Silver – Copper – Phosphorus

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Introduction

Ag-Cu-P alloys have been used for joining copper and brasses. These alloys have found favour because of their low melting temperature and the fact that they can be used to braze copper without use of a flux. Compositions used for fillers range from binary Cu-P alloys to those containing up to 15 mass% Ag. Both Ag and P additions decrease the melting range of an alloy, but P has a greater influence. In order to operate within the melting temperature range reliable information is necessary on the Ag-Cu-P phase diagram (first of all on the liquidus and solidus).

The first reports on the Ag-Cu-P system [1932Mos, 1956Wei, 1963Bal] were summarized by [1977Cha] followed by the MSIT evaluation by [1988Kub].

[1932Mos] determined that three constituents of the Ag-Cu-Cu_3P system have either little or no mutual solubility in the solid. The Ag-Cu_3P section was shown to be quasibinary. Other vertical sections as well as the liquidus surface of Ag-Cu-Cu_3P system were constructed.

Two vertical sections passing through or in the vicinity of the alloys used in soldering (BCuP-3, BCuP-4) were constructed by [1956Wei]. [1963Bal] conducted a study to ascertain the melting ranges of the ternary alloys in the Cu rich region. Flow characteristics were deduced from the data.

High purity materials, such as oxygen free high conductivity copper and 99.99% silver, were used by [1987Tak1, 1987Tak2] for investigation of the Ag-Cu-Cu_3P system to obtain the liquidus surface and several vertical sections. One of the vertical sections constructed by [1956Wei] has been corrected here.

Crystal structure studies by [1965Olo] of ternary alloys with compositions $(Cu_{0.67}Ag_{0.33})P_2$, $(Cu_{0.50}Ag_{0.50})P_2$ and $(Cu_{0.33}Ag_{0.67})P_2$ that had been prepared by sintering mixtures of the binary phosphides at 600°C for 7 days indicated complete mutual solid solubility between CuP_2 and AgP_2.

[1991Zen] studied alloys in the Cu rich part of the system with P contents up to 38 at.%. Alloys were prepared from the components having purities of 99.99, 99.9 and 99.3% for Ag, Cu and P respectively. Some solubility of the components was found. The isothermal section at 500°C was constructed.

A number of reviews of the Ag-Cu-Cu_3P system have been published: [1933Fro, 1949Jae, 1967Mcd, 1973Sis, 1979Dri] citing [1932Mos].

Brief details of the experimental works on the Ag-Cu-P system are listed in Table 1.

Binary Systems

Assessments of the Ag-Cu system by [2002Rom], of the Ag-P system by [2006Per] and of the Cu-P system by [2002Per] are accepted. The Ag-Cu and Cu-P systems as well as the Ag-Cu_3P quasibinary system bounding the Ag-Cu-Cu_3P region [1932Mos] are of the eutectic type.

Solid Phases

Crystallographic data of solid phases are given in Table 2.

Quasibinary Systems

The quasibinary character of the Ag-Cu_3P section (Fig. 1) was established by [1932Mos].

Invariant Equilibria

The data relating to the invariant equilibria in the Ag-Cu-Cu_3P system are given in Table 3. The eutectic temperature of 650°C is accepted from [1991Zen]. The corresponding reaction scheme is shown in Fig. 2.

Liquidus Surface

The liquidus surface of the Ag-Cu-Cu_3P system is shown in Fig. 3, taken from [1932Mos]. Small variations in the phosphorus content affect the liquidus temperature to a great extent in the high phosphorus region.

Isothermal Sections

The isothermal section of the Ag-Cu-Cu_3P system at 500°C is given in Fig. 4, taken from [1991Zen].

Temperature – Composition Sections

Two sections of the Ag-Cu-Cu_3P system, through 6 mass% P and 2 mass% Ag, respectively, are shown in Figs. 5 and 6. However, [1991Zen] ignored the mutual solubility of the components that was previously indicated by them in the isothermal section at 500°C.

