Silver – Copper – Nickel

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Introduction

The system was studied initially by [1913Ces] and [1933Gue]. The latter determined the liquid miscibility gap by chemical analysis and their findings agree, in principle, with those of [1913Ces]. The results obtained by [1913Ces] and [1933Gue] are presented in the review published by [1967McD], which deals with silver alloys. [1977Cha] adjusted the liquidus surface formerly based on [1933Gue], in order to obtain consistency with the currently accepted binary data. By applying improved equipment and techniques, [1977Sie] redetermined the phase equilibria; their results show a somewhat lower ternary solubility limit for Ni below 1000°C. [1993Che] and [1996Luo] applied the diffusion couple method to the study of the interfacial reactions between liquid Ag-Cu alloys and pure nickel substrates. The results obtained at 860, 795 and 700°C confirm that (Ag) has almost no solubility of Ni.

Binary Systems

The Ag-Cu, Ag-Ni and Cu-Ni systems are taken from the recent evaluations made within the MSIT Binary Evaluation Program, by [2002Rom], [2002Iva] and [2002Leb], respectively.

Solid Phases

No intermediate phases have been reported in the binary systems or in the ternary system. The unary phases are listed in Table 1.

Invariant Equilibria

The reaction sequence is illustrated in Fig. 1. The three-phase equilibrium $L_1 + L_2$ + (Ni,Cu) disappears at a critical point of ~1250°C.

Liquidus Surface

According to the chemical analysis data of [1933Gue], the liquid miscibility gap extends from the binary Ag-Ni system to approximately 48 at.% Cu (42 mass% Cu) at 1250°C; see Fig. 2. The locations of some of the isotherms have been modified at the binary edges to ensure agreement with the accepted binary systems.

Isothermal Sections

Figures 3 to 7 present the results obtained by [1933Gue] based on chemical, thermal and metallographic analyses, for temperatures 1440, 1400, 1300, 1250 and 900°C. Some modifications have been made to ensure agreement with the accepted binary diagrams. The solubility of Ni in the liquid phase at 900°C is not accepted in this evaluation, following the more recent findings of [1996Luo] for a temperature of 860°C. Based on the review of [1977Cha] and the calculation of [1991Mur], the isothermal section for 793°C was constructed by [1993Che]. More recently, [1996Luo] confirmed the isothermal section given in [1993Che] and also determined phase equilibria at 860 and 700°C, by both experimental investigation and calculation. It was shown that (Ag) has some solubility of Cu but almost no solubility of Ni and the liquid phase has almost no Ni solubility [1993Che, 1996Luo, 1977Sie]. The isothermal sections established at 860, 795 in [1996Luo] are given in Figs. 8 and 9. The isothermal section for 700°C shown in Fig. 10 is a combination of data from [1933Gue] and [1996Luo].

Notes on Materials Properties and Application

Knowledge of the phase equilibria in the Ag-Cu-Ni system is important because Ni is widely used as a barrier layer material for the Ag-Cu-Sn alloys, which are the most prominent candidates for Pb-free solders. Ag-Sn-Cu/Ni and Ag-Cu/Ni contacts are frequently used in microelectronic products [1993Che, 2004Che]. The Ag-Cu-Ni system is important for the ceramic packaging industry: Ag-Cu alloys are the most commonly used brazes in ceramic packaging, and nickel pads are usually plated on ceramic substrates in order to improve the brazability between the ceramic and the metals [1996Luo].
Ag-Cu/Ni/Ag-Cu clad tapes for YBCO (YBa_2Cu_3) superconducting tape were prepared by [2001Yos]. A high J_c value of about 10^5 A/cm^2 was obtained on Ag-0.1%Cu/Ag-10%Ni clad tape.

