Cobalt – Copper – Manganese

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Introduction

Based on the adjoining binary phase diagrams, [1909Jae] suggested a possible configuration for the Co-Cu-Mn phase diagram. It was characterized by the existence of a three-phase monovariant peritectic transformation region extending from the Cu-Mn side to the γ(Cu,γMn,αCo) ternary solid solution and by the absence of an invariant transformation during crystallization. Such constitution of the Co-Cu-Mn phase diagram was confirmed by the theoretical work of [1942Hir], who used calculations of the free energy of the alloys. The Co-Cu-Mn phase diagram was studied experimentally by [1938Koe] using thermal, magnetic and microstructural analyses in the region from the Co-Cu side up to 40 mass% Mn. A partial liquidus surface and the monovariant line bounding the field of joint crystallization of the γ(Cu,γMn,αCo) and (αCo) solid solutions were constructed. In addition, the isolines of Curie temperature from 20 to 800°C were drawn assuming them as tie lines between the γ(Cu,γMn,αCo) and (αCo) solid solutions. [1938Koe] also constructed four vertical sections at 10, 20, 30 and 40 mass% Mn. [1958Top1, 1958Top2] studied Mn rich alloys with up to 50 mass% Co and up to 50 mass% Cu, which had been annealed at 500°C. The studied alloys contained (αMn) and (γMn) solid solutions. The results of [1958Top1, 1958Top2] contradict, however, the Co-Mn phase diagram through the existence of an extended (βMn) solid solution [1979Cha]. [1982Has] investigated phase compositions of Co-Cu-Mn alloys at several temperatures in the range 877 to 1277°C. Based on their own experimental data, six isothermal sections of the phase diagram were presented. [1979Dri, 1979Cha] reviewed the Co-Cu-Mn phase diagram using data from [1938Koe] and [1958Top1, 1958Top2].
The methods and composition ranges studied in the different investigations are described in Table 1.

Binary Systems

The binary Co-Cu and Cu-Mn systems are accepted from the MSIT Evaluation Program after [2006Ans] and [2005Tur], respectively. The Co-Mn phase diagram is taken from [Mas2].

Solid Phases

No ternary compound has been found in the Co-Cu-Mn system. Three binary ordered phases, γ_1, γ_2 and γ_3, have been established in the Cu-Mn system. There are extended solid solutions based on the separate allotropic forms of the pure metals. Characteristics of the solid phases of the Co-Cu-Mn system are shown in Table 2.

Liquidus, Solidus and Solvus Surfaces

The partial liquidus surface of the Co-Cu-Mn ternary system is shown in Fig. 1. The region adjoining the Co-Cu side is divided by a monovariant line into a surface corresponding to the primary crystallization of the (αCo) and γ primary solid solutions. The monovariant line corresponds to the L + (αCo) ⇌ (Cu) peritectic reaction, the temperature of which falls from 1113.3°C at the Co-Cu binary down to ~800°C on the addition of ~45 at.% Mn. Its location is taken from [1938Koe] with a little correction necessary to meet the accepted Co-Cu binary diagram [2006Ans]. Taking into consideration the binary systems Co-Mn and Cu-Mn, the liquidus surface in the Mn rich region should include a surface of primary crystallization of the (βMn) and (δMn) solid solutions. The location of these surfaces has not been established.
Figure 2 shows the partial solidus surface in the region adjoining the Co-Cu side. It is divided by a double saturation line (which bounds the L + (αCo) + γ three-phase region) into the surface of the joint crystallization of (αCo) + γ and termination of the ternary γ solid solution. The double saturation line bounding the three-phase region is drawn after [1938Koe] with a small correction to meet the binary Co-Cu

[2006Ans]. In accordance with [1938Koe], tie lines corresponding to the isolines of Curie temperature are shown on the concentration field outlined by the double saturation line.

Isothermal Sections

Isothermal sections at different temperatures are presented in Figs. 3-8. They were taken from the calculations of [1982Has] with some corrections to meet the accepted binary phase diagrams.

Temperature – Compositions Sections

Two vertical sections are shown in Figs. 9 and 10. They are drawn according to [1938Koe] with some corrections to meet the accepted binary phase diagrams. In accordance with the accepted Cu-Mn phase diagram, the sections must cross the γ_3, (αMn) + γ_3 and (αMn) + γ_2 areas which are shown in the vertical sections only approximately.

