Copper – Germanium – Nickel

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Introduction

Copper is used extensively for electrical and electronic applications because of its high electrical conductivity. By adding alloying elements producing solid solutions, the resistivity of the alloys can be lowered giving rise to their application as resistance materials. Little work has been carried out on the study of the phase equilibria in the Cu-Ge-Ni system. The earliest and most extensive work was by [1959Bur] who used X-ray analysis and optical microscopy to determine a partial isothermal section at 500°C for Ge contents less than 60 at.%. Later, [1985Boc] used DTA, optical microscopy, X-ray analysis and microhardness measurements to produce a partial isothermal section, also at 500°C (for Cu and Ni contents less than 30 mass%) and isopleths at 75 and 85 mass% Cu. The isothermal sections produced by [1959Bur] and [1985Boc] are in broad agreement with each other but the vertical sections violate the phase rule in that several two-phase regions are missing. Three ternary compounds have been found in the system [1959Bur, 1985Boc, 1986Zav]. The effect of adding Ni to the binary ζ phase in the Cu-Ge system and the apparent valency of the transition metal has been studied by [1961Coc]. Experimental details of the phase diagram studies are summarized in Table 1.

Binary Systems

The Cu-Ni system is isomorphous with complete mutual solubility of both components in the liquid and the fcc solid solution phases, but with a miscibility gap in the latter below 354°C. The Cu-Ni binary system is accepted from [2002Leb]. Both the Cu-Ge and Ge-Ni systems comprise a number of intermetallic compounds. These binary systems are accepted from [Mas2].

Solid Phases

Details of the solid phases are given in Table 2. Three ternary phases were reported by [1959Bur, 1985Boc] to be stable at 500°C, with compositions of $Ni_3Cu_2Ge_2$ (τ_1), $Ni_{15}Cu_{55}Ge_{20}$ (τ_2) and $Ni_{15}Cu_{58}Ge_{22}$ (τ_3). In addition, [1986Zav] reports a ternary compound with the composition $Ni_{16}Cu_{60}Ge_{24}$. This phase has the same γ-brass structure as τ_3 as given by [1959Bur] and is therefore considered to be the same compound. No ternary phases were found by [1961Coc] at 690°C.

[1961Coc] measured the lattice spacings of the binary ζ, Cu_5Ge phase on the addition of Ni. Spectroscopically pure materials were inducton melted under Ar, cast and homogenised at 690°C for 10-14 d before quenching into water. Optical microscopy and XRD of strain relieved fillings of the material using CuKα radiation revealed that Ni addition reduced both the *a* and *c* parameters of the crystal lattice. The relationship between the lattice parameters and Ni content for this phase are shown in Fig. 1. The variation of composition for constant *c/a* ratio is shown in Fig. 2. The binary compound was found to dissolve ~5 at.% Ni at 690°C. It was found that the electron to atom ratio (e/a) for the compound remained constant for constant *c*/*a* ratio, and hence it was possible to determine the contribtion of Ni to the valency electron concentration. At low e/a ratio, the effective Ni valency approaches 1, whereas as e/a increases, the effective valency of Ni decreases (Fig. 3). This decrease begins at lower e/a ratios as the Ni content increases. The explanation given for this observation was that Ni supplies 1 electron/atom to the conduction band at low e/a, but with increasing e/a, the contribution per Ni atom decreases owing to a decrease in the density of states as filling of the first Brillouin zone for the alloy approaches completion. Therefore, it is energetically more favorable for added electrons to be accommodated in a ‘virtual’ bound 3d state assoociated with the individual Ni atoms.

Invariant Equilibria

Five invariant equilibria were given by [1985Boc], one peritectic reaction, three transition reactions and a solid state eutectoid reaction. These are listed in Table 3, but unfortunately, no compositions associated with these reactions were reported in the original work.

