

## Chromium – Copper – Zirconium

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### Introduction

[1956Gla, 1956Zak, 1957Gla, 1957Zak, 1960Gla] investigated the Cu rich corner of the Cr–Cu–Zr diagram up to 3.5 mass% (Cr+Zr) by thermal and metallographic analyses and microhardness measurements. Several isothermal sections within the temperature range from 600 to 1040°C and five vertical sections were constructed. The existence of two invariant eutectic equilibria at 980 and 935°C and a quasibinary Cu–ZrCr<sub>2</sub> section were assumed. The boundaries of the (Cu) solid solution determined in Cr–Cu–Zr system proved much wider than those in the binary Cr–Cu and Cu–Zr systems. Using X-ray diffraction, [1967Kaw, 1972Fed] and [1979Kuz] have established that the ZrCr<sub>2</sub> compound does not occur in the composition field investigated (up to 20 at.% Zr and 5 at.% Cr); therefore the Cu–ZrCr<sub>2</sub> section cannot be quasibinary. [1967Kaw] determined the solubility of Cr and Zr in (Cu) alloys which had been cold worked, solution treated at 900 and 950°C and then quenched, to be 0.26 mass% Cr and 0.11 mass% Zr at 950°C. [1972Fed] obtained higher values for the solubility (0.4 mass% Cr and 0.3 mass% Zr) which appear to be overestimated because these values exceed the solubility of Cr and Zr in (Cu) in the boundary systems. The results of [1967Kaw] are preferential.

Using metallographic analysis, X-ray diffraction, DTA and the electron microprobe technique, [1979Kuz] investigated alloys with a constant Cr content (0.5, 1.5 and 5 at.%) and alloys on the Cu:Zr = 5:1 section. No ternary compounds were found; the presence of eutectic and peritectic invariant equilibria has been established at 963 and 997°C, respectively. Vertical sections and liquidus isotherms have been constructed based on the experimental data and thermodynamic calculations.

The Zr rich corner of the phase diagram (Zr–ZrCr<sub>2</sub>–Zr<sub>2</sub>Cu) has been investigated by [1977Tre, 1979Mal]. Using metallographic, thermal and dilatometric analyses, [1977Tre] constructed two isothermal sections at 900 and 750°C and a projection of a portion of the phase diagram (0 to 10 mass% (Cu+Zr)) on the concentration triangle plane. The materials used were Zr (99.9%), Cr (99.8%) and Cu (99.996%). No ternary phase was found in the system; the existence of a quasibinary section ZrCr<sub>2</sub>–Zr<sub>2</sub>Cu was assumed. Eutectic and eutectoid equilibria occur in the system at 945 ± 15 and 814 ± 8°C, respectively. Using X-ray analysis, [1979Mal] constructed three isothermal sections at 875, 800 and 700°C, confirming the data of [1977Tre].

[1995Zen1] investigated the structure of alloys in the Cu corner after annealing at 940°C for 4 h using microstructural and EDS analyses. The results showed that only three phases, (Cr), ZrCu<sub>5</sub> and (Cu), exist after the heat treatment procedure. This result is in good agreement with [1967Kaw, 1972Fed, 1979Kuz]. Using the CALPHAD method and reliable experimental data, [1995Zen1, 1995Zen2] calculated a number of isothermal and vertical sections together with the liquidus surface. The results of [1995Zen1, 1995Zen2] show that the quasibinary Cu–ZrCr<sub>2</sub> system does not exist.

### Binary Systems

The Cr–Zr, Cr–Cu and Cu–Zr phase diagrams are accepted from the MSIT Evaluation Program [2002Per], [2002Ans] and [2006Sem], respectively.

### Solid Phases

There is no ternary compound in the Cr–Cu–Zr system. The binary phases appearing in the ternary system as discussed are listed in Table 1. The solubility of Cr in the binary phases ZrCu<sub>5</sub>, Zr<sub>14</sub>Cu<sub>51</sub>, [1979Kuz] and Zr<sub>2</sub>Cu [1977Tre], and of Cu in ZrCr<sub>2</sub> [1977Tre] is virtually negligible.

### Quasibinary Systems

The existence of the quasibinary section  $\text{ZrCr}_2\text{--Zr}_2\text{Cu}$  has been assumed by [1977Tre, 1979Mal] where a binary eutectic between these compounds occur. The temperature and composition of this eutectic have not been established experimentally. According to the calculation of [1995Zen2], the eutectic reaction takes place at  $978^\circ\text{C}$  and 66.1 at.% Zr, 3.2 at.% Cr, 30.7 at.% Cu.

### Invariant Equilibria

In the Cu rich corner of the diagram, two invariant equilibria have been found: a transition reaction  $U_3$  at  $997^\circ\text{C}$  and a eutectic reaction  $E_1$  at  $963^\circ\text{C}$  [1979Kuz]. Inside the  $\text{Zr--ZrCr}_2\text{--Zr}_2\text{Cu}$  field, two invariant equilibria have been found. These are a eutectic  $E_2$  at  $945 \pm 15^\circ\text{C}$  and a eutectoid  $E_6$  at  $814 \pm 8^\circ\text{C}$  [1977Tre]. The temperatures of the invariant reactions calculated by [1995Zen2] for  $U_3$  ( $1001^\circ\text{C}$ ) and  $E_1$  ( $963^\circ\text{C}$ ) were close to the experimental data in the Cu corner. In the Zr corner, the calculated values are  $966^\circ\text{C}$  for  $E_2$  and  $807^\circ\text{C}$  for  $E_6$ . [1995Zen2] calculated other invariant equilibria including the three-phase equilibria of the saddle points  $e_5(\text{max})$ ,  $e_9(\text{max})$  and  $e_{10}(\text{max})$ . However, [1995Zen1], [1995Zen2] did not consider the  $\text{Zr}_{13}\text{Cu}_{24}$  compound of the binary Cu–Zr system which was accepted after [2006Sem]. Therefore, we introduce three speculative invariant reactions ( $U_4$ ,  $U_5$ ,  $U_6$ ) in the middle part of Cr–Cu–Zr phase diagram. The reaction scheme is shown in Figs. 1a, 1b. The compositions of the phases of the invariant reactions are presented in Table 2. The compositions of liquid phase are given after [1995Zen2] except for that of point  $E_1$ . The calculated eutectic liquid composition ( $E_1$ ) is 7.717 at.% Zr and 0.706 at.% Cr that is close to 7.8 at.% Zr and 0.5 at.% Cr determined experimentally by [1979Kuz]. The reaction temperatures of points  $E_1$ ,  $E_2$  and  $E_6$  are presented according to [1979Kuz, 1977Tre], the rest after [1995Zen2].

