Phase Diagrams and Thermodynamic Properties of Ternary Copper-Silver Systems

Y. Austin Chang, Daniel Goldberg*, and Joachim P. Neumann

Materials Department, College of Engineering and Applied Science, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

Phase diagram and thermodynamic data for twenty ternary copper-silver-X alloy systems—where X represents Al, Au, Cd, Fe, Ge, In, Mg, Mn, Ni, P, Pb, Pd, Re, S, Sb, Se, Sn, Te, Ti or Zn—were compiled and critically evaluated. Of the twenty ternary systems, thermodynamic data are available for only the seven systems containing Au, Pb, Pd, S, Sn, Te and Zn. The high-temperature phase relationships in the iron-rich region of the Cu-Fe binary system were also evaluated and a recommended phase diagram is presented.

Key words: Critically evaluated data; phase diagrams; ternary copper-silver alloy systems; thermodynamic properties.

Contents

1. Introduction

Phase diagram and thermodynamic data for copper-base alloy systems are of considerable fundamental and practical interest in many aspects of extractive, chemical, and physical metallurgy. These data have been reported for binary copper-base systems in a critical evaluation by Hultgren and Desai [Gen. Ref. 8][1], which forms one of the monographs in the series "The Metallurgy of Copper", sponsored by the International Copper Research Association (INCRA). Since commercial alloys usually consist of more than two components, a considerable effort is being made to extend the work of Hultgren and Desai to ternary copper-base systems. The present paper reflects the first results of this effort. Critical evaluations of 20 ternary Cu-Ag-X systems—where X represents Al, Au, Cd, Fe, Ge, In, Mg, Mn, Ni, P, Pb, Pd, Re, S, Sb, Se, Sn, Te, Ti or Zn—are reported. The evaluations are based on a thorough literature search, mainly using the Chemical Abstracts, up to June 1973. The Index Thermochimique has been used for regular updates since then. However, because the evaluations reported herein were completed at various times between June 1973 and June 1976, the evaluation of each ternary system reflects only the data available for that system at the time of the performance of the evaluation.

*Present affiliation: Westinghouse, Plant Apparatus Division, Pittsburgh, Pa.

[1] Figures in brackets indicate either the General References given in section 3 or the literature references for each particular system after the discussion.

During the evaluation of the Cu-Ag-Fe system, it was noted that some errors and discrepancies exist in the Metals Handbook [Gen. Ref. 1] and in Hultgren and Desai [Gen Ref. 8], concerning the high temperature region of the Cu-Fe binary system. Therefore, a recommended high temperature section of the Cu-Fe binary system is presented here, in addition to the ternary Cu-Ag-Fe system.

2. Format of Presentation

The phase diagram and thermodynamic data have been evaluated for self-consistency, consistency with binary data, and consistency with known phase and thermodynamic relationships. Whenever conflicting data are reported by different groups of investigators, judgment has been made on the basis of the experimental methods used and the detailed experimental information reported by the investigators. The discussion of each system is divided into six sections: Phases and Structures, Phase Diagrams, Thermodynamic Properties, References, Tables, Figures.

2.1. Phases and Structures

Adopting the format of the Metals Handbook [Gen. Ref. 1], the following information is given for each of the binary and ternary intermediate phases: Designation, Composition, Symmetry, Symbol, and Prototype. The phases are listed in the following order: Cu-X binary intermediate phases; Ag-X binary intermediate phases, and Cu-Ag-X ternary intermediate phases. No intermediate phases occur in the Cu-Ag binary system.

The designations of Hansen and Anderko, Elliott, and Shunk [Gen. Refs. 3, 4, 5] are used whenever possible. If their designations cannot be used, they are given in parentheses next to the chemical formula in the composition column. In general, the designation of a disordered and an ordered phase is the same except that the ordered phase is primed. For example, the designation of the disordered high-temperature AgCd phase is β, while that of the ordered low-temperature phase is β'.

Whenever two binary phases with the same crystal structure appear in a ternary system, the same designation is used for both phases; however, they are distinguished by adding the subscripts 1 and 2. For example, in the ternary Cu-Ag-Al system, the bcc phase Cu_3Al in the binary Cu-Al system is designated β_1, while the corresponding phase Ag_3Al in the binary Ag-Al system is designated β_2. For ternary intermediate phases, the designations T_1, T_2, T_3 . . . are used.

If an intermediate phase is stoichiometric or if the stoichiometric composition is derived from structural considerations, the chemical formula is used, for example, CuZn and Cu_3Ti. If the phase is non-stoichiometric, the midpoint composition in wt.% is generally given. If the intermediate phase has a well-known special name, as in the case of minerals, this name is given in parentheses next to the chemical formula. Examples are chalcocite, Cu_2S, and covellite, CuS.

For the abbreviations of crystal symmetry, refer to pp. 243–250 of the Metals Handbook [Gen. Ref. 1].

For the structure symbols (Strukturbericht), refer to Pearson [Gen. Ref. 2].

A prototype phase is given whenever available.

2.2. Phase Diagrams

Following the notation of Rhines [Gen. Ref. 9], the three invariant four-phase equilibria are classified as types I, II, and III. If more than one four-phase equilibrium of the same type occurs, the equilibria are distinguished by adding subscripts to the Roman numerals in order of descending temperature, I_1, I_2, I_3, etc.

The temperatures of the four-phase equilibria and the composition of the coexisting phases are generally given in tabular form. For the presentation of the liquidus projection and the isothermal sections, the Gibbs triangle is used. The element Cu is always located at the left corner of the triangle. The chemical composition is given in wt.% and the temperatures are given in degrees Celsius. Solid lines are used for known phase boundaries, dashed lines for estimated phase boundaries, and dash-dotted lines for magnetic transformations.

In the liquidus projection, the binary eutectics, peritectics and monotectics are designated by e_1, e_2, e_3, . . ., p_1, p_2, p_3, . . ., and m_1, m_2, m_3, . . ., respectively. The inverse peritectic reaction, $\text{solid}_1 \rightarrow \text{solid}_2 +$ liquid, which has been called "metatectic" by Prince [Gen. Ref. 10] and "catatectic" by Wagner and Rigney [Gen. Ref. 11], is designated by p^*. All binary invariant reactions are numbered counter-clockwise, starting at the Cu-corner. The traces of the liquidus valleys, i.e., the uni-variant equilibria, are plotted, and the directions of their slopes toward lower temperature are indicated by arrows inscribed upon the lines. The primary phases of crystallization are given on either side of the traces of these valleys. The types of the four-phase equilibria at the intersections of the traces of the liquidus valleys are indicated by the Roman numerals I, II, or III with the subscripts 1, 2, 3, etc. The melting points of congruently melting binary and ternary phases are marked with solid circles and the corresponding temperatures are given. For ternary saddle points (singular points), open circles are used.

In the isothermal sections, only the single- and two-phase regions are labelled, using the designations for the phases given in section 2.1, Phases and Structures. For the terminal solid solutions, the chemical symbol of the base element in parentheses is used. When complete solid-state miscibility exists between any two elements, the respective chemical symbols, separated by a comma, are enclosed in a single set of parentheses. Liquid phases are designated by the letter L, with the subscripts 1, 2, etc., distinguishing different liquid phases.

In the case of isopleths, all single-, two- and three-phase regions are labelled.

2.3. Thermodynamic Properties

The Kelvin temperature scale is used to represent the temperature instead of the Celsius scale, and atom or mole fractions are used instead of weight percent. If complete thermodynamic data are available for isomorphous systems, iso-activity coefficient curves are presented at constant temperature using the Gibbs triangle. However, if a ternary miscibility gap exists in the system, iso-activity curves are shown, since the activity values for any two coexisting phases are the same. The Gibbs energy and enthalpy are expressed in joules[2] per gram-atom; for pseudo-binary solutions, they are expressed in joules per mole.

Very often the thermodynamic properties of a particular component are known in infinitely dilute solutions. For such cases, the formalism suggested by Wagner [Gen. Ref. 12], to express the excess partial molar Gibbs energy, is used:

$$\ln \gamma_i = \ln \gamma_i^\circ + \epsilon_i^i x_i + \epsilon_i^j x_j, \tag{1}$$

where γ_i is the activity coefficient of the solute i in a ternary dilute solution consisting of the solvent s and the solutes i and j: γ_i° is the limiting activity coefficient of i in the binary system i-s; and the terms x_i and x_j are atom fractions of the solutes i and j. The terms ϵ_i^i and ϵ_i^j are defined as:

$$\epsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{x_s \to 1.0}, \tag{2a}$$

$$\epsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial x_j}\right)_{x_s \to 1.0}. \tag{2b}$$

The Gibbs energy self-interaction parameter ϵ_i^i represents the deviation from Henry's law behavior in the binary $i-s$; the Gibbs energy interaction parameter ϵ_i^j represents the effect of component j on the values of $\ln \gamma_i$ in the limit as the atom fraction of s approaches 1 (pure s). Equation (1) is obtained by using a Taylor series expansion of $\ln \gamma_i$, neglecting the second and higher order terms. Conversions of the ϵ_i^i and ϵ_i^j values to e_i^i and e_i^j values, using wt.% as the composition coordinate, may be carried out readily by using the relationships of Lupis and Elliott [Gen. Ref. 13].

For the partial molar enthalpy, a relationship similar to eq (1) is used [Gen. Ref. 13]:

$$\Delta\bar{H}_i = \Delta\bar{H}_i^\circ + \eta_i^i x_i + \eta_i^j x_j, \tag{3}$$

where $\Delta\bar{H}_i$ is the relative partial molar enthalpy of the solute i in a ternary dilute solution consisting of the solvent s and the solutes i and j; $\Delta\bar{H}_i^\circ$ is the limiting partial molar enthalpy of i in the binary system i-s; and η_i^i and η_i^j are the enthalpy self-interaction parameter and the enthalpy interaction parameter, respectively. They are defined as:

$$\eta_i^i = \left(\frac{\partial\, \Delta\bar{H}_i}{\partial x_i}\right)_{x_s \to 1.0}, \tag{4a}$$

$$\eta_i^j = \left(\frac{\partial\, \Delta\bar{H}_i}{\partial x_j}\right)_{x_s \to 1.0}. \tag{4b}$$

For pseudo-binary systems with complete solubility, the thermodynamic activities of the two binary phases are given as a function of the mole fraction of one of the binary phases. The standard states are the pure binary phases.

2.4. References

The literature references which are pertinent to each particular system are given after the discussion. A number of frequently occurring references are cited as "General References"; they are listed in section 3.

2.5. Tables

Generally, the types and temperatures of the known invariant equilibria, as well as the compositions of the coexisting phases, are given in a table. From this information, the given isothermal sections, and the liquidus projection, additional isothermal sections may be derived.

2.6. Figures

If the information is available, figures of the phase diagrams are generally presented in the following order: liquidus projection—isothermal sections—isopleths, including quasi-binaries. Graphical representations of the thermodynamic properties are given last.

3. General References

[1] *Metals Handbook*, 8th Ed., Vol. 8, "Metallography, Structures and Phase Diagrams", American Society for Metals, Metals Park, Ohio, 1973.

[2] Pearson, W. B., *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vols. 1 and 2, Pergamon Press, London, 1958 and 1967.

[3] Hansen, M., and Anderko, K., *Constitution of Binary Alloys*, 2nd Edition, McGraw-Hill, New York, 1958.

[4] Elliott, R. P., *Constitution of Binary Alloys*, First Supplement, McGraw-Hill, New York, 1965.

[5] Shunk, F. A., *Constitution of Binary Alloys*, Second Supplement, McGraw-Hill, New York, 1969.

[2] 1 joule = 0.2390 calories.

[6] Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., and Kelley, K. K., *Selected Values of the Thermodynamic Properties of Binary Alloys*, American Society for Metals, Metals Park, Ohio, 1973.
[7] Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D., *Selected Values of the Thermodynamic Properties of the Elements*. American Society for Metals, Metals Park, Ohio, 1973.
[8] Hultgren, R., and Desai, P. D., INCRA Monograph I, *Selected Thermodynamic Values and Phase Diagrams for Copper and Some of Its Binary Alloys*, The International Copper Research Association, Inc., New York, 1971.
[9] Rhines, F., *Phase Diagrams in Metallurgy, Their Development and Application*, McGraw-Hill, New York, 1956.
[10] Prince, A., *Alloy Phase Equilibria*, Elsevier, Amsterdam-London-New York, 1966.
[11] Wagner, S., and Rigney, D. A., Metall. Trans. **5**, 2155 (1974).
[12] Wagner, C., *Thermodynamics of Alloys* (Translated by Mellgren, S., and Westbrook, J. H.), Addison-Wesley, Reading, Mass., 1952.
[13] Lupis, C. H. P., and Elliott, J. F., Trans. Met. Soc. AIME **233**, 829; 1200 (1965).

4. Personnel

Personnel who contributed to this work are Y. A. Chang ((YAC), U. V. Choudary (UVC), D. Goldberg (DG), D. K. Gupta (DKG), H. Ipser (HI), and J. P. Neumann (JPN). The evaluation of each system was the primary responsibility of one of the team members, whose initials are placed on the last page of the evaluation, following the list of references. Each final evaluation was reviewed by other members of the group before being accepted. The line drawings were done by Ms. L. Bickerstaff and the typing by Ms. J. Kenney and Ms. V. Bargenquast.

Dr. D. Goldberg is now with Westinghouse, Plant Apparatus Division, Pittsburgh, Pennsylvania; Dr. D. K. Gupta is now with Howmet Corporation, Whitehall, Michigan; and Dr. H. Ipser is now with the Institut für Anorganische Chemie, Universität Wien, Austria.

5. Acknowledgments

Financial support was provided primarily by INCRA. The authors wish to thank Dr. L. McDonald Schetky of INCRA for his interest in this work and his initiation of support for the project. Financial support of the Graduate School of the University of Wisconsin-Milwaukee on the overall research activities of Professor Y. A. Chang also helped to bring this work to fruition. The authors also wish to thank Dr. H. Ipser for his critical and meticulous review of all evaluations.

One of the authors (YAC) wishes to thank Dr. R. G. Griskey, former Dean of the College of Engineering and Applied Science, for his interest in this work.

6. Phase Diagrams and Thermodynamic Properties of Ternary Copper-Silver-X Systems

Cu-Ag-Al

Phases and Structures

The following intermediate phases appear in the Cu-Al and Ag-Al binary systems. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
β_1	$AlCu_3(\beta)$	bcc	A2	W
γ	~ 11% Al	fcc or cu	A1 or A13	Cu or β-Mn
χ	~ 16% Al	ord bcc	Like $D8_{1-3}$	γ-brass
κ	~ 17% Al(γ_1)	ord bcc	Like $D8_{1-3}$	γ-brass
λ	$Al_4Cu_9(\gamma_2)$	cu	$D8_3$	Al_4Cu_9
δ	~ 22% Al	unknown		
ϵ	~ 22% Al(ϵ_1)	unknown		
σ	$Al_2Cu_3(\epsilon_2)$	pseudo cu(?)		
ζ	~ 25% Al(ζ_1)	hex	Like $D8_3$	Al_4Cu_9
ν	~ 25% Al(ζ_2)	mono (?)		
η	$AlCu(\eta_1)$	ortho		
π	$AlCu(\eta_2)$	eco		
θ	Al_2Cu	bct	C16	Al_2Cu
β_2	$Ag_3Al(HT)(\beta)$	bcc	A2	W
μ	$Ag_3Al(LT)$	cu	A13	β-Mn
ρ	$Ag_2Al(\zeta)$	hcp	A3	Mg

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

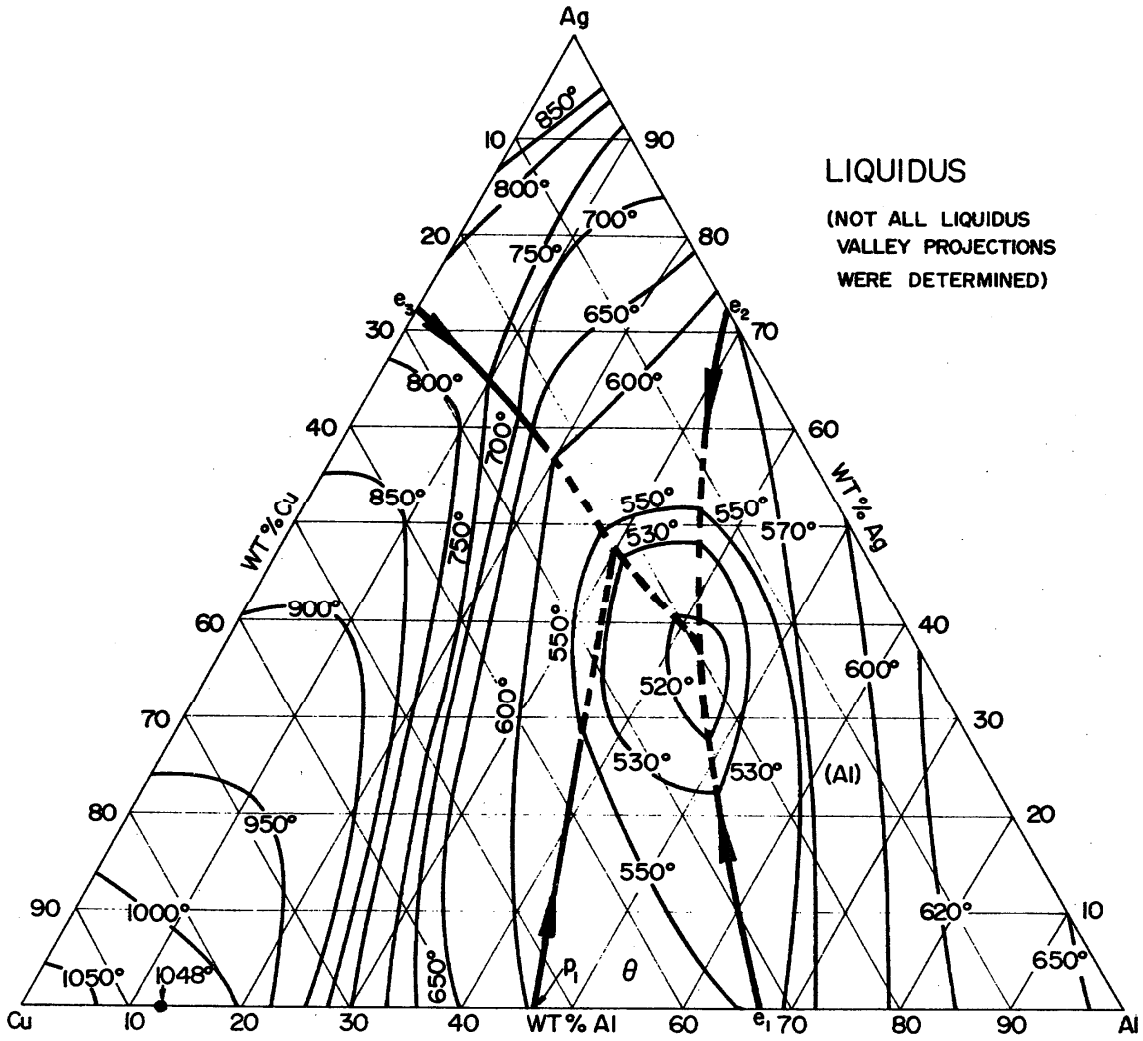
The liquidus was investigated in the early work of Ueno [1], whose data are in fair agreement with the accepted binary liquidus measurements. However, significant corrections were made along the Cu-Al side of the diagram to be consistent with the current binary data. Ueno's investigation was made before the binary phase diagrams were accurately established, thus the isotherms on the liquidus should be regarded as only approximate, and those liquidus valley projections which were determined (extending from the binary eutectics e_1, e_2, and e_3, and from the binary peritectic p_1) are suspect near the middle of the ternary diagram. Ueno's two suggested four-phase equilibria are also highly questionable. For these reasons, the liquidus valley projections are indicated by dashed lines in the questionable region. Ueno also determined a number of vertical sections, but these are not accurate because of lack of knowledge of the binaries.

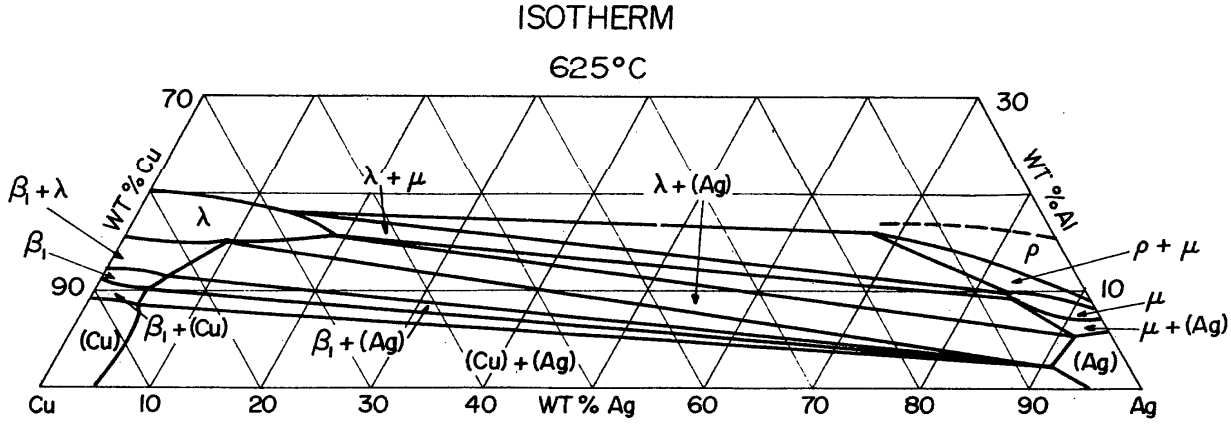
The 625 °C isotherm in the 0 to 20% Al region is from Massalski and Perepezko [2]. They also determined the 570 °C isotherm, which is essentially similar to the one shown except for a small 3-phase (Ag) + μ + ρ region just inside the Ag-Al binary line at about 10% Ag. The vertical sections in the Cu-rich corner determined by Panseri and Leoni [3] do not agree with the more recent work of [2].

References

[1] Ueno, S., Anniversary Vol. Dedicated to M. Chikashige, Kyoto Imp. Univ. 57 (1930).
[2] Massalski, T. B., and Perepezko, J. H., Z. Metallk. **64**, 176 (1973).
[3] Panseri, C., and Leoni, M., Alluminio **30**, 289 (1961).

DG


Ag
LIQUIDUS
(NOT ALL LIQUIDUS VALLEY PROJECTIONS WERE DETERMINED)
WT % Cu
WT % Ag
WT % Al
Cu
Al
(Al)
e_1
e_2
e_3
P_1
θ


ISOTHERM
625°C
WT % Cu
WT % Ag
WT % Al
$\beta_1 + \lambda$
β_1
λ
$\lambda + \mu$
λ + (Ag)
ρ
$\rho + \mu$
μ
μ + (Ag)
(Cu)
β_1 + (Cu)
β_1 + (Ag)
(Cu) + (Ag)
(Ag)
Cu
Ag

Cu-Ag-Au

Phases and Structures

No intermediate phases were found in any of the three binary systems or in the ternary system. However, in the Cu-Au binary system, at low temperatures, the following ordered phases appear:

Designation	Composition	Symmetry	Symbol	Prototype
α'_{I}	$AuCu_3$I (LT)	ord fcc	$L1_2$	$AuCu_3$I
α'_{II}	$AuCu_3$II (HT)	ord fct		
α''_{I}	AuCuI (LT)	ord fct	$L1_0$	AuCuI
α''_{II}	AuCuII (HT)	ord fco		
α'''	Au_3Cu	ord fcc	$L1_2$	$AuCu_3$I

The above crystal structure data are from the Metals Handbook [Gen. Ref. 1], except for $AuCu_3$II, for which the data have been taken from Hultgren [Gen. Ref. 8].

Phase Diagrams

Phase diagram investigations of the ternary system Cu-Ag-Au have been carried out by Sistare [1], Jänecke [2], Sterner-Rainer [3], Masing and Kloiber [4], Raub [5], and McMullin and Norton [6]. The liquidus diagram is from the Metals Handbook [Gen. Ref. 1] and from Sterner-Rainer [3]. A correction has been made in the liquidus diagram to take into account the change in the minimum liquidus temperature on the copper-gold side from 889 °C to 911 °C as reported by Hultgren [Gen. Ref. 8]. The end point of the eutectic valley is not exactly known.

The solvus diagram, which shows the miscibility gap in the solid state between (Cu) and (Ag), is taken from McMullin and Norton [6]. According to Masing and Kloiber [4], the tie lines in the miscibility gap are nearly parallel to the copper-silver side. Raub [5] observed that the ordering temperature of the copper-gold superlattice structures is lowered by the addition of silver.

Thermodynamic Properties

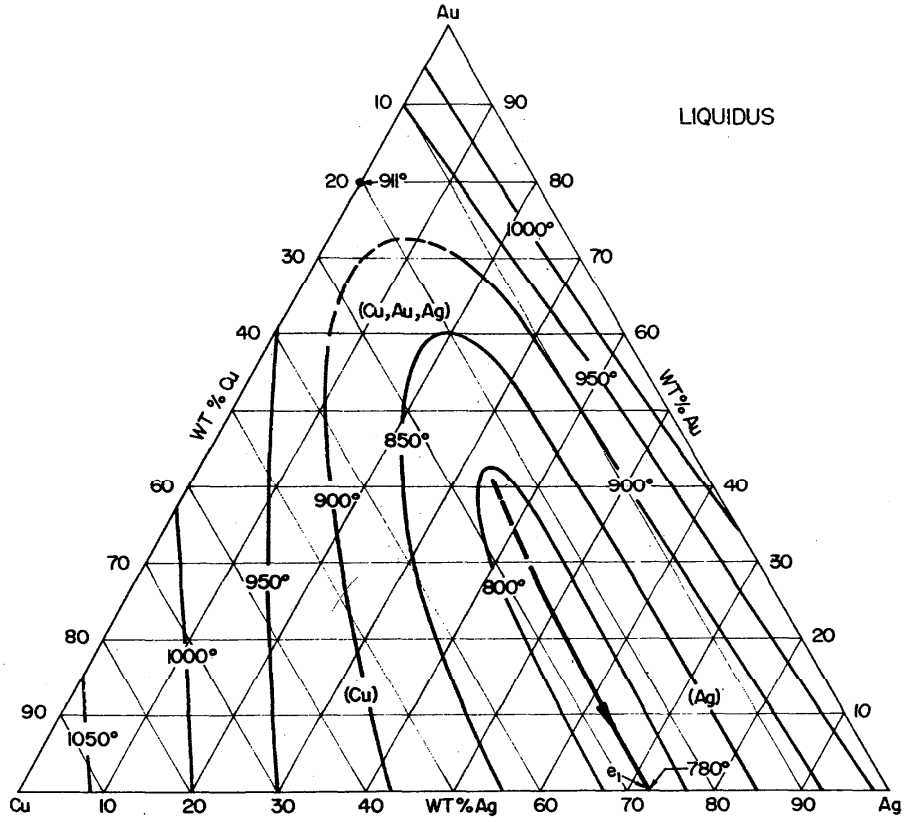
Bolsaitis and Skolnick [7] have employed the Knudsen effusion technique to measure the vapor pressure of silver over ternary liquid Cu-Ag-Au alloys at 1350 K. Their results, expressed in terms of the activity coefficient, γ_{Ag}, are shown in the graph.

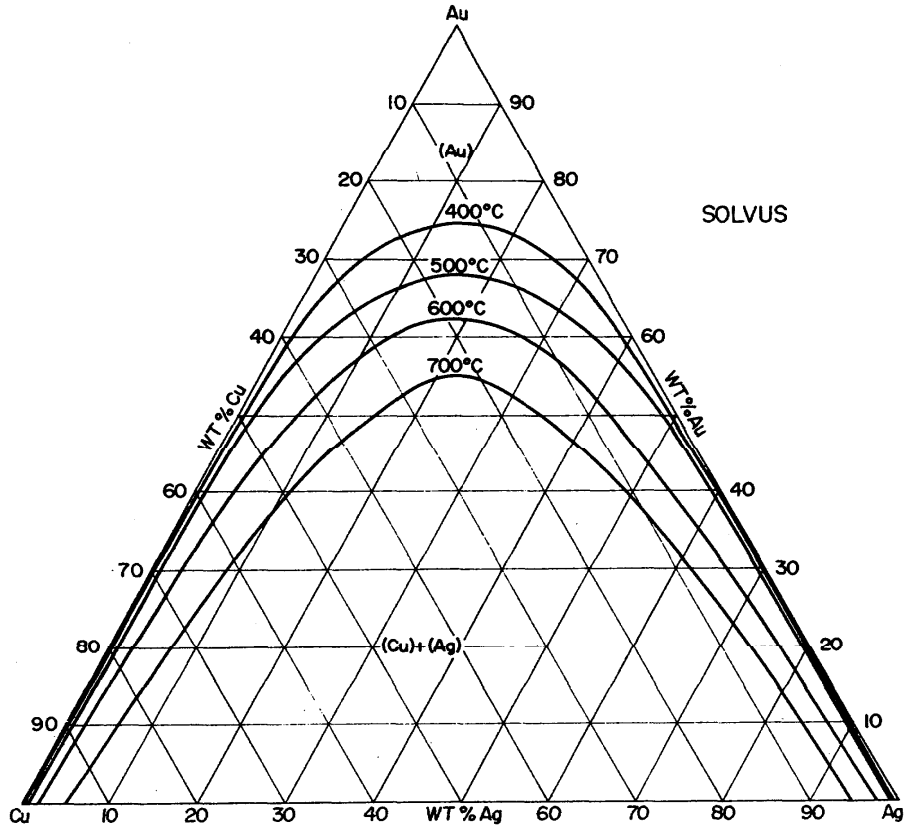
The authors used the vapor pressure data furthermore, to estimate the integral excess free energy, the integral enthalpy of formation and the activities of copper and gold in the ternary system.