Isothermal Sections

Partial isothermal sections for 500°C were presented by [1959Bur] and [1985Boc]. Both are in broad agreement with each other. The more extensive is that by [1959Bur] but the Ge-Ni binary edge of the section does not agree with the accepted binary. In the original work, the *B*8 phase is mistakenly labelled as Ni_2Ge. However, in the accepted binary system, the Ni_2Ge phase has the Strukturbericht designation *C*23. The *B*8 phases are actually the εNi_5Ge_3 and Ni_3Ge_2 phases which are separated by the $Ni_{19}Ge_{12}$ phase. It is most likely, therefore, that the *B*8 phase in [1959Bur], which is capable of dissolving up to about 20 at.% Cu at 500°C according to the experimental studies, refers to the εNi_5Ge_3 phase; the Ni_3Ge_2 phase being unstable at this temperature. In a further complication, the real Ni_2Ge phase, which appears at a composition of 33.5 at.% Ge in the accepted binary system, is missing in this isothermal section. According to [Mas2], this compound decomposes peritectoidally at 506°C. The possibility then, is that the experimental study was made at a slightly higher temperature than 500°C. The isothermal section is given in Fig. 4 with amendments to equilibria at the Ge-Ni side of the diagram to bring it into agreement with the accepted binary; but for a temperature slightly higher than 500°C (above the peritectoid decomposition temperature of the Ni_2Ge phase). Minor alterations have also been made to the Cu-Ge side to maintain consistency with the accepted Cu-Ge phase diagram. [1961Coc] presented a partial isothermal section for 690°C. This is shown in Fig. 5 with appropriate modifications to ensure agreement with the edge binary phase diagrams.

Notes on Materials Properties and Applications

Microhardness measurements were used by [1985Boc] to distinguish the visually similar ternary phases. A pyramidal diamond indenter was used and gave values of 4230 MPa for $Ni_{15}Cu_{65}Ge_{10}$, 5310 MPa for $Ni_{15}Cu_{58}Ge_2$and 7210 MPa for $Ni_3Cu_2Ge_2$. Details of experimental studies of materials properties are given in Table 4.

Miscellaneous

[2000Gie] studied the diffusion of Cu and Ni into (Ge) between 700 and 900°C, using rapid isothermal lamp annealing and spreading-resistance profiling. Typical double-hump diffusion profiles were found for both Cu and Ni.

[2000Wan] studied the effect of Cu clusters on nucleation on an undercooled $Ge_{73.7}Ni_{26.3}$ alloy. In the binary alloy, solidification begins at a maximum undercooling of 205 K resulting in a eutectic mixture of Ge and NiGe, as opposed to a mixture of primary Ge crystals and eutectic that would result from normal cooling directly from the melt. However, by sputtering Cu on the undercooled melt, solidification begins at an undercooling of 136 K, suggesting that the Cu clusters interfere with the nucleation process.