### Liquidus and Solvus Surfaces

The calculated liquidus surface is presented in Fig. 2. It is based on data of [1995Zen1, 1995Zen2], however, the part of the liquidus surface between points  $U_6$  and  $U_4$  was constructed here speculatively. Figures 3 and 4 show the projection of the solvus surfaces of the ( $\beta\text{Zr}$ ) and (Cu) phases, respectively. The solvus surfaces of the ( $\alpha\text{Zr}$ ) phase are also displayed, which appear below  $822^\circ\text{C}$  ( $e_{16}$ ) (Fig. 3). The compositions of the ( $\beta\text{Zr}$ ) phase and the (Cu) phase at points  $E_2$ ,  $E_1$  and  $E_6$  were calculated by [1995Zen2].

### Isothermal Sections

The isothermal section at room temperature is given in Fig. 5 as an overview, based on all the reported solid state equilibria. The homogeneity range of  $\alpha\text{ZrCr}_2$  ( $\sim 66$  to  $\sim 68$  at.% Cr at  $300^\circ\text{C}$ , [2002Per]) is disregarded. The mutual solubilities of the other phases are small. The equilibria are estimated based on the presented reaction scheme (Fig. 1). In the Cu rich corner, two isothermal sections have been constructed by [1967Kaw] at  $950$  and  $900^\circ\text{C}$  (Fig. 6 and Fig. 7). The solubilities in (Cu) are (0.2 mass% Cr + 0.1 mass% Zr) at  $950^\circ\text{C}$  and ( $\sim 0.14$  mass% Cr +  $\sim 0.08$  mass% Zr) at  $900^\circ\text{C}$ .

### Temperature – Composition Sections

Two vertical sections at 0.5 and 1.5 at.% Cr are presented in Fig. 8 and Fig. 9 [1979Kuz]. The section with constant Cr content of 0.5 at.% passes through the ternary eutectic point  $E_1$ .

### Notes on Materials Properties and Applications

The Cr–Cu–Zr alloys have long been known as a series of copper alloys that possesses high strength and high conductivity. In particular, the high electrical and thermal conductivity of these alloys have been used for many applications such as trolley wire, electrode material for resistance welding and materials for thermonuclear reactors. The properties of Cr–Cu–Zr alloys depend on the methods of preparation and the heat treatment conditions. These questions have been the subject of much discussion in the literature.

[2002Dur, 2002Iva, 2002Mer] investigated the physico-mechanical properties (electrical conductivity, hardness, strength and ductility) of Cr-Cu-Zr alloys as a function of cooling rate after solution annealing, [2002Iva], the temperatures of heat treatment, [2002Mer], cold deformation before aging [2002Dur].

[1999Mor] gave a review of spray deposition of high conductivity Cr-Cu-Zr alloys. Two features of interest in spray formed and processed Cr-Cu-Zr alloys have been reported: the possibility for ductile Cr globules to elongate as fine strengthening fibres during hot and cold mechanical working and the possibility of improving specific properties by the presence of dispersed oxide particles.

[1995Sou] considered the possibility of using a composition of  $\text{Zr}(\text{Cr}_{1-x}\text{Cu}_x)_2$  at  $x = 0.1; 0.2$  synthesized with the C14 or C15 type structures as electrodes in hydride batteries.

[1972Suz] investigated the precipitation processes of Cr-Cu-Zr alloys after quenching at  $950^\circ\text{C}$  with subsequent aging. The precipitation diagram (the time-temperature transformation, TTT, diagram) was constructed, which was used to account for the property changes during isothermal aging. [1987Har] reviewed copper-based materials (in particular, Cr-Cu-Zr alloys) for use in fusion reactors. [1997Fab] investigated the effects of neutron irradiation on the mechanical properties of Cr-Cu-Zr alloys for use in thermonuclear reactors.

A series of works were devoted to the study of Cr-Cu-Zr alloys with an ultra fine grain structure [1972Sar, 1993Bat, 1993Spa, 1994Cor, 1997Cor, 1997Anz1, 1997Anz2, 1997Lop, 2000Hol, 2001Tu, 2002Vin, 2003Qi, 2004Vin]. The structure, thermal stability and properties of Cr-Cu-Zr alloys with ultra fine grains produced by equal-channel angular pressing have been investigated as a function of alloying element concentration by [2002Vin, 2004Vin]. A non-linear relationship between the parameters of the rapidly solidified aging processes and mechanical and electrical properties of Cr-Cu-Zr alloys was established by use of an artificial neural network [2003Su, 2004Su]. [2001Tu, 2003Qi] investigated the friction and wear behavior of peak aged Cr-Cu-Zr alloys by dry sliding against a brass counterface on a pin-on-disk tester.

The formation of fine and coherent precipitates in the Cu-matrix improve the hardness and wear resistance of the Cr-Cu-Zr alloys. [2000Hol] estimated that a fine dispersion of precipitates with a mean size of 2.3 nm produced after hot isostatic pressing of Cu-base alloys with 0.75 mass% Cr and 0.105 mass% Zr are responsible for the mechanical strength of the aged alloy. [1997Anz1, 1997Anz2] investigated the possibility of attaining a homogeneous fine cellular structure during continuous casting of a Cu base alloy having 1.11 mass% Cr and 0.12 mass% Zr, for the achievement of the required mechanical properties. [1994Cor, 1997Cor] produced the Cr-Cu-Zr alloy powders by water atomization and consolidation by warm extrusion. The strengthening observed was interpreted in terms of theories of precipitation and dispersion strengthening. [1993Spa] showed the strong influence of cooling and solidification rates on the structure of a cast Cr-Cu-Zr alloy. [1997Lop] showed that rapidly solidified and aged Cr-Cu-Zr alloys have a good combination of electrical properties, conductivity and microhardness.