Notes on Materials Properties and Applications

Due to the possible application of Ag-Cu-P alloys as soldering materials, the investigation of their electro-physical, electro-chemical and mechanical properties has been carried out in parallel with the phase diagram studies. The effect of phosphorus additions on physical and chemical properties of the Ag-Cu-P alloys was investigated by [1932Fro, 1945Coo, 1956Wei, 1963Bal, 1981Ple].
According to the diagram of shear strength for the Ag-Cu-P alloys, the best characteristics were observed for compositions with 15Ag-Cu-(30-40)Cu_3P (mass%). The diagram of ductility suggested that the most conductive compositions were those rich in Ag (~85 mass% Ag) and those with 40-60 mass% Ag and 7-15 mass% Cu_3P [1956Wei]. The14.5Ag-Cu-7P alloy was chosen as the most ductile by [1981Ple]. It was noted that being less strong and ductile 2-6 mass% Ag alloys could be applied for somewhat lower brazing temperatures.
The alloys of the Ag-Cu-P system richest in Ag were investigated by [1932Fro]. Alloys containing 83.5 mass% Ag and between 0.3-1 mass% P, quenched from 520 and 600°C showed an appreciable combination of the tensile strength and elongation. Maximum elongation was seen for alloys with 50 mass% Ag and 1 mass% P, whereas tensile strength was found to increase with increasing P content. Minimum Brinell hardness was found for alloys containing 83.5 mass% Ag and quenched from 520, 600 and 700°C when the P content was 0.3 mass%. For the alloys with 50 mass% Ag the P content giving minimum hardness was about 1 mass% P. The deep extension of these alloys did not depend much on the phosphorous content (0-3 mass%). Corrosion resistance of the alloys with 80 mass% Ag and 0-1.0 mass% P was increased in acetic acid and decreased in nitric acid with increasing phosphorus content.
[1945Coo] studied the effect of small additions of P (< 0.2 mass%) on physical and mechanical properties of the 1 mass% Ag-Cu alloy in the wrought and deposited states. Phosphorous was shown not to have an appreciable effect upon the melting range of the ternary alloys as well as upon density of the materials in the wrought condition. The increase in the P content from 0.025 to 0.19 mass% in the deposited state and in the welds resulted in a decrease in the density. The tensile strength of the wrought alloys was observed to increase with phosphorus addition, while it did not notably affect the ductility. The strength of the alloys in the deposited state was reduced when the phosphorous content exceeded about 0.1 mass% and the alloys with higher P content were exposed to hot shortness. On decreasing the Ag content (from 14.5 to 2 mass%) with simultaneous increasing of P (from 4.5 to 6 mass%) the ductility of the ternary alloys fell, the yield stress and breaking point decreased while electrical resistance increased [1981Ple].
There was observed no correlation between flow characteristics with changing Ag content (0-15 mass%), whereas a higher P content (5-7.3 mass%) resulted in higher fluidity. The largest spread was at 10 Ag and 7.3 P (mass%) [1963Bal].

From the work of [1987Tak1, 1987Tak2] it follows that the spread area of the Ag-Cu-7P filler metals on copper plate does not depend on Ag content (10 or 15 mass%) at a brazing temperature 700°C. It reaches the same size at 670°C for an alloy with 15% Ag. The best result at 700°C was obtained for a 15Ag-Cu-8.5P alloy.
The capillarity rise did not deteriorate with phosphorus in the presence of Ag, but without Ag all characteristics of wettability deteriorated [1981Ple].

Miscellaneous

The eutectic alloy, having the lowest temperature of melting, was found to be useless for practical purposes owing to its extreme brittleness [1956Wei].

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Table 1: Investigation of the Ag-Cu-P Phase Relations, Structures and Thermodynamics

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1932Mos]	Thermal analysis, metallography	600 - 1100°C, in Ag-Cu-Cu_3P region
[1956Wei]	Thermal analysis, metallography	600 - 1100°C, in Ag-Cu-Cu_3P region
[1963Bal]	Determination of liquidus surface, establishing of melting ranges	700 - 1100°C, in copper rich area; up to about 10 mass% (4.7 at.%) P and 20 mass% (30.7 at.%) Ag
[1965Olo]	X-ray diffraction	AgP_2-CuP_2 section
[1987Tak1, 1987Tak2]	DTA, optical microscopy, EPMA, X-ray analyses	650 - 900°C, Cu - 15 mass% (23 at.%)Ag - 8 mass% (3.4 at.%) P
[1991Zen]	X-ray diffraction, μDTA, metallography	500-1083°C, in Ag-Cu-Cu_3P region