References

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Table 1: Investigations of the Cu-Ge-Ni Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1959Bur]	Metallography, X-ray diffraction	Isothermal section at 500°C; < 30 at.% Ge
[1961Coc]	X-ray diffraction	Isothermal section at 690°C; 25 at.% Ni and < 40 at.% Ge. Change in lattice parameters with Ni dissolved in ζ,Cu_5Ge
[1985Boc]	Metallography, X-ray diffraction, DTA, hardness measurements	Isothermal section at 500°C; > 70 at.% Cu. Isopleth at 75 and 85 mass% Cu
[1986Zav]	X-ray diffraction	Crystal structure of $Ni_{15}Cu_{65}Ge_{20}$ and $Ni_{16}Cu_{60}Ge_{24}$. Compounds prepared at 597°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, $(Ni_{1-x}Cu_x)$	*cF*4 *Fm*$\bar{3}$*m* Cu		
(Ni) < 1455		*a* = 352.4	pure Ni at 25°C [2002Leb]. Dissolves 12 at.% Ge at 1124°C [Mas2]
(Cu) < 1084.62		*a* = 361.46	at 25°C [Mas2] Dissolves 12 at.% Ge at 824°C [Mas2]
(δGe)	*cI*16 *Im*$\bar{3}$*m* γSi	*a* = 692	LT, 12 GPa [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γGe)	*tP*12 $P4_12_12$ γGe	*a* = 593 *c* = 698	at 25°C, 12 GPa→1 atm [Mas2]
(βGe)	*tI*4 $I4_1/amd$ βSn	*a* = 488.4 *c* = 269.2	at 25°C, 12 GPa [Mas2]
(αGe) < 938.3	*cF*8 $Fd\bar{3}m$ C (diamond)	*a* = 565.74	at 25°C [Mas2]
ζ, Cu_5Ge < 824	*hP*2 $P6_3/mmc$ Mg	*a* = 260.5 *c* = 422.6	[Mas2], [V-C2]
$ε_2$, Cu_3Ge 636 - 698	*cF*16 $Fm\bar{3}m$ BiF_3	*a* = 590.6	73.5-73.95 at.% Cu [Mas2], [V-C2]
$ε_1$, Cu_3Ge < 638	*oP*8 *Pmnm* $βCu_3Ti$	*a* = 418.8 *b* = 452.7 *c* = 262.4	74.9-76.9 at.% Cu [Mas2], [V-C2]
ε, Cu_3Ge 549.5 - 747	*hP*8 $P6_3/mmc$ $IrAl_3$	*a* = 416.9 *c* = 749.9	76.2-76.9 at.% Cu [Mas2], [V-C2]
NiGe < 850	*oP*8 *Pnma* FeAs	*a* = 538.1 *b* = 342.8 *c* = 581.1	[Mas2], [V-C2]
Ni_3Ge_2 515 - 990	*hP*6 $P6_3/mmc$ Ni_2In	*a* = 386.3 *c* = 499.8	41-43 at.% Ge [Mas2], [V-C2]
$Ni_{19}Ge_{12}$ 382 - 1050	*mC*62 *C*121 $Ni_{19}Ge_{12}$	*a* = 1163.1 *b* = 671.5 *c* = 1004.8	38-41 at.% Ge [Mas2], [V-C2]
$εNi_5Ge_3$ 290 - 1195	*hP*6 $P6_3/mmc$ Ni_2In	*a* = 393.4 *c* = 505.6	35-44 at.% Ge [Mas2], [V-C2]
ε´Ni_5Ge_3 < 394	*mC*32 *C*121 Ni_5Ge_3	*a* = 1168.2 ± 0.6 *b* = 673.7 ± 0.3 *c* = 636.4 ± 0.3 β = 52.11 ± 0.01°	~37 at.% Ge [Mas2], [V-C2]
Ni_2Ge < 506	*oP*12 *Pnma* Co_2Si	*a* = 511.3 ± 0.3 *b* = 383.0 ± 0.2 *c* = 726.4 ± 0.4	33.5 at.% Ge [Mas2], [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δNi_5Ge_2 1045 - 1110	*hP*42 $P6_3cm$ Pd_5Sb_2	 a = 682.7 ± 0.3 c = 1239.5 ± 0.5	28 at.% Ge [Mas2]. [V-C2] Max temp. given incorrectly in [Mas2] as 1082
γNi_3Ge 1082 - 1118	*cF*16 $Fd\bar{3}m$ NaTl	a = 574.36	25.6 at.% Ge, [Mas2], [V-C2]
βNi_3Ge < 1132	*cP*4 $Pm\bar{3}m$ $AuCu_3$	a = 357.0	22.5-25 at.% Ge [Mas2], [V-C2]
* τ_1, $Ni_3Cu_2Ge_2$	*hP*42 $P6_3cm$ Ni_5As_2	a = 689.2 c = 1255.0	Quenched from 500°C. ~10-~46 at.% Cu [1959Bur], [V-C2] (as $Ni_{47}Cu_{25}Ge_{28}$)
* τ_2, $Ni_{15}Cu_{65}Ge_{20}$	*cP*20 $P4_132$ βMn or Au_4Al	a = 627.3 a = 627.1	Quenched from 500°C [1959Bur], [V-C2] (as $Ni_3Cu_{13}Ge_4$) [1986Zav] quenched from 597°C
* τ_3, $Ni_{15}Cu_{58}Ge_{25}$	*c*** - Cu_9Al_4	a = 826.7 a = 866.1	[1959Bur], [V-C2] (as $Ni_{15}Cu_{58}Ge_{22}$). [1986Zav] (as $Ni_{16}Cu_{60}Ge_{24}$)

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)*		
				Cu	Ge	Ni
L + (Cu) + $\tau_1 \rightleftharpoons \tau_2$	830	P	-	-	-	-
L + (Cu) $\rightleftharpoons \zeta + \tau_2$	785	U	-	-	-	-
L + $\tau_2 \rightleftharpoons \zeta + \tau_3$	745	U	-	-	-	-
L + $\zeta \rightleftharpoons \varepsilon_1 + \tau_3$	712	U	-	-	-	-
$\varepsilon_1 \rightleftharpoons \varepsilon + \zeta + \tau_3$	515	E	-	-	-	-