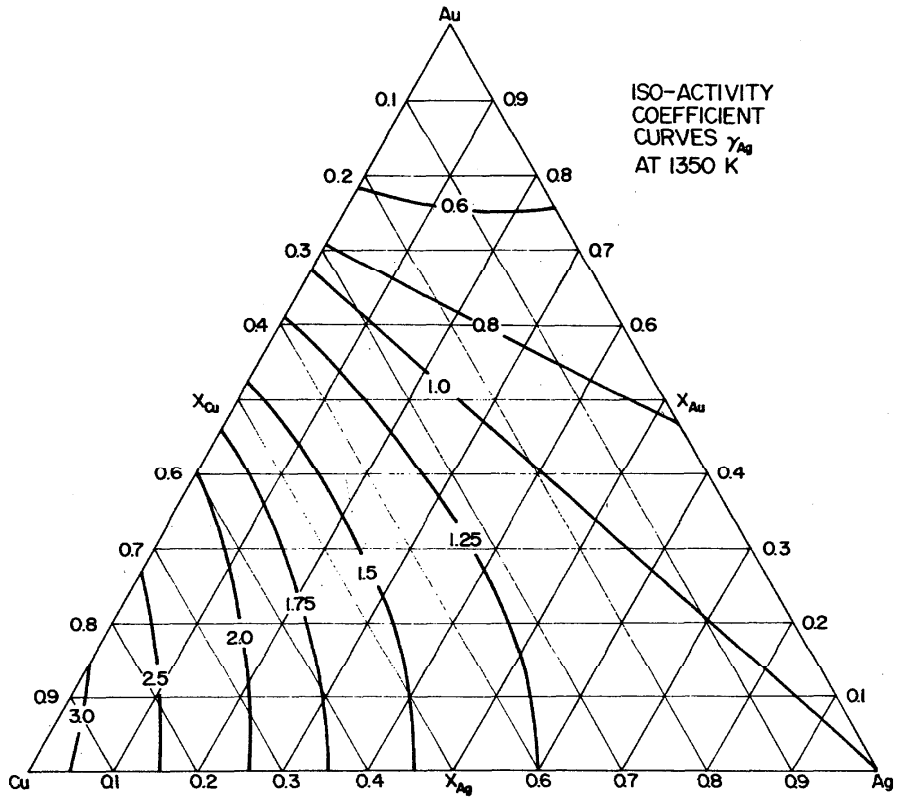
References

[1] Sistare, G. H., cited in Gen. Ref. 1, p. 377.
[2] Jänecke, E., Metallurgie **8**, 597 (1912).
[3] Sterner-Rainer, L., Z. Metallk. **18**, 143 (1926).
[4] Masing, G., and Kloiber, K., Z. Metallk. **32**, 125 (1940).
[5] Raub, E., Z. Metallk. **40**, 46 (1949).
[6] McMullin, J. G., and Norton, J. T., J. Metals **1**, 46 (1949).
[7] Bolsaitis, P., and Skolnick, L., Trans. Met. Soc. A.I.M.E. **242**, 225 (1968).

JPN


Au
LIQUIDUS
911°
1000°
950°
900°
850°
800°
(Cu,Au,Ag)
(Cu)
(Ag)
e1
780°
1050°
WT % Cu
WT % Au
WT % Ag
Cu
Ag


Au
SOLVUS
(Au)
400°C
500°C
600°C
700°C
(Cu)+(Ag)
WT % Cu
WT % Au
WT % Ag
Cu
Ag



Cu-Ag-Cd

Phases and Structures

The following intermediate phases appear in the Cu-Cd and Ag-Cd binary systems. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
δ	Cu_2Cd	hex	C36	$MgNi_2$
η	Cu_4Cd_3	comp cu		
γ_1'	$Cu_5Cd_8(\gamma)$	ord bcc	$D8_2$	γ-brass
θ	$CuCd_3$	comp hex		
β	AgCd(HT)	bcc	A2	W
ζ	AgCd(MT)	hcp	A3	Mg
β'	AgCd(LT)	ord bcc	B2	CsCl
ϕ	AgCd(VLT)	ortho	Like B19	β'-AuCd
γ	Ag_5Cd_8(HT)	ord bcc	$D8_2$	γ-brass
γ_2'	Ag_5Cd_8(LT)(γ')	ord bcc	Like $D8_2$	variant of γ-brass
ϵ	$AgCd_3$	hcp	A3	Mg

The crystal structures of the Cu-Cd phases are from the Metals Handbook [Gen. Ref. 1], and the structures of the Ag-Cd phases are from Pearson [Gen. Ref. 2], with the γ_2'-Ag_5Cd_8(LT) structure from Hansen [Gen. Ref. 3]. The Metals Handbook contains several inconsistencies, with respect to the phase designations in the binary system silver-cadmium, between the phase diagrams and the list of phases. The nature of the γ-γ' transformation in this system is not clear.

The β'-phase undergoes at sub-zero temperatures a martensitic transformation to the orthorhombic structure ϕ.

Phase Diagrams

Earlier studies of the ternary phase diagram Cu-Ag-Cd by Losana and Goria [1], Keinert [2], and Weigert [3], were superseded by the more extensive investigations by Gebhardt and Petzow [4, 5]. In their first investigation, Gebhardt and Petzow established the liquidus and five isopleths at 25% Cd, 35% Cd, 45% Cd, 55% Cd and 65% Cd. In their second paper, they gave three isothermal sections at 600 °C, 500 °C, and 300 °C; isopleths at 5% Cu and 5% Ag, and all the four-phase reaction equilibria. Petzow and Gebhardt [6] also represented the ternary constitution diagram using three-dimensional models for ease of visualization but no additional phase investigation was made. The isothermal sections at 600°, 500°, and 300 °C, the liquidus projection and the 25% Cd isopleth given here are those of Gebhardt and Petzow [4, 5].

The liquidus projection shows three binary eutectics e_1, e_2, and e_3 and seven binary peritectics, p_1 to p_7. These three-phase binary reactions continue into the ternary field to form six four-phase equilibria, one

type I and five type II. The compositions of the coexisting phases and the temperatures of the four-phase planes are given in table I.

In the solid state, there are four four-phase equilibria, two of which are type I (I_2 and I_3) and two of which are type II (II_4 and II_7). Their temperatures and the compositions of the co-existing phases, estimated from relatively small graphs in [4], are also given in table I. The difference in the structure between the γ- and γ'-phases in the silver-cadmium system is not clear. For this reason, no distinction is made between them in the ternary system; both are designated as γ.

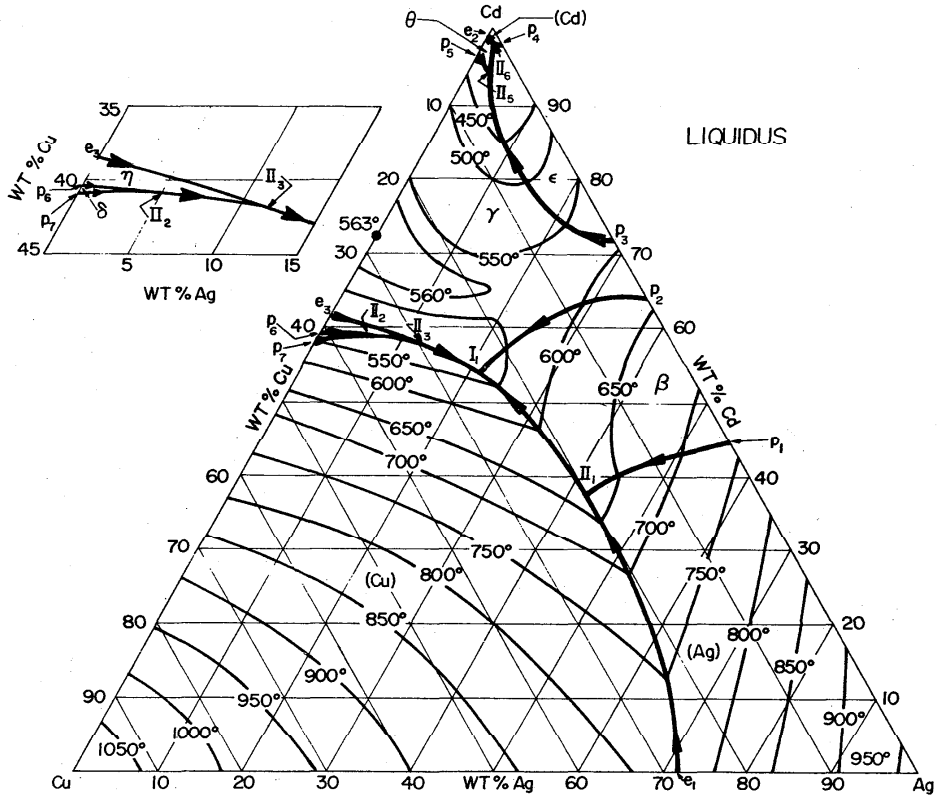
References

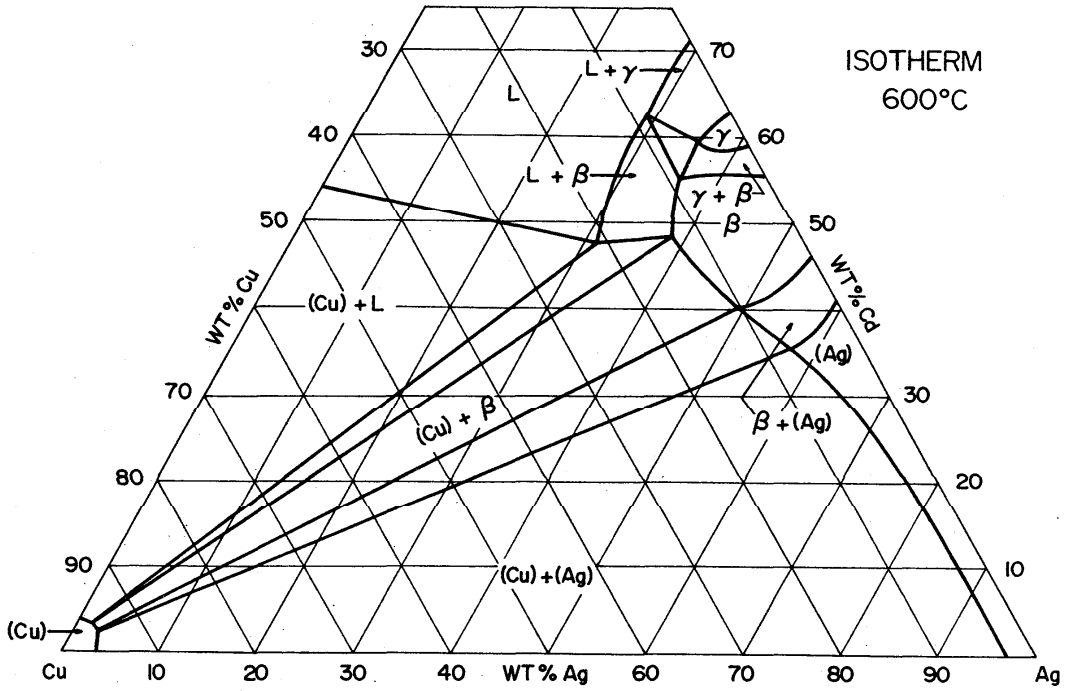
[1] Losana, L., and Goria, C., L'Industria Chimica **9**, 1603 (1934).
[2] Keinert, M., Z. physik. Chem. **A162**, 289 (1932).
[3] Weigert, K. M., Weld. J. **34**, 420 (1955).
[4] Gebhardt, E., and Petzow, G., Z. Metallk. **47**, 901 (1956).
[5] Gebhardt, E., and Petzow, G., Z. Metallk. **47**, 751 (1956).
[6] Petzow, G., and Gebhardt, E., Z. Metallk. **50**, 704 (1959).

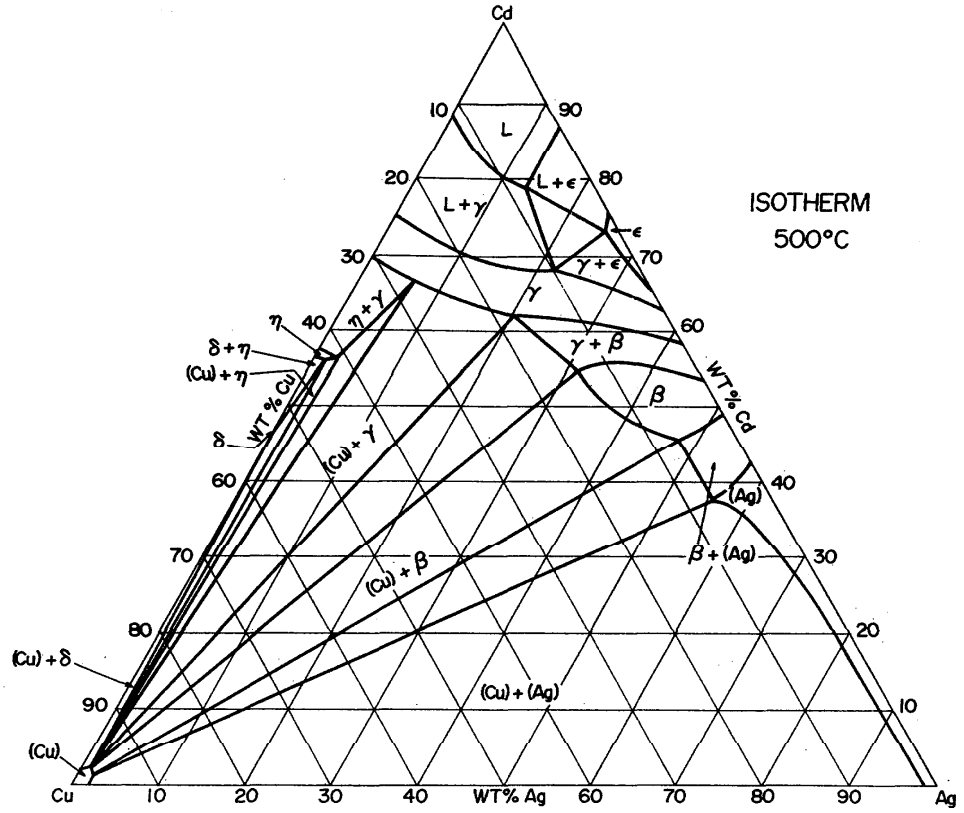
YAC

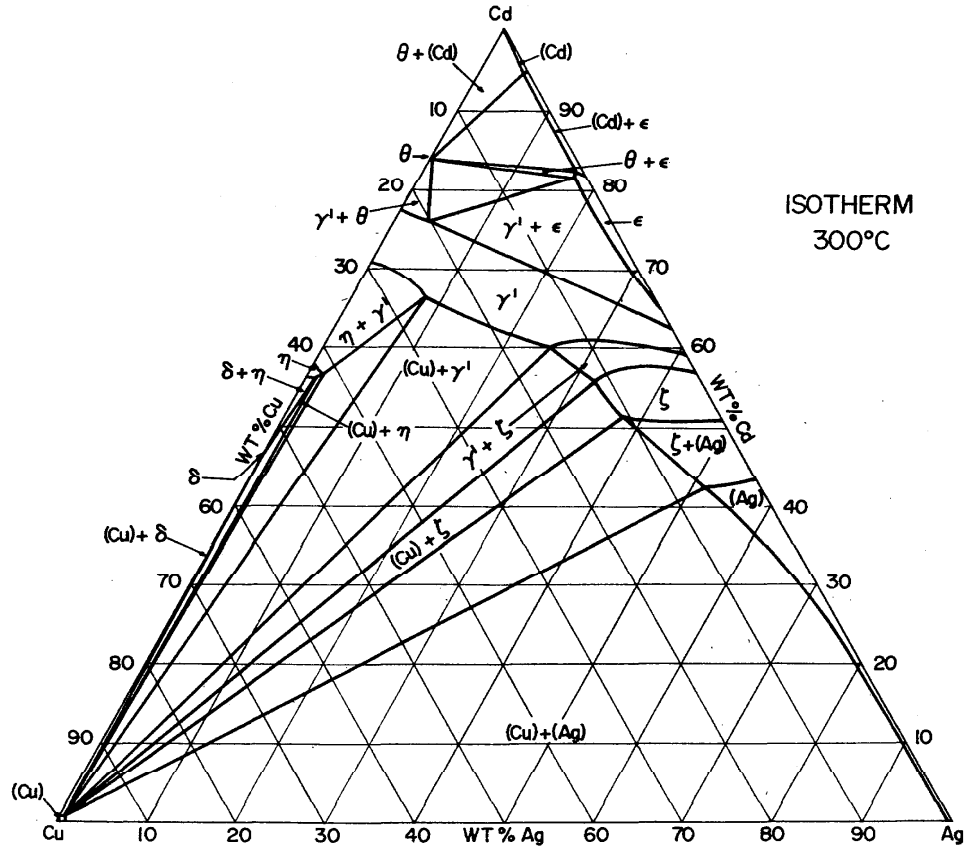
TABLE I. Four-phase equilibria in the Cu-Ag-Cd system

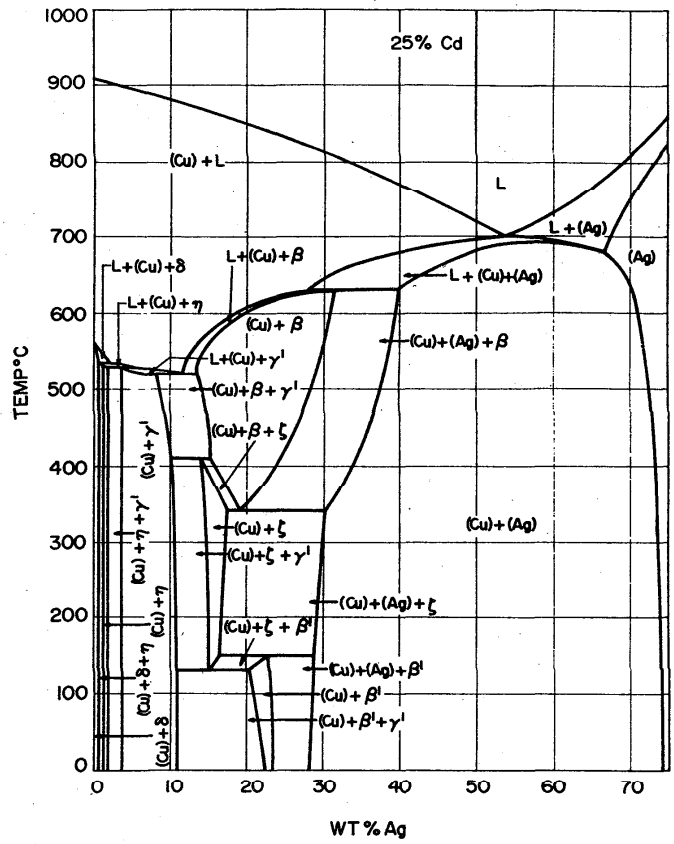
Reaction	Temp. °C	Coexisting phases	Composition of phases		
			Wt. % Cu	Wt. % Ag	Wt. % Cd
II_1: $L + (Ag) = (Cu) + \beta$	630	L	20.5	42.5	37
		β	12	49.5	38.5
		(Cu)	95	2.5	2.5
		(Ag)	6	58	36
II_2: $L + \delta = (Cu) + \eta$	535	L	36	5	59
		η	43	1	56
		δ	53	0	47
		(Cu)	96	1	3
II_3: $L + \eta = (Cu) + \gamma'$	530	L	30	12	58
		γ'	28.5	6	65.5
		η	41.5	1.5	57
		(Cu)	95.5	1.5	3
I_1: $L = (Cu) + \beta + \gamma'$	525	L	24	23	53
		γ'	21	18.5	60.5
		β	16	29.5	54.5
		(Cu)	96	1.5	2.5
II_4: $\beta + \gamma' = \zeta + (Cu)$	410	γ'	16	23.5	60.5
		ζ	12	31.5	56.5
		β	13	33	54
		(Cu)	96	2	2
II_5: $L + \gamma' = \epsilon + \theta$	350	L	3	3	94
		θ	15.5	0.5	84
		ϵ	2	15.5	82.5
		γ'	21.5	3.5	75
I_2: $\beta = \zeta + (Cu) + (Ag)$	340	β	16	37	47
		ζ	11	37	52
		(Cu)	96	2	2
		(Ag)	6	52	42
II_6: $L + \epsilon = \theta + (Cd)$	325	L	1	1	98
		ϵ	1	16	83
		θ	14.5	0.5	85
		(Cd)	0.5	7	92.5
II_7: $(Ag) + \zeta = (Cu) + \beta'$	150	ζ	12	36	52
		β'	6	46	48
		(Cu)	98	1	1
		(Ag)	8	50	42
I_3: $\zeta = (Cu) + \beta' + \gamma'$	130	ζ	12	33	55
		β'	6	43	51
		γ'	12	27	61
		(Cu)	98	1	1


LIQUIDUS
Cd
(Cd)
θ
WT % Cu
WT % Ag
WT % Cd
Cu
Ag
(Cu)
(Ag)


ISOTHERM
600°C
L
L + γ
L + β
γ + β
β
(Cu) + L
(Cu) + β
(Cu) + (Ag)
β + (Ag)
(Ag)
(Cu)
WT % Cu
WT % Cd
WT % Ag
Cu
Ag


Cd
L
L+ϵ
L+γ
ϵ
γ+ϵ
γ
γ+β
β
η
η+γ
δ+η
(Cu)+η
δ
(Cu)+γ
(Ag)
β+(Ag)
(Cu)+β
(Cu)+δ
(Cu)+(Ag)
(Cu)
Cu
WT% Cu
WT% Cd
WT% Ag
Ag
ISOTHERM
500°C


Cd
θ+(Cd)
(Cd)
(Cd)+ϵ
θ
θ+ϵ
γ'+θ
γ'+ϵ
ϵ
γ'
η+γ'
(Cu)+γ'
δ+η
η
(Cu)+η
γ'+ζ
ζ
ζ+(Ag)
(Ag)
δ
(Cu)+δ
(Cu)+ζ
(Cu)+(Ag)
(Cu)
Cu
WT%Cu
WT%Cd
WT% Ag
Ag
ISOTHERM
300°C



Cu-Ag-Fe

Phases and Structures

No intermediate phases have been reported in the binary systems or in the ternary system.

Phase Diagrams

The diagram showing the miscibility gap between two liquids ($L_1 + L_2$) is from Lüder [1]. The gap in the miscibility of Cu-Ag-Fe alloys in the liquid state extends over most of the diagram. The alloys separate into two liquids, one of which consists almost entirely of Fe and the other of Ag and Cu with very little Fe, as shown by the tie lines determined at the indicated temperatures.

Since the binary system Cu-Fe, which forms the basis for the ternary Cu-Fe-X systems in this compilation, is subject to certain controversy, particularly on the Fe-rich side, a brief discussion of it is given at this point. Hansen [Gen. Ref. 3] gives a nearly vertical γ-Fe solidus curve between the two peritectic equilibria at ~1484 °C [L+(δ-Fe)=(γ-Fe)] and at ~1094 °C [L+(γ-Fe)=(Cu)]. The vertical solidus curve was confirmed by Hellawell and Hume-Rothery [2] but it does not agree with the retrograde solidus curve observed by Bochvar et al. [3], which lies at higher Cu concentrations.

Furthermore, two mistakes appear in literature evaluations of this system, involving the conversion between wt.% and at.%. The Metals Handbook [Gen. Ref. 1] contains an error concerning the peritectic equilibrium L + (δ-Fe) = (γ-Fe) at 1480 °C. According to the figure on p. 293 of Gen. Ref. 1, the phases have the following compositions:

	wt.% Cu
δ-Fe:	6.7
γ-Fe:	8.3
L:	10.3

These data were apparently taken from reference [2]; however, in this reference the compositions are given in at.% and the conversion to wt.% would yield the following values:

	wt.% Cu
δ-Fe:	7.5
γ-Fe:	9.3
L:	11.6

In a later publication by Hume-Rothery and Buckley [4], the solubility of Cu in δ-Fe was reported as 7.2 at.%, which corresponds to 8.1 wt.%.

Hultgren [Gen. Ref. 6] contains an error concerning the peritectic equilibrium L + (γ-Fe) = (Cu), at ~1094 °C and the eutectoid equilibrium (γ-Fe) = (Cu) + (α-Fe) at ~850 °C.

According to the figure on page 739 of Gen. Ref. 6, the solubility limits of Cu in γ-Fe and α-Fe are as follows:

		at.% Cu
At 1094 °C:	γ-Fe:	7.5
At 850 °C:	γ-Fe:	3.0
	α-Fe:	2.4

These data were apparently taken from figure 8 of Speich et al. [5], who, unfortunately, made a mistake when converting wt.% to at.%. The correct compositions should be:

		wt.% Cu	at.% Cu
At 1094 °C:	γ-Fe:	6.8	6.0
At 850 °C:	γ-Fe:	2.6	2.3
	α-Fe	2.1	1.9

Already, Speich et al. [5] have pointed out that their solubility data of Cu in γ-Fe are lower than those selected by Hansen [Gen. Ref. 3]. The corrected Fe-rich side of the Cu-Fe phase diagram is shown in the figure.

References

[1] Lüder, E., Z. Metallk. **16**, 61 (1924).

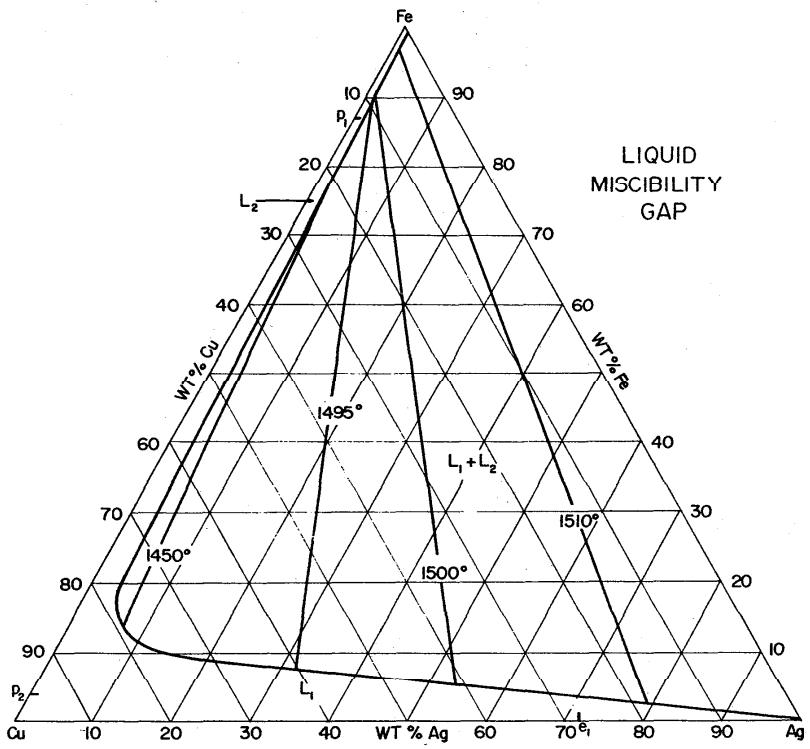
[2] Hellawell, A., and Hume-Rothery, W., Phil. Trans. Roy. Soc. London **A249**, 417 (1957).

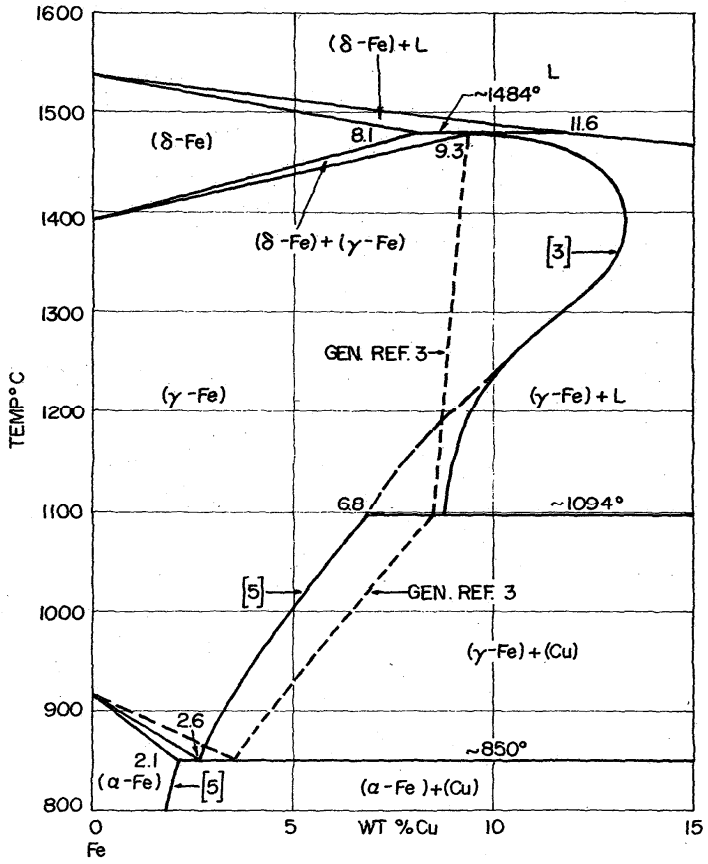
[3] Bochvar, A. A., Ekatova, A. S., Panchenko, E. V., and Sidokhin, Yu. F., Dokl. Adad. Nauk SSSR **174**, 863 (1967).

[4] Hume-Rothery, W., and Buckley, R. A., J. Iron Steel Inst. **202**, 531 (1964).

[5] Speich, G. R., Gula, J. A., and Fisher, R. M., in: *The Electron Microprobe* (Eds.: T. D. McKinley, K. F. J. Heinrich, D. B. Wittry), p. 525, Wiley, New York, 1966.

JPN





Cu-Ag-Ge

Phases and Structures

The following intermediate phases appear in the Cu-Ge binary system. No ternary compounds have been found.

Designation	Composition	Symmetry	Symbol	Prototype
ζ	Cu_5Ge	hcp	A3	Mg
ϵ	Cu_3Ge(HT)	trigonally distorted bcc	A2	W
ω	Cu_3Ge(LT)(ϵ_1)	ortho		β.Cu_3Ti
ψ	~31% Ge(ϵ_2)	bcc	A2	W

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

The isotherm at 500 °C is based upon the work of Nowotny and Bachmayer [1]. Their estimated liquidus, constructed from thermal analysis of only nine samples, was revised to be consistent with the currently accepted binaries and is also shown. There are four four-phase equilibria involving the liquid phase, two type-I and two type-II, as listed in table I. The composition of the phases involved was not determined.