Notes on Materials Properties and Applications

The Co-Cu-Mn system forms part of the commercial alloy SA04 (AP Cu-Mn-28Ni-29Co5-Si-B) used for the soldering of hot and corrosion resistant steels and alloys. The soldering temperature is 1050°C and its seal strength is 350 MPa.
[1947Fre] discovered the propensity for alloys containing 2-4 mass% Co and up to 15 mass% Mn to age harden at temperatures of 480, 540 and 595°C.
[1973Mas] established the anti-ferromagnetic behavior of Mn rich Co-Cu-Mn alloys and their Elinvar characteristics. Nonmagnetic ternary alloys of 32.8 - ~87.5% Mn and less than 67% Cu and 24% Co (mass%) were found to have pronounced Elinvar characteristics and fairly good corrosion resistance.
[1976Ano] reported that Co-Cu-Mn alloys with a typical composition of 10%Co-58%Cu-31.5%Mn (mass%) can be successfully used as brazing materials for gas turbine applications in place of alloys containing expensive precious metals.
[2003Cao] investigated the magnetic properties of the Mn layer-doped Co/$Cu_{92}Mn_8$/Co layered structures. Their behavior in magnetic fields was established.
A summary of studies of the materials properties and applications related to the Co-Co-Mn alloys is presented in Table 3.

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Table 1: Investigations of the Co-Cu-Mn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1938Koe]	Thermal, magnetic, microstructural analyses	Alloys with constant Mn = 10, 20, 30, 40 mass%. Temperature - composition sections at constant Mn = 10, 20, 30, 40 mass%. Liquidus surface with monovariant peritectic line and miscibility gap in solid state.
[1958Top1, 1958Top2]	Melting in a high - frequency furnace in pressed and sintered magnesite crucibles, casting in mild steel mold, homogenization at 900-800-700-600-500°C for 1 day at each temperature and added 500°C for 20 days in sealed quartz ampoules. Metallographic, hardness, resistivity, dilatometry.	Alloys in the Mn corner (100 - 50 mass% Mn) up to 50 mass% Co and 50 mass% Cu. These alloys have a two-phase structure in the annealed state: (αMn) and (γMn,αCo)
[1982Has]	Ternary diffusion couple technique, computer calculation	Experimental results on the miscibility gap (γ and γ^f) between 877 and 1077°C and on the γ/L equilibrium between 1277 and 977°C. Six calculated isothermal sections at 1177, 1077, 977, 877, 777 and 577°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, (Cu,γMn,αCo) < 1495	*cF*4 $Fm\bar{3}m$ Cu		
(Cu) < 1084.62		*a* =361.46	pure Cu at 25°C [Mas2] dissolves 9.1 at.% Co at 1113,3°C [Mas2] and 100% Mn [2005Tur]
(γMn) 1138 - 1087		*a* = 386.0	pure γMn [Mas2] dissolves up to 5 at.% Co at 1138°C [Mas2] and 100 at.% Cu [2005Tur]
(αCo) 1495 - 422		*a* = 354.47 *a* = 356.88	[Mas2] at 520°C [2006Ans] dissolves 11.7 at.% Cu at 1113.3°C and ~59 at.% Mn at 1161°C [Mas2]
(εCo) < 422	*hP*2 $P6_3/mmc$ Mg	*a* = 250.71 *c* = 406.86	at 25°C [Mas2]
(δMn) 1246 - 1138	*cI*12 $Im\bar{3}m$ W	*a* = 308.0	dissolves 9.0 at.% Co at ~1185°C [Mas2] and 13 at.% Cu at 1097°C [2005Tur]
(βMn) 1087 - 707	*cP*20 $P4_132$ βMn	*a* = 631.52	dissolves 41 at.% Co at 1161°C [Mas2] and 2.03 at.% Cu at 706°C [2005Tur]
(αMn) < 707	*cI*58 $I\bar{4}3m$ αMn	*a* = 891.26	dissolves up to 3 at.% Co [Mas2] and 2.3 at.% Cu at 706°C [2005Tur]
γ_3 (Cu-Mn phase) ≤ 700	*c***	-	[2005Tur]
γ_2, $MnCu_3$ ≤ 450	*c***	-	[2005Tur]
γ_1, $MnCu_5$	*c***	-	[2005Tur]