* phase compositions unknown

Table 4: Investigations of the Cu-Ge-Ni Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1985Boc]	Microhardness measurements	Microhardness
[2000Gie]	Rapid isothermal lamp annealing and spreading-resistance profiling	Diffusion of Cu and Ni into Ge between 700 and 900°C

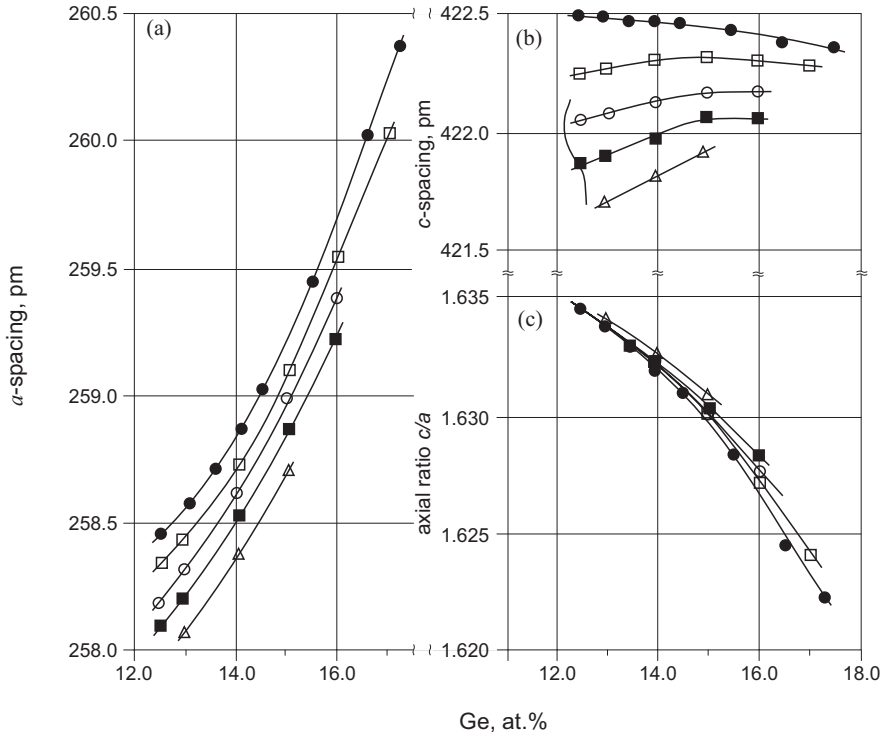

Fig. 1: Cu-Ge-Ni. Variation of (a) *a* lattice parameter, (b) *c* lattice parameter and (c) *c/a* ratio of ζ, Cu_5Ge with Ge content for 0 (filled circles), 1 (open squares), 2 (open circles), 3 (filled squares) and 4 (open triangles) at.% Ni.