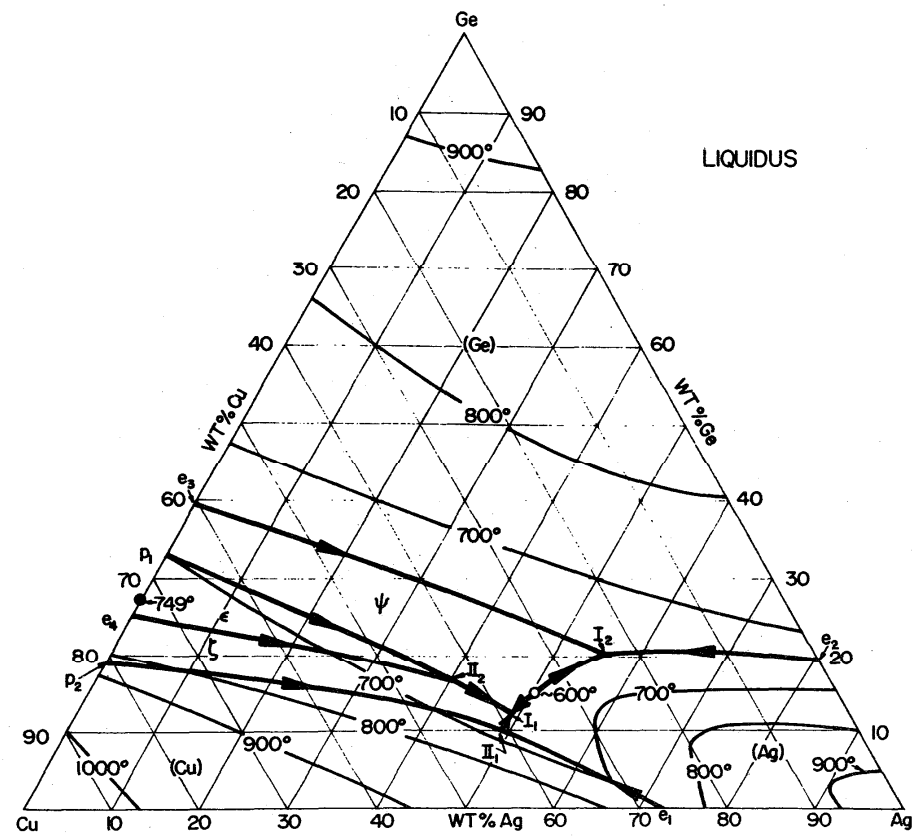
Reference

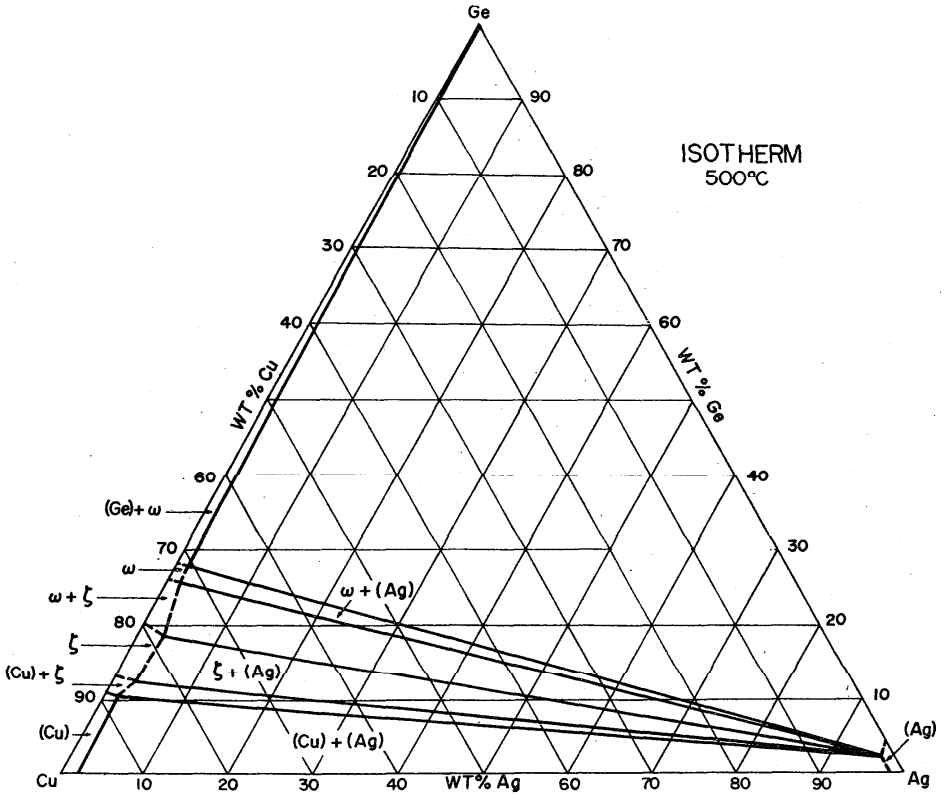
[1] Nowotny, H., and Bachmayer, K., Monatsh. Chem. **81**, 669 (1950).

DG

TABLE I. Four-phase equilibria with the liquid in the Cu-Ag-Ge System

Reaction	Temp. °C
II_1: $L+(Cu)=(Ag)+\zeta$	685
II_2: $L+\epsilon=\zeta+\psi$	640
I_1: $L=(Ag)+\zeta+\psi$	545
I_2: $L=(Ag)+(Ge)+\psi$	520


Ge
LIQUIDUS
900°
800°
700°
(Ge)
WT% Cu
WT% Ge
WT% Ag
Cu
Ag
e3
e4
e2
e1
p1
p2
749°
ψ
ζ
ε
I2
II2
I1
II1
~600°
1000°
(Cu)
(Ag)


Ge
ISOTHERM
500°C
WT% Cu
WT% Ge
WT% Ag
Cu
Ag
(Ge)+ω
ω
ω+ζ
ζ
(Cu)+ζ
(Cu)
ω+(Ag)
ζ+(Ag)
(Cu)+(Ag)
(Ag)

Cu-Ag-In

Phases and Structures

The following intermediate phases appear in the Cu-In and Ag-In binary systems. No ternary compounds have been found.

Designation	Composition	Symmetry	Symbol	Prototype
β_1	$Cu_4In(\beta)$	bcc	A2	W
γ_1	~42% In(γ)	ord bcc	$D8_{1-3}$	γ-brass
δ	~43% In	ambiguous		
η	Cu_2In	hex	$B8_2$	Ni_2In
ϕ	~56% In	unknown		
α'	Ag_3In	cu or ord fcc	$L1_2$	$AuCu_3I$
β_2	Ag_3In(HT)	bcc	A2	W
ζ	Ag_3In(LT)	hcp	A3	Mg
γ_2	$Ag_2In(\gamma)$	ord cu	$D8_{1-3}$	γ-brass
θ	$AgIn_2(\phi)$	bct	C16	Al_2Cu

The above crystal structures are from the Metals Handbook [Gen. Ref. 1]. In addition, Gauneau and Graf [1] report a monoclinic phase with composition 83.2 wt.% Cu and 16.8 wt.% In, stable below about 475 °C. Jain et al. [2] report the existence of five separate phases in the η-phase region of the Cu-In system, between 48 and 54 wt.% In.

Phase Diagrams

The liquidus and isopleths at 10% In and 20% In were taken from Gebhardt and Dreher [3]. The isotherms at 450 °C, 500 °C, and 550 °C and isopleths at 25% In and 30% In were taken from the additional work of Gebhardt and Dreher [4]. They report two type I and four type II four-phase equilibria, with temperatures and compositions listed in Table I below. The binary eutectic (e_1) and peritectics (p_1 to p_3) in the composition region studied are indicated on the liquidus diagram. The liquidus valleys extend from these points into the ternary diagram and intersect at the points II_1 and II_2, corresponding to the 4-phase equilibria involving the liquid phase.

References

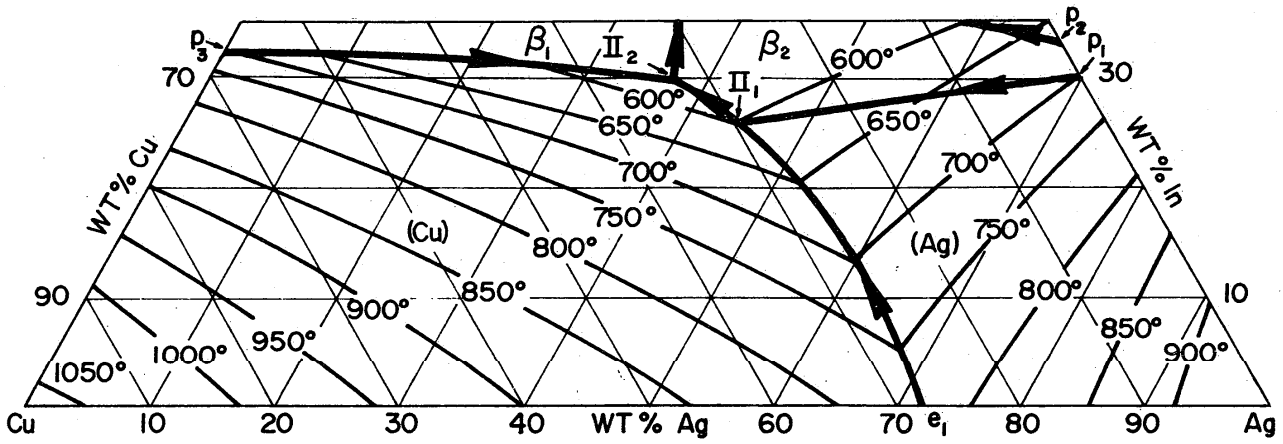
[1] Gauneau, M., and Graf, R., Compt. rend., Ser. B **266,** 1397 (1968).
[2] Jain, K. C., Ellner, M., and Schubert, K., Z. Metallk. **63,** 456 (1972).
[3] Gebhardt, E., and Dreher, M., Z. Metallk. **42,** 230 (1951).
[4] Gebhardt, E., and Dreher, M., Z. Metallk. **43,** 357 (1952).

DG

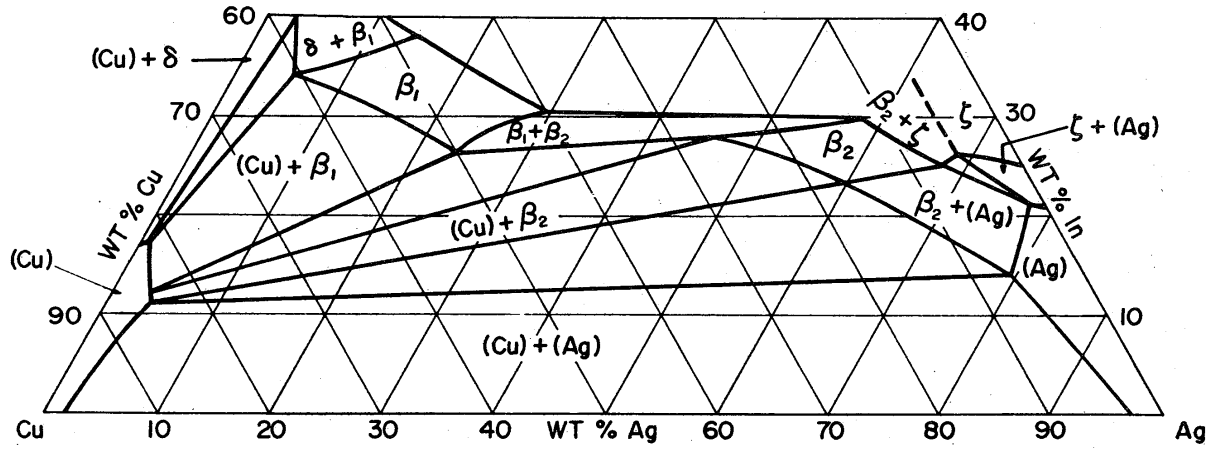
TABLE I. Four-phase equilibria in the Cu-Ag-In system

Reaction	Temp. °C	Coexisting phases	Composition of phases Wt. % Cu	Wt. % Ag	Wt. % In
II_1: $L + (Ag) = (Cu) + \beta_2$	600	(Cu)	71.6	17.7	10.7
		(Ag)	9.1	80.2	10.7
		β_2	17.3	60.0	22.7
		L	28.5	46.0	25.5
II_2: $L + (Cu) = \beta_1 + \beta_2$	575	(Cu)	64.1	17.5	18.4
		β_1	44.0	29.1	26.9
		β_2	28.4	43.5	28.1
		L	34.1	36.6	29.3
II_3: $L + \beta_2 = \zeta + \beta_1$	560	Not reported			
I_1: $\beta_1 = (Cu) + \beta_2 + \delta$	490	(Cu)	87.1	1.8	11.1
		β_2	22.5	51.4	26.1
		δ	51.0	8.5	40.5
		β_1	54.7	14.0	31.3
II_4: $\beta_2 + \gamma_1 = (Ag) + \delta$	485	Not reported			
I_2: $\beta_2 = (Cu) + (Ag) + \delta$	475	(Cu)	87.1	1.8	11.1
		(Ag)	4.0	76.0	80.0
		δ	45.0	8.4	46.6
		β_2	17.0	56.2	26.8

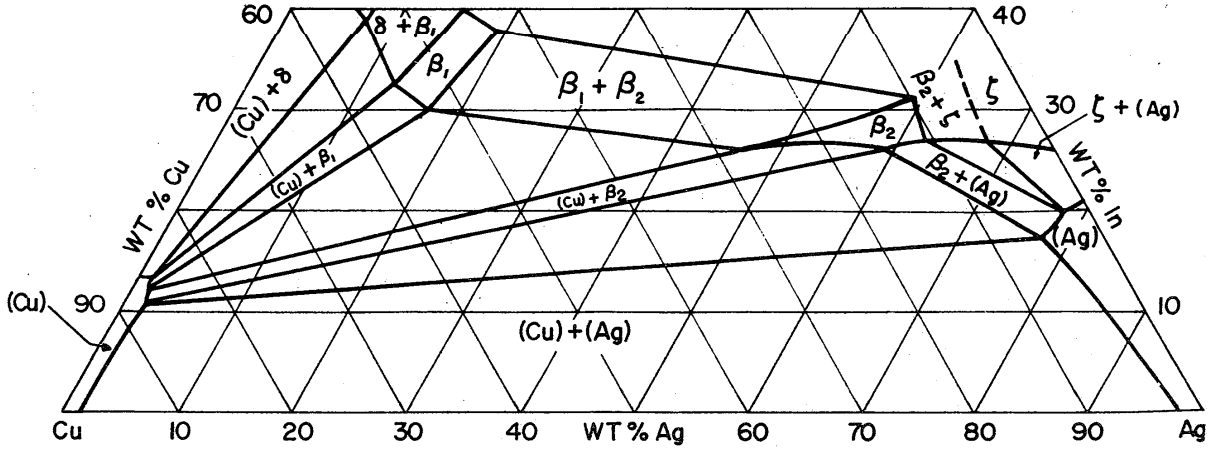
LIQUIDUS

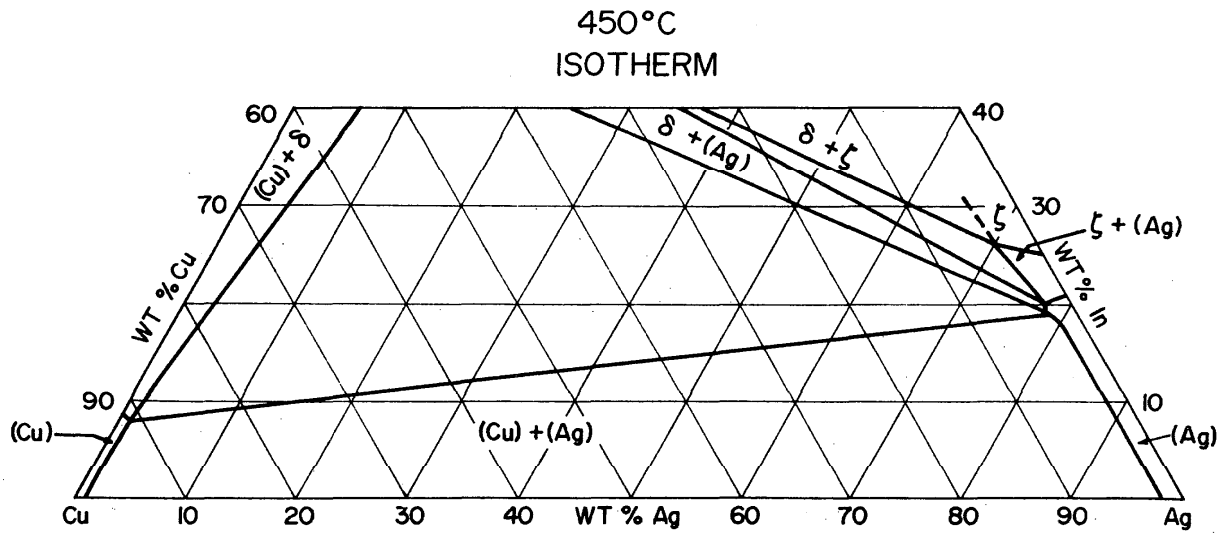


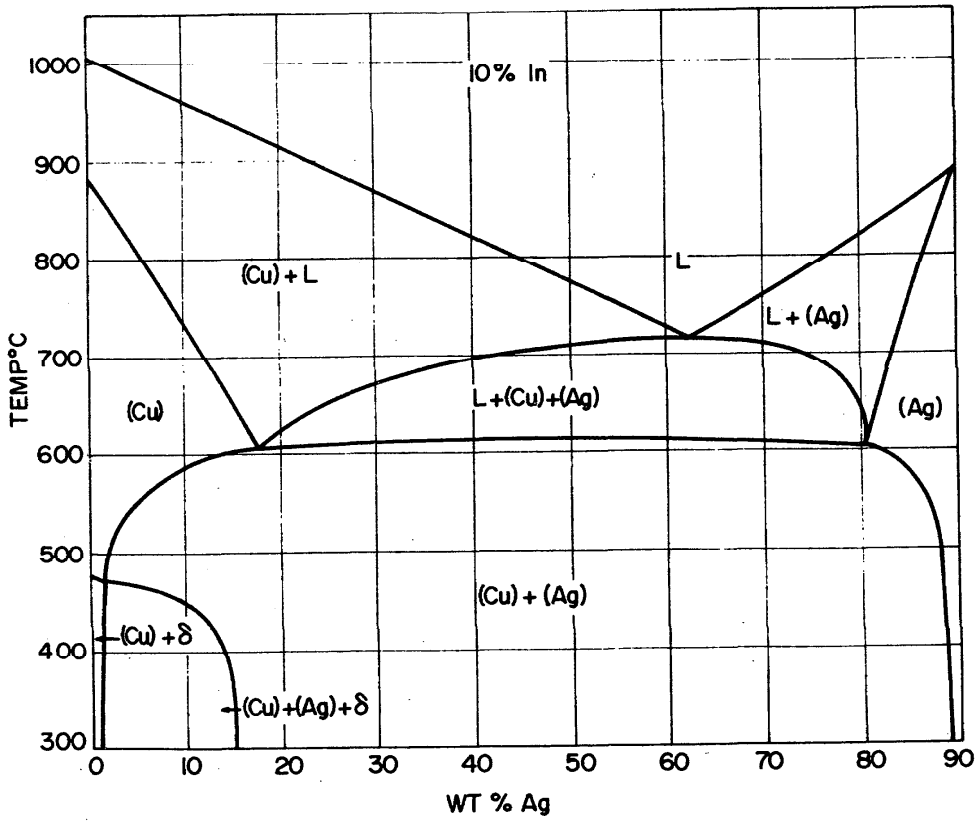
550°C ISOTHERM

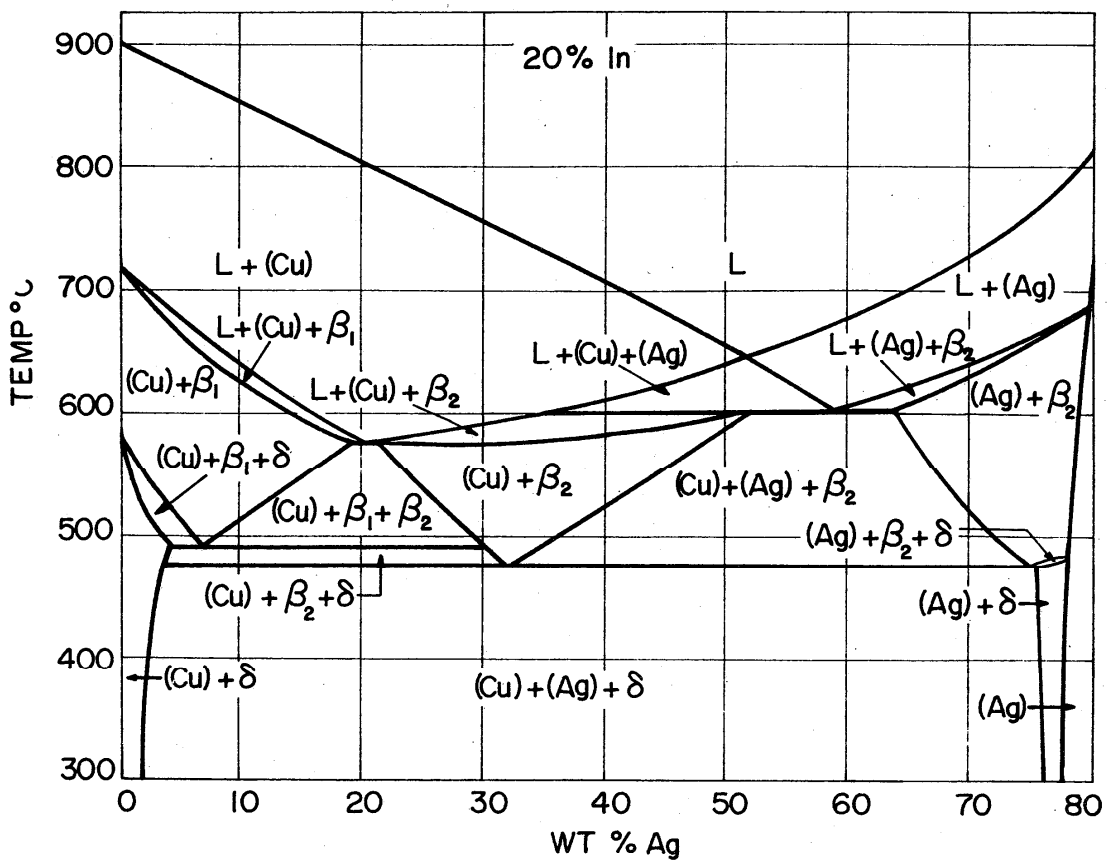


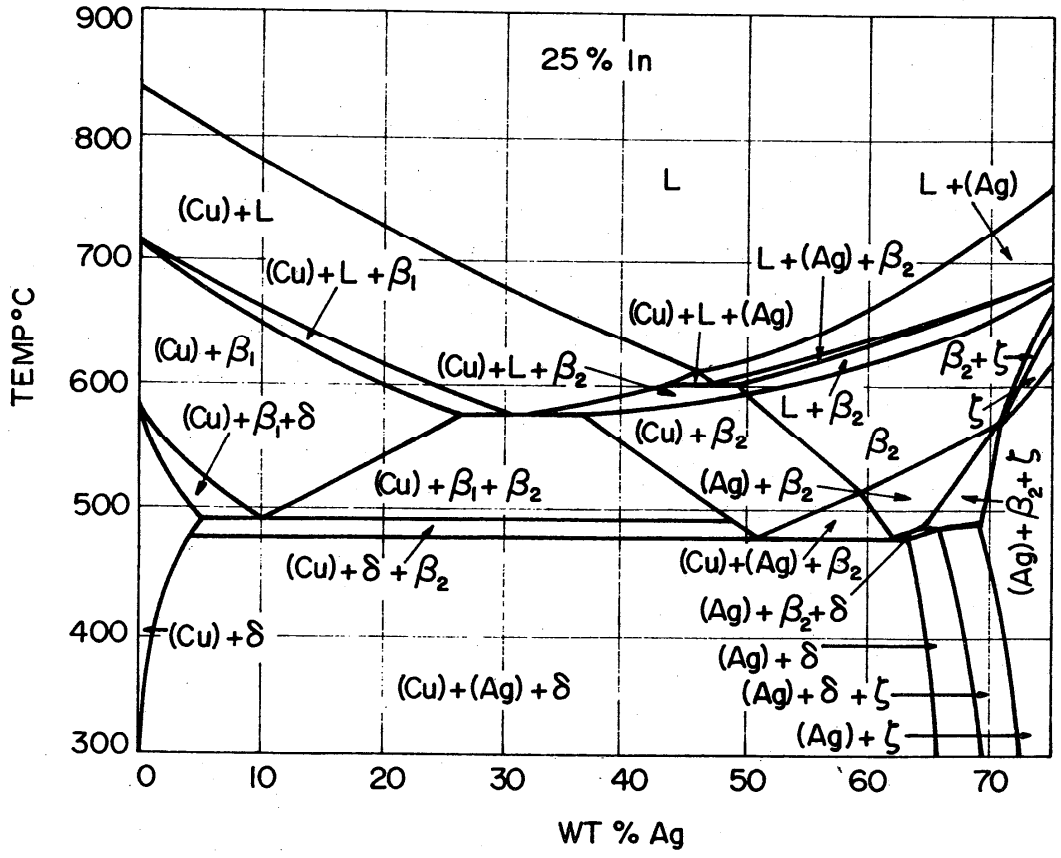
500°C ISOTHERM

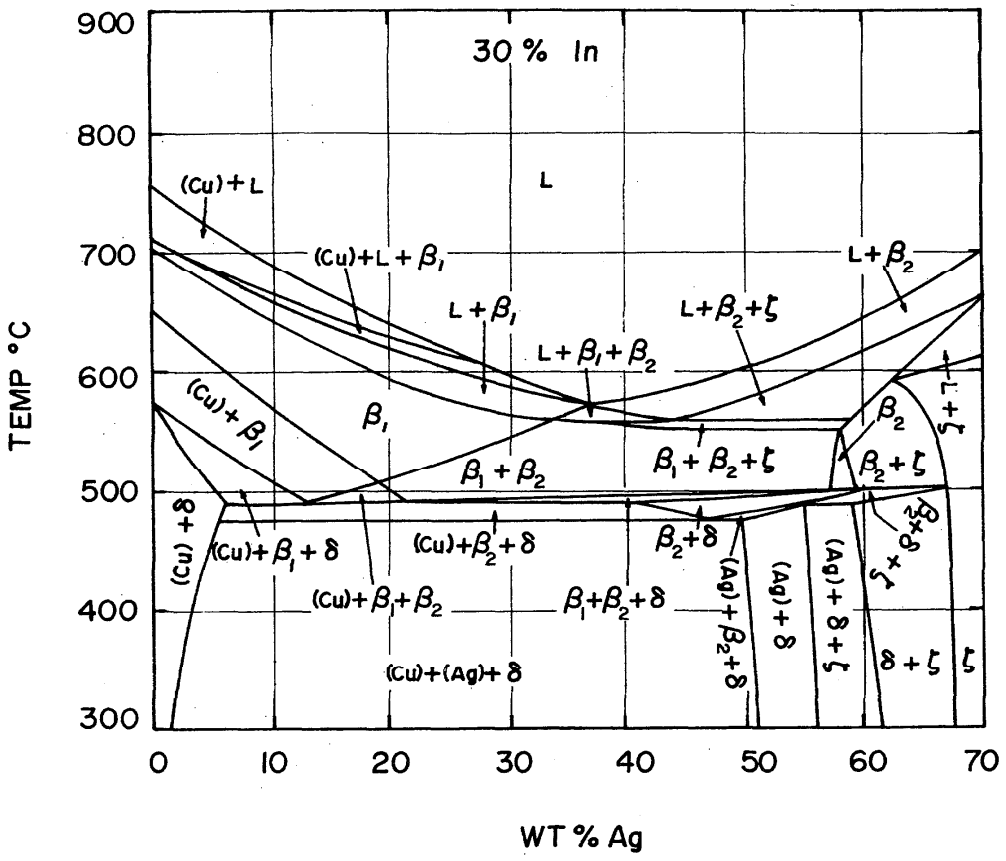



450°C
ISOTHERM
60
70
80
90
40
30
20
10
WT % Cu
WT % In
(Cu)+δ
δ +(Ag)
δ +ζ
ζ
ζ + (Ag)
(Cu)
(Cu) +(Ag)
(Ag)
Cu
10
20
30
40
WT % Ag
60
70
80
90
Ag


10% In
1000
900
800
700
600
500
400
300
TEMP°C
(Cu) + L
L
L + (Ag)
(Cu)
L+(Cu)+(Ag)
(Ag)
(Cu) + (Ag)
(Cu) +δ
(Cu)+(Ag)+δ
0
10
20
30
40
50
60
70
80
90
WT % Ag


20% In
L
L + (Cu)
L + (Ag)
L+(Cu)+β1
L+(Cu)+(Ag)
L+(Ag)+β2
(Cu)+β1
L+(Cu)+β2
(Ag)+β2
(Cu)+β1+δ
(Cu)+β2
(Cu)+(Ag)+β2
(Cu)+β1+β2
(Ag)+β2+δ
(Cu)+β2+δ
(Ag)+δ
(Cu)+δ
(Cu)+(Ag)+δ
(Ag)
TEMP°C
WT % Ag
900
800
700
600
500
400
300
0
10
20
30
40
50
60
70
80


25% In
L
(Cu)+L
L +(Ag)
(Cu)+L +β1
L+(Ag)+β2
(Cu)+L+(Ag)
(Cu)+β1
(Cu)+L+β2
β2+ζ
L+β2
ζ
(Cu)+β1+δ
(Cu)+β2
β2
(Cu)+β1+β2
(Ag)+β2
(Ag)+β2+ζ
(Cu)+δ+β2
(Cu)+(Ag)+β2
(Ag)+β2+δ
(Cu)+δ
(Ag)+δ
(Cu)+(Ag)+δ
(Ag)+δ+ζ
(Ag)+ζ
TEMP°C
WT % Ag
900
800
700
600
500
400
300
0
10
20
30
40
50
60
70



Cu-Ag-Mg

Phases and Structures

The following phases appear in the binary systems Cu-Mg and Ag-Mg. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
μ	$CuMg_2$	ord ortho		
σ	Cu_2Mg	ord fcc	C15	Cu_2Mg
α'	Ag_3Mg	pseudo cu or: ord bct	$L1_2$ (distorted) DO_{23}	$AuCu_3I$ Al_3Zr
β'	AgMg	ord bcc	B2	CsCl
ϵ	$AgMg_3$	hex		

The above crystal structures are from the Metals Handbook [Gen. Ref. 1].

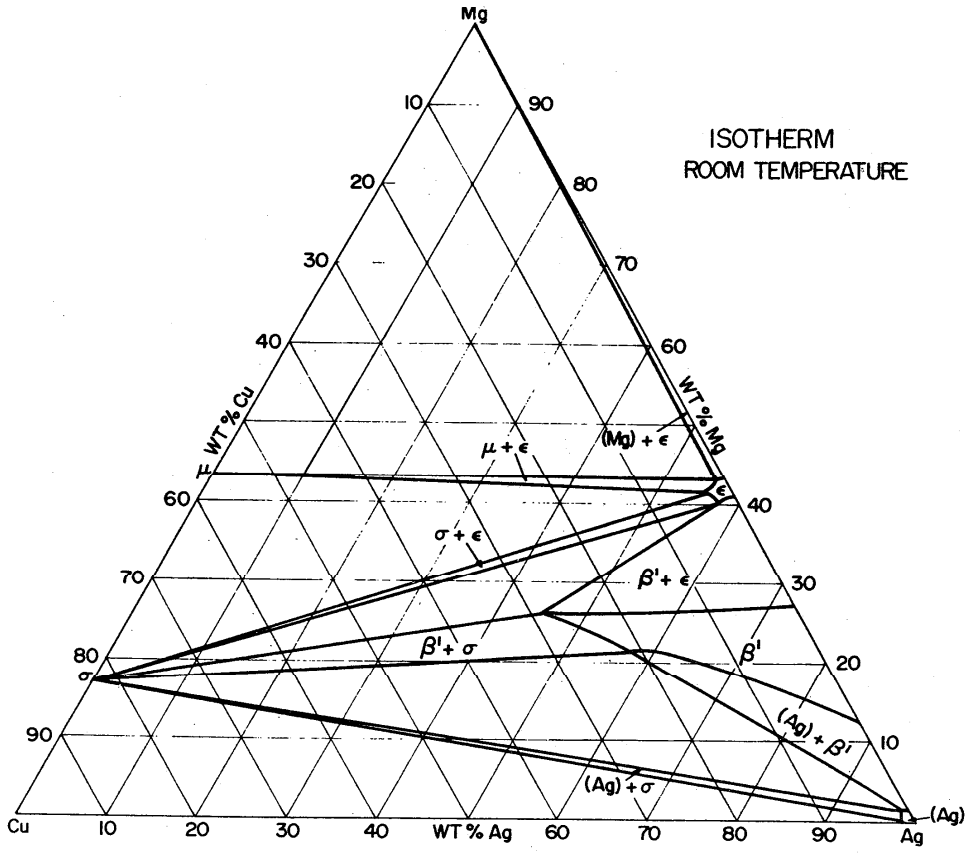
Phase Diagrams

The isotherm is from Guertler and Rassmann [1]. The heat treatment of the alloys consisted of an anneal at 400 °C, followed by slow cooling to room temperature.