Table 3: Investigations of the Co-Cu-Mn Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1947Fre]	Melting in a high - frequency induction furnace, cold - worked and solution - treated for 0.5 h at temperatures varying from 650 to 980°C, aging at temperatures from 315 to 650°C for times of 0.5, 1, 2, 4, 8, 16, 24 and 48 h	Time - hardness curves at various aging temperatures for cold - reduced and annealed Co-Cu-Mn alloys with 2, 3 and 4 mass% Co and 1 and 10 mass% Mn
[1973Mas]	Measurement of Young's modulus at –150 - ~400°C, rigidity modulus and hardness at room temperature. The resonance frequency 470 - 880 Hz. Annealing temperature - 900°C, cold working or water quenching and reheating for 1 h at 200, 400, 600 and 800°C	Elinvar characteristics for Co-Cu-Mn alloys of 0 - ~40.0 mass% Co, 0.1 - ~67.0 mass% Cu, 38.0 - ~88 mass% Mn subjected to various heat treatments and cold working. Nonmagnetic Elinvar - type alloys consisted of less than 67 mass% Cu, 24 mass% Co and 32.8 - ~87.5 mass% Mn and have fairly good corrosion resistance
[1976Ano]	Tensile, shear and fatigue strength	The alloy with10 mass% Co, 58 mass% Mn and 31.5 mass% Cu can be used as brazing materials in place of alloys of precious metals
[2003Cao]	Magnetic Properties	Giant magnetoresistance in Mn layer - doped Co/Cu/Co multilayers