For the development of materials with high conductivity and high strength, [1998Mih] investigated the solidification structure, cold worked structure and aging characteristics of a Cu base alloy with 15 mass% Cr and 0.15 mass% Zr. [1991Pia] carried out tensile tests at different temperatures on a heat treatable Cu base alloy having 0.6 mass% Cr and 0.08 mass% Zr, of interest for nuclear fusion reactor applications as a primary heat sink material. [1996Tsu] tested a Cu-base alloy having 1 mass% Cr and 1 mass% Zr as heat sink material for the surface heat flux in the first wall in high power density devices.

### Miscellaneous

[1974Nov] investigated the morphology and structure of the precipitated phases in a Cu-0.33 mass% Cr-0.07 mass% Zr alloy during aging, using the method of diffraction electron microscopy.

A structural analysis of the hardening phases precipitated in the Cu matrix of Cr-Cu-Zr alloys after different heat treatments was undertaken by [2000Zha, 2001Bat, 2003Bat, 2003Hua]. Using a scanning electronic microscope and energy dispersive X-ray spectroscopy and a transmission electron microscope, [2003Hua] has shown some types of phases in specimens of a Cu-base alloy having 0.31 mass% Cr and 0.21 mass% Zr after quenching and aging; Cu matrix, (Cr), the coarse precipitation of  $\text{ZrCu}_5$  and the fine precipitation of  $\text{Zr}_{14}\text{Cu}_{51}$ . [2001Bat, 2003Bat] has shown that precipitation in a Cu base alloy with 1 mass% Cr and 1 mass% Zr, takes place through the formation of a metastable ordered phase. [2000Zha] has shown that it

enhances the precipitation hardening effect. The major mechanism of this enhancement may be through an increase in the Cr rich precipitate nucleation rate and precipitate/matrix interfacial energy.

The recrystallization kinetics of Cr-Cu-Zr alloys was investigated by [1973Nag, 1979Fed, 1994Mor].

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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	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 361.46$	dissolves 0.12 at.% Zr at 1000°C [2006Sem] and 0.82 at.% Cr at 1075°C [2002Ans] pure Cu at 25°C [Mas2]
(Cr) < 1863	<i>cI2</i> <i>Im<math>\bar{3}m</math></i> W	$a = 288.48$	Dissolves 0.6 at.% Zr at 1592°C] [2002Per] and 0.28 at.% Cu at 1800°C [2002Ans] pure Cr at 25°C [Mas2]
( $\beta$ Zr) 1855 - 863	<i>cI2</i> <i>Im<math>\bar{3}m</math></i> W	$a = 360.90$	dissolves up to 5.7 at.% Cu at 995°C [2006Sem] and 8.4 at.% Cr at 1332°C [2002Per] [2006Sem]
( $\alpha$ Zr) < 863	<i>hP2</i> <i>P6<math>_3</math>/mmc</i> Mg	$a = 323.16$ $c = 514.75$	Dissolves ~ 0.2 at.% Cu at 822°C [2006Sem] and 0.5 at.% Cr at 831°C [2002Per] at 25°C [Mas2]
ZrCu <sub>5</sub> < 1032	<i>cF24</i> <i>F<math>\bar{4}3m</math></i> AuBe <sub>5</sub>	$a = 687.0$	[2006Sem]
Zr <sub>14</sub> Cu <sub>51</sub> < 1112	<i>hP68</i> <i>P6/m</i> Gd <sub>14</sub> Ag <sub>51</sub>	$a = 1124.44$ $c = 828.15$	[2006Sem]
Zr <sub>3</sub> Cu <sub>8</sub> < 1028	<i>oP44</i> <i>Pnma</i> Hf <sub>3</sub> Cu <sub>8</sub>	$a = 786.93$ $b = 815.47$ $c = 998.48$	[2006Sem]
Zr <sub>13</sub> Cu <sub>24</sub> 960 - 915	<i>o*37</i>	$a = 1119.0$ $b = 791.2$ $c = 646.0$	[2006Sem]
Zr <sub>7</sub> Cu <sub>10</sub> < 935	<i>oC68</i> <i>C2ca</i> Zr <sub>7</sub> Ni <sub>10</sub>	$a = 1267.29$ $b = 931.63$ $c = 934.66$	[2006Sem]

Phase Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ZrCu 960 - 725	<i>cP2</i> <i>Pm<math>\bar{3}m</math></i> CsCl	$a = 325.87$	[2006Sem]
Zr <sub>2</sub> Cu(h) 1025 - 950	<i>tI6</i> <i>I4/mmm</i> MoSi <sub>2</sub>	$a = 322.04$ $c = 1118.32$	[2006Sem]
Zr <sub>2</sub> Cu(r) < 950	<i>tP150</i>	$a = 1592.4$ $c = 1132.8$	[2006Sem]
$\gamma$ ZrCr <sub>2</sub> 1677 - 1624	<i>hP12</i> <i>P6<sub>3</sub>/mmc</i> MgZn <sub>2</sub>	$a = 507.2$ $c = 828.9$	[2002Per]
$\beta$ ZrCr <sub>2</sub> 1624 - 1546	<i>hP24</i> <i>P6<sub>3</sub>/mmc</i> MgNi <sub>2</sub>	$a = 510.0$ $c = 1661$	[2002Per]
$\alpha$ ZrCr <sub>2</sub> < 1560	<i>cF24</i> <i>Fd<math>\bar{3}m</math></i> MgCu <sub>2</sub>	$a = 720.4$	[2002Per]