Miscellaneous

A number of Ag-Cu-Ni alloys exhibit age-hardening phenomena. For this reason, [1934Pfi1] studied the Cu rich Ag-Cu-Ni alloys and [1934Pfi2] the precipitation in ternary alloys. [1981Duk] and [1981Pav] studied the dendritic segregation of silver-copper alloys with the addition of nickel. Knowledge of phase equilibria of the Ag-Cu-Ni ternary system is also important for the understanding of the interfacial reactions in Ag-Cu/Ni contacts, which are frequently encountered in microelectronic products. [1993Che] studied the interfacial reaction between liquid Ag-Cu eutectic alloys and pure nickel substrates at 793°C. [1996Luo] determined the phases formed at the interfaces of Ni and Ag-Cu alloys at three different temperatures: 860, 795 and 700°C. The diffusion paths proposed by the author are in agreement with the isothermal sections. [1997Zhu] reports experimental results obtained at 850 and 800°C, in terms of kinetics and microstructures of the products formed at the interface of Cu/Ni/Ag-Cu eutectic melts. Using Auger Electron Spectroscopy, [2000Weh] determined the depth distributions of each element in either Ni/Ag-Cu or Ag/Ni-Cu samples. [2004Che] used the isothermal section at 250°C taken from [1977Cha] and [1996Luo] to obtain a representation of the phase equilibria in the Ag-Cu-Ni-Sn quaternary system with the aim of better understanding the reactions occurring at the Ag-Cu-Sn/Ni interfaces. Isoplethal sections at 60, 70, 80 and 90 at.% Sn of the 250°C isothermal section of the Ag-Cu-Ni-Sn quaternary system are represented.

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
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	*a* = 408.57	pure Ag at 25°C [Mas2]
$(Ni_{1-x}Cu_x)$	*cF*4 $Fm\bar{3}m$		$0 \le x \le 1$
(Ni) < 1455	Cu	*a* = 352.40	pure Ni at 25°C [Mas2]
(Cu) < 1084.62		*a* = 361.46	pure Cu at 25°C [Mas2] melting point [1994Sub]