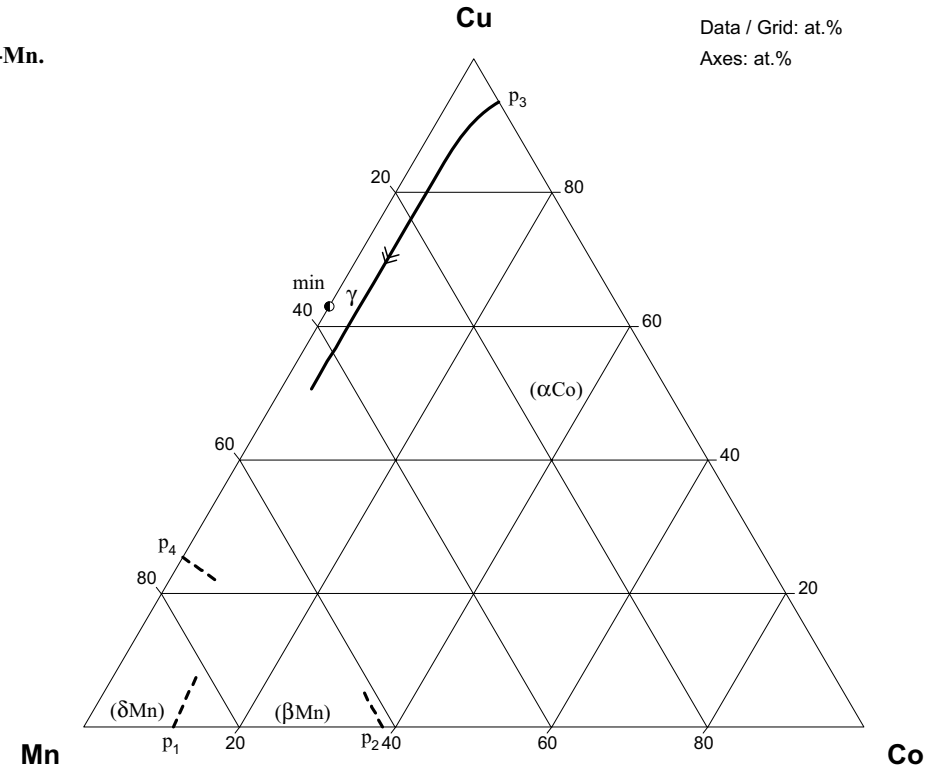

Fig. 1: Co-Cu-Mn. Liquidus surface projection

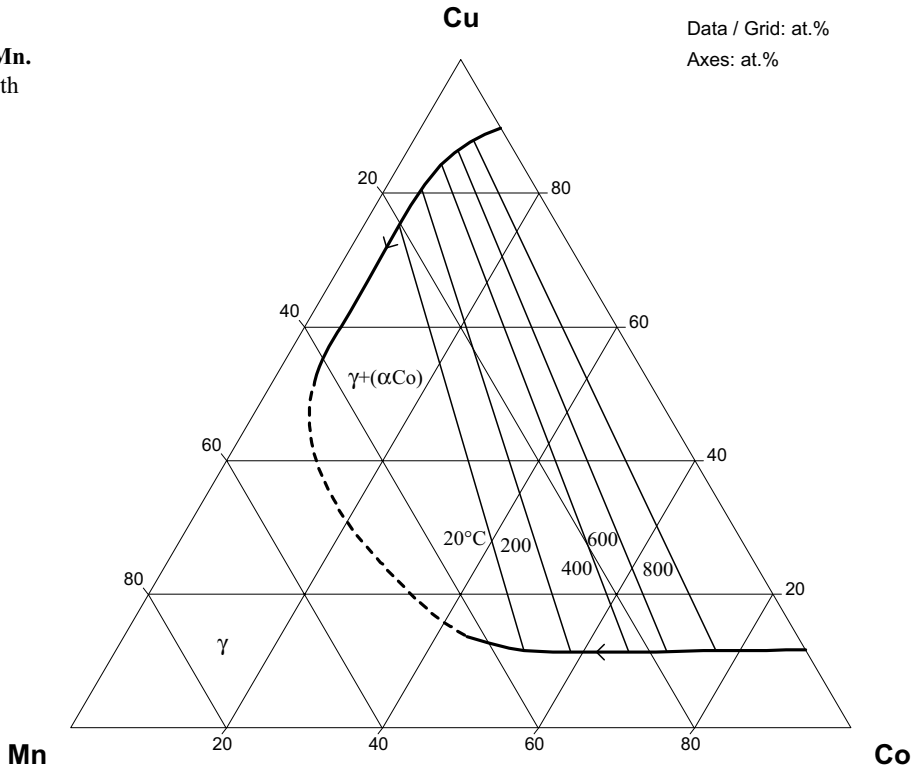

Fig. 2: Co-Cu-Mn. Solidus surface with isolines of Curie temperature