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comment/References
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	*a* = 408.57 *a* = 403.95 *a* = 402.1	at 25°C, pure Ag at 12.1 at.% Cu at 12.6 at.% Cu, at 7 GPa, at 890°C, dissolves 14 at.% Cu [2002Rom]; liquid Ag dissolves 9.7 at.% P at 880°C [2006Per]; at 500°C dissolves 1.02 at.% Cu [1991Zen]
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	*a* = 361.46 *a* = 363.7 *a* = 366.3	pure Cu at 19°C at 500°C dissolves 2.6 at.% Ag and 0.54 at.% P [1991Zen] at 3.7 at.% Ag at 4 at.% Ag, 7 GPa, 890°C [2002Rom]
(P) (I)	*cP*1 $Pm\bar{3}m$ Po	*a* = 237.7 *a* = 229	high pressure phase, above ~10 GPa [2006Per]
(P) (II)	*hR*6 $R\bar{3}m$ As	*a* = 337.7 *c* = 880.6	high pressure phase 5 to 11.1 GPa [2006Per]
(P) (red)	*c**66	*a* = 1131	subl. at 417C, 1 bar [2006Per]
(P) (white) < 44.14	*c** ? P (white)	*a* = 718	at 25°C, common form of elemental P, less stable than P (red) at this temperature [2006Per]
(P) (black)	*oC*8 *Cmca* P (black)	*a* = 331.6 *b* = 1047.8 *c* = 437.63	at 25°C [2006Per]
Ag_3P_{11} ≲ 458	*m** *Cm*	*a* = 1299.9 *b* = 755.5 *c* = 661.2 β = 118.84	[2006Per]
βCu_3P < 1022	*hP*8 $P\bar{3}m1$ Cu_3P	*a* = 409.2 *c* = 718.6	at 560°C, congruent melting at 1 bar, 25 to 31 at.% P, at ~833°C [2002Per]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comment/References
αCu_3P	*hP*24 $P6_3cm$ Cu_3P	 *a* = 695.93 *c* = 714.3	low temperature phase [2002Per]
$(Ag_xCu_{1-x})P_2$	*mP*12 $P2_1/c$ CuP_2		0 ≤ *x* ≤ 100 [1965Olo]
AgP_2 ≲ 554		*a* = 621.8 *b* = 505.6 *c* = 780.4 β = 113.48	[2006Per]
CuP_2 < 891		*a* = 580.04 *b* = 480.63 *c* = 752.63 β = 112.70	congruent melting at 15.2 bar [2002Per]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition, at.%		
				Ag	Cu	P
L ⇌ (Ag) + Cu_3P	796	e_1(max)	-	-	-	-
L ⇌ (Ag) + (Cu) + Cu_3P	650	E	L	10.6	74.6	14.8