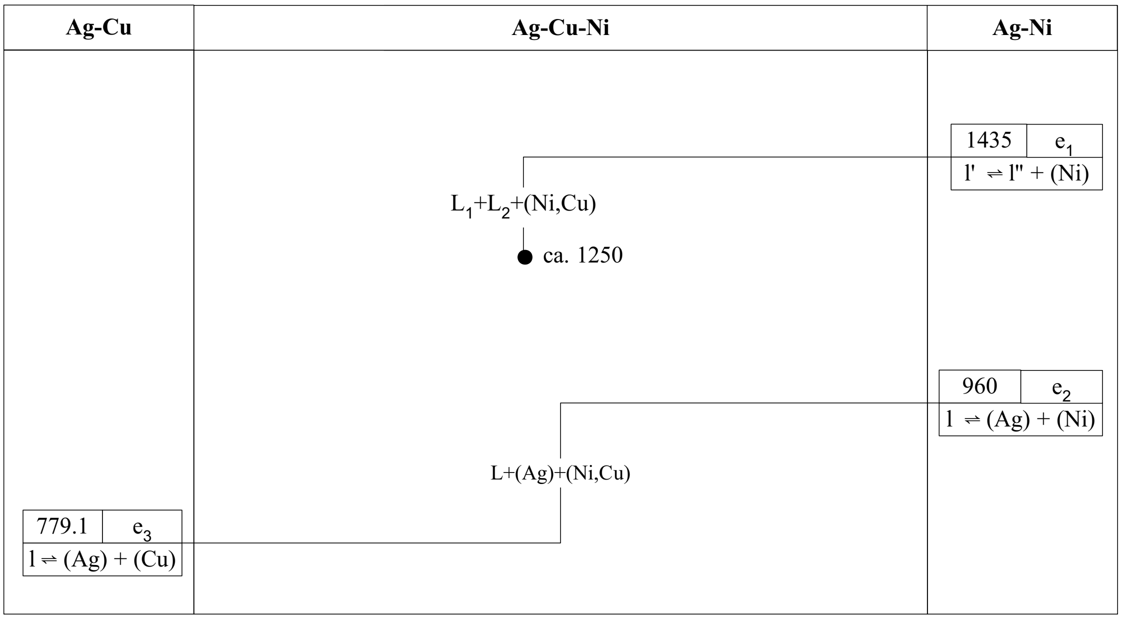

Fig. 1: Ag-Cu-Ni. Reaction scheme

Fig. 2: Ag-Cu-Ni. Liquidus surface projection

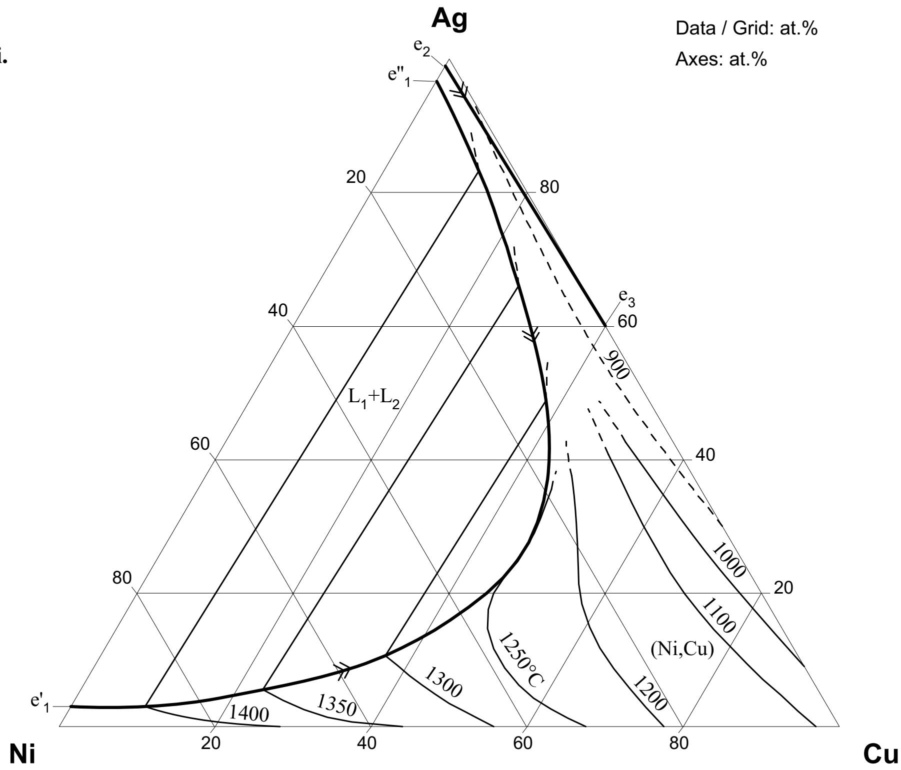