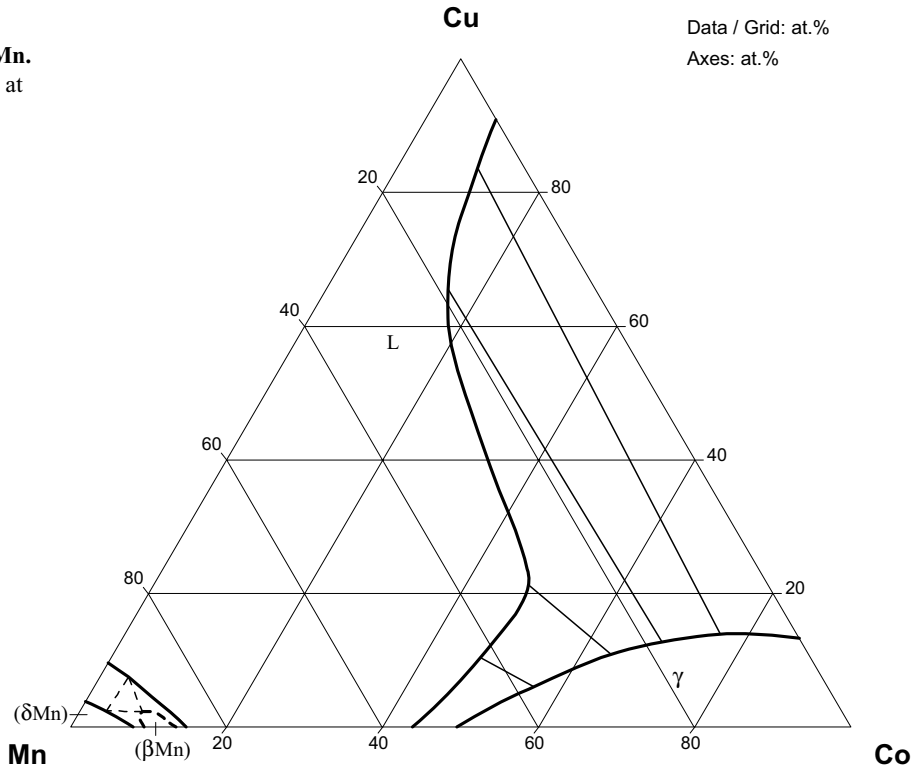

Fig. 3: Co-Cu-Mn. Isothermal section at 1777°C

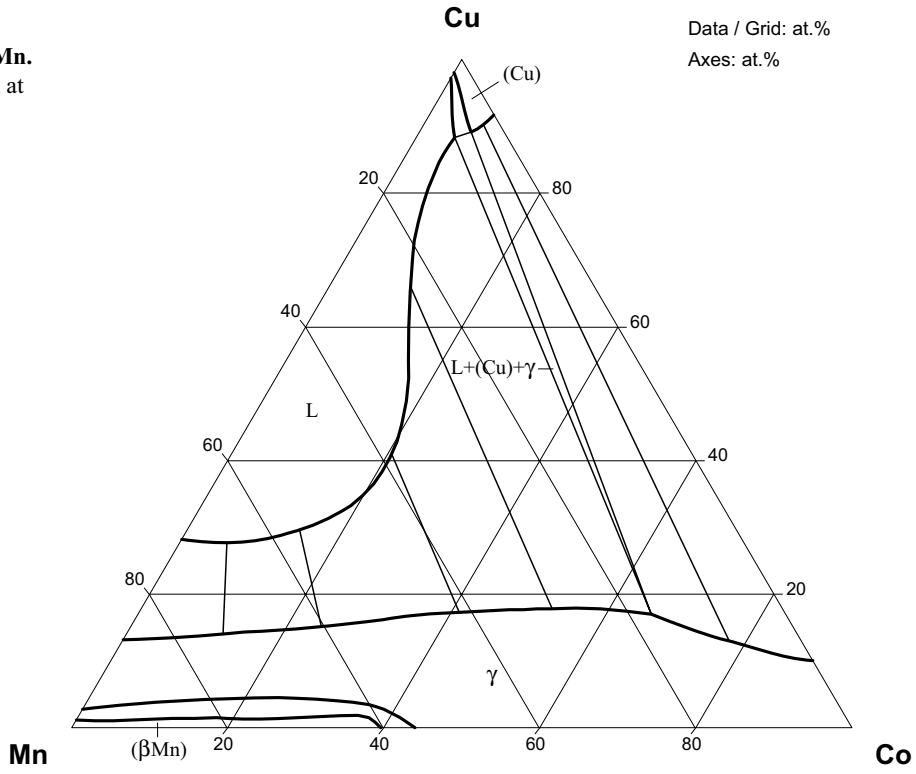

Fig. 4: Co-Cu-Mn. Isothermal section at 1077°C