**Table 2:** Invariant Equilibria

Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Zr	Cr	Cu
$L + \beta\text{ZrCr}_2 \rightleftharpoons (\text{Cr}) + \alpha\text{ZrCr}_2$	1547	$U_1$	L	18.3	75.6	6.1
			$\beta\text{ZrCr}_2$	~33.3	~66.7	~0
			(Cr)	~0	~100	~0
			$\alpha\text{ZrCr}_2$	33.3	66.7	0
$L + \alpha\text{ZrCr}_2 \rightleftharpoons \text{Zr}_{14}\text{Cu}_{51}$	1100	$e_5$ (max)	L	20.5	1.4	78.1
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{Zr}_{14}\text{Cu}_{51}$	21.54	~0	78.46
$L + \alpha\text{ZrCr}_2 \rightleftharpoons (\text{Cr}) + \text{Zr}_{14}\text{Cu}_{51}$	1092	$U_2$	L	18.0	1.4	80.6
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			(Cr)	~0	~100	~0
			$\text{Zr}_{14}\text{Cu}_{51}$	21.54	0	78.46
$L + \text{Zr}_{14}\text{Cu}_{51} \rightleftharpoons \text{ZrCu}_5 + (\text{Cr})$	997 *	$U_3$	L	10.2	0.8	89.0
			$\text{Zr}_{14}\text{Cu}_{51}$	21.54	0	78.46
			$\text{ZrCu}_5$	16.7	0	83.3
			(Cr)	~0	~100	~0
$L \rightleftharpoons \alpha\text{ZrCr}_2 + \text{Zr}_2\text{Cu}$	978	$e_9$ (max)	L	66.1	3.2	30.7
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{Zr}_2\text{Cu}$	66.7	0	33.3



Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Zr	Cr	Cu
$L \rightleftharpoons \alpha\text{ZrCr}_2 + \text{Zr}_2\text{Cu} + (\beta\text{Zr})$	$945 \pm 15$ *	$E_2$	L	70.3	4.0	25.7
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{Zr}_2\text{Cu}$	66.7	0	33.3
			$(\beta\text{Zr})$	94.9	1.4	3.7
$L \rightleftharpoons \text{ZrCu}_5 + (\text{Cu}) + (\text{Cr})$	963 *	$E_1$	L	7.8 *	0.5 *	91.7 *
			$\text{ZrCu}_5$	16.7	0	83.3
			(Cu)	0.11	0.36	99.53
			(Cr)	~0	~100	~0
$L \rightleftharpoons \alpha\text{ZrCr}_2 + \text{ZrCu}$	927	$e_{10}(\text{max})$	L	48.7	0.6	50.7
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{ZrCu}$	50	0	50
$L \rightleftharpoons \alpha\text{ZrCr}_2 + \text{ZrCu} + \text{Zr}_2\text{Cu}$	$\leq 915$	$E_4$	L	53.7	0.8	45.5
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{ZrCu}$	50	0	50
			$\text{Zr}_2\text{Cu}$	66.7	0	33.3
$L \rightleftharpoons \alpha\text{ZrCr}_2 + \text{Zr}_7\text{Cu}_{10} + \text{ZrCu}$	887.6	$E_5$	L	42.7	0.3	57
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$\text{Zr}_7\text{Cu}_{10}$	41.18	0	58.82
			$\text{ZrCu}$	50	0	50
$(\beta\text{Zr}) \rightleftharpoons \alpha\text{ZrCr}_2 + (\alpha\text{Zr}) + \text{Zr}_2\text{Cu}$	$814 \pm 8$ *	$E_6$	$(\beta\text{Zr})$	97.2	0.99	1.81
			$\alpha\text{ZrCr}_2$	~33.3	~66.7	~0
			$(\alpha\text{Zr})$	~99.6	~0.2	~0.2
			$\text{Zr}_2\text{Cu}$	66.7	0	50