References

[1] Guertler, W., and Rassmann, G., Metallwirtschaft **22**, 34 (1943).

JPN



Cu-Ag-Mn

Phases and Structures

The following ordered phases appear in the Cu-Mn system. No ternary compounds have been found.

Designation	Composition	Symmetry	Symbol	Prototype
γ'	13% Mn	ord fcc	Al	Cu
γ''	22% Mn	ord fcc	Al	Cu

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

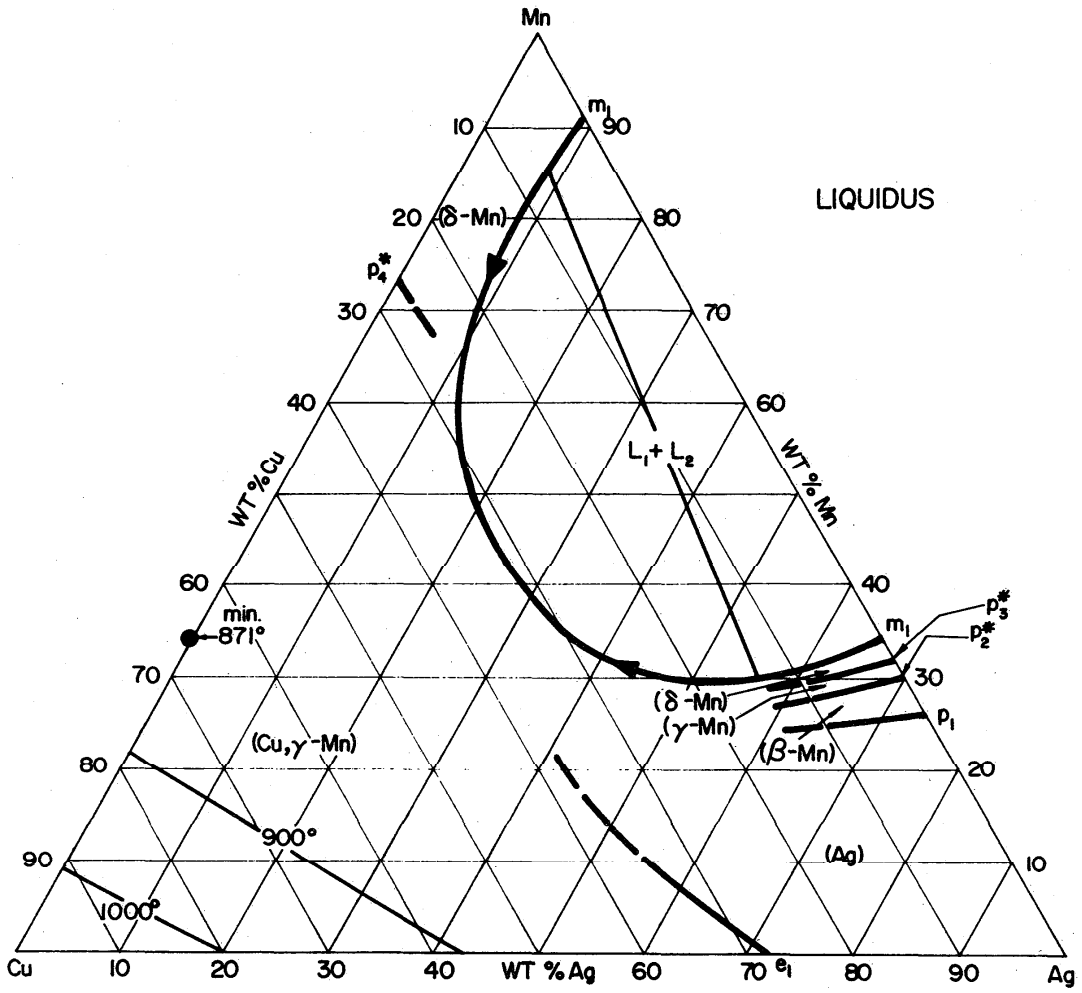
The melting experiments of Keinert [1] indicate that the binary Ag-Mn liquid miscibility gap extends into the ternary phase diagram to a maximum at about 30% Cu at an unspecified temperature. The liquidus projection of the ternary system can only be estimated.

The information concerning the three-phase equilibria in the Ag-Mn binary system is from Hultgren [Gen. Ref. 6]. The temperatures of m_1, p_3^*, p_2^*. and p_1 are 1208 °C, 1131 °C, 1070 °C, and 987 °C, respectively. The Ag-Mn binary phase diagram shown in the Metals Handbook [Gen. Ref. 1] is in error. It indicates that at 1071 °C four phases are in equilibrium—liquid, (Ag), (γ-Mn), and (β-Mn); this is a violation of the phase rule.

References

[1] Keinert, M., Z. physik. Chem. Abt.A. **156**, 291 (1931).

JPN



Cu-Ag-Ni

Phases and Structures

There are no intermediate phases in any of the binary systems or in the ternary system.

Phase Diagrams

The liquidus diagram is based on the thermal analysis data of De Cesaris [1], and the work by Guertler and Bergmann [2]. Adjustments have been made to obtain consistency with the currently accepted binary data.

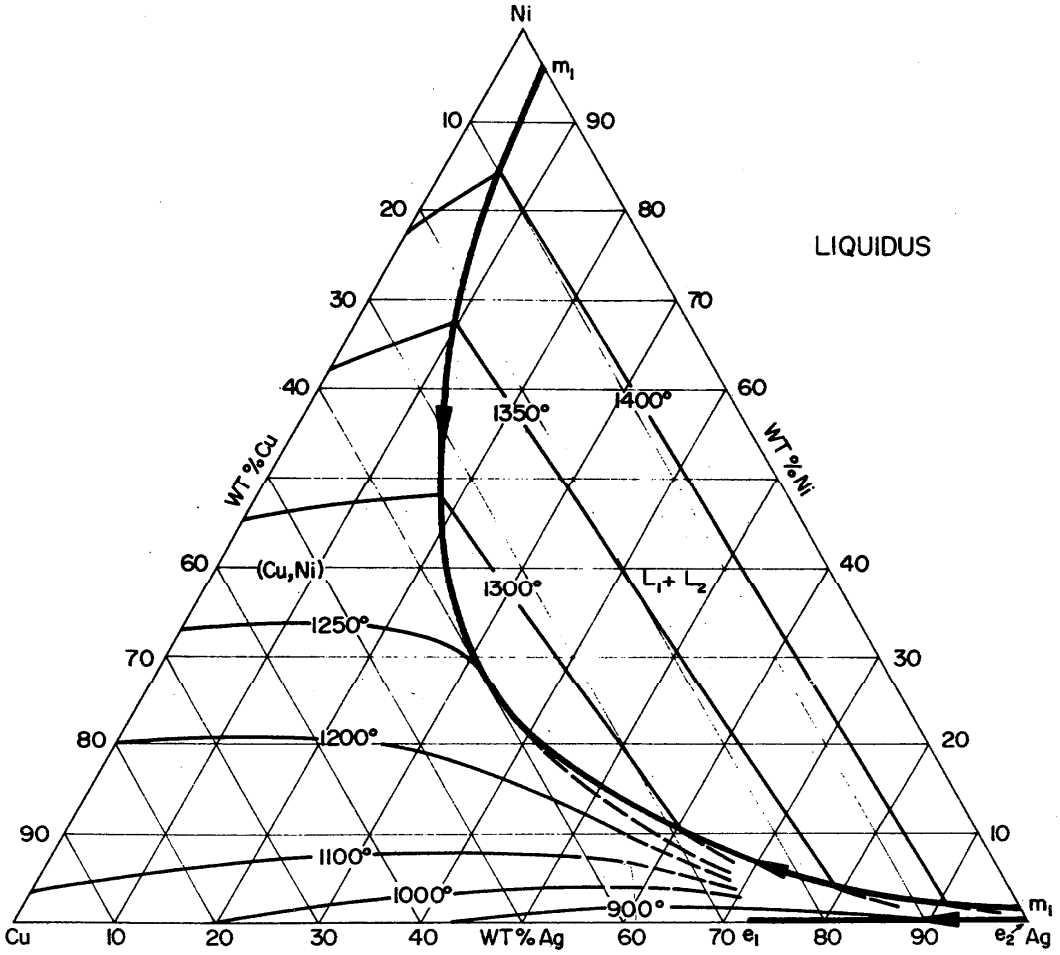
According to the chemical analysis data by Guertler and Bergmann [2], the liquid miscibility gap extends from the binary silver-nickel system to approximately 40 wt.% copper at 1250 °C. The extent of the primary field of crystallization of silver is virtually limited to the binary system copper-silver.

Three of Guertler and Bergmann's isothermal sections are schematically shown.

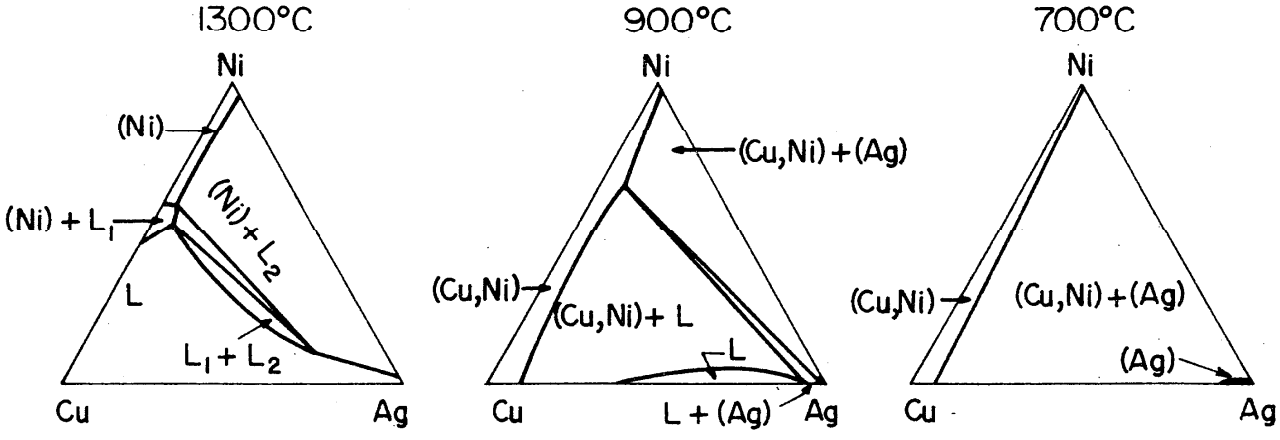
References

[1] De Cesaris, P., Gazz. Chim. Ital. **43**, 365 (1913).
[2] Guertler, W., and Bergmann, A., Z. Metallk. **25**, 53 (1933).

JPN



SCHEMATIC ISOTHERMS



Cu-Ag-P

Phases and Structures

The binary Cu-Ag and pseudobinary Cu-Cu_3P and Ag-Cu_3P systems are all of the simple eutectic type.

Phase Diagrams

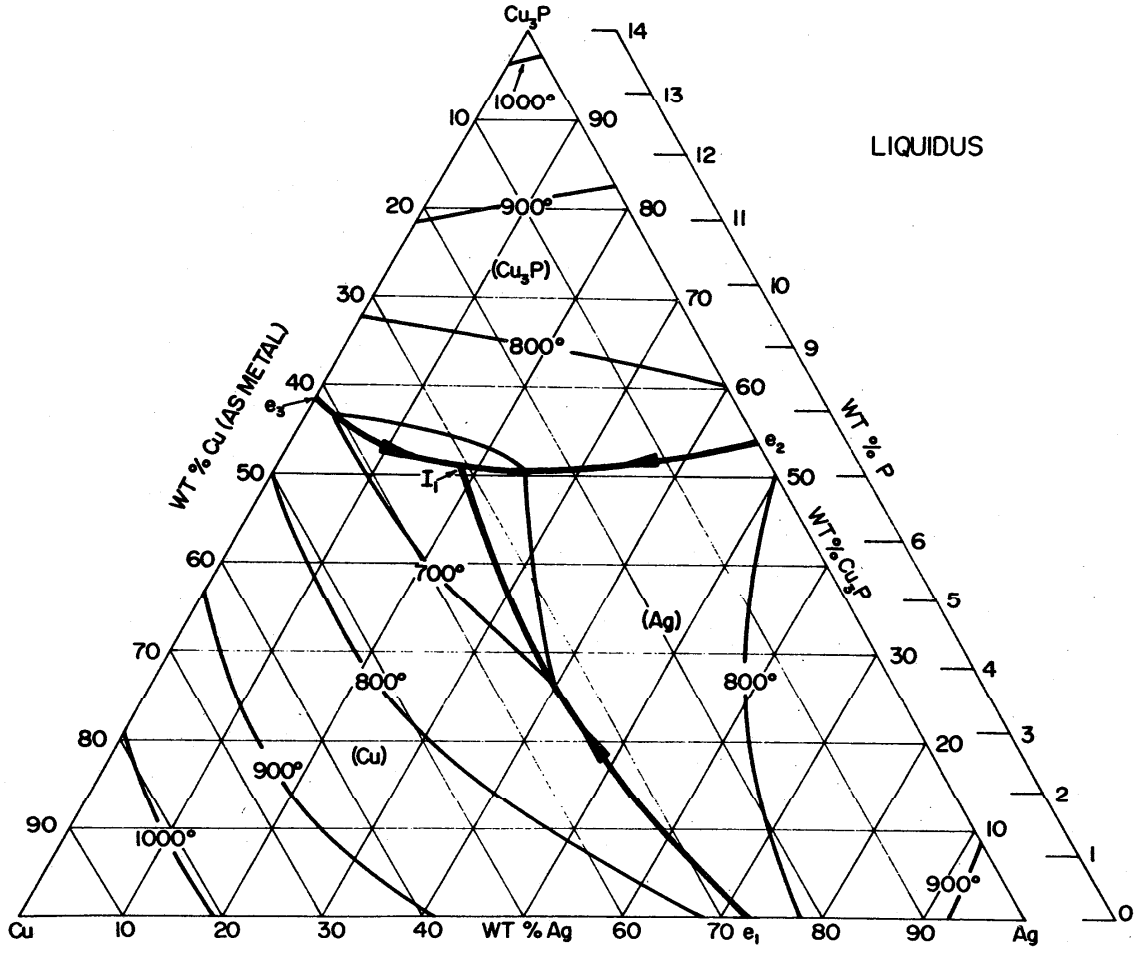
The liquidus is based on data of Moser, Fröhlich, and Raub [1], Weigert [2], and Ballentine [3]. The liquidus valleys extend from the binary eutectics e_1, e_2, and e_3 (at 780 °C, 796 °C, and 714 °C, respectively) to the ternary eutectic point I_1, at 646 °C. The ternary eutectic has the composition 31% Cu, 51% Cu_3P (7.1% P), and 18% Ag.

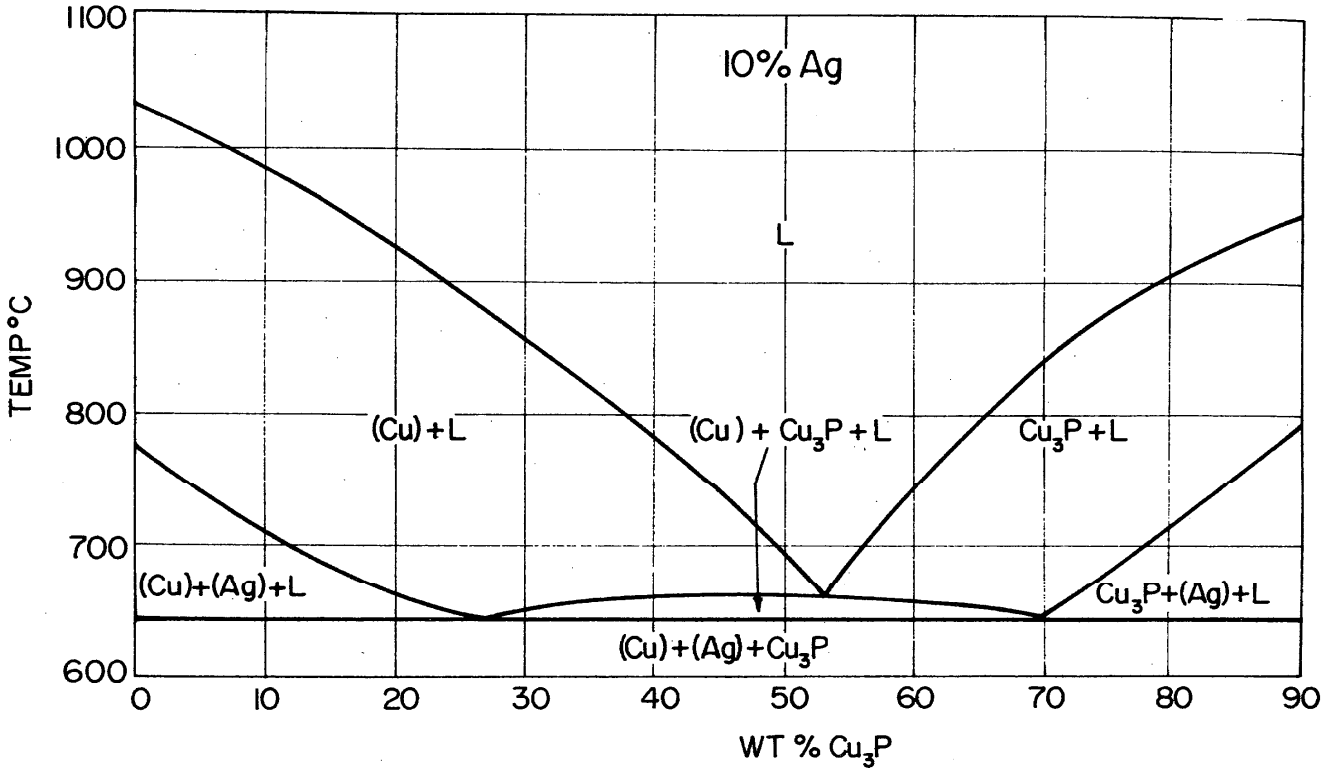
The isopleth at 10% Ag is from Moser et al. [1], who give also isopleths at 25% Cu and 11% Cu_3P. Weigert [2] gives an isopleth at 5% Ag and determines some mechanical properties of alloys with respect to their usefulness for brazing. The three constituents of this system have little or no solubility in the solid state.

References

[1] Moser, H., Fröhlich, K. W., and Raub, E., Z. anorg. allg. Chem **208**, 225 (1932).
[2] Weigert, K. M., Weld. J. **35**, 672 (1956).
[3] Ballentine, R. E., Machinery **69**, 138 (1963).

DG





Cu-Ag-Pb

Phases and Structures

No intermediate phases have been reported in the binary systems or in the ternary system.

Phase Diagrams

The liquidus diagram is from Jänecke [1]. The three binary eutectics e_1 (780 °C), e_2 (304 °C), and e_3 (326 °C) extend into the ternary system, forming a four-phase equilibrium I_1, which is located near the binary silver-lead eutectic at about 2 wt.% Ag and 0.5 wt.% Cu, at a temperature of about 302 °C.

A liquid miscibility gap extends from the copper-lead system to approximately 30 wt.% Ag. A redetermination of the miscibility gap by Hubicki and Lechowski [2] shows some discrepancies with the data given by [1]. Llewelyn [3] found that alloys containing approximately equal weight fractions of the three components are suitable as bearing material. In the solid state, lead is virtually insoluble in both silver and copper.

Thermodynamic Properties

The activity of lead in dilute liquid copper-silver alloys was determined by Hayashi, Azakami, and Kameda [4] by means of the Knudsen effusion method at 1403 K. The measurements, which extended up to solute concentrations of $x_{Pb,\,Ag} = 0.05$, yield the following values for the activity coefficient of lead and its compositional dependence (reference state, liquid Pb):

$$\gamma^{\circ}_{Pb} = 4.3$$

$$\epsilon^{Pb}_{Pb} = 0.0$$

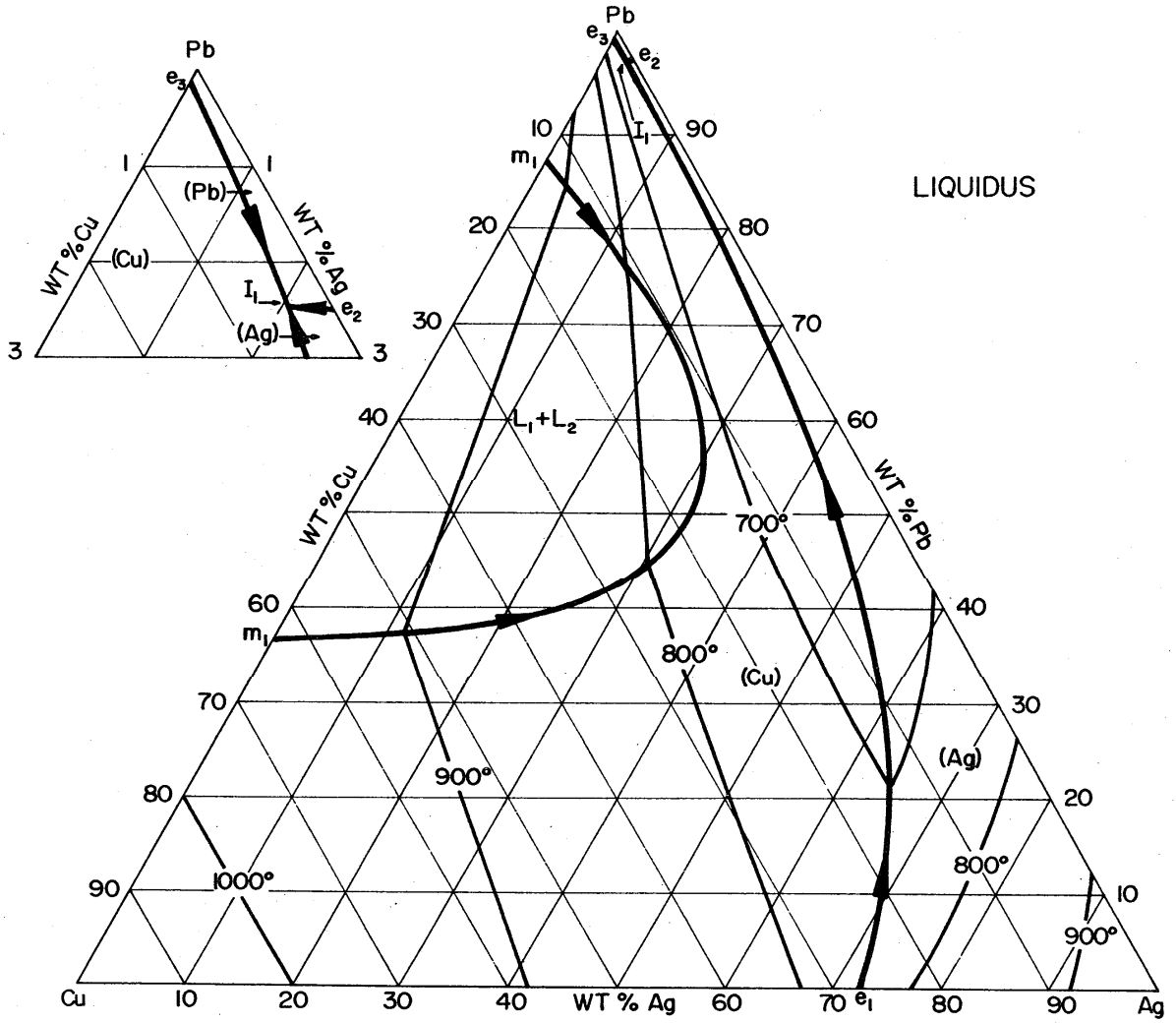
$$\epsilon^{Ag}_{Pb} = -10.2$$

Hultgren [Gen. Ref. 8] reports a value of $\gamma^{\circ}_{Pb} = 5.27$ at 1473 K.

References

[1] Jänecke, E., Kurzgefasstes Handbuch aller Legierungen, Otto Spamer Verlag, Leipzig, 1937.
[2] Hubicki, W., and Lechowski, M., Ann. Univ. Mariae Curie–Sklodowska, Lublin, Poland, Sect. AA **2**, 33 (1947).
[3] Llewelyn, G., Metallurgia **48**, 215 (1953).
[4] Hayashi, M., Azakami, T., and Kameda, M., J. Japan Inst. Metals **90**, 51 (1974).

JPN



Cu-Ag-Pd

Phases and Structures

The following intermediate phases appear in the Cu-Pd binary system. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
α'	~24% Pd	ord fcc	$L1_2$	$AuCu_3I$
α''	~33% Pd	ord tet	Distortion of $L1_2$	
β'	~54% Pd	ord bcc	B2	CsCl

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

The phase diagram has been investigated by Wise et al. [1], Glander [2], Raub and Wörwag [3], Nemilov et al. [4], and Khera et al. [5]. Summaries have been given by Wise [6] and Guertler et al. [7].

The liquidus is based on the most recent work by [4], it agrees reasonably well with the data by Wise [1], [6].

The eutectic valley rises from 780 °C in the binary system Cu-Ag to about 940 °C at 30% Pd. At this critical point, the miscibility gap in the solid has closed, and the liquid is in equilibrium with a solid containing about 45% Pd. According to [2], the temperature and the palladium concentrations at the critical point are slightly lower. Nemilov et al. [4] measured also the Brinell hardness and the electrical resistivity in the ternary system. The maximum hardness occurred at 25% Cu, 25% Ag, and 50% Pd; Wise [6] reported the maximum of the Vickers hardness at 30% Cu, 30% Ag, and 40% Pd.

The phase relationships in the solid state, in particular the extent of the copper-silver miscibility gap have been investigated by [2], [3], [4], and [5]. The location of the solidus and solvus curves of the miscibility gap between 900 °C and 400 °C as determined by Glander [2], were confirmed in general by [3] and [4]. The main difference between the authors concerns the maximum

extent of the miscibility gap, which, at 400 °C, lies at 70% Pd, 65% Pd and 55% Pd, according to [3], [2], and [4], respectively. However, the maximum in the electrical resistivity at 70% Pd [4] suggests that the gap extends up to the higher palladium concentration.

The work by Raub and Wörwag [3] and Khera et al. [5] confirmed the principal direction of the tie-lines reported earlier by Glander [2].

Of the diagrams shown, the two isopleths and the 400 °C isotherm are from [3], while the 727 °C isotherm is from [5].

The order-disorder temperature of β'-CuPd (54% Pd) is distinctly increased by the addition of silver [3].

Thermodynamic Properties

The activity of copper at 1000 K was measured by Pratt et al. [8], using a solid electrolyte (CSZ) galvanic cell. The directions of their iso-activity curves within the miscibility gap are in excellent agreement with the tie-lines by Khera et al. [5], two of which are shown for comparison. A Gibbs-Duhem integration was used by [8], to calculate the integral free energy of formation of the alloys. The free energy exhibits a minimum of 14 kJ/g-atom at $x_{Cu}=0.5$, $x_{Ag}=0.1$ and $x_{Pd}=0.4$. This is possibly related to the observation that the β'-CuPd phase is stabilized by small additions of silver.

References

[1] Wise, E. M., Crowell, W. G., and Eash, J. T., Trans. AIME **99**, 363 (1932).

[2] Glander, F., Metallwirtschaft **18**, 337 (1939).

[3] Raub, E., and Wörwag, G., Z. Metallk. **46**, 52 (1955).

[4] Nemilov, V. A., Grigorev, A. T., and Sokolovskaya, E. M., Izvest. Akad. Nauk SSSR, Sekt. Platiny **29**, 163 (1955).

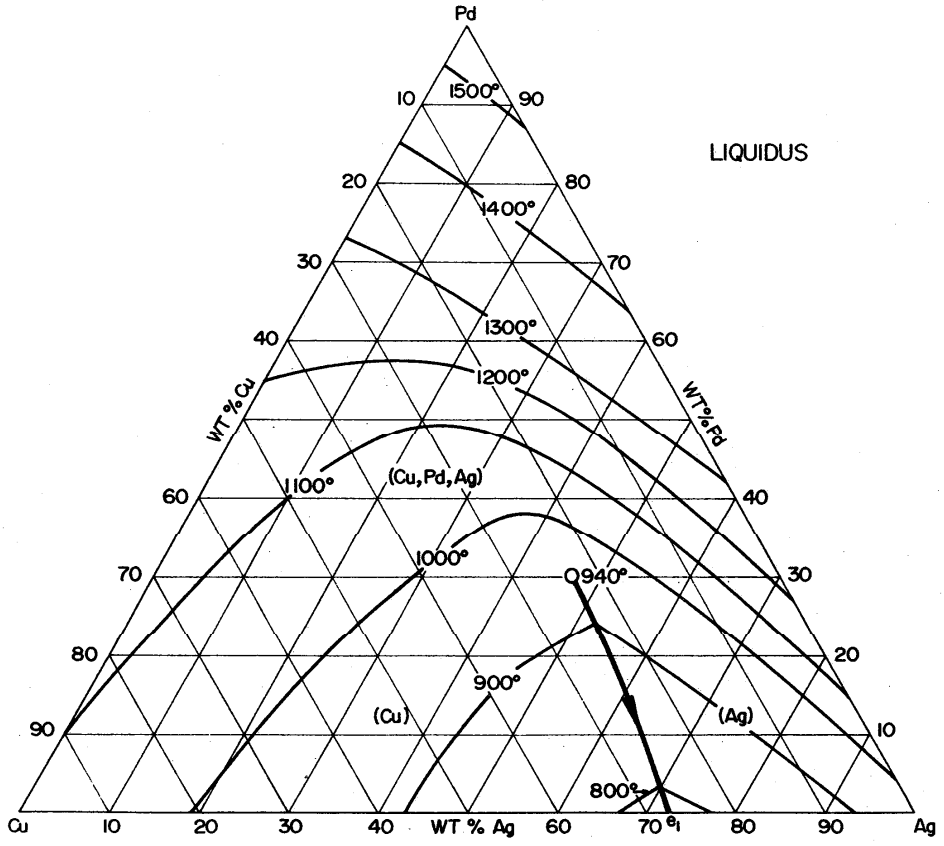
[5] Khera, S. K., Tank, R. N., and Nayar, P. K. K., Trans. Indian Inst. Metals **25**(3), 105 (1972).