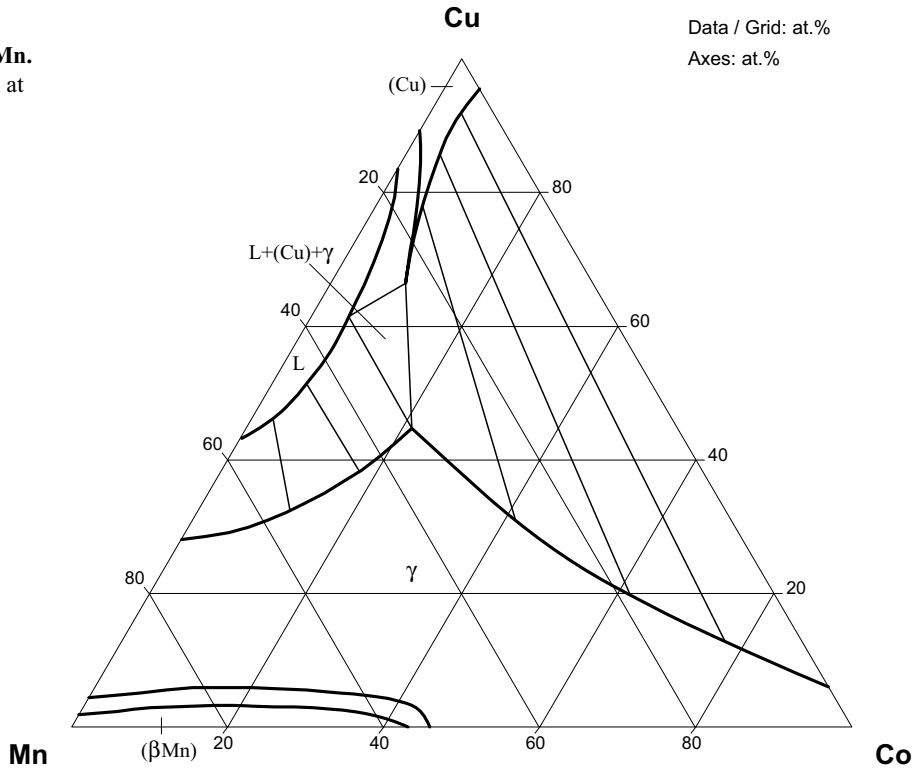

Fig. 5: Co-Cu-Mn. Isothermal section at 977°C

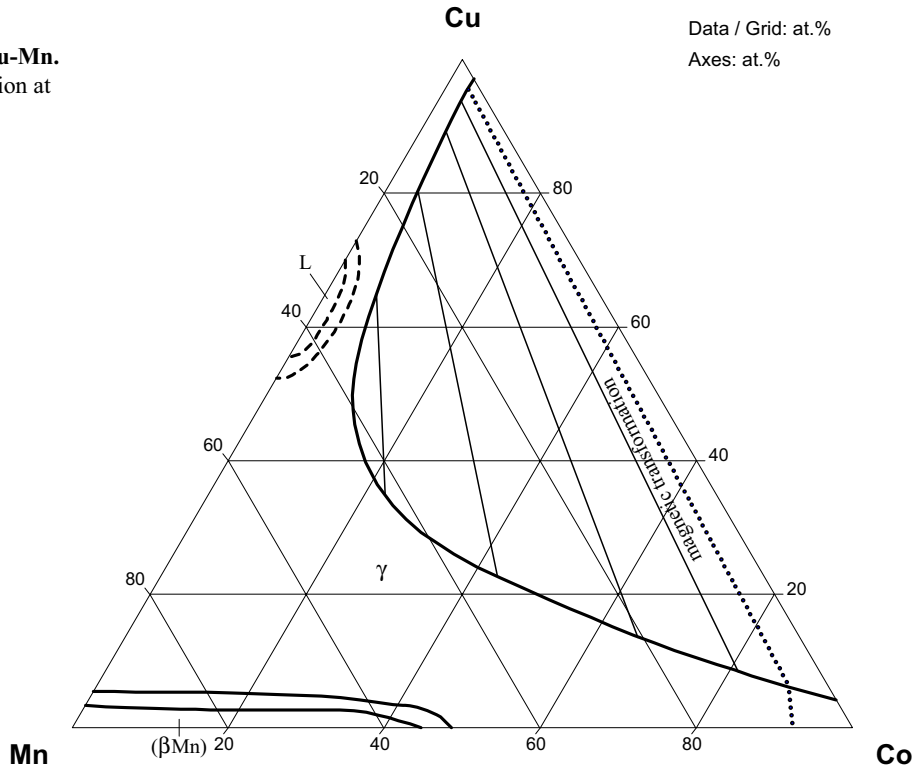

Fig. 6: Co-Cu-Mn. Isothermal section at 877°C

