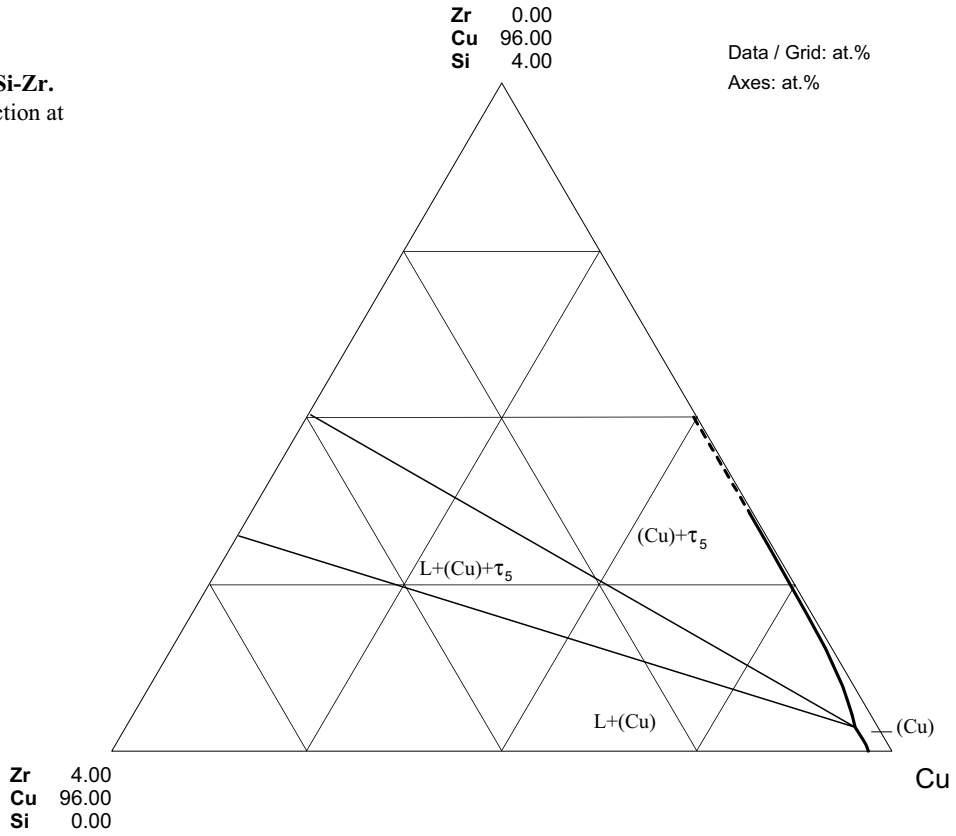

Fig. 4: Cu-Si-Zr. Isothermal section at 1000°C

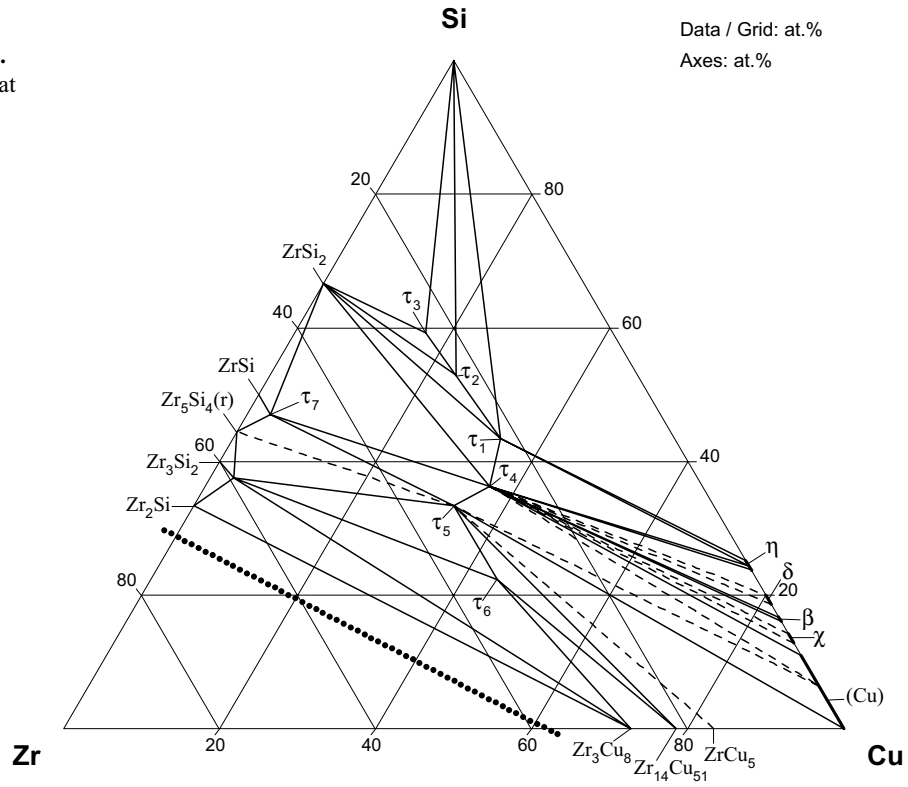

Fig. 5: Cu-Si-Zr. Isothermal section at 800°C