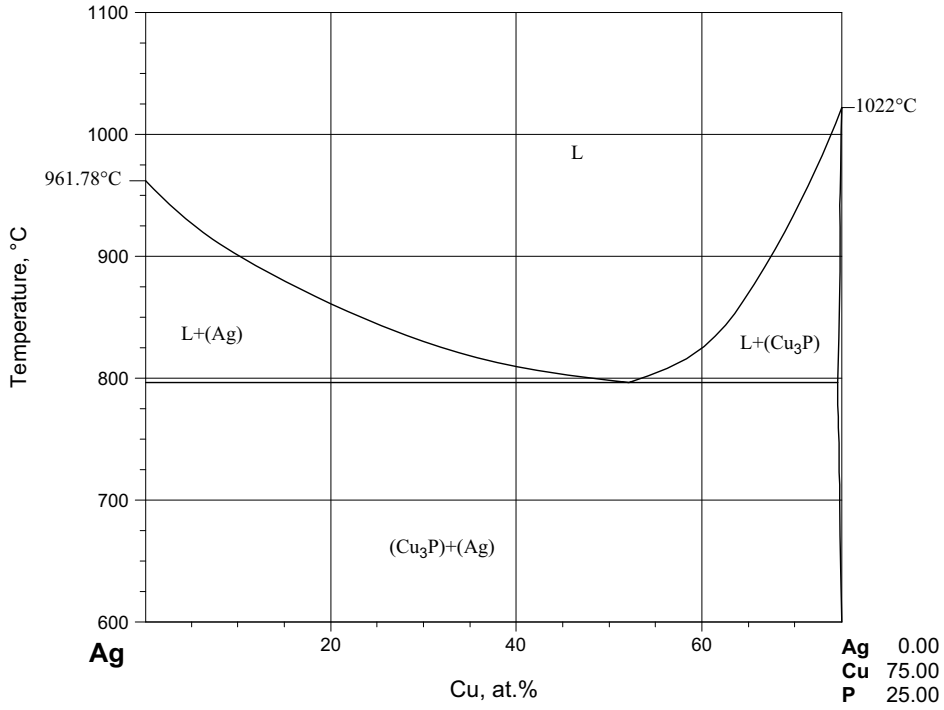

Fig. 1: Ag-Cu-P. The quasibinary system Ag - Cu_3P

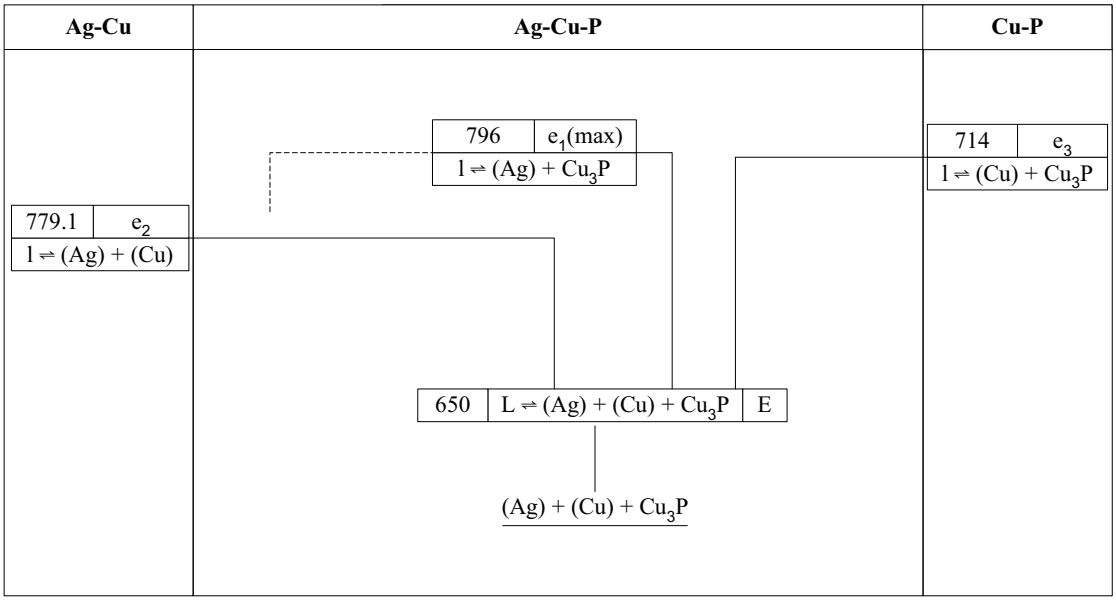

Fig. 2: Ag-Cu-P. Partial reaction scheme in the Ag - Cu - Cu_3P region