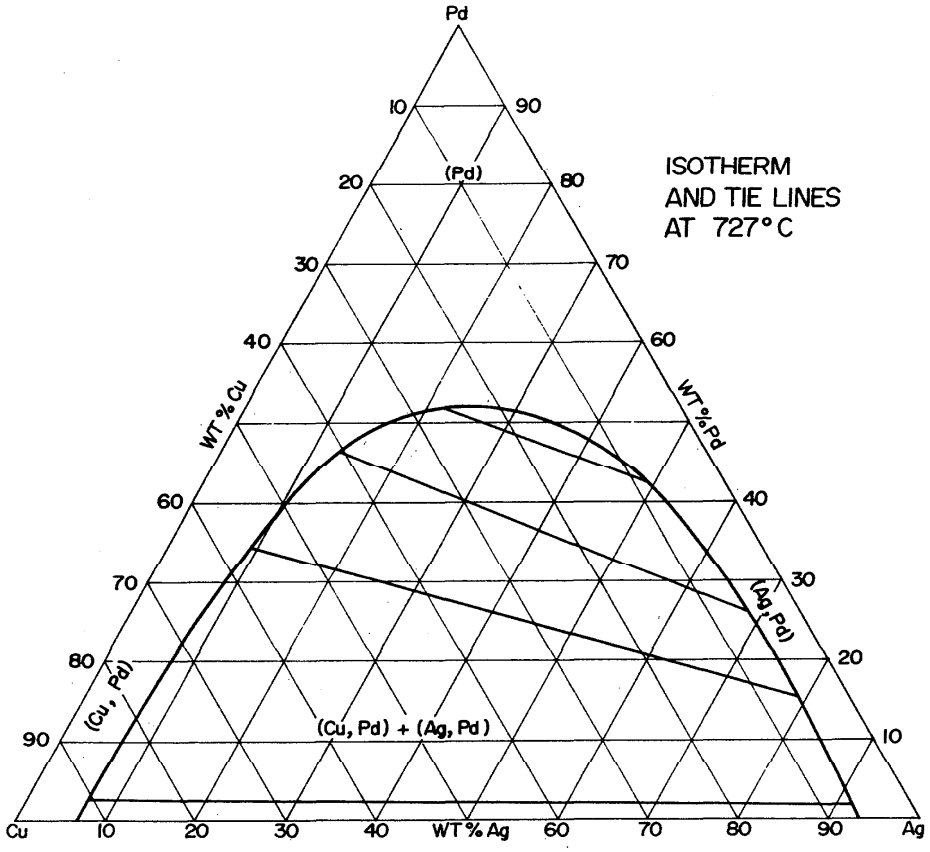
[6] Wise, E. M., Metals Handbook, Amer. Soc. Metals (1948) pp. 1128 and 1241.

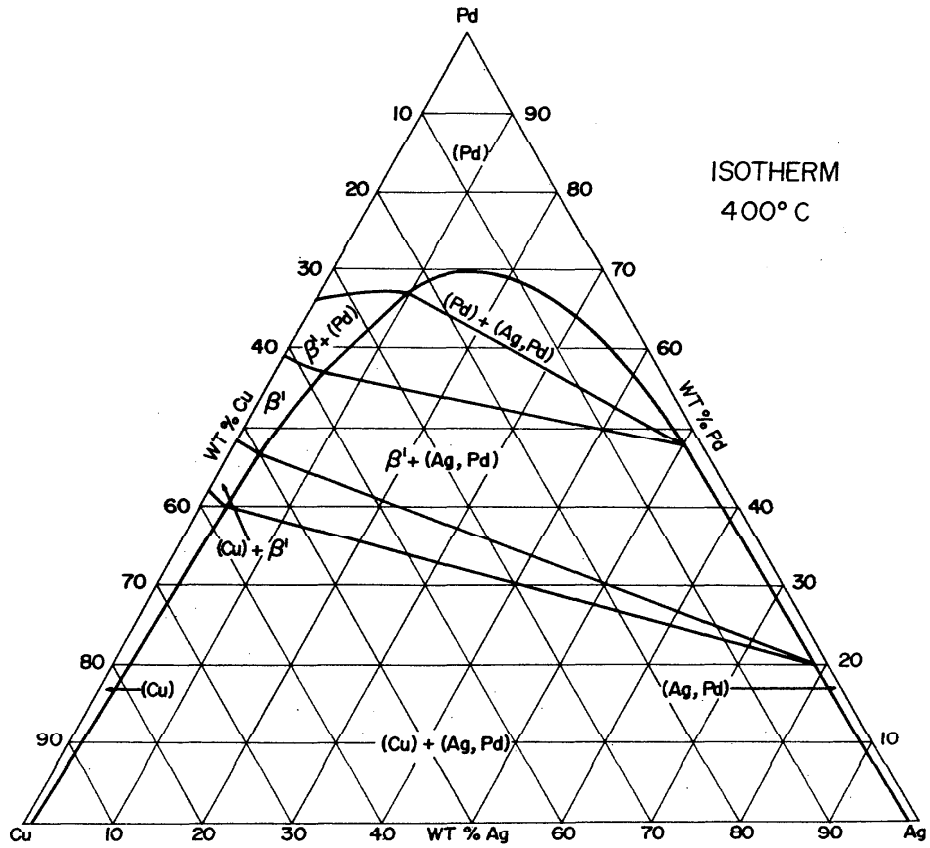
[7] Guertler, W., Guertler, M., and Anastasiadias, E., A Compendium of Constitutional Ternary Diagrams of Metallic Systems, Israel Program for Scientific Translations, Jerusalem (1969) pp. 250 and 614.

[8] Pratt, J. N., Bryant, A. W., and Bugden, W. G., Final Technical Report, United States Army. Contract DAJA37-68-C-0027, Nov. 1968, Department of Physical Metallurgy and Science of Materials, University of Birmingham, England.

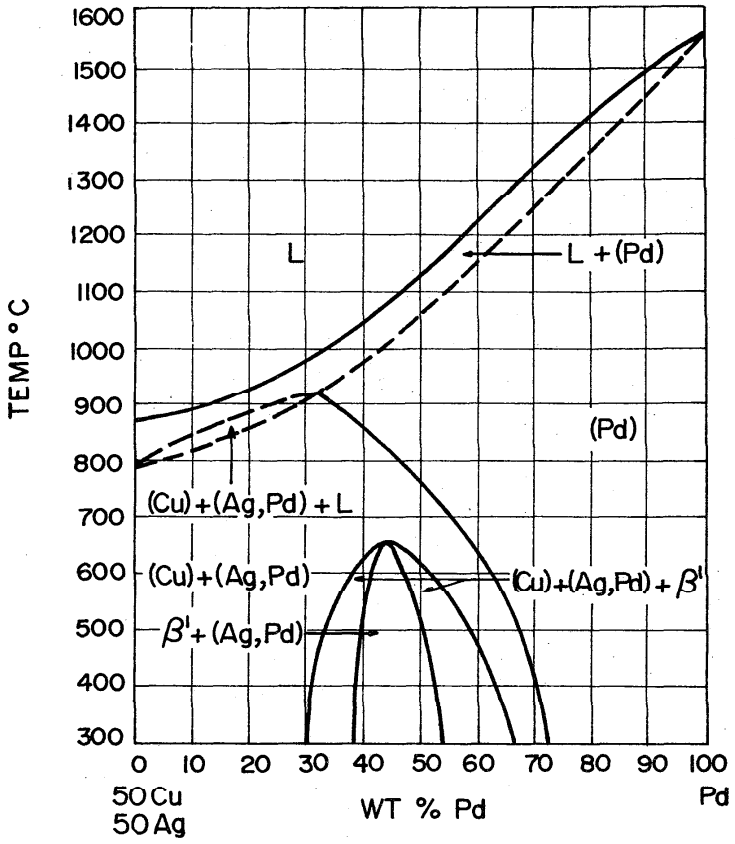
JPN

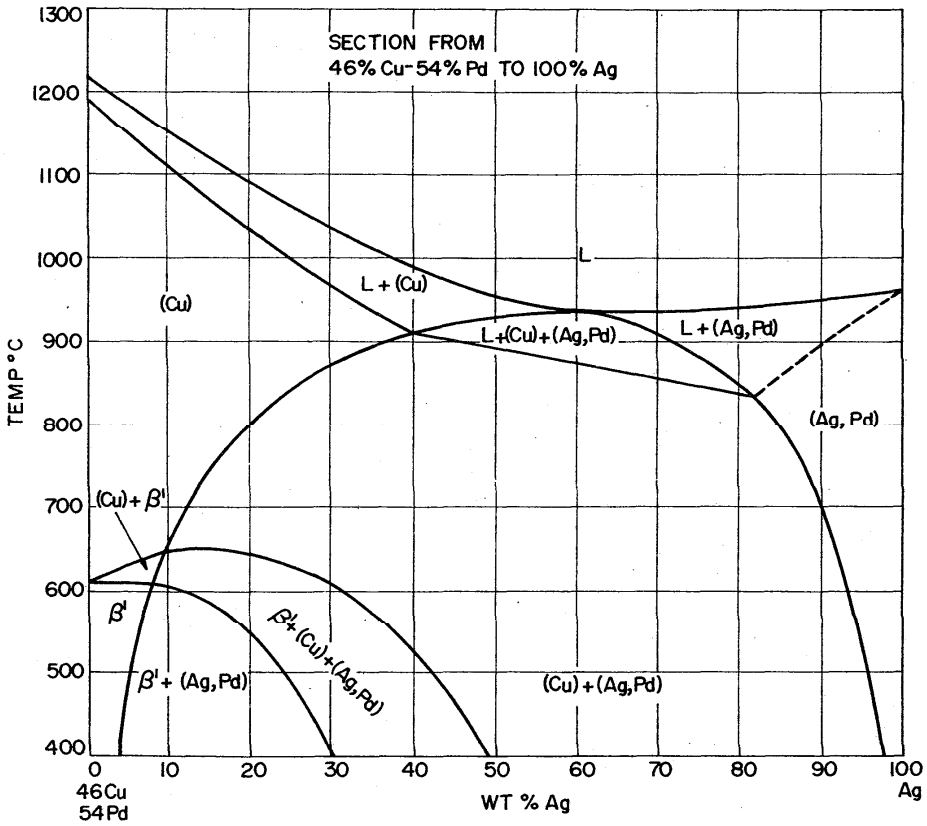


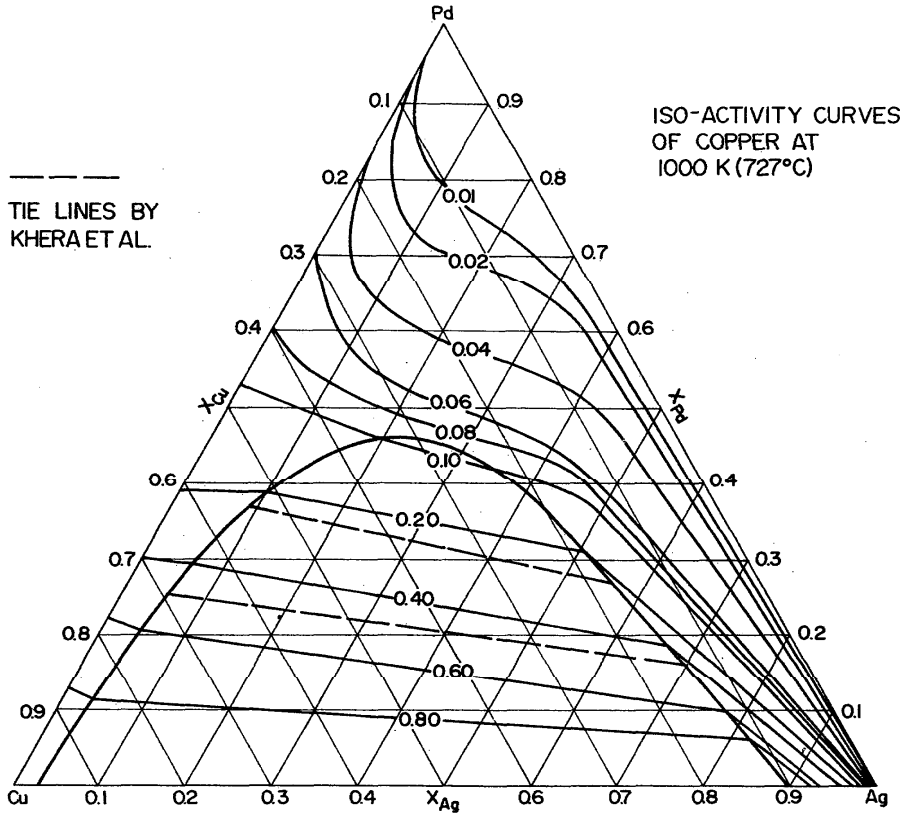

Pd
ISOTHERM
AND TIE LINES
AT 727° C
(Pd)
WT % Cu
WT % Pd
(Cu, Pd)
(Ag, Pd)
(Cu, Pd) + (Ag, Pd)
Cu
WT % Ag
Ag


Pd
ISOTHERM
400° C
(Pd)
β' + (Pd)
(Pd) + (Ag, Pd)
β'
WT % Cu
WT % Pd
β' + (Ag, Pd)
(Cu) + β'
(Cu)
(Ag, Pd)
(Cu) + (Ag, Pd)
Cu
WT % Ag
Ag

SECTION FROM
50% Cu-50% Ag TO 100% Pd







Cu-Ag-Re

Phases and Structures

No intermediate phases are reported in the binary systems or in the ternary system.

Phase Diagrams

It was concluded by Holland-Nell and Sauerwald [1] that no useful binary or ternary alloys of these metals could be produced, because of the very limited solubility of Re in Cu and Ag.

References

[1] Holland-Nell, U., and Sauerwald, F., Z. anorg. Chem. **276**, 155. (1954).

DKG

Cu-Ag-S

Phases and Structures

The following intermediate phases appear in the Cu-S and Ag-S binary systems and in the Cu-Ag-S ternary system.

Designation	Composition	Symmetry	Symbol	Prototype
μ_1	$Cu_{2-x}S$(HT) (digenite)	fcc	Cl	CaF_2
γ	Cu_2S(MT) (chalcocite)	hex		
β	Cu_2S(LT) (chalcocite)	eco		
ν	$Cu_{1.96}S$ (djurleite)	ortho or mono		
δ	$Cu_{1.8}S$ (digenite)	rhom		
ϵ	CuS (covellite)	hex	B18	CuS
μ_2	$\sim Ag_{2-x}S$(HT) (argentite)	fcc	Cl	CaF_2
ϕ	$\sim Ag_2S$(MT) (argentite)	bcc		
θ	Ag_2S(LT) (acanthite)	mono		
π	Ag_2S(LT)	mono		
T_1	$Cu_{0.45}Ag_{1.55}S$ (jalpaite)	bct		
T_2	$Cu_{0.8}Ag_{1.2}S$ (mckinstiyite)			
T_3	$Cu_{1.07}Ag_{0.93}S$ (stromeyerite)	ortho		

The crystal structures of the Cu-S binary system are from the Metals Handbook [Gen. Ref. 1]. The structure of the ν ($Cu_{1.96}S$) phase, stable below ~93 °C, is from Roseboom [1]. The tetragonal, higher temperature modification of this phase, which is listed in the Metals Handbook, has been shown to be metastable by Roseboom [1] and by Djurle [2]. However, according to the unpublished work by Skinner, quoted by Roseboom [1], this phase may be stable at high pressure. The mineralogical names of these phases are taken from Barton [3].

The crystal structures of the Ag-S binary phases and of the ternary phases are from Pearson [Gen. Ref. 2], while the mineralogical names are from Craig and Scott [4]. As shown in the Cu_2S-Ag_2S pseudo-binary diagram, the ternary phases T_1, T_2, and T_3 are stable only at low temperatures. T_1 transforms at 112 °C congruently to the bcc solid solution of ϕ-Ag_2S, while T_3 transforms at 90 °C congruently to the hex solid solution of γ-Cu_2S. T_2 decomposes at 94 °C peritectoidally into T_1 and γ-Cu_2S.

Phase Diagrams

After earlier studies by Lüder [5], Jänecke [6], Suhr [7], and Djurle [2], the system was extensively reinvestigated by Skinner [8]. The Cu_2S-Ag_2S pseudo-binary diagram and the isothermal sections at 25 °C and 250 °C are from Skinner [8], while the miscibility gap at 1200 °C is from Gerlach et al. [9]. The 250 °C isotherm given by Skinner [8] is based on the room temperature observation of samples quenched from 250 °C. It shows a miscibility gap in the μ-$(Cu,Ag)_2S$ phase near the Cu-rich end which is highly improbable since the thermodynamic activities of Cu_2S and Ag_2S in the μ-phase show a negative deviation from ideality at higher temperatures. The 250 °C isotherm as given by Skinner was therefore modified to show a continuous solid solution of the μ-phase from pure μ-Cu_2S to the composition where it is in equilibrium with ϕ-Ag_2S. The liquidus and solidus lines of the Cu_2S-Ag_2S pseudo-binary diagram are from Krestovnikov et al. [10].

Thermodynamic Properties

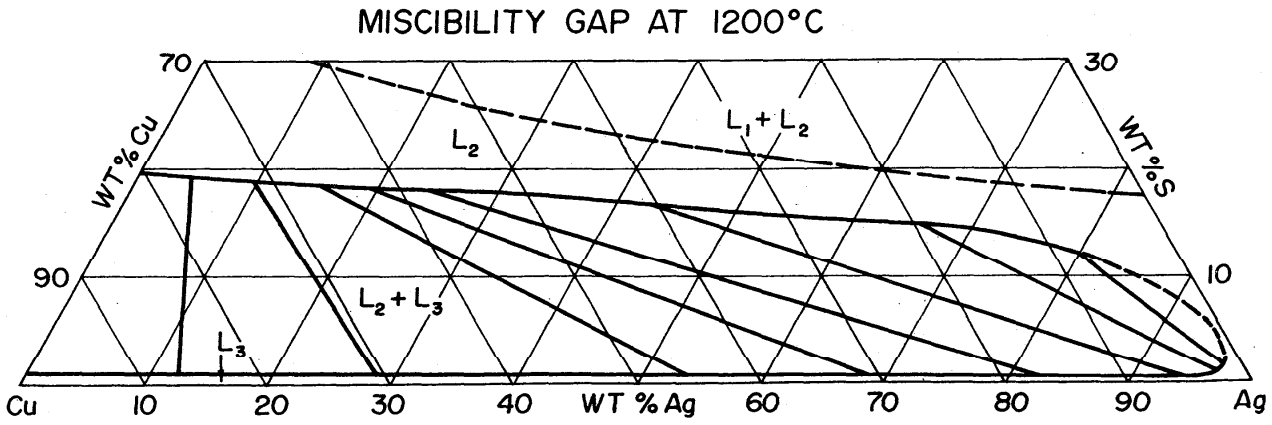
Perrot and Jeannot [11] reported the activities of Ag_2S (standard state: solid Ag_2S) in the Cu_2S-Ag_2S solid solution at 703, 790, 928, and 980 K; the activities show negative deviations from Raoult's law at all four temperatures. The activity of Cu_2S (standard state: solid Cu_2S) obtained from the Gibbs-Duhem integration is shown together with that of Ag_2S at 928 K.

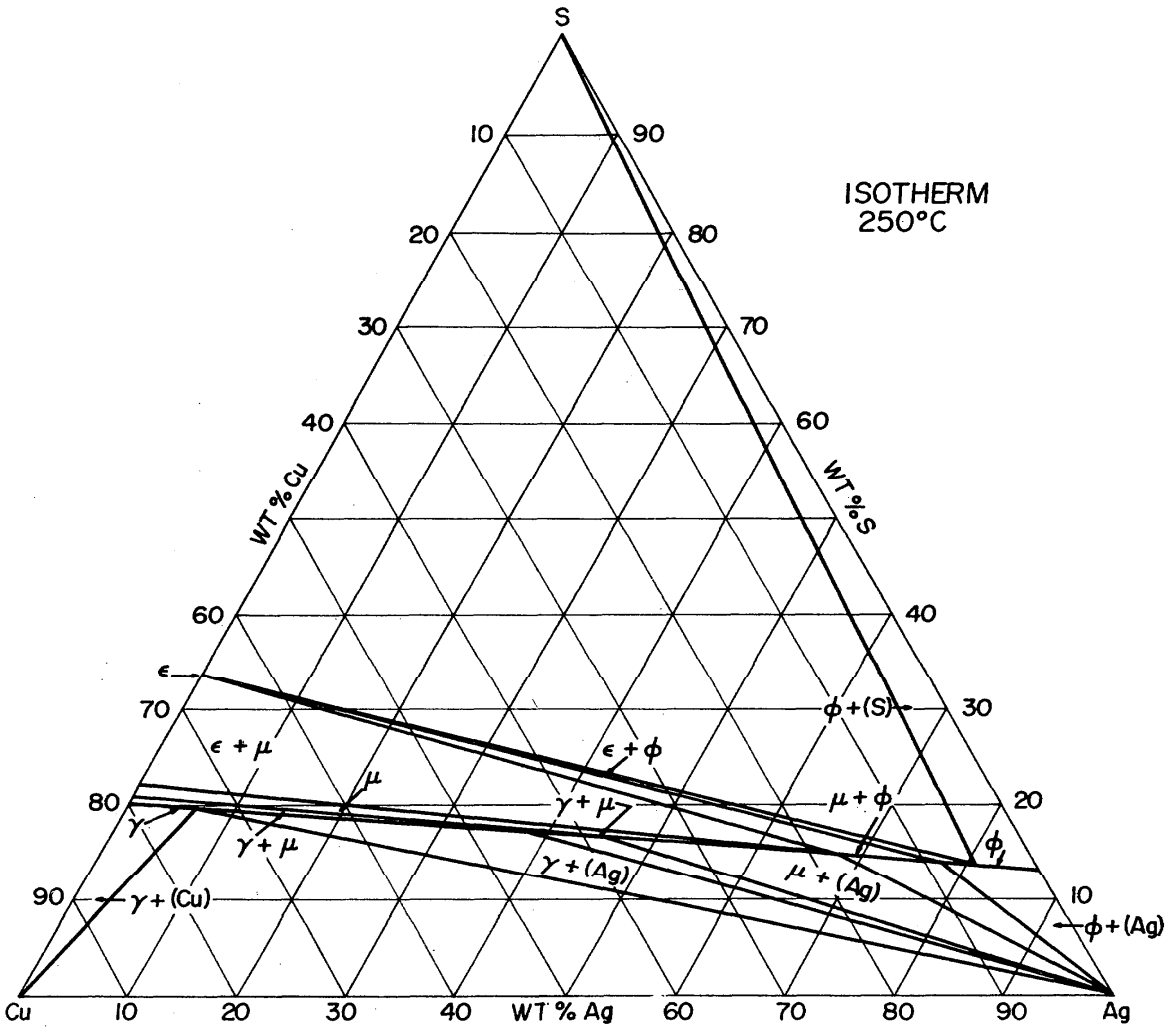
From the phase diagram, Mendelevich et al. [12] computed the regular solution parameters for the Cu_2S-Ag_2S pseudo-binary system in the solid and liquid states as −2.43 and −13.7 kJ/mol, respectively.

References

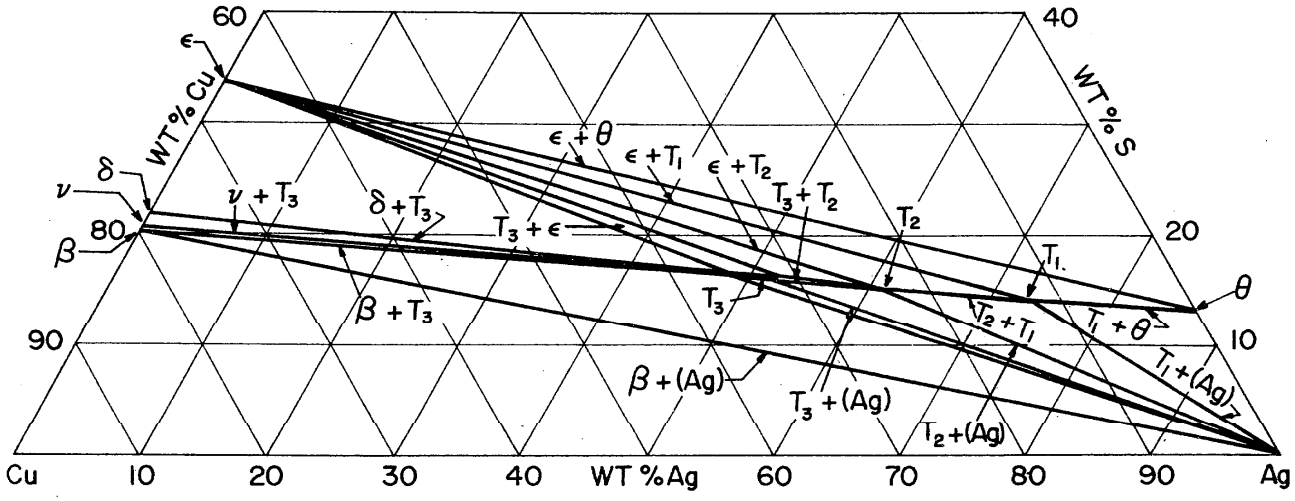
[1] Roseboom, E. H., Jr., Econ. Geol. **61**, 641 (1966).
[2] Djurle, S., Acta Chem. Scand. **12**, 1415 and 1427 (1958).
[3] Barton, P. B., Jr., Econ. Geol. **68**, 455 (1973).
[4] Craig, J. R., and Scott, S. D., in: *Sulfide Mineralogy* (Ed.: P. H. Ribbe), Short Course Notes, Vol. 1, Chapter 5, Mineralogical Society of America, Washington, D.C., 1974.
[5] Lüder, E., Metall u. Erz **21**, 133 (1924).
[6] Jänecke, E., Z. Elektrochem. **42**, 373 (1936).
[7] Suhr, N., Econ. Geol. **50**, 347 (1955).
[8] Skinner, B., Econ. Geol. **61**, 1 (1966).
[9] Gerlach, J., Hennig, U., and Trettin, K., Erzmetall **19**, 458 (1966).
[10] Krestovnikov, A. N., Mendelevich, A. Yu, and Glazov, V. M., Izv. Akad. Nauk SSSR, Neorg. Mater. **4**, 1189 (1968).
[11] Perrot, P., and Jeannot, C., Rev. Chim. Min. **8**, 87 (1971).
[12] Mendelevich, A. Yu, Krestovnikov, A. N., and Glazov, V. M., Zh. Fiz. Khim. **43**, 3067 (1969).

UVC

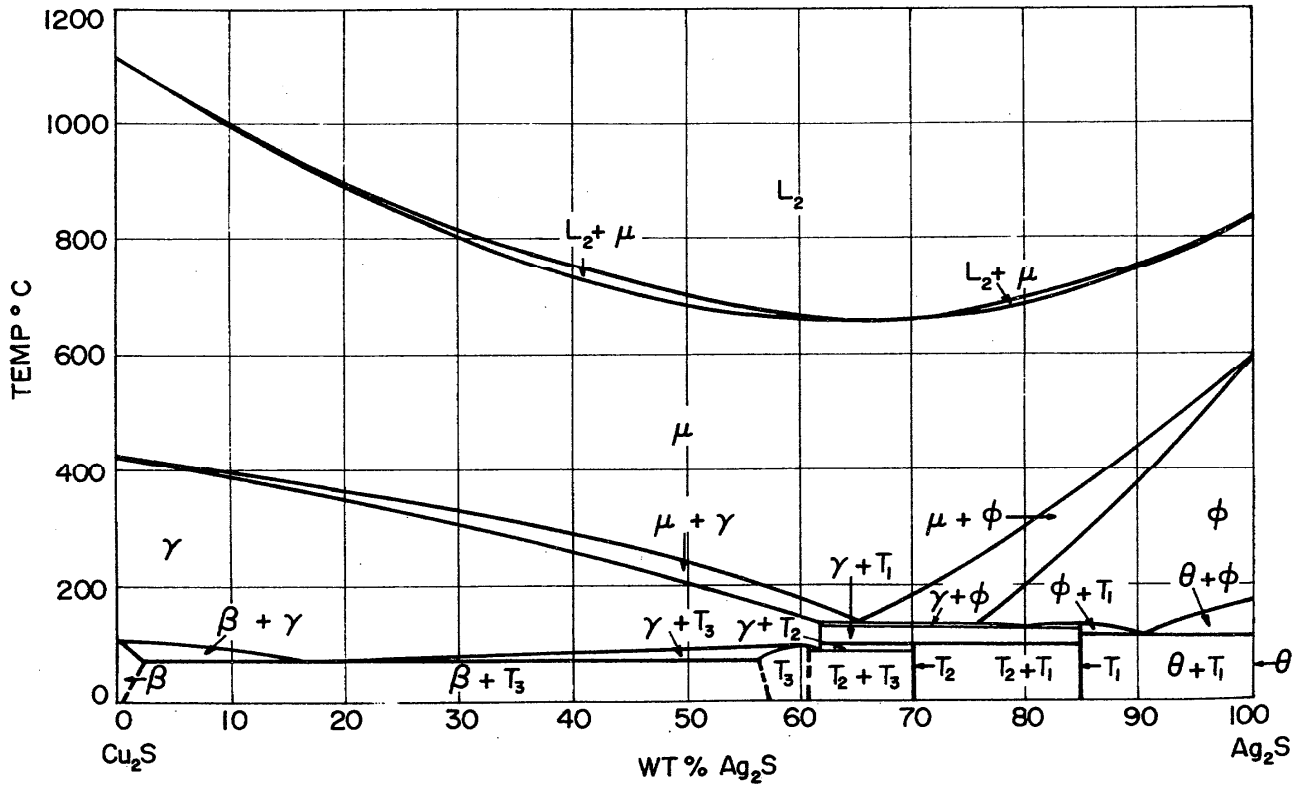


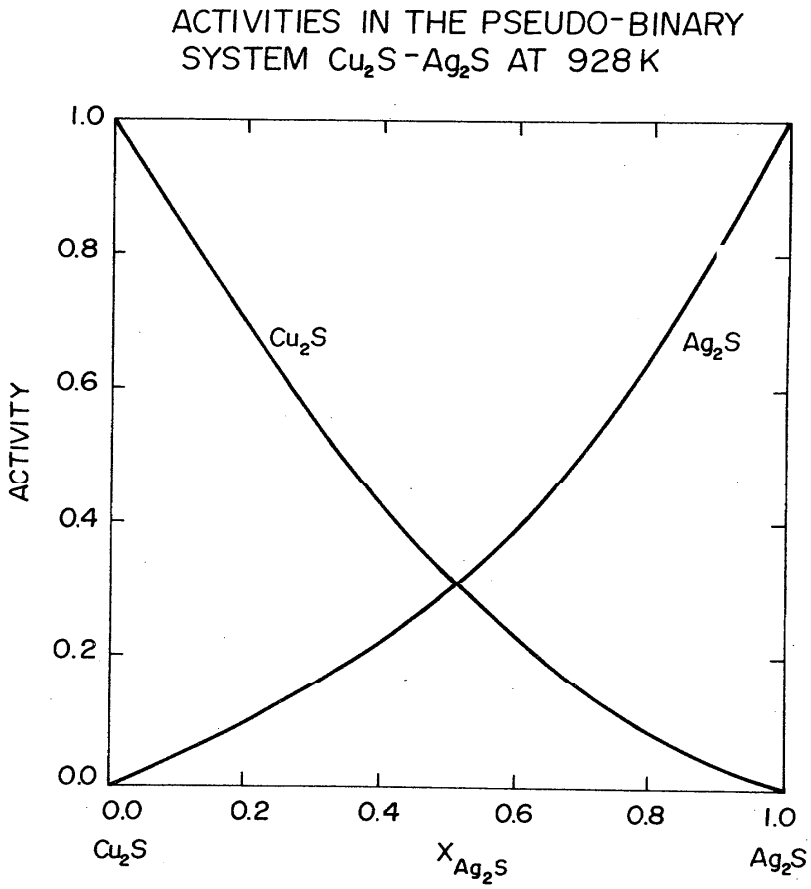

S
ISOTHERM
250°C
WT % Cu
WT % S
WT % Ag
Cu
Ag
10
20
30
40
60
70
80
90
ϵ
ϵ + μ
μ
γ
γ + μ
ϵ + ϕ
γ + μ
ϕ + (S)
μ + ϕ
ϕ
γ + (Cu)
γ + (Ag)
μ + (Ag)
ϕ + (Ag)

ISOTHERM
25° C



PSEUDO-BINARY SYSTEM Cu_2S-Ag_2S





Cu-Ag-Sb

Phases and Structures

The following intermediate phases appear in the binary Cu-Sb and Ag-Sb phase diagrams. No ternary phases have been reported.