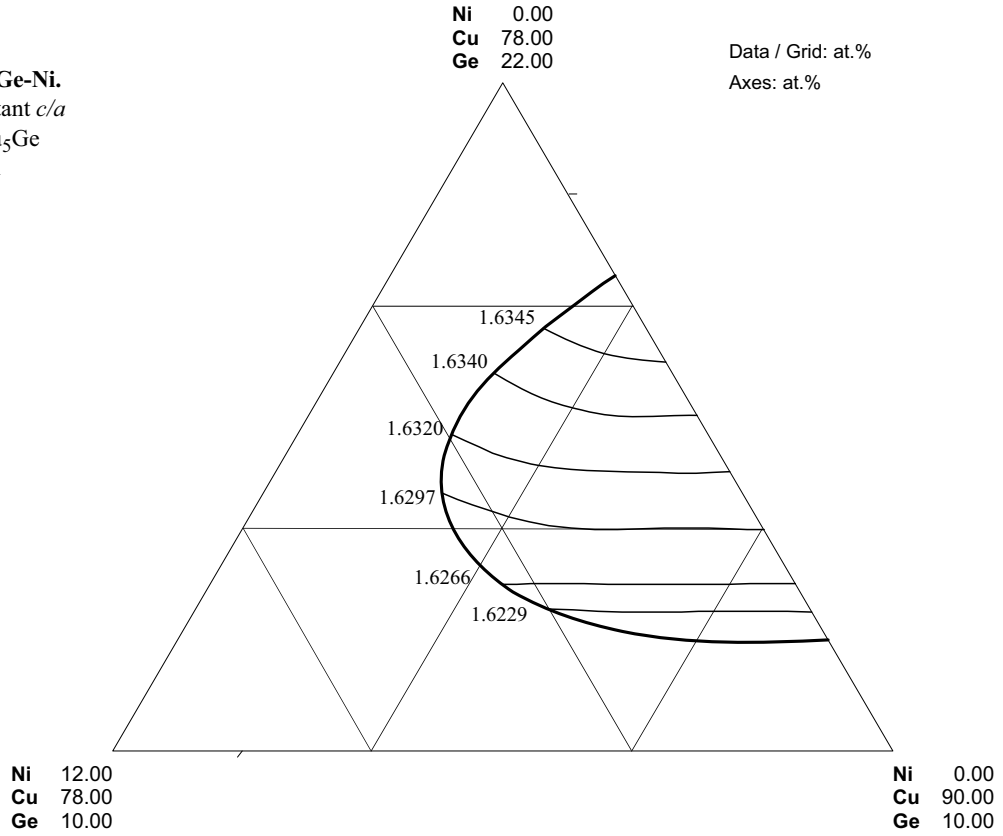

Fig. 2: Cu-Ge-Ni. Lines of constant *c/a* ratio for ζ, Cu_5Ge with added Ni

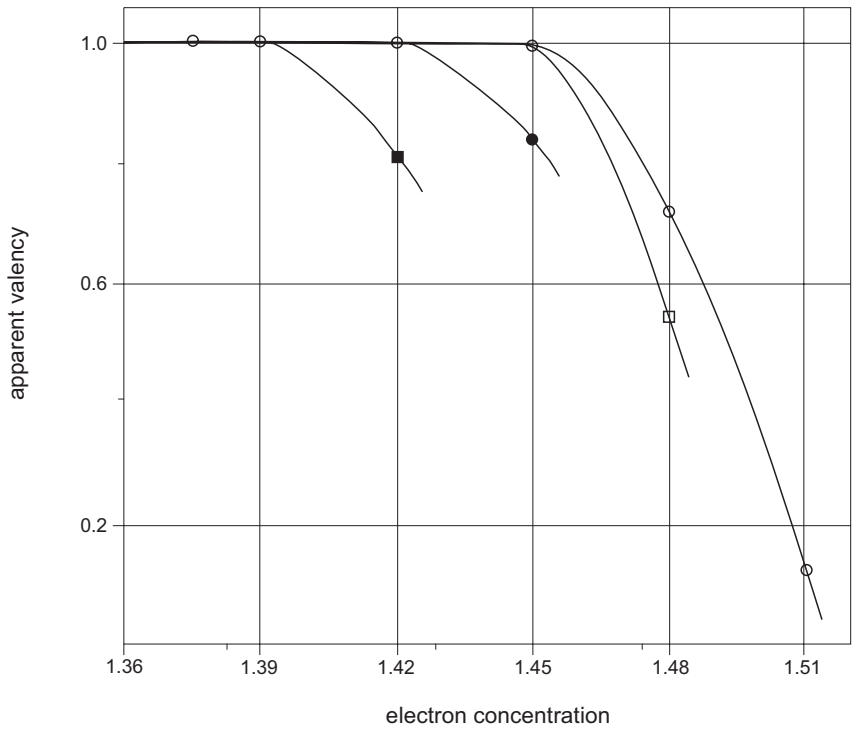

Fig. 3: Cu-Ge-Ni. Variation with electron concentration and composition of the apparent valency of Ni dissolved in ζ, Cu_5Ge