Fig. 3: Ag-Cu-Ni.
Isothermal section
at 1440°C

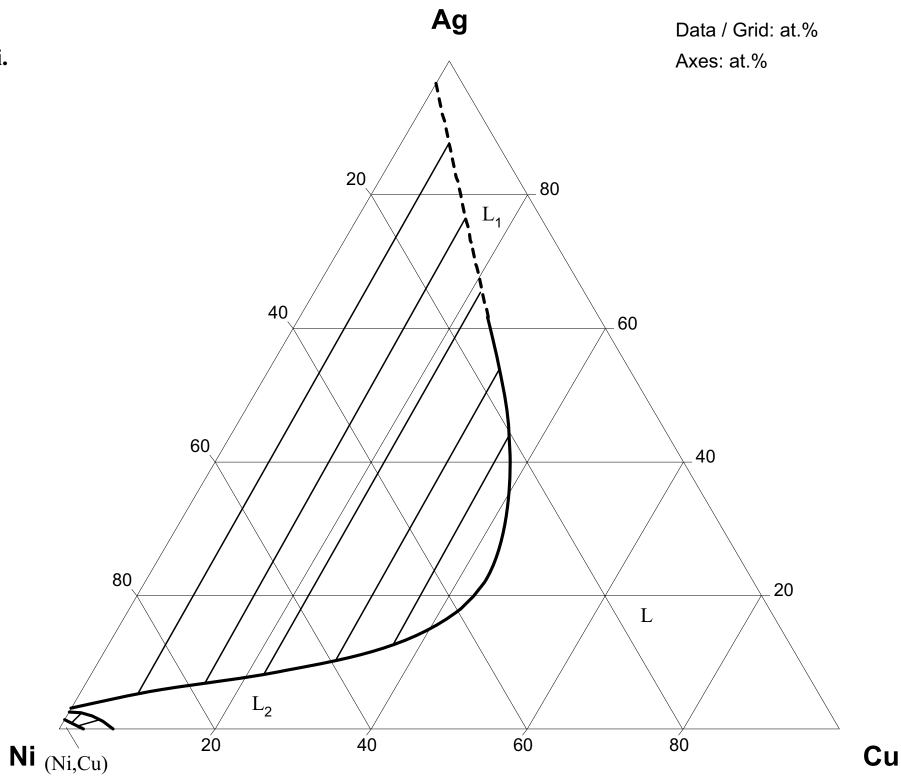

Fig. 4: Ag-Cu-Ni.
Isothermal section
at 1400°C

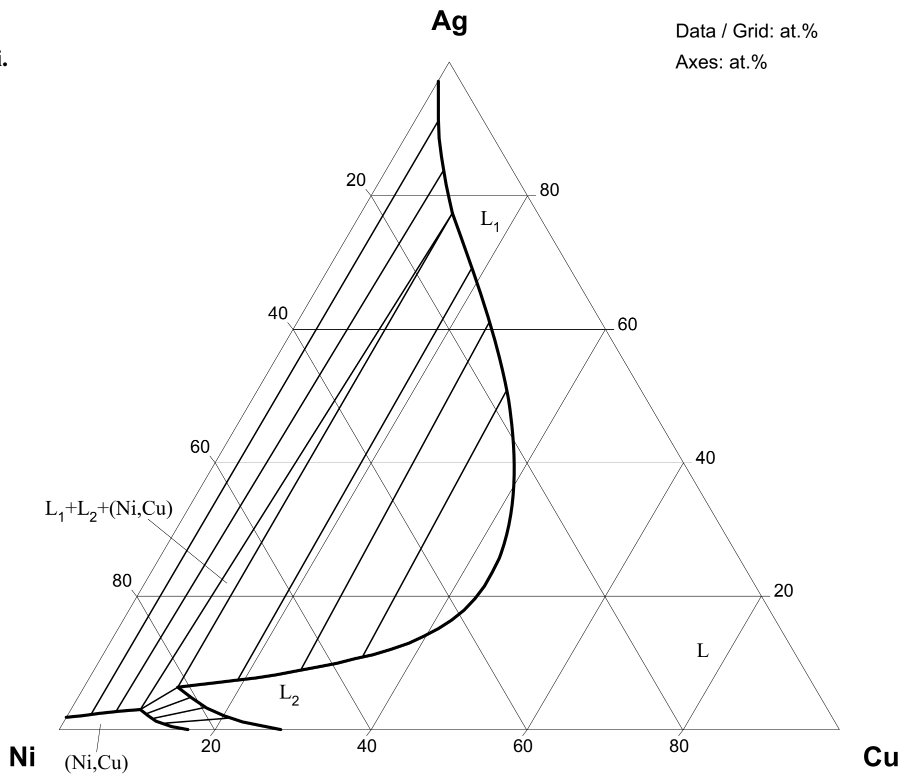