\* - experimental data, the rest – calculated data

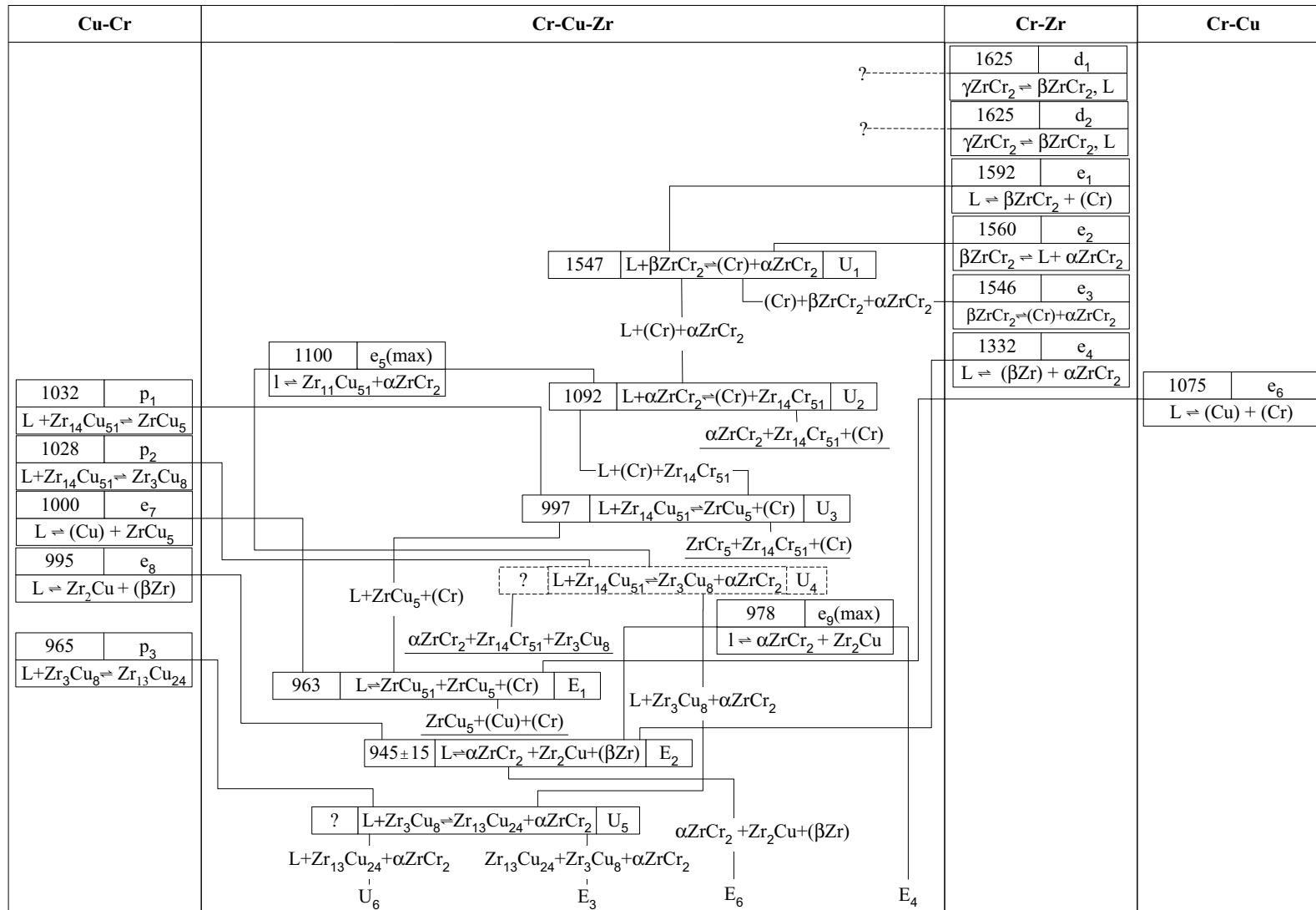
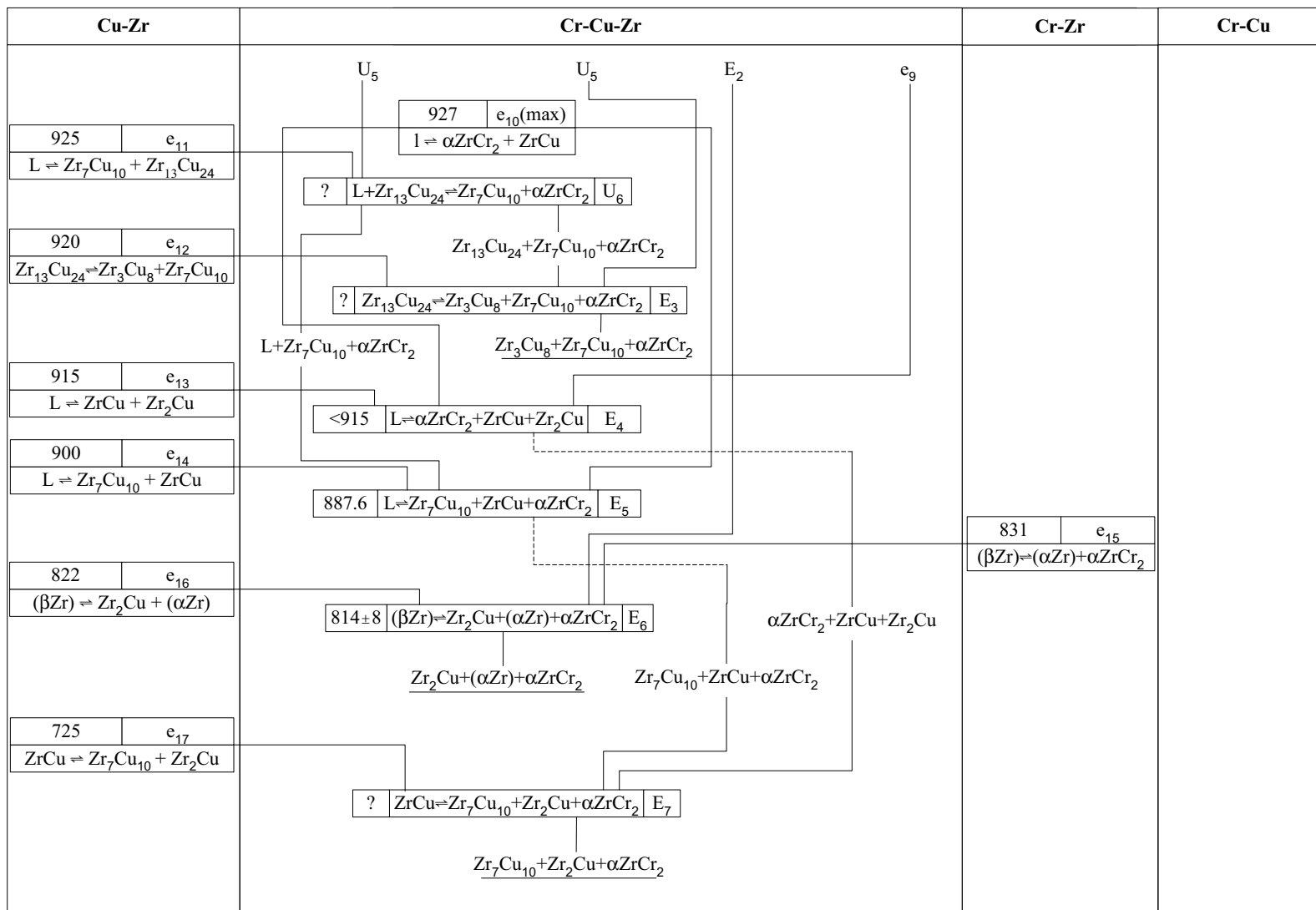
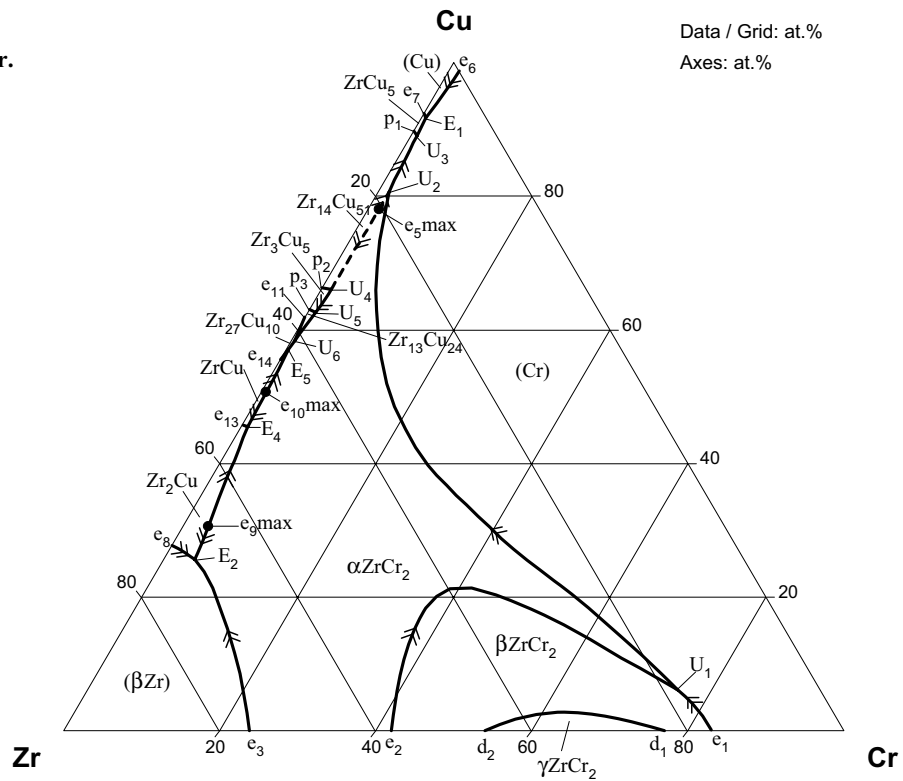