Designation	Composition	Symmetry	Symbol	Prototype
η	$Cu_{5.5}Sb$	hcp	A3	Mg
ϵ	$Cu_{4.5}Sb$	hex	Related to DO_{19}	Ni_3Sn
λ	$Cu_{3.3}Sb(\epsilon')$	hcp	Based on A3	Mg
β	Cu_3Sb	ord fcc	DO_3	BiF_3
κ	Cu_3Sb	ortho		Cu_3Ti
θ	Cu_2Sb	ord tet	C38	Cu_2Sb
ζ	~12% Sb	hcp	A3	Mg
γ	$Ag_3Sb(\epsilon)$	ortho		Both like β' Cu_3Ti(HT)
γ'	$Ag_3Sb(\epsilon')$	ord ortho		

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

Guertler and Rosenthal [1] studied the 400 °C isotherm, and were able to establish only that the θ-phase (Cu_2Sb) is in equilibrium with the ζ-phase and the γ'-phase of the binary system silver-antimony.

Reference

[1] Guertler, W., and Rosenthal, W., Z. Metallk. **24**, 7, 30, (1932).

DG

Cu-Ag-Se

Phases and Structures

The following intermediate phases appear in the Cu-Se and Ag-Se binary systems, and in the Cu-Ag-Se ternary system:

Designation	Composition	Symmetry	Symbol	Prototype
β	$Cu_{2-x}Se$(HT)	fcc for $x \cong 0.2$	Cl	CaF_2
γ	Cu_2Se(LT)	rhom (?)		
δ	Cu_3Se_2	tet		
ϵ	CuSe(HT)	ortho (?)		
ϵ'	CuSe(LT)	hex	B18	CuS
ζ	$CuSe_2$	ortho	C18	FeS_2
ν	Ag_2Se(HT)	bcc		
θ	Ag_2Se or $Ag_{16}Se_7$(LT)	ortho		
T_1	AgCuSe	ortho		

The binary Cu-Se phase diagrams given in the Metals Handbook [Gen. Ref. 1] and in Hansen [Gen. Ref. 3] have been greatly modified by the work of Heyding [1], Bernardini et al. [2], and Ogorelec et al. [3], which are in relatively good agreement. The crystal structure of the γ-Cu_2Se(LT) phase is from Bernardini et al. [2]; the structures of the δ-Cu_3Se_2, ϵ-CuSe, ϵ'-CuSe, and ζ-$CuSe_2$ phases are from Heyding [1], who confirmed the structure of ζ-$CuSe_2$ reported by Gattow [4]; and the β-$Cu_{2-x}Se$(HT) phase is from Pearson [Gen. Ref. 2]. Many older studies of the crystal structures of the β-$Cu_{2-x}Se$(HT) and γ-Cu_2Se(LT) phases (as reported by Pearson [Gen. Ref. 2], Hansen [Gen. Ref. 3], and Shunk [Gen. Ref. 5]) are in disagreement, because many different metastable structures can be obtained depending on stoichiometry, thermal history, and sample preparation. The other crystal structures listed above are from Pearson [Gen. Ref. 2].

Phase Diagrams

The predominant feature of the system at high temperatures is the liquid miscibility gap where the binary Cu-Se and Ag-Se monotectic solubility gaps extend across the entire ternary diagram. The 1200 °C isotherm was determined by Asano et al. [5], whose reported tie-lines are in essential agreement with those of Emicke [6] at 950 °C.

From the binary eutectics e_1, e_2, and e_3, three liquidus valleys extend into the ternary diagram, forming two type-I four-phase equilibria (I_1 and I_2):

I_1 (822°): L_2 (33.4% Cu, 35.8% Ag, 30.8% Se)
$= L_1$ (14.8% Cu, 82.6% Ag, 2.6% Se) + (Ag) + β

I_2: (770°): L_1 (30.0% Cu, 69.0% Ag, 1.0% Se)
$= (Cu) + (Ag) + \beta$.

The $(L_1 + L_2)$ 2-phase region converges to a minimum tie-line at 822 °C, below which the L_2 phase disappears according to reaction I_1.

Asano et al. [5] observed a continuous bcc solid solution (β) between Ag_2Se and $Cu_{2-x}Se$ in this pseudo-binary system. The phase diagram is of the azeotropic type with a minimum at 25.8% $Cu_{2-x}Se$ at 736 °C. An earlier investigation by Mendelevich, Krestovnikov, and Glazov [7], which placed the minimum at 700 °C, is probably in error. In either case, the existence of a continuous solid solution between the fcc $Cu_{2-x}Se$ phase and bcc Ag_2Se is highly improbable, unless both studies actually had a non-equilibrium bcc $Cu_{2-x}Se$ phase, which is possible, depending on thermal history and sample preparation.

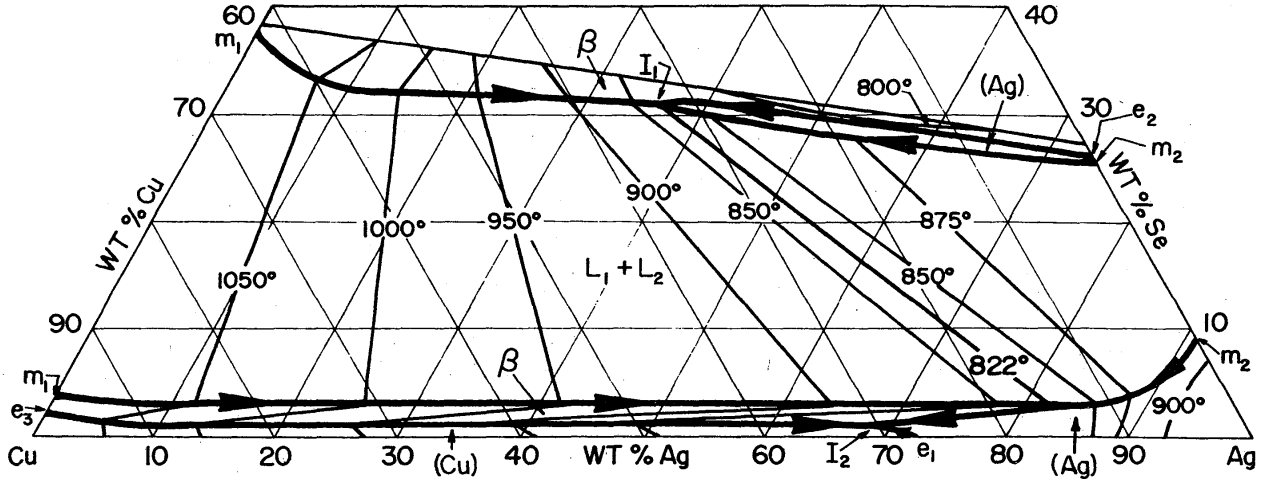
A considerably different pseudobinary diagram was obtained by Agaev, Alekperova, and Zargarova [8], whose liquidus data give a eutectic at 730 °C and 36 mole % Cu_2Se, and a peritectic at 760 °C and 44 mole % Cu_2Se. The two regions are separated by the ternary compound AgCuSe. Asano et al. [5], also mention the existence of the compound AgCuSe, and it is not clear why their diagrams do not show this compound. Three of their six isopleths are shown here, although the presence of the β solid solution and the absence of CuAgSe should be regarded as questionable. Valverde [9] reports a solubility gap at 300 °C in the Cu_2Se-Ag_2Se pseudobinary, between 69–79 mole % Ag_2Se, and does not detect AgCuSe.

References

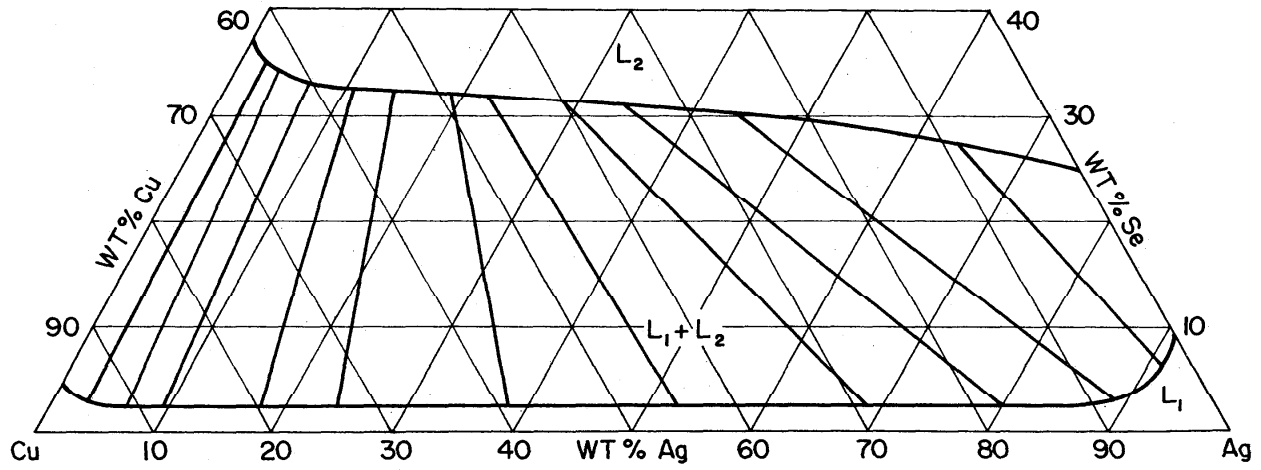
[1] Heyding, R. D., Can. J. Chem. **55**, 1233 (1966).
[2] Bernardini, G. P., Corsini, F., and Trosti, R., Period. Mineral. **41**, 565 (1972).
[3] Ogorelec, Z., Mestnik, B., and Devcic, D., J. Mater. Sci. **7**, 967 (1972).
[4] Gattow, G., Naturwissenschaften **52**, 258 (1965).
[5] Asano, N., Wase, K., and Nomura, T., Nippon Kogyo Kaishi **87**, 485 (1971).
[6] Emicke, K., Erzmetall **15**, 15 (1962).
[7] Mendelevich, A. Yu., Krestovnikov, A. N., and Glazov, V. M., Zh. Fiz. Khim. **43**, 3067 (1969).
[8] Agaev, M. I., Alekperova, Sh. M., and Zargarova, M. I., Dokl. Akad. Nauk Azerb. SSR **27**, 20 (1971).
[9] Valverde, N., Z. phys. Chem. Neue Folge **61**, 92 (1968).

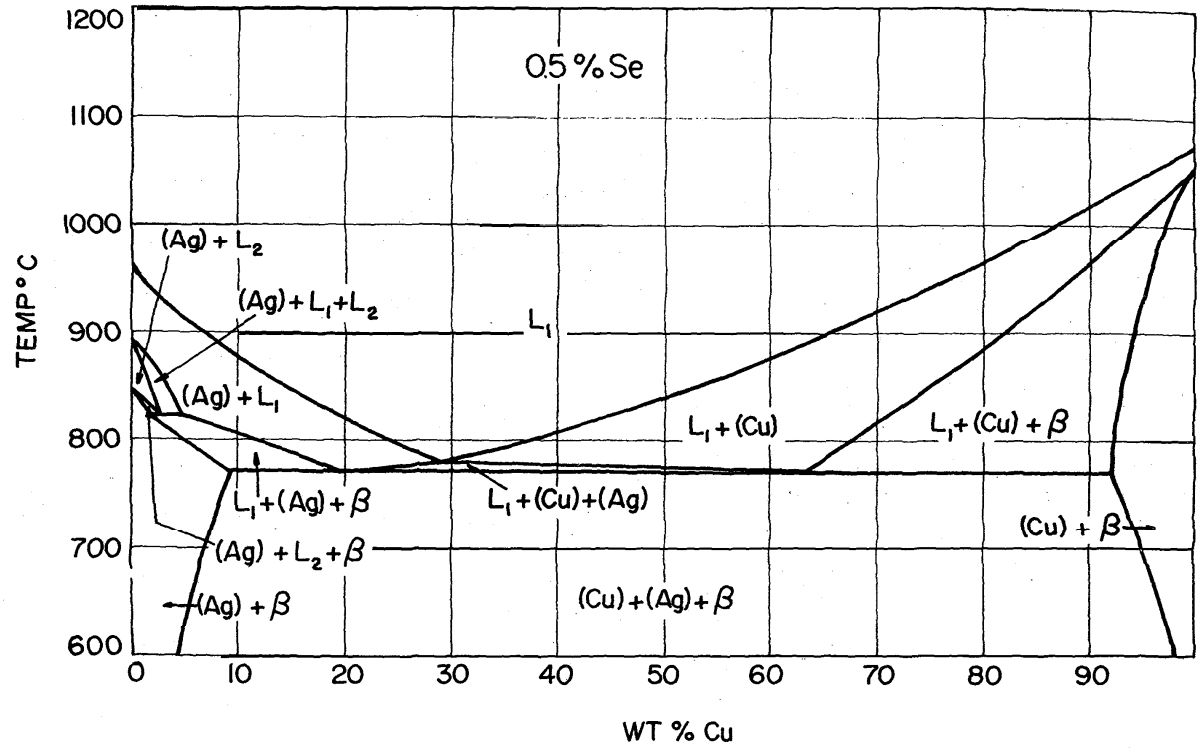
DG

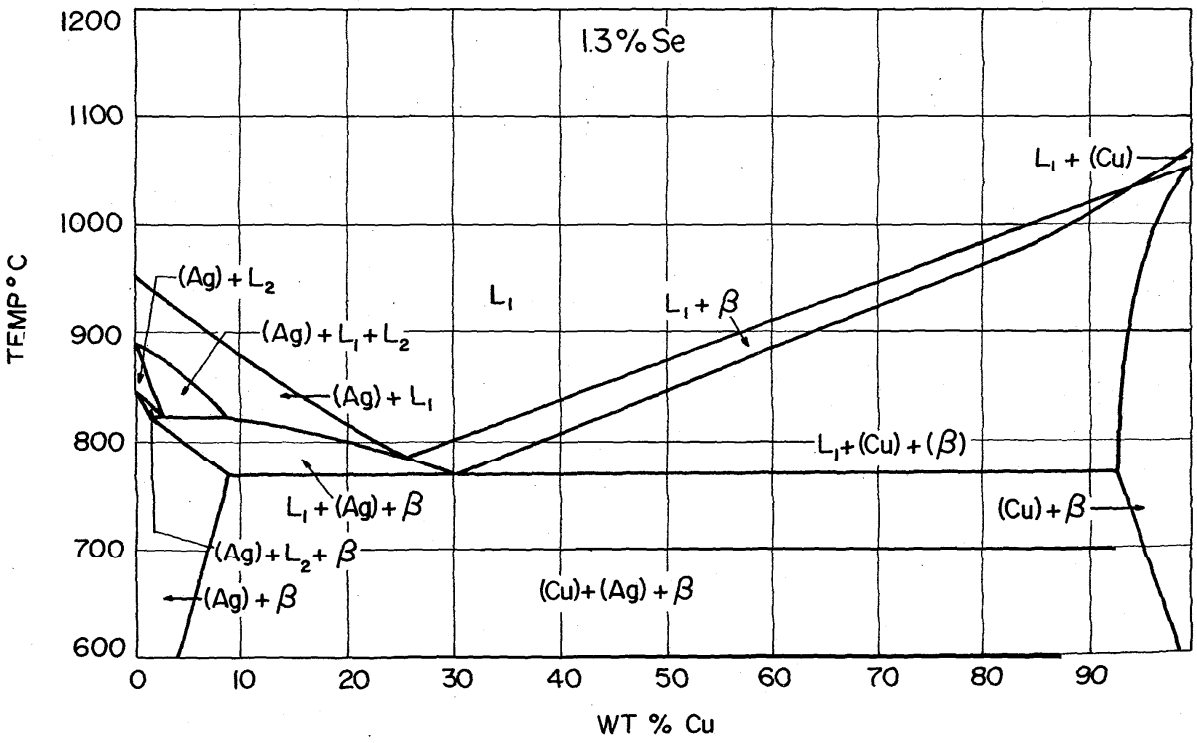
LIQUIDUS

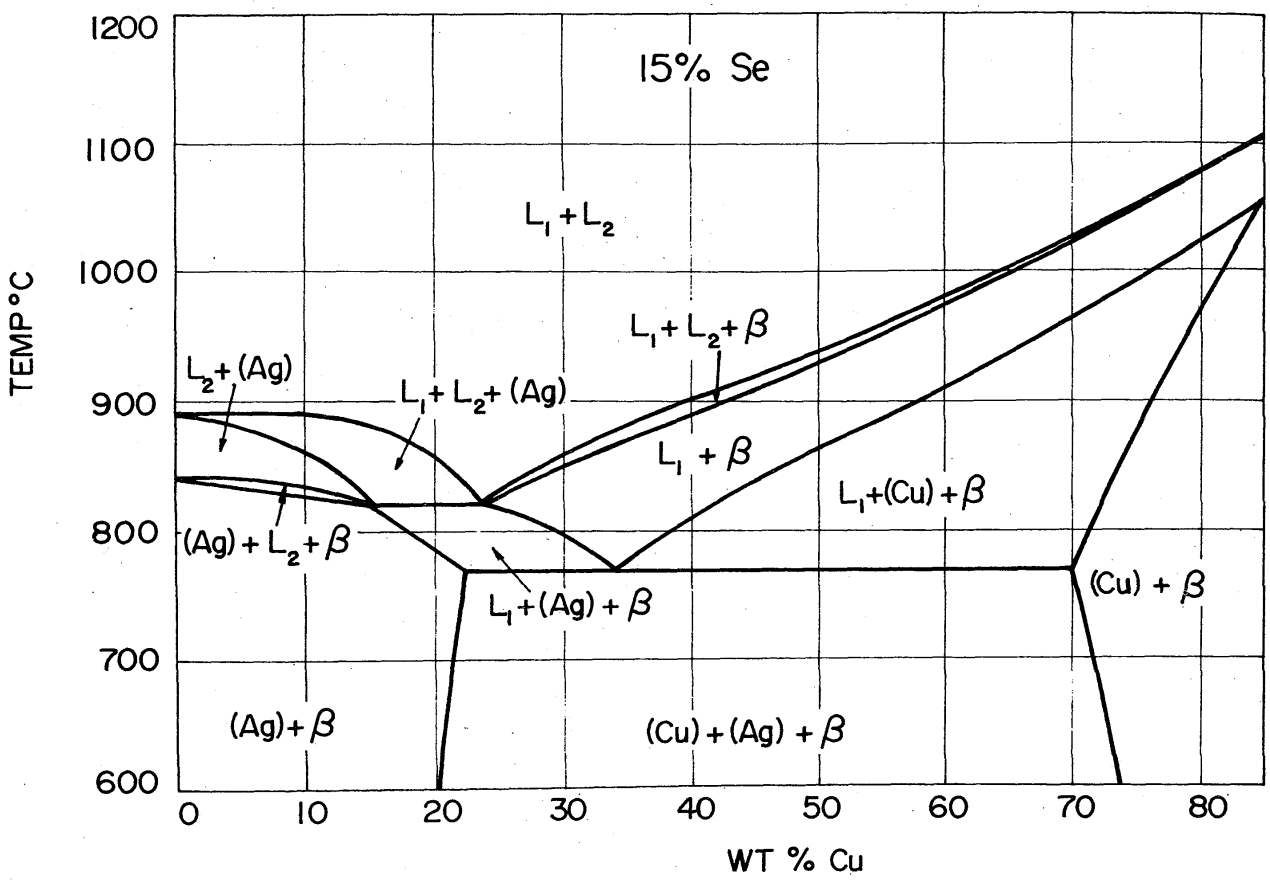


1200°C MISCIBILITY GAP
WITH TIE LINES




0.5 % Se
TEMP° C
WT % Cu
(Ag) + L2
(Ag) + L1 + L2
L1
(Ag) + L1
L1 + (Cu)
L1 + (Cu) + β
L1 + (Ag) + β
L1 + (Cu) + (Ag)
(Ag) + L2 + β
(Cu) + β
(Ag) + β
(Cu) + (Ag) + β


1.3 % Se
TEMP° C
WT % Cu
L1 + (Cu)
(Ag) + L2
L1
L1 + β
(Ag) + L1 + L2
(Ag) + L1
L1 + (Cu) + (β)
L1 + (Ag) + β
(Cu) + β
(Ag) + L2 + β
(Ag) + β
(Cu) + (Ag) + β



Cu-Ag-Sn

Phases and Structures

The following intermediate phases appear in the Cu-Sn and Ag-Sn binary systems. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
β	~23% Sn	bcc	A2	W
γ	Cu_3Sn	fcc	DO_3	BiF_3
δ	$Cu_{31}Sn_8$	cu	Like $D8_{1-3}$	γ-brass
ϵ_1	$Cu_3Sn(\epsilon)$	pseudo hex	A3	Mg
ζ	$Cu_{20}Sn_6$	trig		
η	Cu_6Sn_5(HT)	hex	$B8_1$	NiAs
η'	Cu_6Sn_5(LT)	hex (long period superlattice)		
ϵ_2	~15% Sn(ζ)	hcp	A3	Mg
θ	$Ag_3Sn(\epsilon)$	ortho		

The crystal structures are from the Metals Handbook [Gen. Ref. 1] except those of the η and η' phases, which were taken from Gangulee, Das, and Bever [6]. The designations of the two Ag-Sn phases are interchanged in the Metals Handbook (Gen. Ref. 1, p. 243 and p. 341), but the formulas and crystal structures are listed correctly.

Phase Diagrams

This system was originally investigated by Guertler and Bonsack [1] before the Cu-Sn binary was accurately established, and more recently was completely reinvestigated by Gebhardt and Petzow [2], whose results are shown here. The liquidus includes some results of unpublished work by Wagner [3], quoted by [2]. The liquidus valleys extend from the three binary eutectic points e_1 to e_3, and the six binary peritectics p_1 to p_6. The valleys meet at points II_1 to II_7, each point corresponding to the liquid composition in a type II four-phase equilibrium. The four-phase reactions, temperatures, and compositions of the coexisting phases are listed in table I.

In the solid state, there are five type-I four-phase equilibria (I_1 to I_5) and four type-II four-phase equilibria (II_8 to II_{11}). These reactions are also listed in table I. The composition of each phase in the solid state reactions should be regarded as only approximate, as they are taken from Gebhardt and Petzow's estimated drawings. Also shown are the isotherms at 500° and 600°, and isopleths at 5%, 10%, 15%, and 20% Sn.

Thermodynamic Properties

The enthalpies of solution of Cu(s) and Ag(l) in liquid Sn were measured calorimetrically at 720 K by Shen, Spencer, and Pool [4] for solute concentrations up to $x_{Cu,Ag}=0.04$. The data were used to calculate the partial enthalpies of solution of Cu and Ag in Sn at infinite dilution, as well as the interaction coefficients η_{Cu}^{Cu}, η_{Ag}^{Ag}, η_{Cu}^{Ag}, and η_{Ag}^{Cu}.

For the solution of Cu in Sn, the following values were obtained:

$$\Delta\bar{H}^{\circ}_{Cu(s)} = 11.8 \text{ kJ/g-atom } (\pm 0.3),$$

$$\eta_{Cu}^{Cu} = -17 \text{ kJ/g-atom } (\pm 8),$$

$$\eta_{Cu}^{Ag} = -40 \text{ kJ/g-atom } (\pm 15).$$

For the solution of Ag in Sn, the following values were obtained:

$$\Delta\bar{H}^{\circ}_{Ag(l)} = 4.3 \text{ kJ/g-atom } (\pm 0.3),$$

$$\eta_{Ag}^{Ag} = -40 \text{ kJ/g-atom } (\pm 5),$$

$$\eta_{Ag}^{Cu} = -38 \text{ kJ/g-atom } (\pm 15).$$

The thermodynamic requirement that $\eta_{Cu}^{Ag}=\eta_{Ag}^{Cu}$, is satisfied within the experimental precision; the value of η_{Ag}^{Cu} is believed to be more reliable.

Assuming an enthalpy of melting for Cu, $\Delta H_m=13$ kJ/g-atom, invariant with temperature, the value $\Delta\bar{H}^{\circ}_{Cu(s)}=11.8$ kJ/g-atom corresponds to $\Delta\bar{H}^{\circ}_{Cu(l)}=-1.2$ kJ/g-atom. This value is in good agreement with the value of -1.1 kJ/g-atom selected by Hultgren [Gen. Ref. 8] at 723 K.

The value $\Delta\bar{H}^{\circ}_{Ag(l)}=4.3$ kJ/g-atom is in good agreement with the value of 4.0 kJ/g-atom at 723 K, obtained previously by Spencer and Pool [5].

References

[1] Guertler, W., and Bonsack, W., Z. anorg. allg. Chem. **162,** 22 (1927).

[2] Gebhardt, E., and Petzow, G., Z. Metallk. **50,** 597 (1959).

[3] Wagner, F., unpublished research, quoted in reference 2.

[4] Shen, S. S., Spencer, P. J., and Pool, M. J., Trans. AIME **245,** 603 (1969).

[5] Spencer, P. J., and Pool, M. J., Trans. AIME **242,** 291 (1968).

[6] Cangulee, A., Das, C. C., and Bever, M. B., Metall. Trans. **4,** 2063 (1973).