Fig. 5: Ag-Cu-Ni.
Isothermal section
at 1300°C

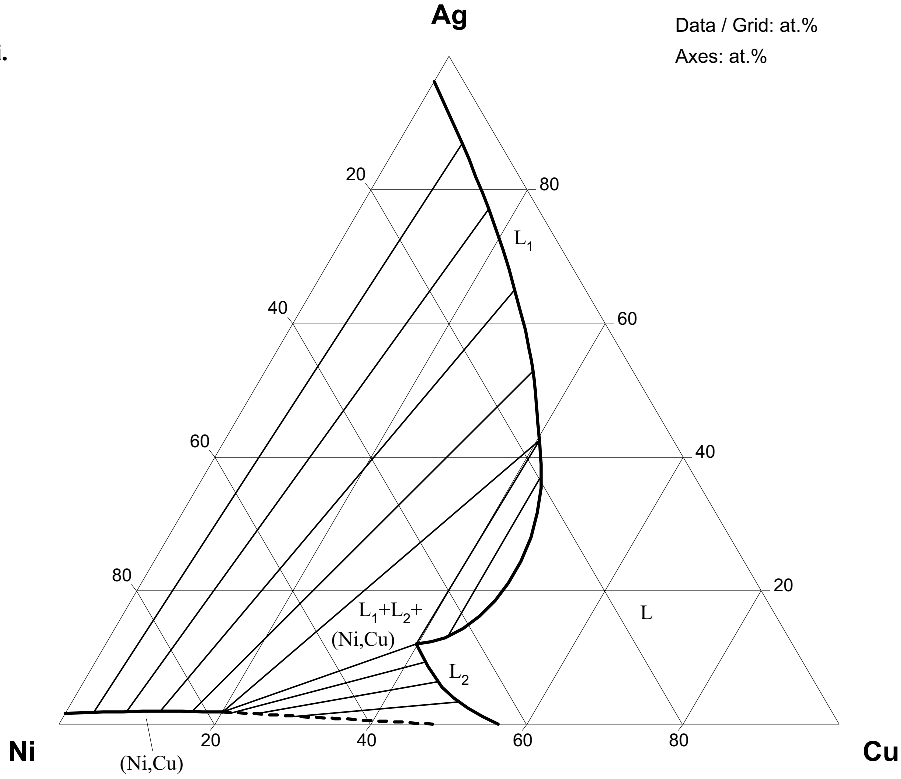

Fig. 6: Ag-Cu-Ni.
Isothermal section
at 1250°C