Fig. 1a: Cr-Cu-Zr. Reaction scheme, part 1

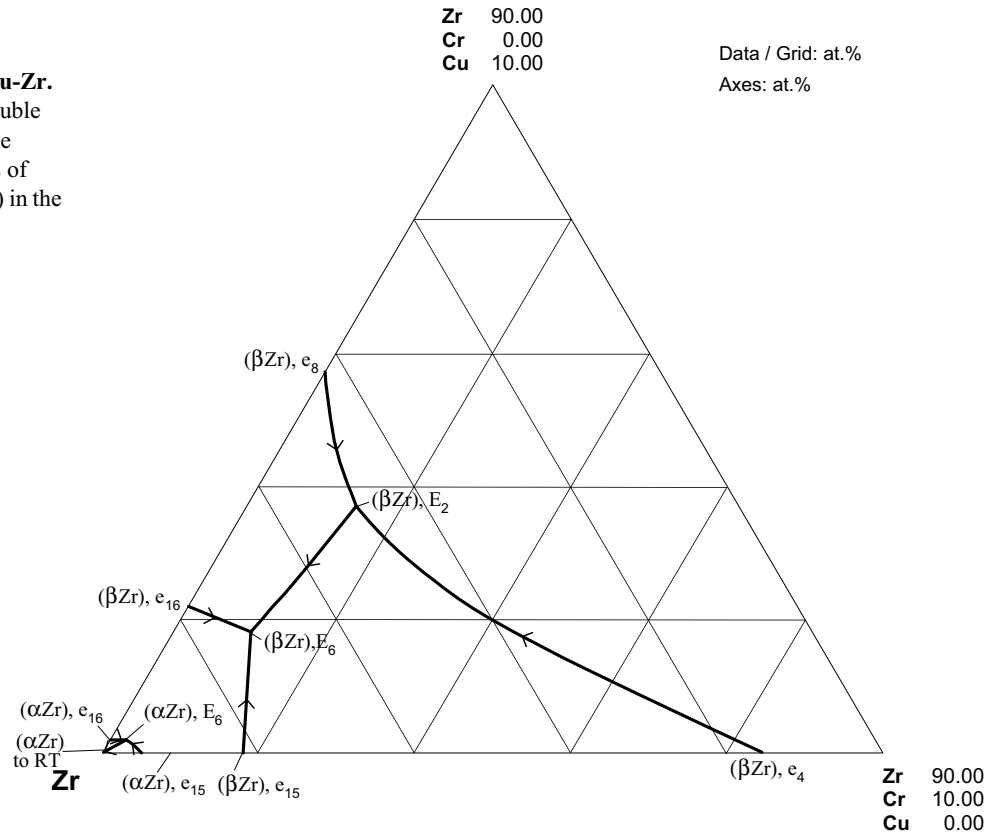


**Fig. 1b: Cr-Cu-Zr.** Reaction scheme, part 2

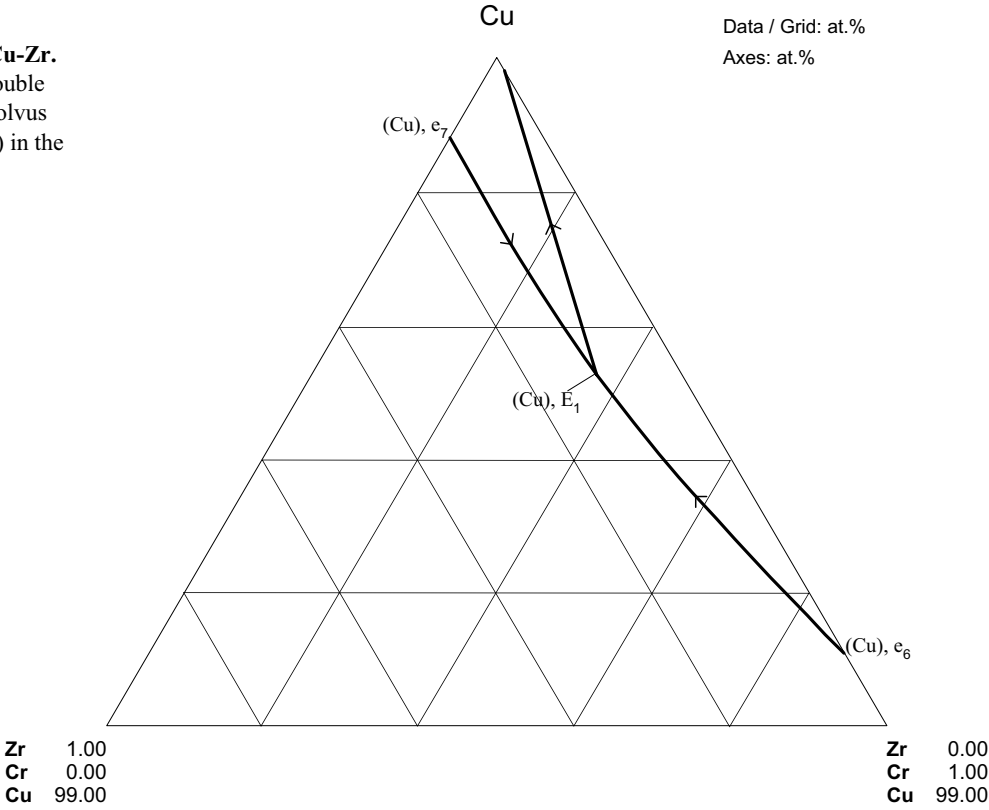
**Fig. 2: Cr-Cu-Zr.**  
Liquidus surface