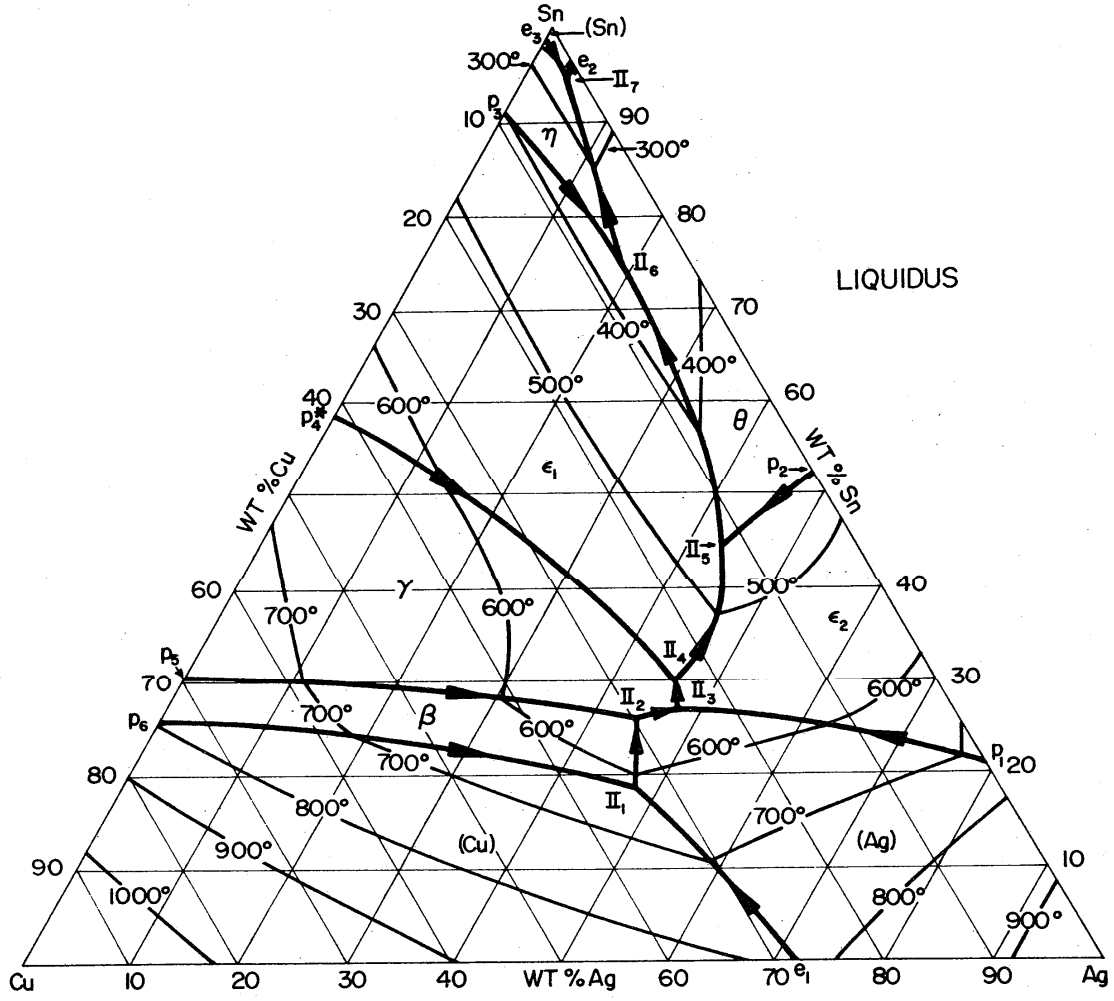
DG

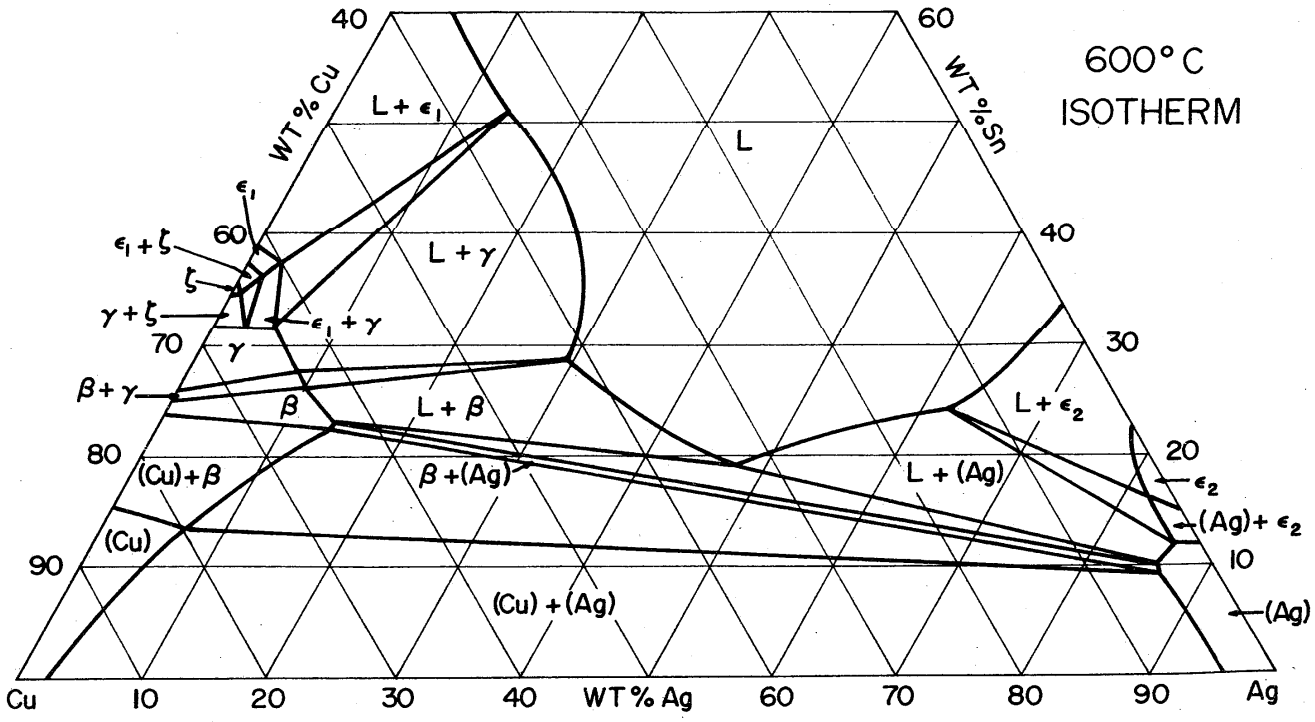
TABLE I. Four-phase equilibria in the Cu-Ag-Sn system

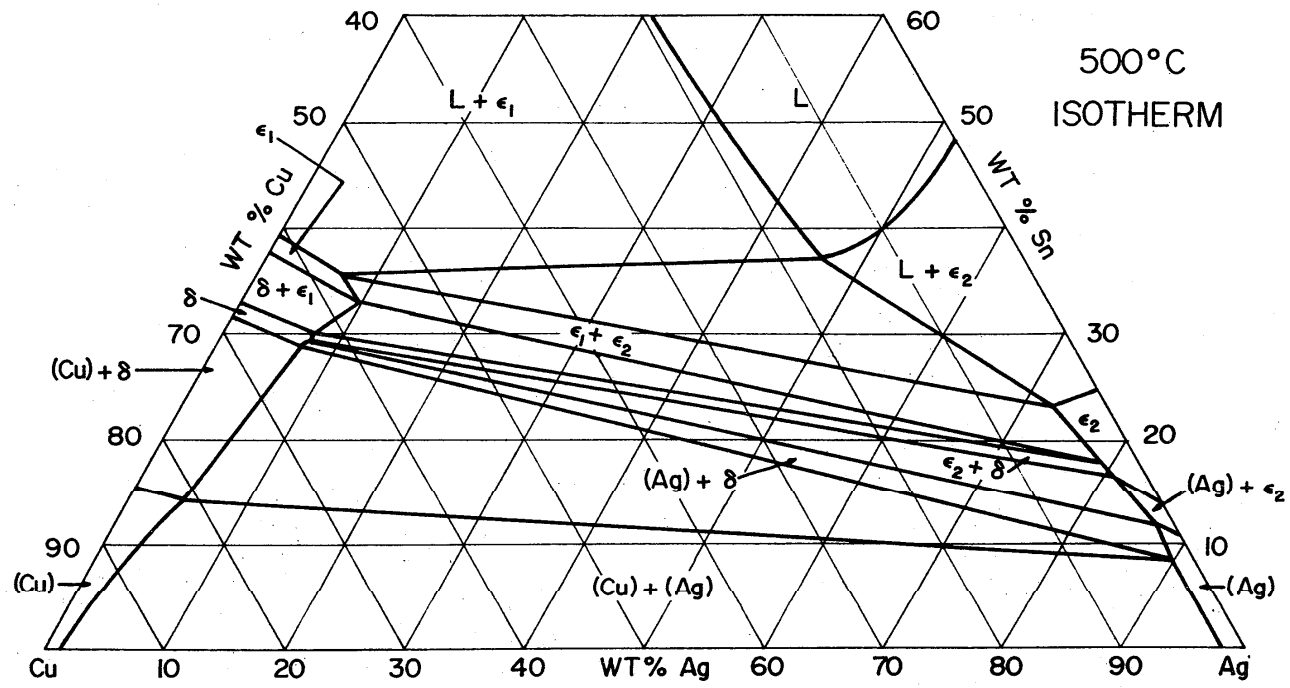
Reaction	Temp. °C	Coexisting phases	Composition of phases		
			Wt.% Ag	Wt.% Cu	Wt.% Sn
II_1: L + (Cu) = (Ag) + β	605	L	48	33.5	18.5
		(Cu)	6.5	80.5	13
		(Ag)	87	4	9
		β	14	63	23
II_2: L + β = (Ag) + γ	560	L	44.5	29.5	26
		β	14	62	24
		(Ag)	86	3.5	10.5
		γ	13	60	27
II_3: L + (Ag) = ϵ_2 + γ	550	L	47.5	25.5	27
		(Ag)	85	2.5	12.5
		ϵ_2	80.5	3.5	16
		γ	12	59	29
II_4: L + γ = ϵ_2 + ϵ_1	540	L	46	24	30
		γ	11	58	31
		ϵ_2	78	4	18
		ϵ_1	11	53	36
II_5: L + ϵ_2 = θ + ϵ_1	440	L	43.5	12	44.5
		ϵ_2	73	4	23
		θ	71.5	2.5	26
		ϵ_1	10	52	38
II_6: L + ϵ_1 = θ + η	350	L	20	6	74
		ϵ_1	8	54	38
		θ	71	2	27
		η	4	38	58

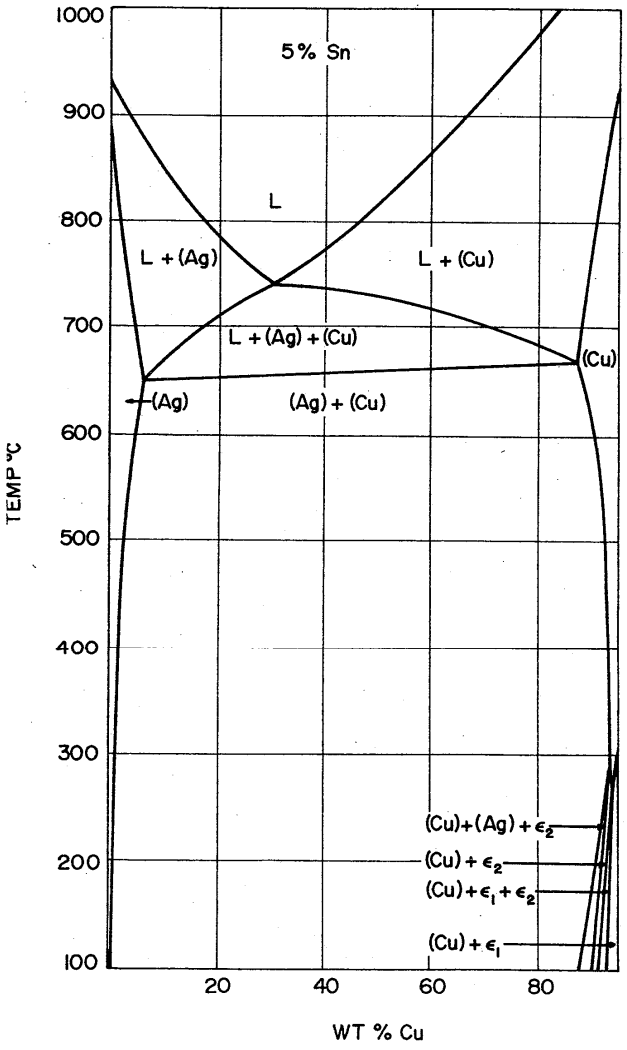
TABLE I. Four-phase equilibria in the Cu-Ag-Sn system—Continued

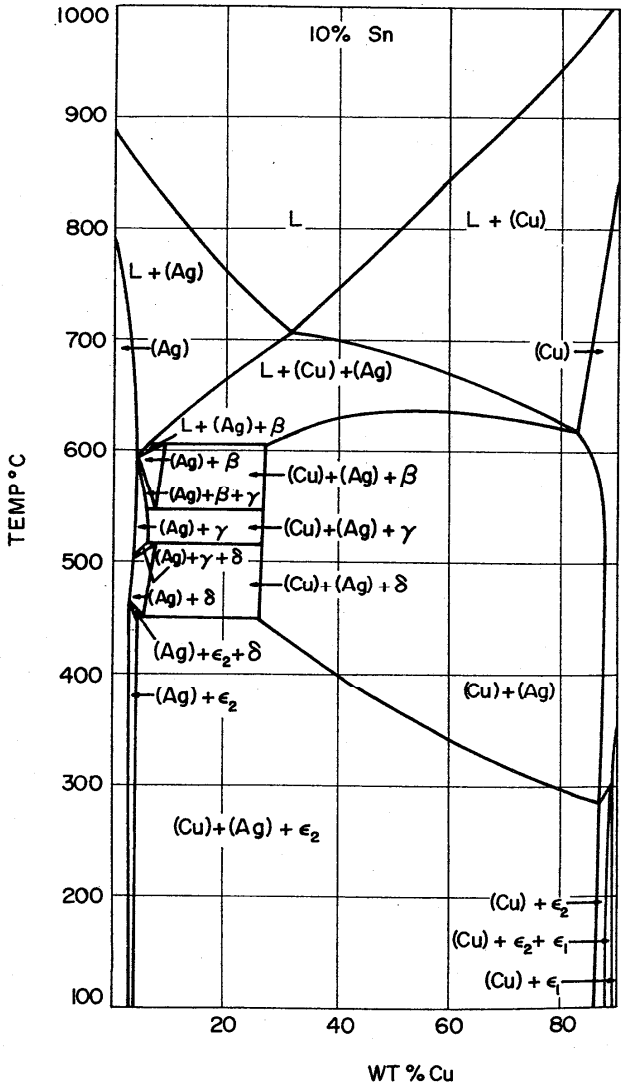
Reaction	Temp. °C	Coexisting phases	Composition of phases		
			Wt. % Ag	Wt. % Cu	Wt. % Sn
II_7: $L+\eta=\Theta+(Sn)$	225	L	4	0.5	95.5
		η	2.5	37.5	60
		θ	71	1.5	27.5
		(Sn)	0.5	1	98.5
I_1: $\zeta=\delta+\gamma+\epsilon_1$	570	ζ	3	65	32
		δ	2	67	31
		γ	4	67	29
		ϵ_1	4	62	34
I_2: $\beta=(Cu)+(Ag)+\gamma$	545	β	14	63	23
		(Cu)	7	81	12
		(Ag)	88	3	9
		γ	21	62	17
II_8: $\gamma+\epsilon_1=\delta+\epsilon_2$	525	γ	9	62	29
		ϵ_1	9	57	34
		δ	5	61	34
		ϵ_2	78	5	17
II_9: $(Cu)+\gamma=(Ag)+\delta$	515	(Cu)	5	83	12
		γ	14	59	27
		(Ag)	87	5	8
		δ	6	66	28
I_3: $\gamma=(Ag)+\epsilon_2+\delta$	505	γ	18	55	27
		(Ag)	84	4	12
		ϵ_2	82	3	15
		δ	7	64	29
II_{10}: $(Ag)+\delta=(Cu)+\epsilon_2$	450	(Ag)	88	3	9
		δ	8	63	29
		(Cu)	4	83	13
		ϵ_2	82	4	14
I_4: $\delta=(Cu)+\epsilon_2+\epsilon_1$	300	δ	7	63	30
		(Cu)	2	87	11
		ϵ_2	82	3	15
		ϵ_1	3	62	35
II_{11}: $\epsilon_1+\eta=\theta+\eta'$	170	ϵ_1	8	54	38
		η	3	38	59
		η'	2	40	58
		θ	71	3	26
I_5: $\eta=\theta+\eta'+(Sn)$	150	η	3	37	60
		θ	70	3	27
		η'	2	39	59
		(Sn)	0	0	100

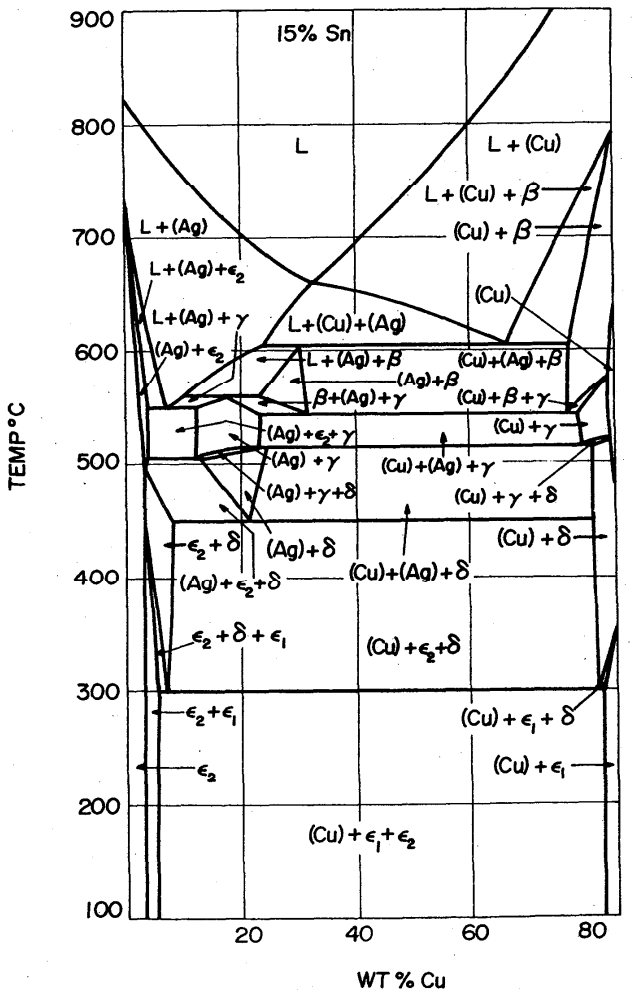

LIQUIDUS
Sn
(Sn)
e_3
e_2
e_1
p_1
p_2
p_3
p_4
p_5
p_6
Π_1
Π_2
Π_3
Π_4
Π_5
Π_6
Π_7
η
θ
ϵ_1
ϵ_2
γ
β
(Cu)
(Ag)
300°
400°
500°
600°
700°
800°
900°
1000°
WT % Cu
WT % Sn
WT % Ag
Cu
Ag

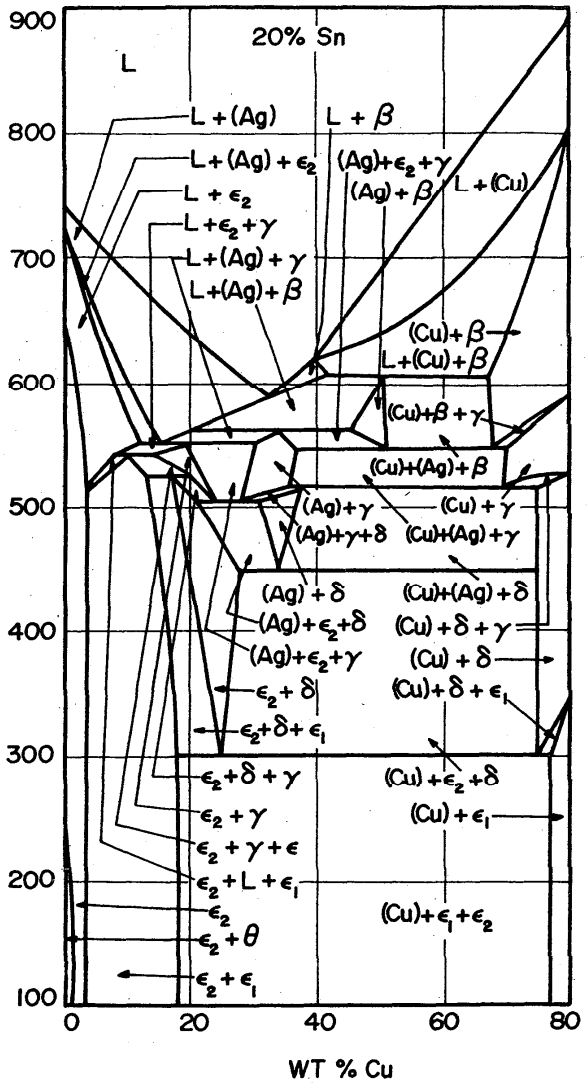

600° C
ISOTHERM
L
$L + \epsilon_1$
$L + \gamma$
$L + \beta$
$L + \epsilon_2$
$L + (Ag)$
ϵ_1
$\epsilon_1 + \zeta$
ζ
$\gamma + \zeta$
$\epsilon_1 + \gamma$
$\beta + \gamma$
$\beta + (Ag)$
(Cu) + β
(Cu)
(Cu) + (Ag)
ϵ_2
(Ag) + ϵ_2
(Ag)
WT % Cu
WT % Sn
WT % Ag
Cu
Ag


500°C
ISOTHERM
L + ε1
L
L + ε2
δ + ε1
ε1 + ε2
ε2
ε2 + δ
(Cu) + δ
(Ag) + δ
(Ag) + ε2
(Cu)
(Cu) + (Ag)
(Ag)
WT % Cu
WT % Sn
WT % Ag
Cu
Ag


5% Sn
L
L + (Ag)
L + (Cu)
L + (Ag) + (Cu)
(Ag)
(Ag) + (Cu)
(Cu)
(Cu) + (Ag) + ε2
(Cu) + ε2
(Cu) + ε1 + ε2
(Cu) + ε1
TEMP °C
WT % Cu


10% Sn
L
L + (Cu)
L + (Ag)
(Ag)
(Cu)
L + (Cu) + (Ag)
L + (Ag) + β
(Ag) + β
(Cu) + (Ag) + β
(Ag) + β + γ
(Ag) + γ
(Cu) + (Ag) + γ
(Ag) + γ + δ
(Cu) + (Ag) + δ
(Ag) + δ
(Ag) + ε2 + δ
(Ag) + ε2
(Cu) + (Ag)
(Cu) + (Ag) + ε2
(Cu) + ε2
(Cu) + ε2 + ε1
(Cu) + ε1
TEMP °C
WT % Cu


15% Sn
L
L + (Cu)
L + (Cu) + β
(Cu) + β
L + (Ag)
L+(Ag)+ε2
L+(Ag) + γ
(Ag)+ε2
L+(Cu)+(Ag)
L+(Ag)+β
(Cu)+(Ag)+β
(Ag)+β
β+(Ag)+γ
(Cu)+β+γ
(Cu)
(Cu)+γ
(Ag)+ε2+γ
(Ag) +γ
(Cu)+(Ag)+γ
(Ag)+γ+δ
(Cu) + γ + δ
(Cu) + δ
ε2 + δ
(Ag)+δ
(Ag)+ε2+δ
(Cu)+(Ag)+δ
ε2 + δ + ε1
(Cu)+ε2+δ
ε2+ε1
(Cu) + ε1 + δ
ε2
(Cu) + ε1
(Cu) + ε1+ε2
TEMP°C
WT % Cu
100
200
300
400
500
600
700
800
900
20
40
60
80


20% Sn
L
L + (Ag)
L + β
L+(Ag) + ε2
(Ag)+ε2+γ
(Ag) + β
L + (Cu)
L + ε2
L+ε2+γ
L+(Ag) + γ
L+(Ag)+β
(Cu)+β
L+(Cu)+β
(Cu)+β+γ
(Cu)+(Ag)+β
(Ag)+γ
(Cu) + γ
(Ag)+γ+δ
(Cu)+(Ag) +γ
(Ag) + δ
(Cu)+(Ag) + δ
(Ag)+ε2+δ
(Cu) +δ+γ
(Ag)+ε2+γ
(Cu) + δ
ε2+ δ
(Cu)+δ + ε1
ε2+δ+ε1
ε2+δ+γ
(Cu) +ε2 +δ
ε2 + γ
(Cu) + ε1
ε2 + γ + ε
ε2 + L + ε1
ε2
(Cu)+ε1+ε2
ε2 + θ
ε2 + ε1
TEMP°C
WT % Cu
100
200
300
400
500
600
700
800
900
0
20
40
60
80

Cu-Ag-Te

Phases and Structures

The results of the structural investigations in the binary systems Cu-Te and Ag-Te and in the ternary system are very often contradictory and more work is required to clarify the phase relationships. The following phases have been reported.

Designation	Composition	Symmetry	Symbol	Prototype
β_1	Cu_2Te(HT)	fcc		
$\gamma, \gamma', \gamma''$	Cu_2Te(LT)	hex		
δ	Cu_4Te_3 (rickardite)	tet	C38	Cu_2Sb
ϵ_1	CuTe	ortho		
β_2	Ag_2Te(HT) (β)	fcc		
ζ	Ag_2Te(HT)	bcc		
η	Ag_2Te(LT)(α) (hessite)	mono		
θ	Ag_5Te_3	hex		
ϵ_2	AgTe (empressite)	ortho		
T_1(?)	AgCuTe			
T_2	$AgCuTe_2$	ortho		

The crystal structures are from Pearson [Gen. Ref. 2]. A ternary compound AgCuTe was reported by Agaev, Alekperova, and Zargarova [1], but no structure was given and its existence is questionable. Rustamov et al. [2] did not detect this phase in their investigation. A second ternary compound, $AgCuTe_2$, is reported by Avilov and Baranova [3].

Phase Diagrams

The liquidus and solidus were determined by Rustamov et al. [2], Krestovnikov, Mendelevich and Glazov [4], and by Mendelevich et al. [5]. All these investigations report an isomorphous-type phase diagram with a minimum at 35–36 mole % Cu_2Te at 842 ± 3 °C. Agaev, Alekperova, and Zargarova [1] report the existence of the AgCuTe compound (m. p. 850 °C) at 50 mole % Cu_2Te, dividing the pseudobinary phase diagram into two parts: (a) Cu_2Te to AgCuTe: a eutectic at 800 °C and 56 mole % Cu_2Te; (b) a peritectic at 850 °C and 50 mole % Cu_2Te (see figure). The diagram shown should be regarded as questionable, pending the confirmation of the AgCuTe phase.

Insufficient data are available to give any reliable solid-state phase relations.

Thermodynamic Properties

The vapor pressure of Cu_2Te-Ag_2Te solid solutions was measured by Glazov and Korenchuk [6]. They report a negative deviation from Raoult's Law, which suggests the formation of a superlattice or of the compound AgCuTe. However, they make no mention of this compound.

References

[1] Agaev, M. I., Alekperova, S. M., and Zargarova, M. I., Dokl. Akad. Nauk Azerb. SSR **27**, 15 (1971).

[2] Rustamov, P. G., Rustamov, A. G., Ibragimova, P. G., and Babaev, S. Kh., Elektronnaya Tekhnika, Ser. 12 **5**, 3 (1970).

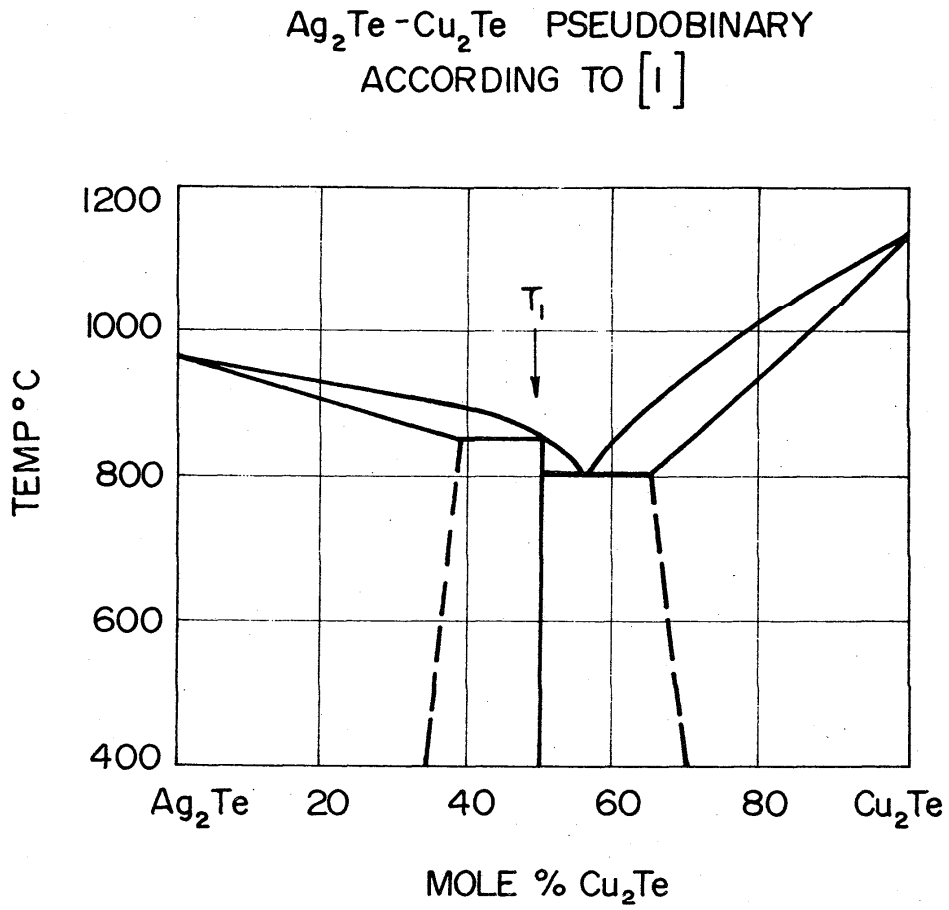
[3] Avilov, A. S., and Baranova, R. V., Kristallografiya **17**, 219 (1972).

[4] Krestovnikov, A. N., Mendelevich, A. Yu., and Glazov, V. M., Izv. Akad. Nauk SSSR, Neorg. Mater. **4**, 1804 (1968).

[5] Mendelevich, A. Yu., Krestovnikov, A. N., and Glazov, V. M., Zh. Fiz. Khim. **43**, 3067 (1969).

[6] Glazov, V. M., and Korenchuk, N. M., Zh. Fiz. Khim. **45**, 2107 (1971).

DG



Cu-Ag-Ti

Phases and Structures

The following intermediate phases appear in the Cu-Ti and Ag-Ti binary systems. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
γ	Cu_7Ti_2(?)	rhom or ortho		Au_4Zr(?)
δ(?)	Cu_2Ti	ortho		Au_2V
ϵ	Cu_3Ti_2	tet		Al_3Os_2
λ	Cu_4Ti_3	tet		
ζ	CuTi	ord tet	B11	CuTi
η_1	$CuTi_2$	tet	$C11_b$	$MoSi_2$
β	AgTi	ord fct	$L1_0$	AuCuI
η_2	$AgTi_2$(?)	tet	$C11_b$	$MoSi_2$

The crystal structures of the Cu-Ti binary phases are from Hultgren [Gen. Ref. 6], and the structures of the Ag-Ti binary phases are from the Metals Handbook [Gen. Ref. 1]. There is still considerable uncertainty in the Cu-Ti binary system. The γ phase (Cu_7Ti_2) has also been reported as Cu_4Ti and Cu_3Ti. The existence of the δ phase (Cu_2Ti) is questionable. In addition, Pearson [Gen. Ref. 2] lists four other phases, β'-Cu_3Ti(HT), β-Cu_3Ti(LT), δ-CuTi(Ll_0), and ϵ-$CuTi_3$; some of them are doubtful. The η_2 phase ($AgTi_2$) has also been reported as $AgTi_3$. Many of the reported crystal structures are not in agreement. Eremenko, Buyanov, and Panchenko [1] report a continuous solid solution $(Cu,Ag)Ti_2$, designated here as η, connecting the isostructural $CuTi_2(\eta_1)$ and $AgTi_2(\eta_2)$ binary compounds.

Phase Diagrams

The system has been investigated by Eremenko, Buyanov, and Panchenko [1, 2, 3] whose diagrams are the basis for the ones shown here. There is serious disagreement between Eremenko et al.'s original diagrams and the currently recommended binary Cu-Ti and Ag-Ti phase diagrams of Hultgren [Gen. Ref. 6] and the Metals Handbook [Gen. Ref. 1], respectively, near the liquidus temperatures. Eremenko et al. seem to have confused eutectic and peritectic points in the Cu-Ti binary, and indicated a eutectic on the Ag-Ti binary where only a eutectoid has been detected. For these reasons, their liquidus valley projections are suspect and are not shown here. For lack of any other data, their liquidus is shown, but is adjusted to be consistent with the binaries. It is also felt that the invariant reactions listed in table I below should be regarded as tentative.

The liquid state is marked by the presence of a miscibility gap, as shown in the isotherm at 1300 °C. An unusual feature of the liquidus is the "hump" in the base of the $L_1 + L_2$ region. This is caused by the liquidus surface being raised (to maximum at 970 °C) by the congruently melting compound CuTi(ζ). Four four-phase equilibria (two type-I and two type-II) were reported (see table I). The liquid compositions are estimated from the diagrams of the original paper and should be considered approximate. A vague reference is made to seven other invariant equilibria involving the liquid, but neither the nature of the reactions nor the coexisting phases were described.

In the solid state, the 700 °C isotherm shown here appears to be reliable. Eremenko et al. [1], have unaccountably omitted the $\epsilon(Cu_3Ti_2)$ phase from their isotherm at 700 °C. There is a continuous solid solution $(Ag,Cu)Ti_2$, designated η, which extends across the whole diagram. The silver solid solution (Ag) is in equilibrium with all the phases which exist at this temperature, except Ti.