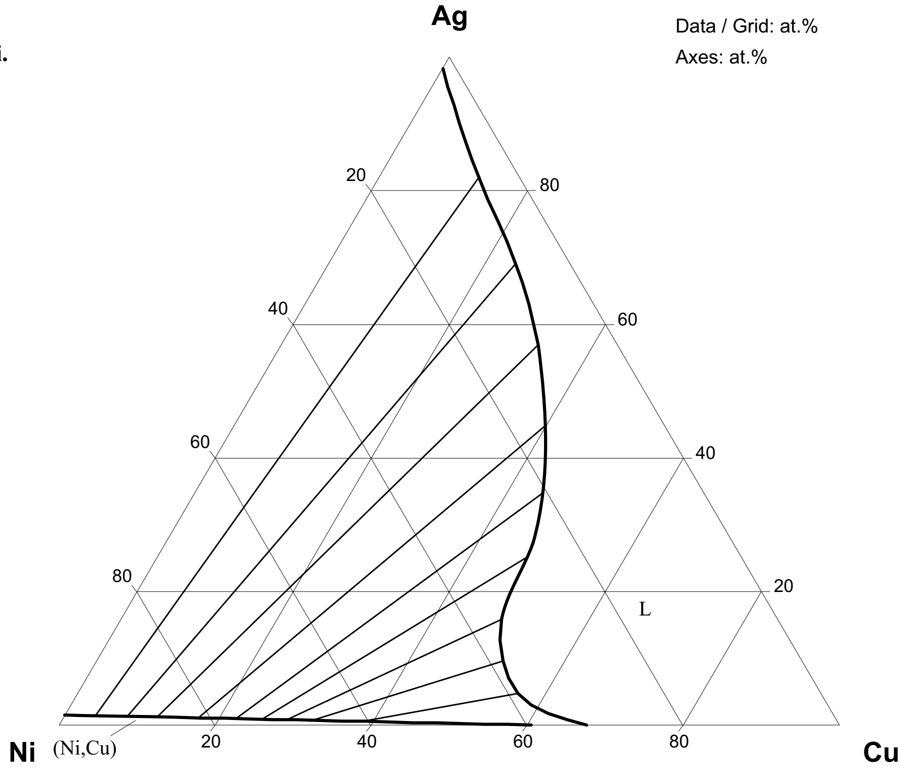

Fig. 7: Ag-Cu-Ni.
Isothermal section
at 900°C

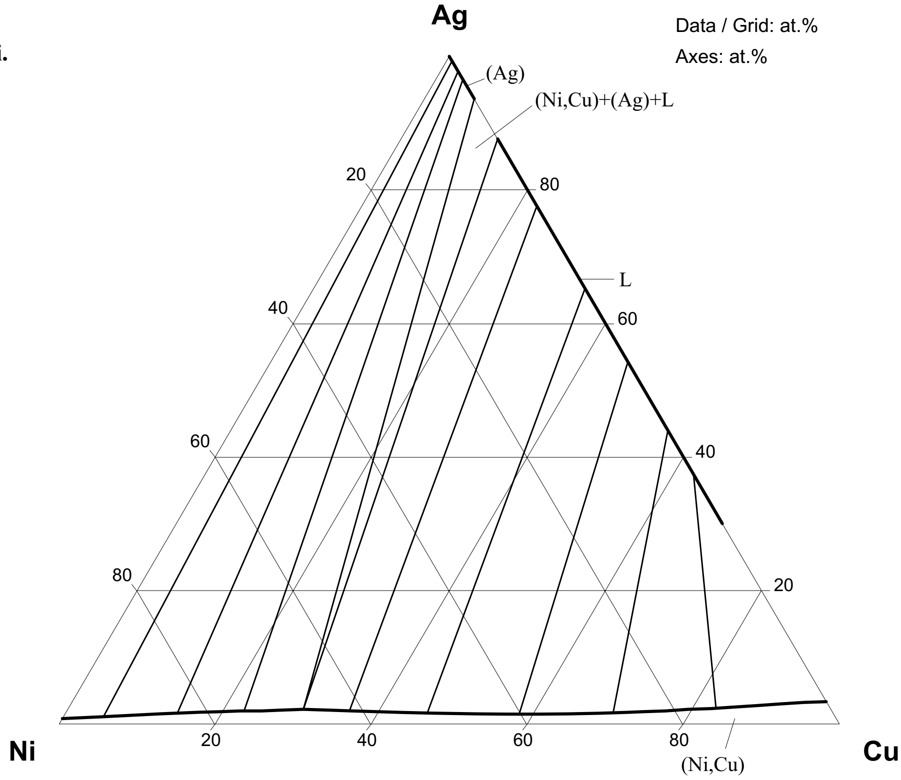

Fig. 8: Ag-Cu-Ni.
Isothermal section
at 860°C