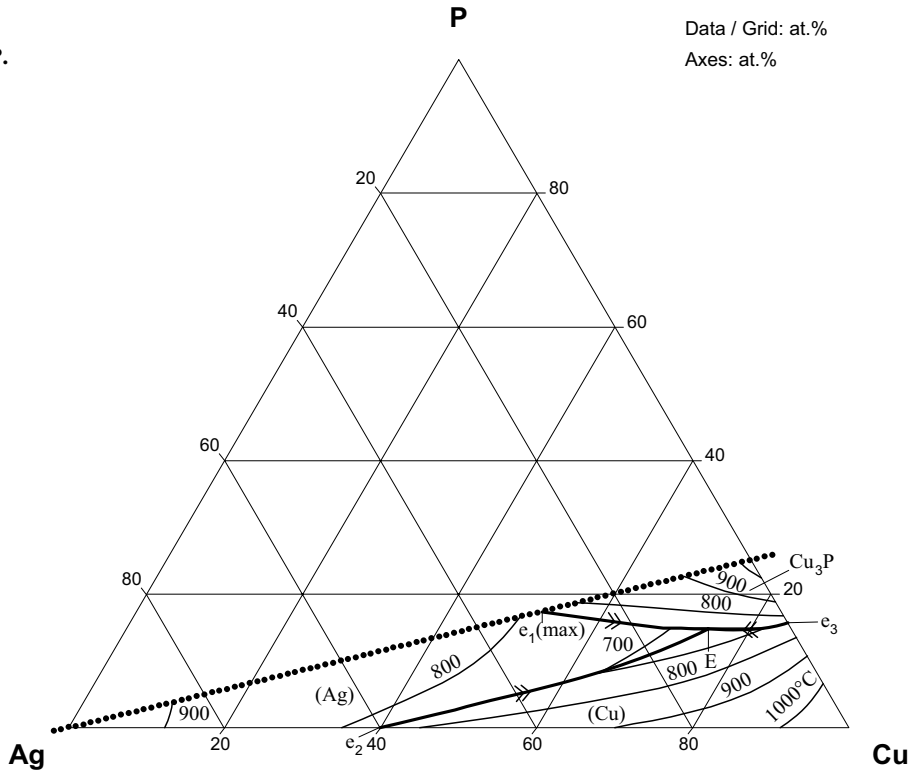

Fig. 3: Ag-Cu-P. Partial liquidus surface projection

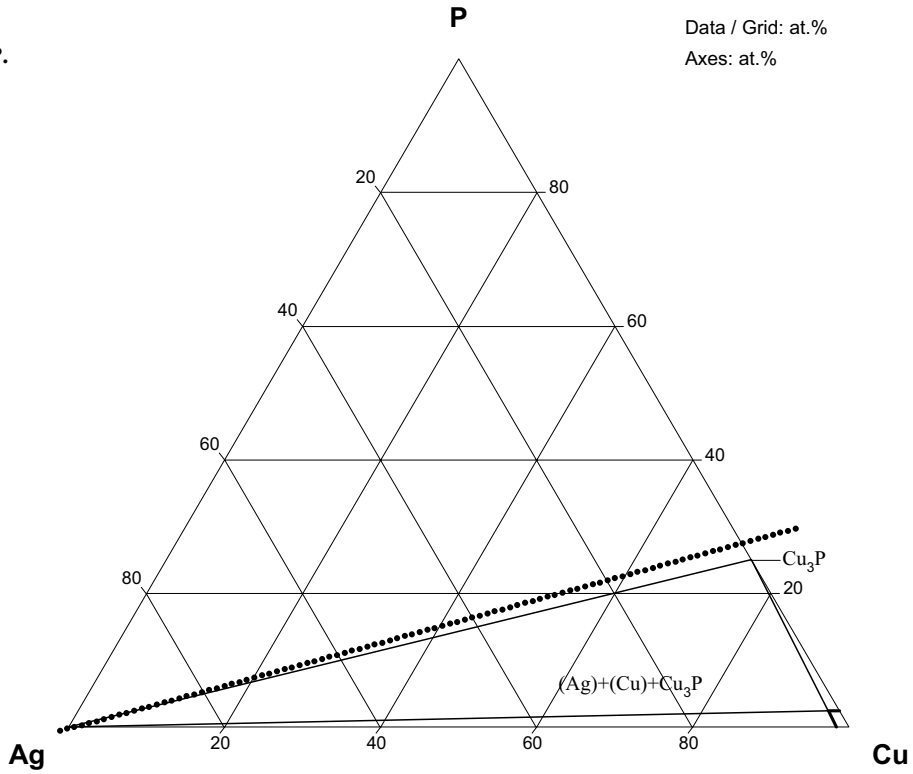

Fig. 4: Ag-Cu-P. Partial isothermal section at 500°C