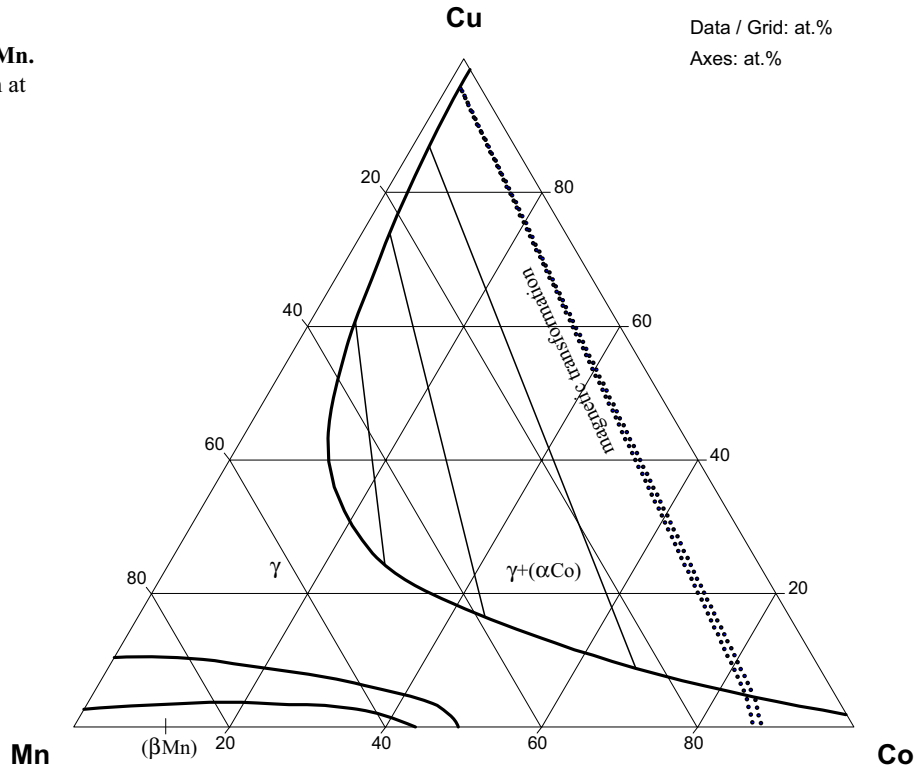

Fig. 7: Co-Cu-Mn. Isothermal section at 777°C

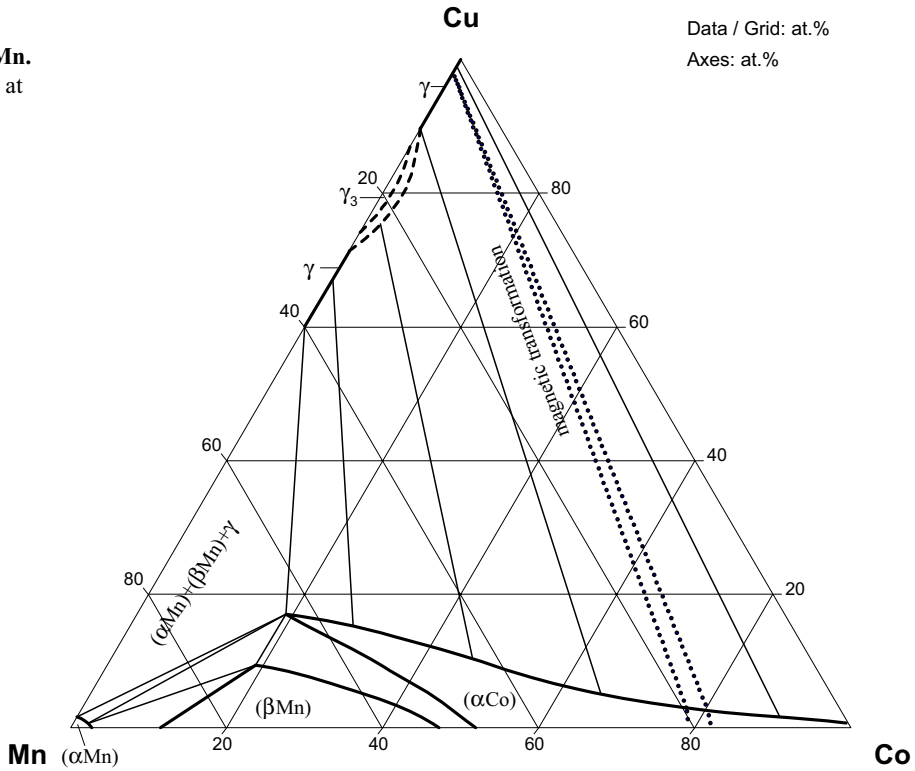

Fig. 8: Co-Cu-Mn. Isothermal section at 577°C

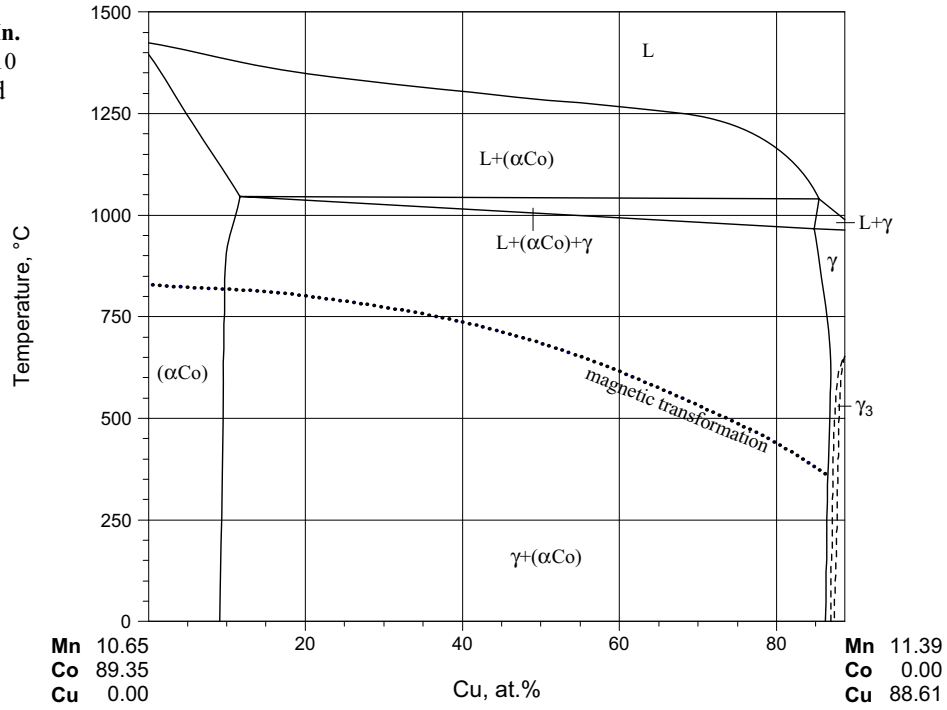