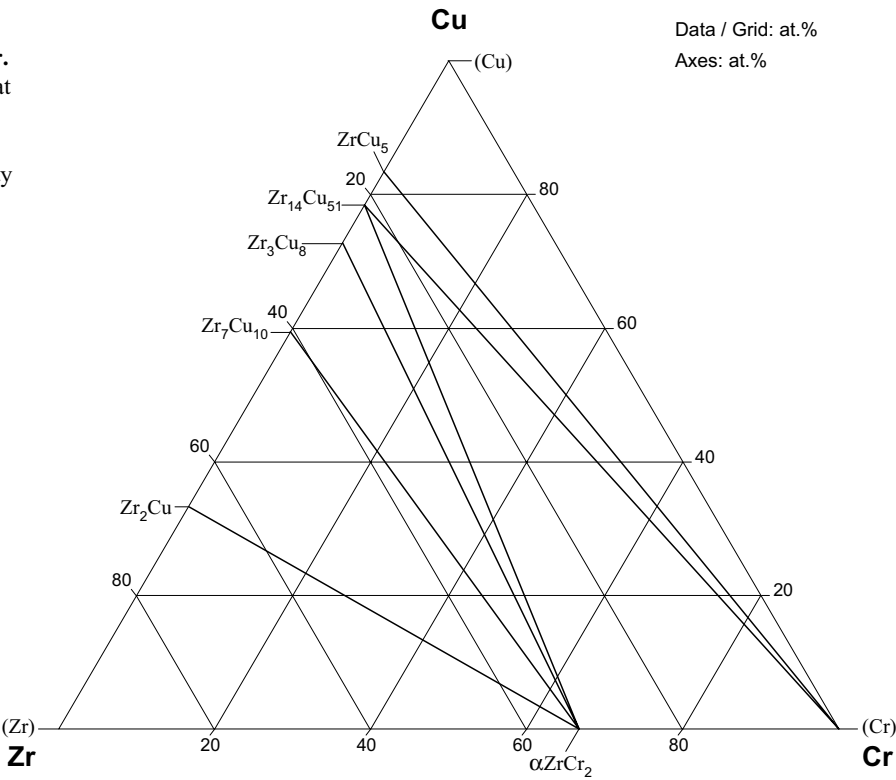
**Fig. 3: Cr-Cu-Zr.**  
The lines of double saturation of the solvus surfaces of ( $\beta$ Zr) and ( $\alpha$ Zr) in the Zr rich corner



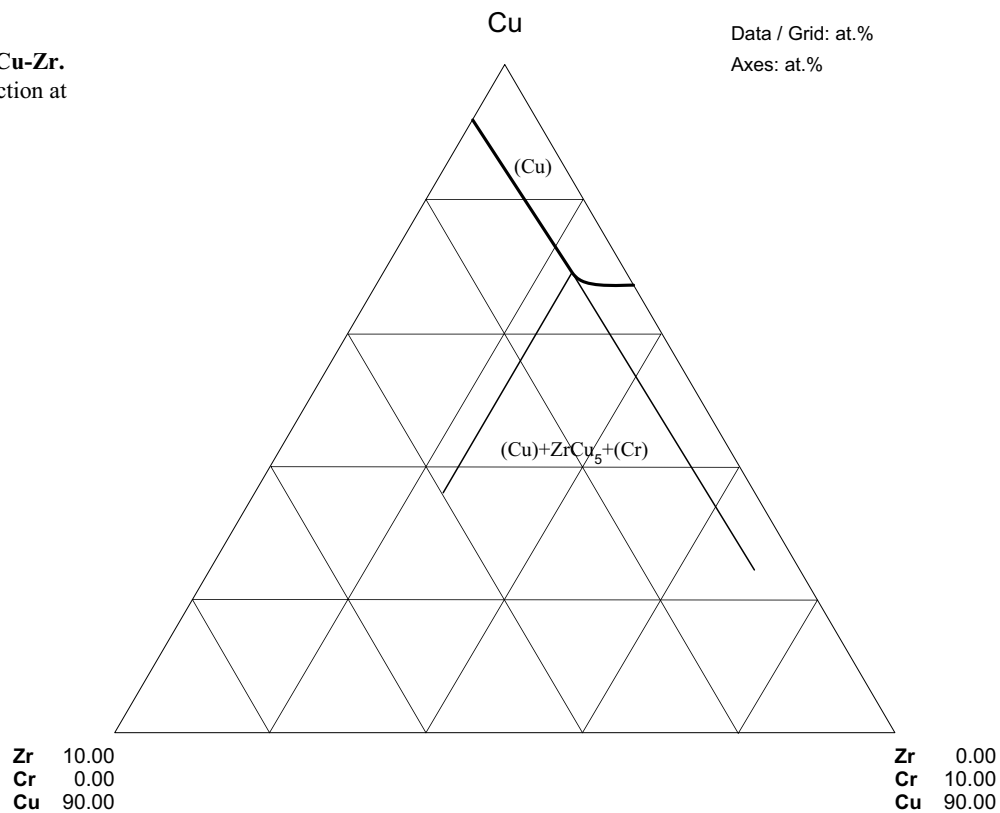
**Fig. 4: Cr-Cu-Zr.**  
The lines of double saturation of solvus surface of (Cu) in the Cu rich corner