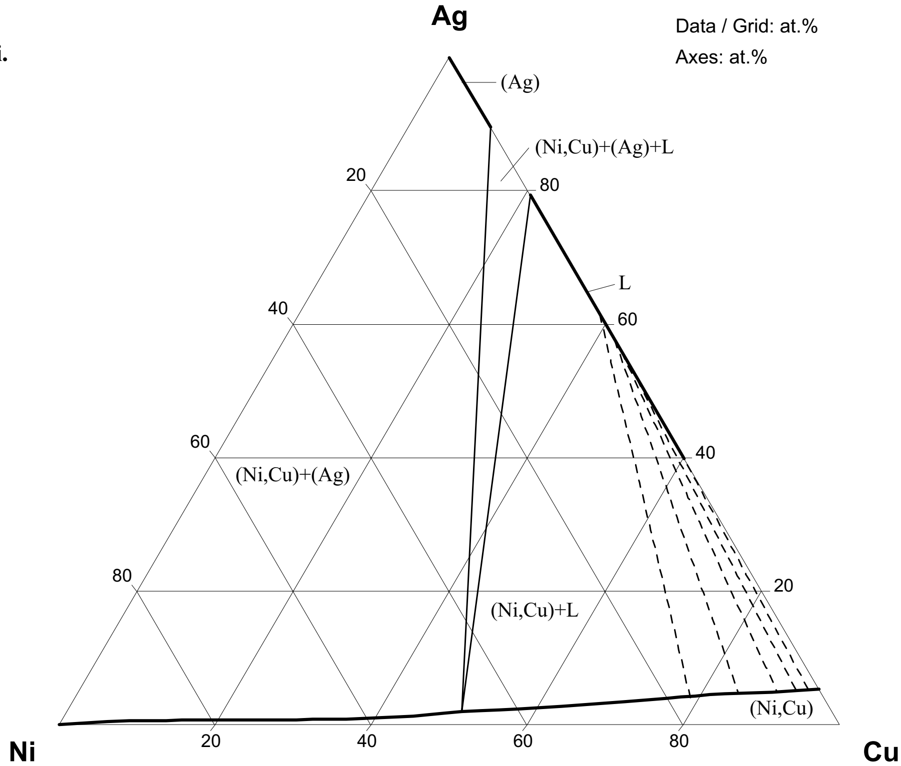

Fig. 9: Ag-Cu-Ni.
Isothermal section
at 795°C

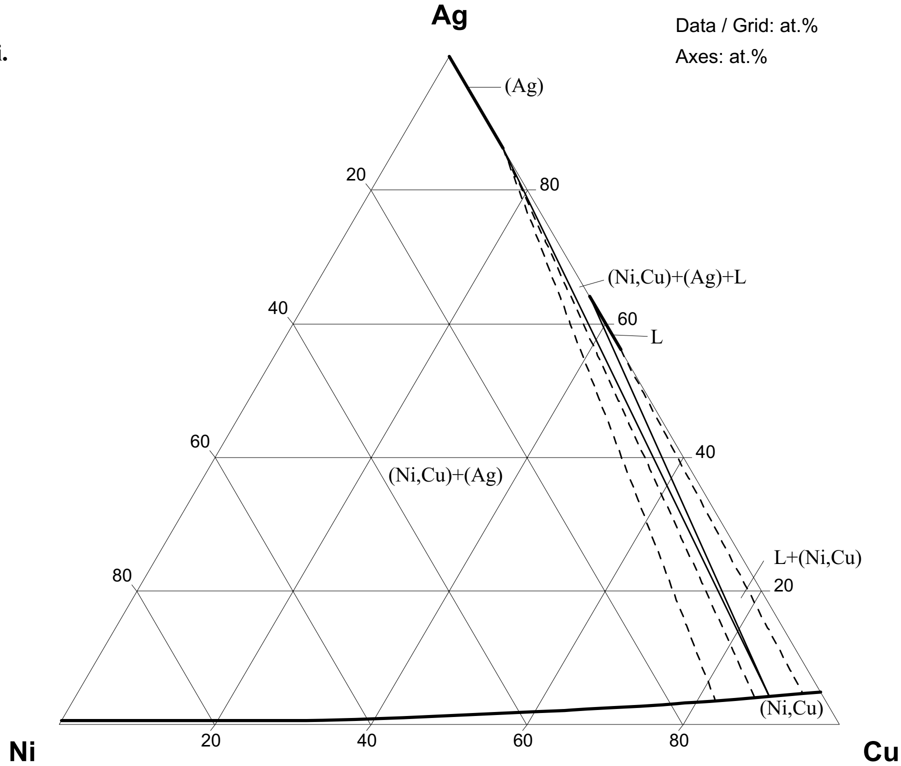

Fig. 10: Ag-Cu-Ni.
Isothermal section
at 700°C