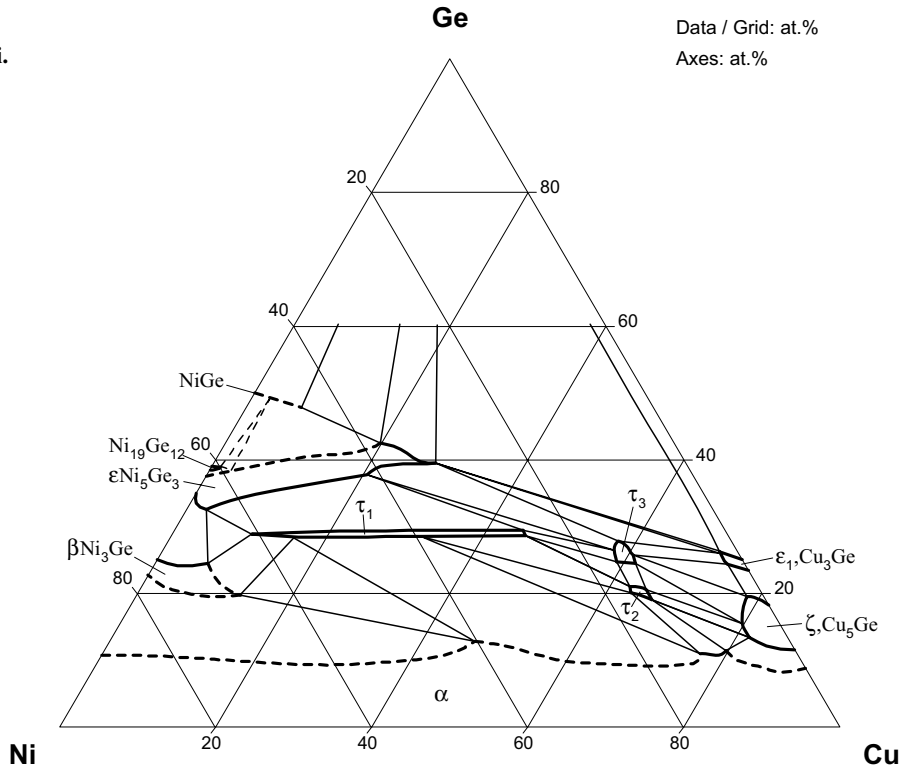

Fig. 4: Cu-Ge-Ni. Partial isothermal section at around 500°C

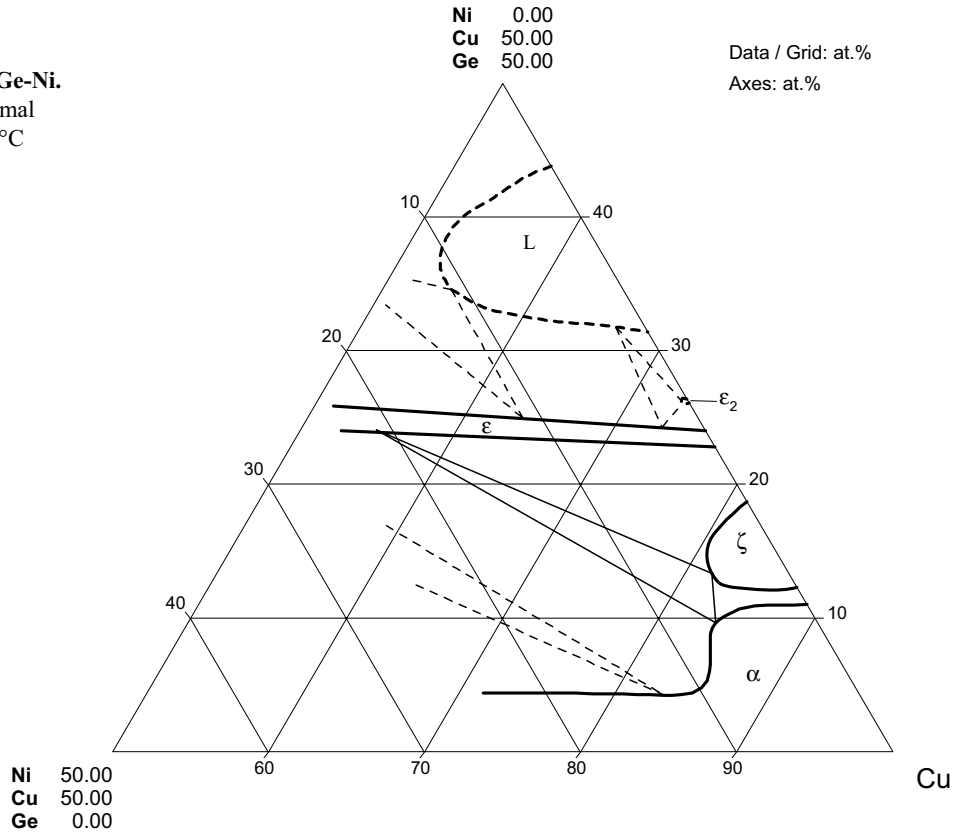

Fig. 5: Cu-Ge-Ni. Partial isothermal section at 690°C