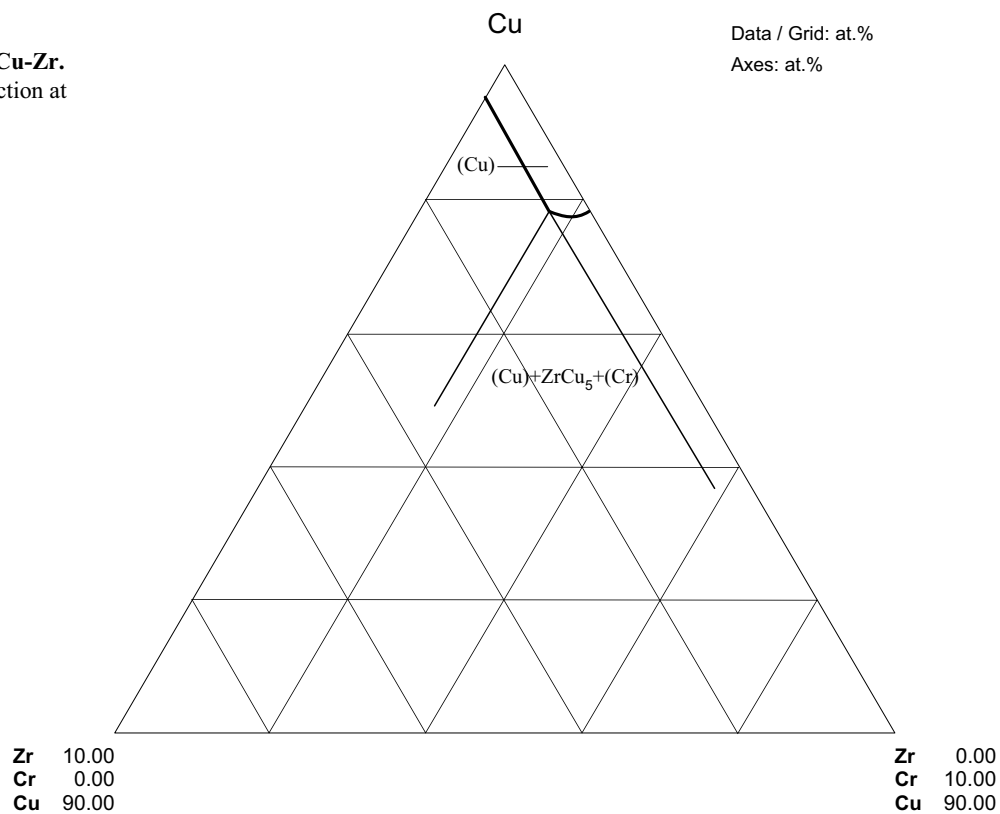
**Fig. 5: Cr-Cu-Zr.**  
Isothermal section at room temperature, disregarding the  $\alpha\text{ZrCr}_2$  homogeneity range



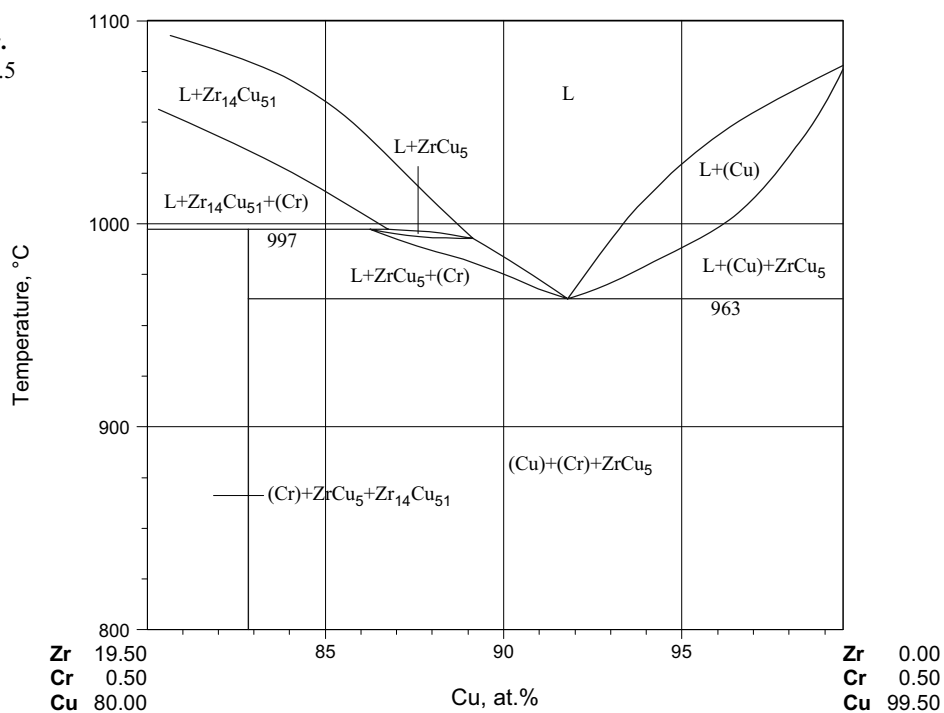
**Fig. 6: Cr-Cu-Zr.**  
Isothermal section at  
950°C



**Fig. 7: Cr-Cu-Zr.**  
Isothermal section at  
900°C



**Fig. 8: Cr-Cu-Zr.**  
Vertical section at 0.5 at.% Cr



**Fig. 9: Cr-Cu-Zr.**  
Vertical section at 1.5 at.% Cr