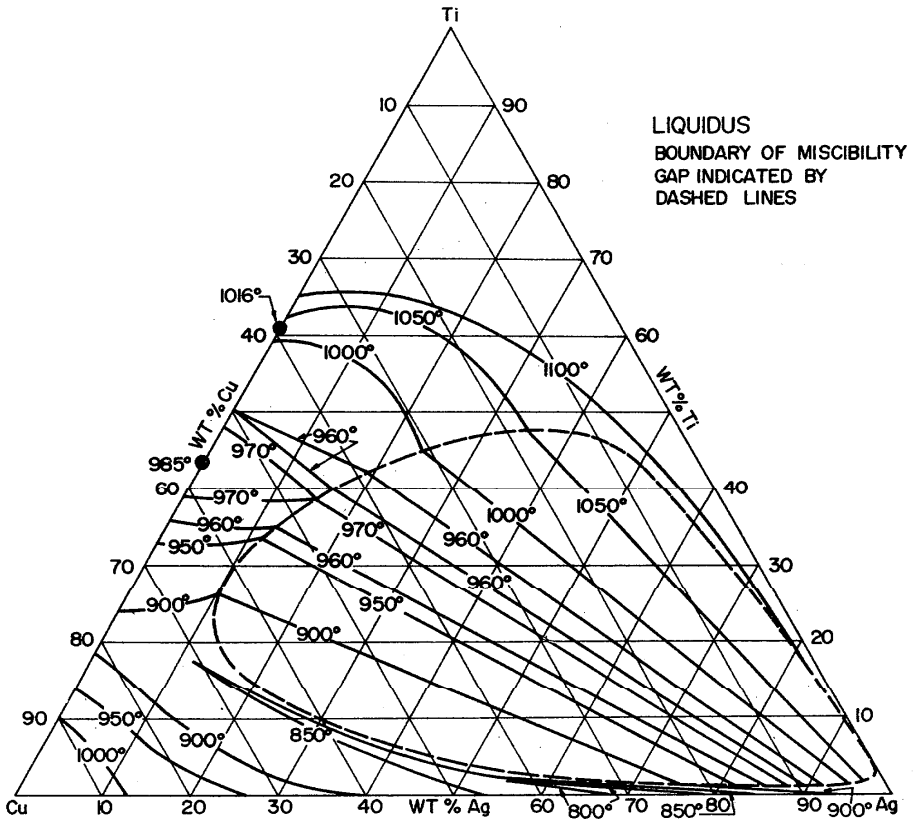
References

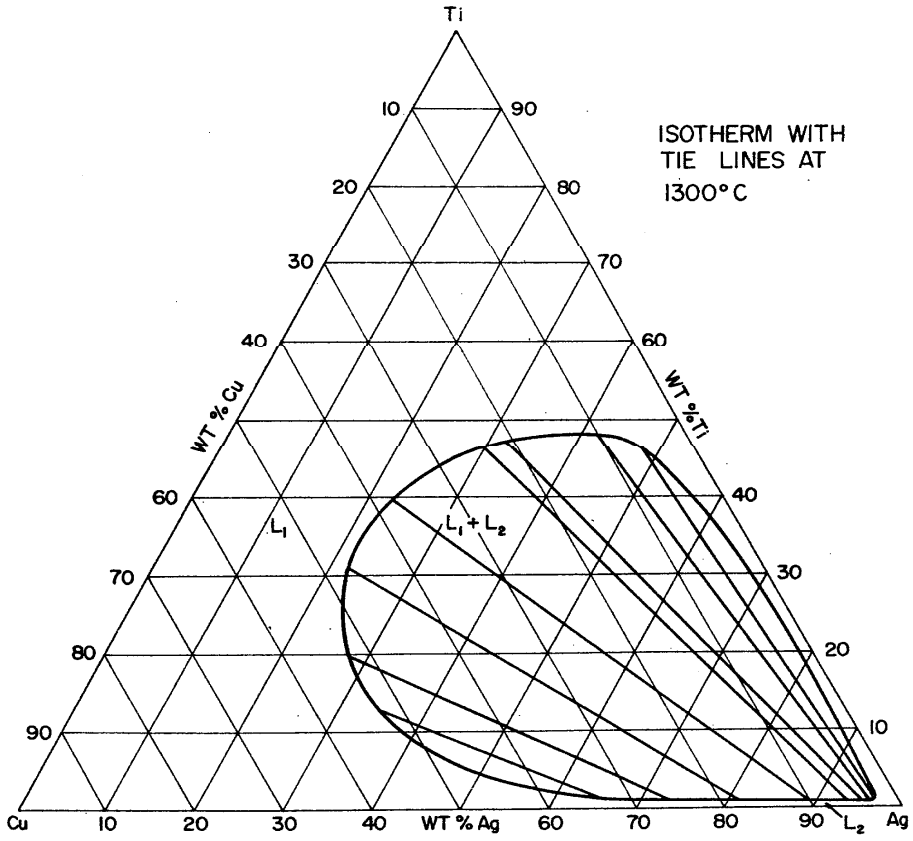
[1] Eremenko, V. N., Buyanov, Yu. I., and Panchenko, N. M., Izv. Akad. Nauk SSSR, Metal. No. 3, 188 (1969).
[2] Eremenko, V. N., Buyanov, Yu. I., and Panchenko, N. M., Izv. Akad. Nauk SSSR, Metal. No. 3, 200 (1969).
[3] Eremenko, V. N., Buyanov, Yu. I., and Panchenko, N. M., Porosh. Met. **10**, 44 (1970).

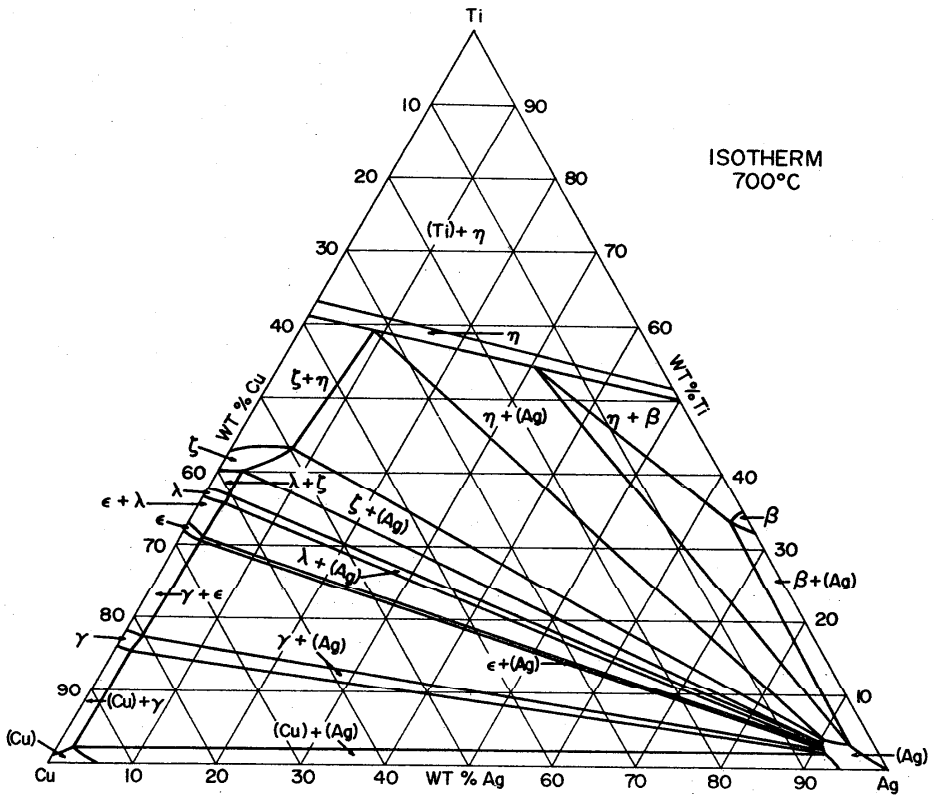
DG

TABLE I. Some proposed four-phase equilibria in the Cu-Ag-Ti system

Reaction	Temp. °C	Coexisting phases	Composition of phases		
			Wt. % Cu	Wt. % Ag	Wt. % Ti
II_1: $L_1 + (Ti) = L_2 + \eta$	982	L_1	32	23	45
		L_2	6	93	1
		(Ti)			
		η			
I_1: $L_1 = L_2 + \eta + \zeta$	954	L_1	40	18	42
		L_2	9	90	1
		η			
		ζ			
II_2: $L_1 + \zeta = L_2 + \lambda$	900	L_1	63	11	26
		L_2	22	77	1
		ζ			
		λ			
I_2: $\delta = L + \epsilon + \gamma$	851	L	73	9	18
		δ			
		ϵ			
		γ			


Ti
LIQUIDUS
BOUNDARY OF MISCIBILITY GAP INDICATED BY DASHED LINES
WT % Cu
WT % Ti
WT % Ag
Cu
Ag
1016°
1050°
1000°
1100°
985°
970°
960°
950°
900°
850°
800°


Ti
ISOTHERM WITH TIE LINES AT 1300°C
WT % Cu
WT % Ti
WT % Ag
Cu
Ag
L1
L1 + L2
L2



Cu-Ag-Zn

Phases and Structures

The following intermediate phases appear in the Cu-Zn and Ag-Zn binary systems. No ternary phases have been found.

Designation	Composition	Symmetry	Symbol	Prototype
β_1	CuZn (HT) (β)	bcc	A2	W
β'	CuZn (LT)	ord bcc	B2	CsCl
γ_1	Cu_5Zn_8 (γ)	ord bcc	$D8_2$	γ-brass
δ	$CuZn_3$	ord bcc	B2	CsCl
ϵ_1	~ 83% Zn (ϵ)	hcp	A3	Mg
β_2	AgZn (HT) (β)	bcc	A2	W
ζ	AgZn (LT)	ord hex		
γ_2	Ag_5Zn_8 (γ)	ord bcc	$D8_2$	γ-brass
ϵ_2	~ 70% Zn (ϵ)	hcp	A3	Mg

The crystal structures are from the Metals Handbook [Gen. Ref. 1].

Phase Diagrams

After early investigations by Ueno [1], Keinert [2], and Weigert [3], Gebhardt, Petzow, and Krauss [4] later on thoroughly reexamined the phase relations in the ternary system. The liquidus, the isotherms at 600°, 500°, and 350 °C, and the isopleths at 20% Ag and 20% Zn by [4] are shown here. Gebhardt et al. also gave isopleths at 40% Ag, 60% Ag, 40% Cu, and 60% Cu.

The liquidus diagram shows the liquidus valleys extending from the binary eutectic or peritectic points into the ternary field. Two continuous valleys (from p_8 to p_2 and from p_4 to p_5) are formed, the other valleys meet on planes of four-phase equilibria. The invariant reaction temperatures and compositions of the coexisting phases are shown in table I.

In the solid state, the isotherms show that continuous solid solutions, designated β, γ, and ϵ, connect the isostructural β_1 and β_2, γ_1 and γ_2 and ϵ_1 and ϵ_2 binary phases, respectively. On the 350 °C isotherm, the β and β' (ordered) regions were labelled incorrectly as β' and β, respectively, in the original paper [4]. No solid-state four-phase equilibria exist in this system.

The β' to β order-disorder transition temperature of $Cu_{0.53-x}Ag_xZn_{0.47}$ alloys was investigated by Murakami, Nakanishi, and Kachi [5]. The transition temperature decreases with increasing Ag content from about 465 °C at $Cu_{0.53}Zn_{0.47}$ to about 223 °C at $Ag_{0.53}Zn_{0.47}$. The latter temperature is estimated from an extrapolation to 0% Cu.

Thermodynamic Properties

The partial pressure of zinc over the terminal (Cu) and (Ag) solid solutions at 1000 K were measured by

Argent and Lee [6]. For the terminal copper solid solution, the data yield the following values:

$$\gamma^{\circ}_{Zn(l)} = 0.051,$$

$$\epsilon^{Zn}_{Zn} = +6.5,$$

$$\epsilon^{Ag}_{Zn} \simeq 0.$$

The few data available in the terminal silver solid solution do not permit a reliable evaluation of the activity coefficients; the values given must be considered as estimates:

$$\gamma^{\circ}_{Zn(l)} = 0.27,$$

$$\epsilon^{Zn}_{Zn} \simeq 0,$$

$$\epsilon^{Cu}_{Zn} \simeq -3.5.$$

For the solid solution of zinc in copper, Hultgren [Gen. Ref. 6] reports a value of 0.014 for $\gamma^{\circ}_{Zn(s)}$ at 773 K, which corresponds to $\gamma^{\circ}_{Zn(l)} = 0.048$ at 1000 K. The data by [6] are in good agreement with this value. For the solid solution of zinc in silver, however, Hultgren [Gen. Ref. 6] reports a value of 0.199 for $\gamma^{\circ}_{Zn(s)}$ at 873 K, which corresponds to $\gamma^{\circ}_{Zn(l)} = 0.36$ at 1000 K. This value is quite different from the one obtained from the data by Argent and Lee. Values for the partial enthalpies and partial entropies of zinc are also given by [6]. An insufficient number of data was taken to calculate integral properties.

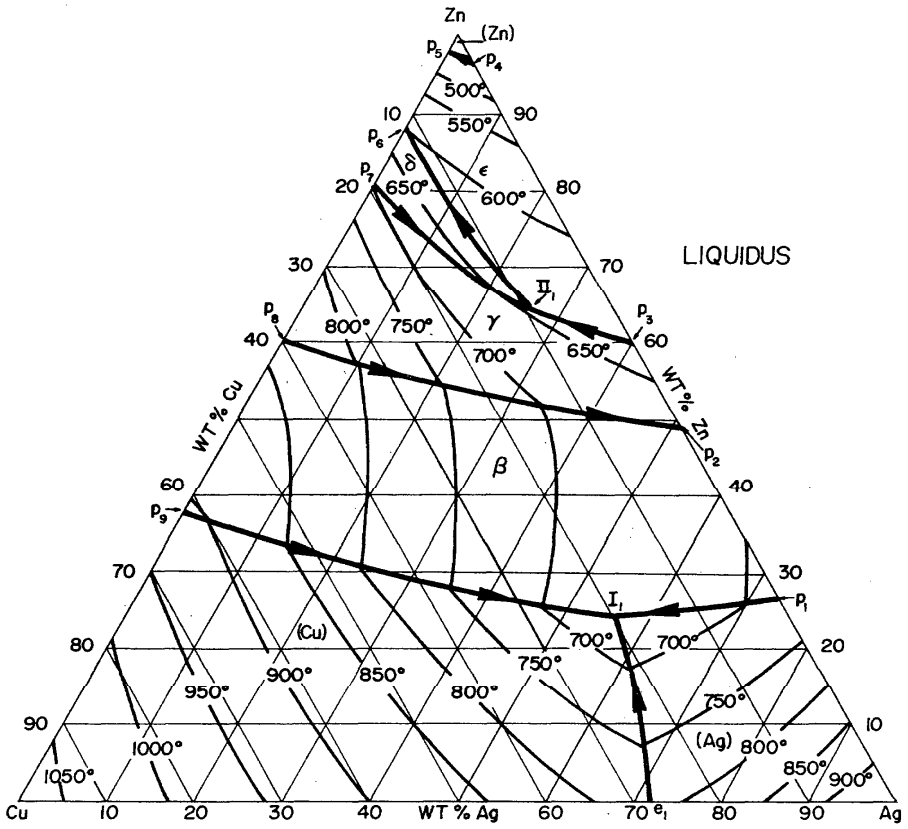
References

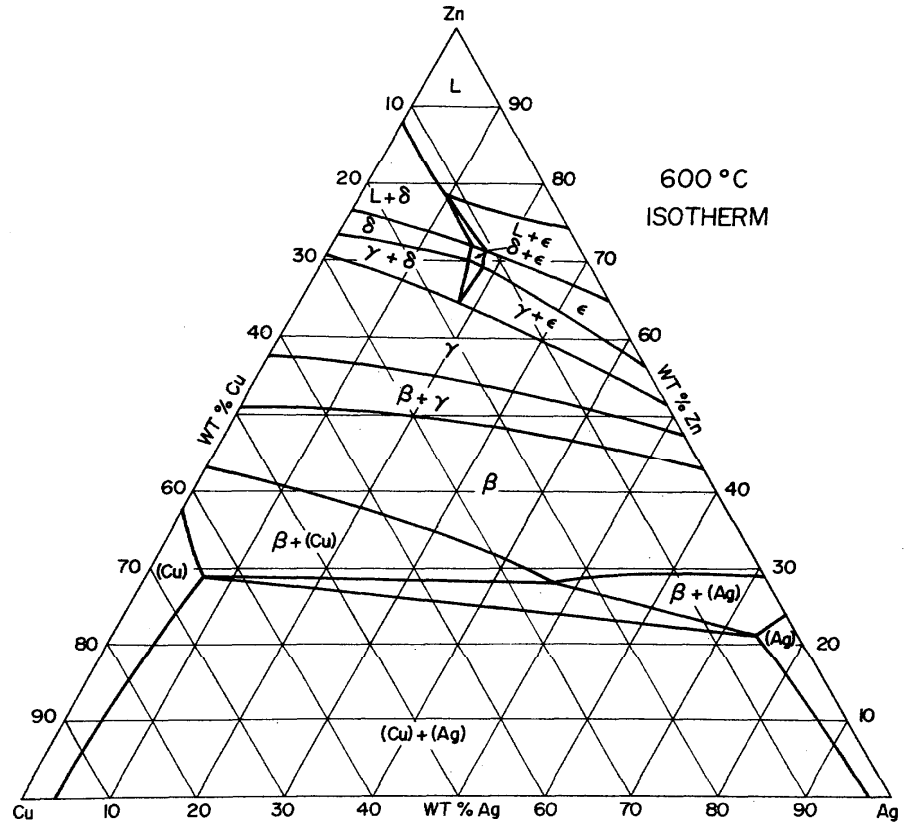
[1] Ueno, S., Mem. Coll. Sci. Kyoto Imp. Univ. **12A,** 347 (1929).
[2] Keinert, M., Z. physik. Chem. **A160,** 15 (1932).
[3] Weigert, K. M., Trans. AIME **200,** 233 (1954).
[4] Gebhardt, E., Petzow, G., and Krauss, W., Z. Metallk. **53,** 372 (1962).
[5] Murakami, Y., Nakanishi, N., and Kachi, S., Acta Met. **19,** 93 (1971).
[6] Argent, B. B., and Lee, K. T., Trans. Faraday Soc. **61,** 826 (1965).

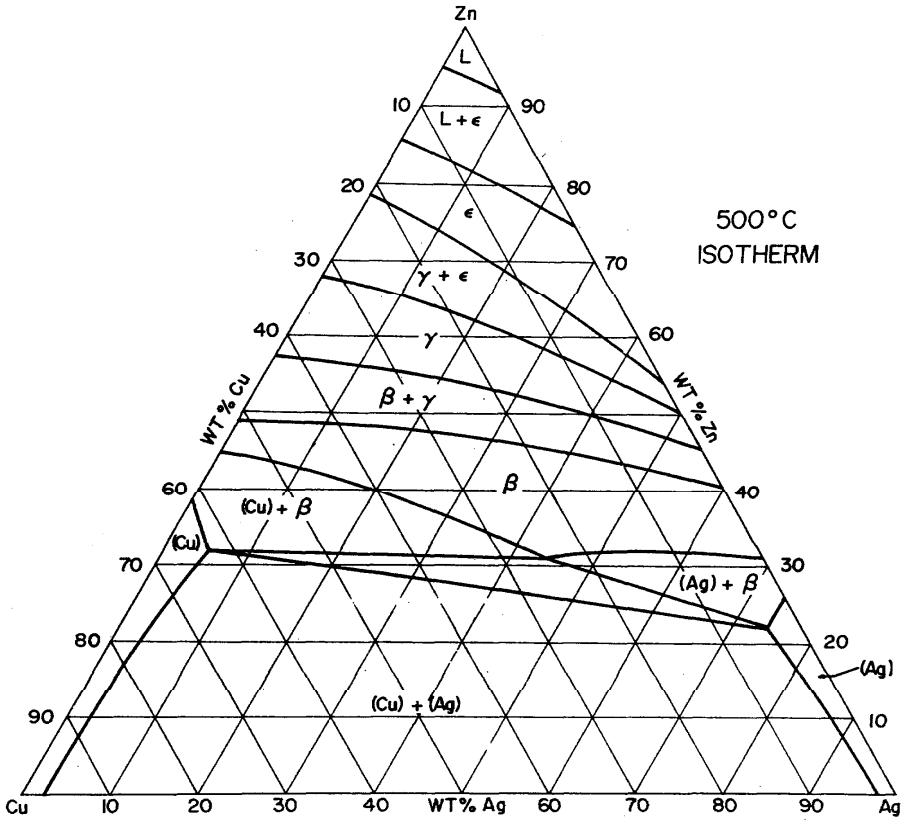
DG

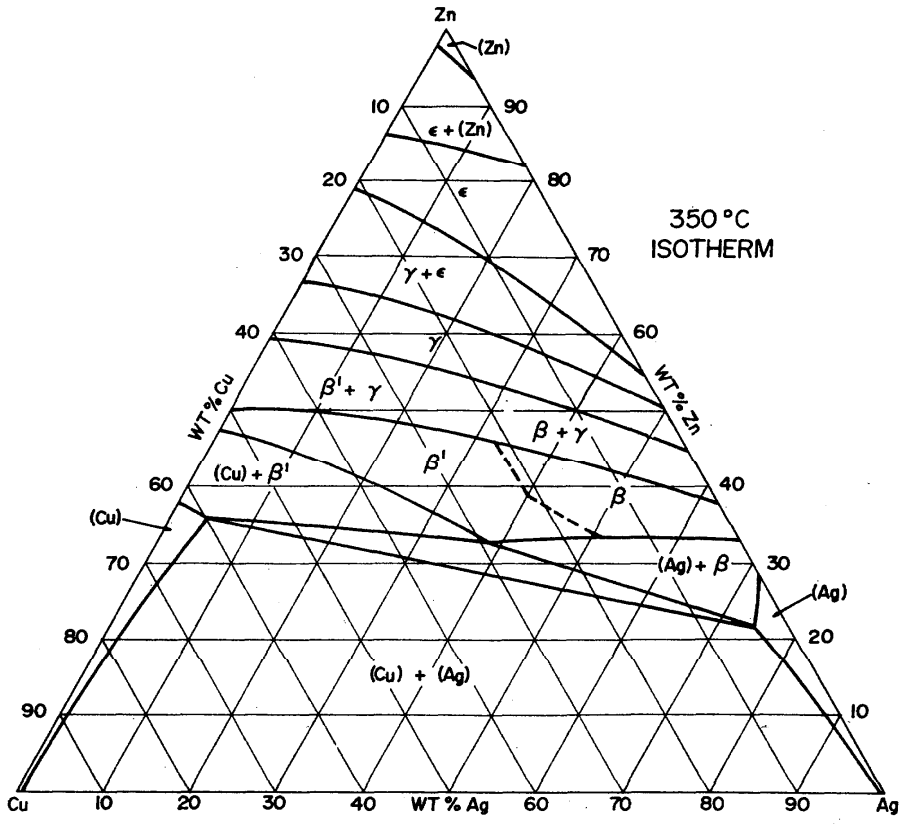
TABLE I. Four-phase equilibria in the Cu-Ag-Zn system

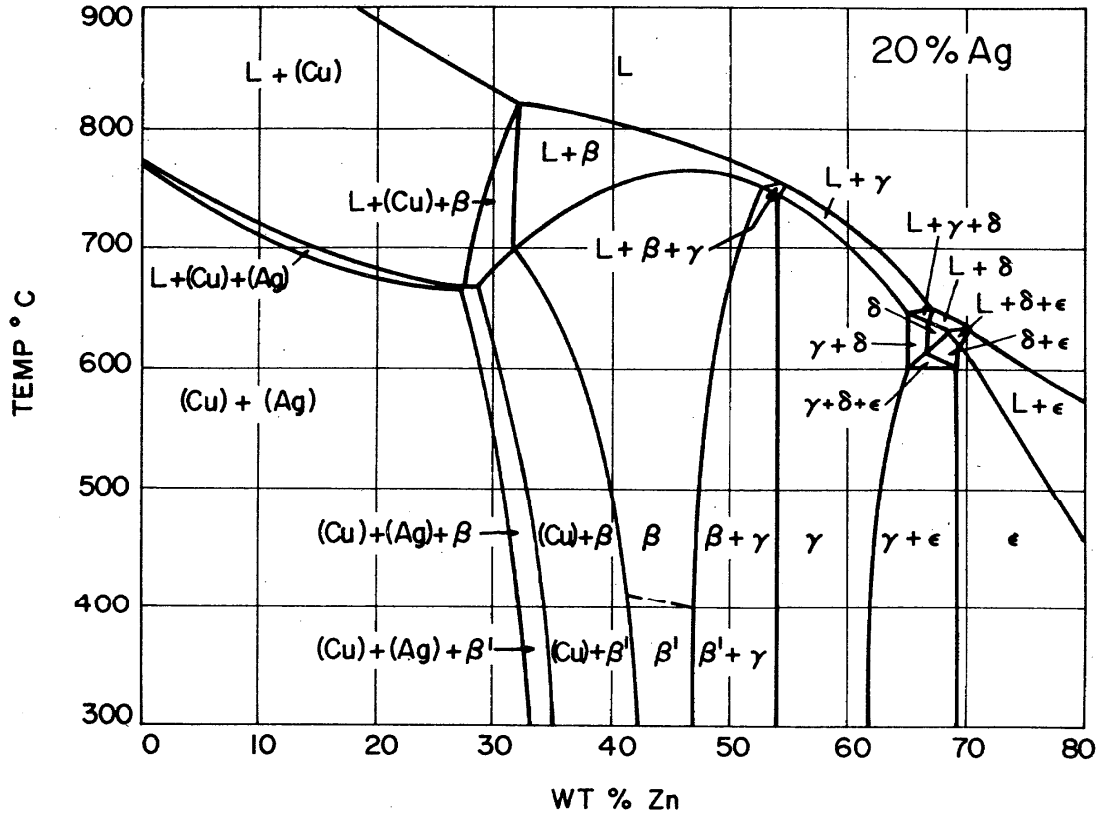
Reaction	Temp. °C	Coexisting phases	Composition of Phases		
			Wt.% Cu	Wt.% Ag	Wt.% Zn
I_1: $L = (Cu) + (Ag) + \beta$	665	L	20	56	24
		(Cu)	63	9	28
		(Ag)	5	75	20
		β	23	50	27
II_1: $L + \gamma = \epsilon + \delta$	630	L	9.5	26	64.5
		γ	12	25	63
		ϵ	10.5	26	63.5
		δ	11	25	64

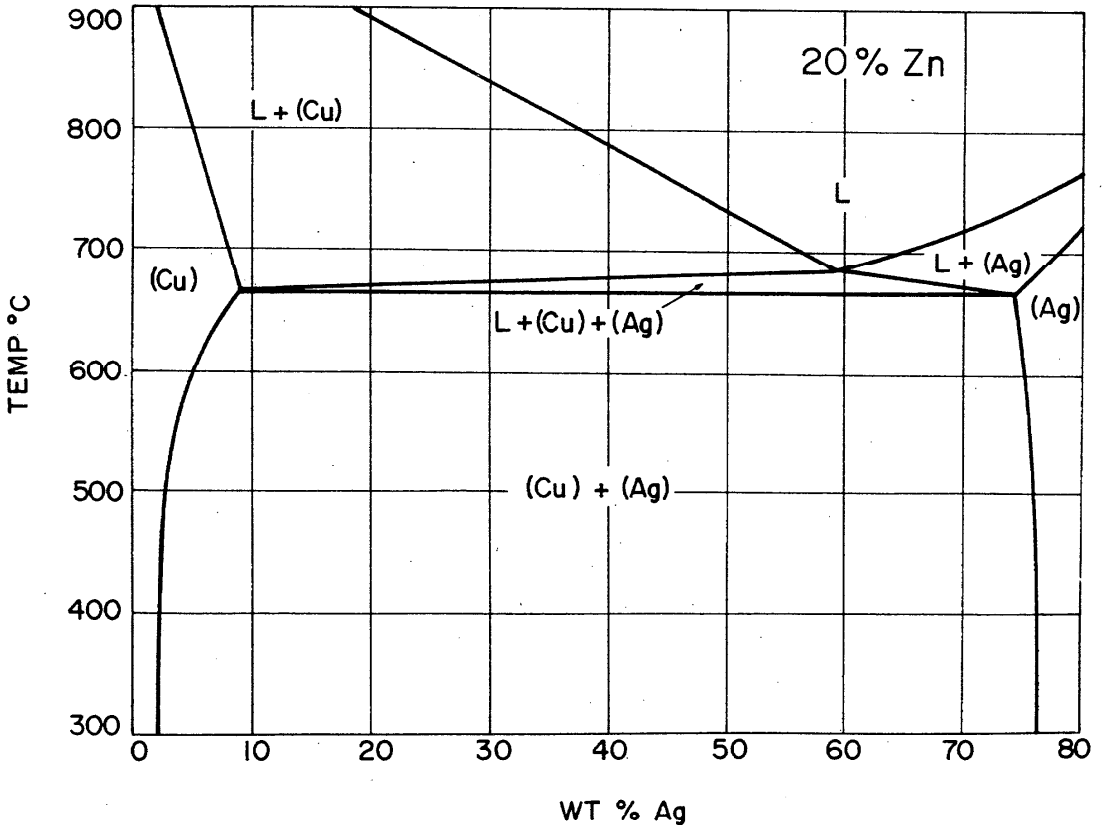

Zn
(Zn)
p_5
p_4
500°
550°
p_6
p_7
δ
ε
650°
600°
LIQUIDUS
Π_1
γ
p_8
800°
750°
700°
650°
p_3
WT % Cu
WT % Zn
β
p_2
p_9
I_1
p_1
(Cu)
700°
700°
750°
950°
900°
850°
800°
750°
(Ag)
800°
850°
900°
1000°
1050°
Cu
WT % Ag
e_1
Ag


Zn
L
600 °C
ISOTHERM
L+δ
δ
L+ε
δ+ε
γ+δ
γ+ε
ε
γ
β+γ
β
β+(Cu)
(Cu)
β+(Ag)
(Ag)
(Cu)+(Ag)
WT % Cu
WT % Zn
Cu
WT % Ag
Ag


Zn
L
L + ε
ε
γ + ε
γ
β + γ
β
(Cu) + β
(Cu)
(Ag) + β
(Ag)
(Cu) + (Ag)
500°C
ISOTHERM
WT % Cu
WT % Zn
WT % Ag
Cu
Ag
10
20
30
40
60
70
80
90


Zn
(Zn)
ε + (Zn)
ε
γ + ε
γ
β' + γ
β + γ
β'
(Cu) + β'
β
(Cu)
(Ag) + β
(Ag)
(Cu) + (Ag)
350°C
ISOTHERM
WT % Cu
WT % Zn
WT % Ag
Cu
Ag
10
20
30
40
60
70
80
90


20 % Ag
L + (Cu)
L
L+β
L+(Cu)+β
L + γ
L+γ+δ
L + β + γ
L + δ
L+(Cu)+(Ag)
δ
L +δ+ϵ
γ + δ
δ+ϵ
(Cu) + (Ag)
γ+δ+ϵ
L+ϵ
(Cu)+(Ag)+β
(Cu)+β
β
β + γ
γ
γ + ϵ
ϵ
(Cu)+(Ag)+β'
(Cu)+β'
β'
β'+ γ
TEMP °C
WT % Zn


20 % Zn
L + (Cu)
L
L + (Ag)
(Cu)
L +(Cu) + (Ag)
(Ag)
(Cu) + (Ag)
TEMP °C
WT % Ag