Fig. 9: Co-Cu-Mn. Vertical section at 10 mass% Mn, plotted in at.%

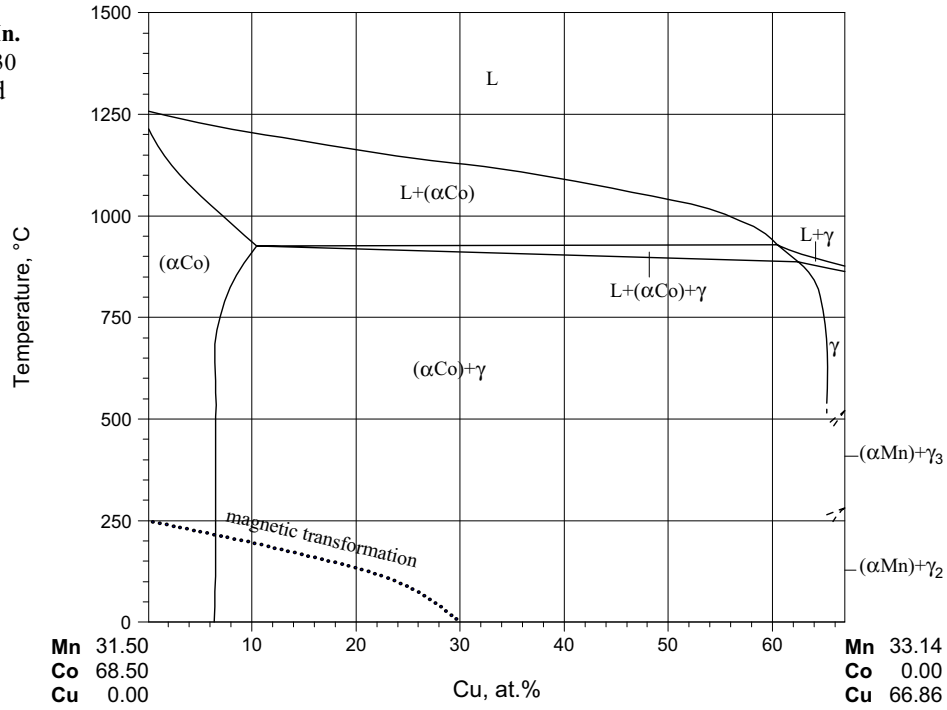

Fig. 10: Co-Cu-Mn. Vertical section at 30 mass% Mn, plotted in at.%