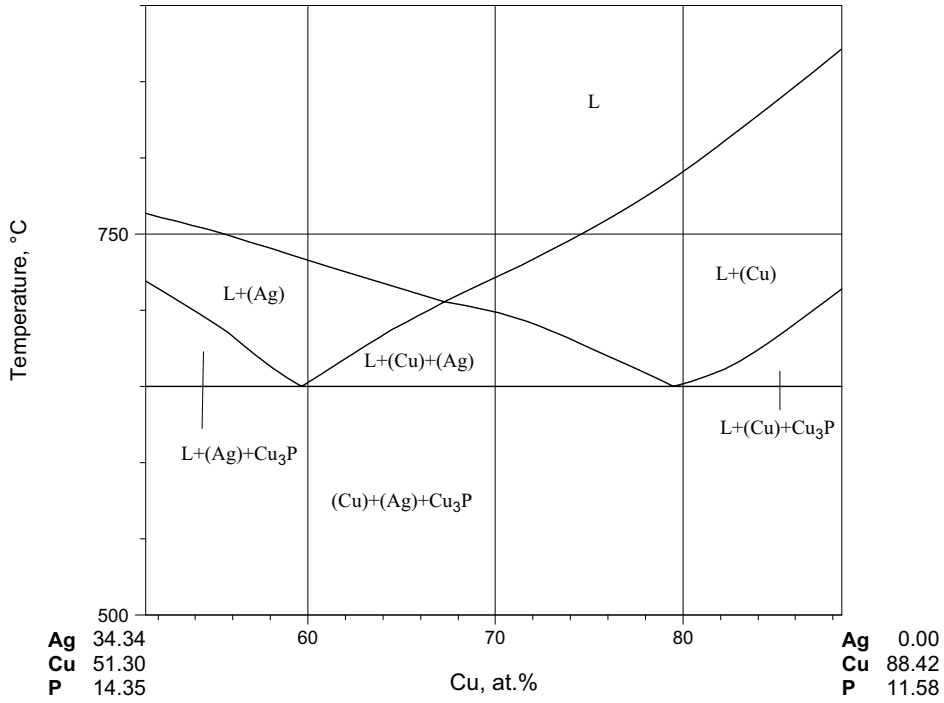

Fig. 5: Ag-Cu-P. Isopleth through 6 mass% P, plotted in at.%

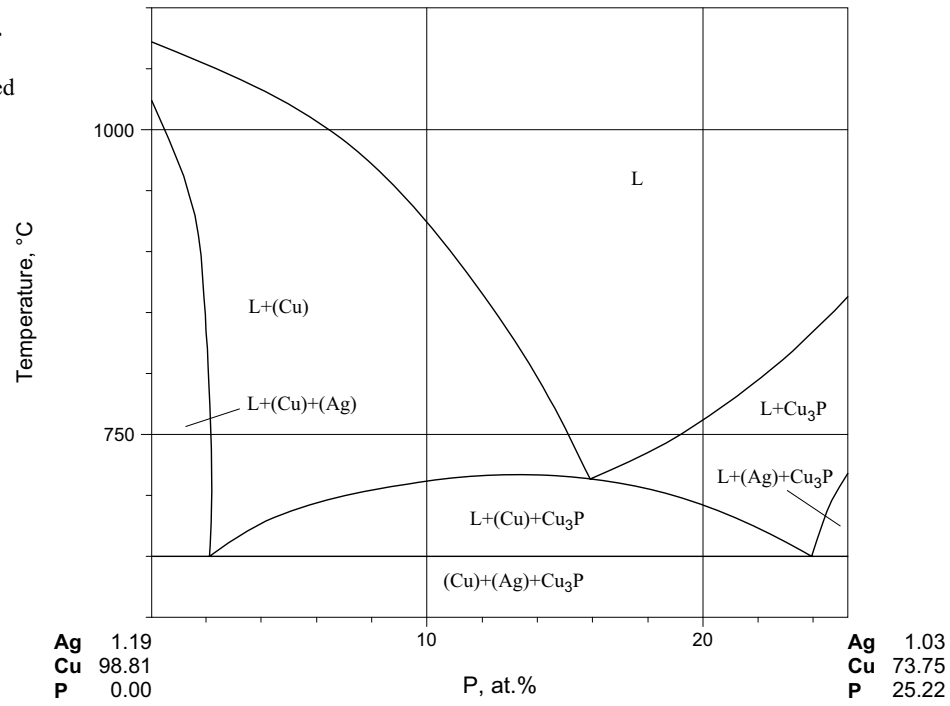

Fig. 6: Ag-Cu-P. Isopleth through 2 mass% Ag, plotted in at.%