Copper – Manganese – Nickel

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Introduction

The earliest recorded experimental studies were made by [1912Par, 1913Par] who determined the liquidus and solidus surfaces of the Cu-Mn-Ni phase diagram using thermal analysis. The surfaces were constructed for the full concentration range, assuming the existence of a continuous solid solution between the three components immediately below solidus surface. Resulting from this study, isotherms of the liquidus and solidus surfaces were drawn. Six vertical sections of the liquidus and solidus surfaces were also presented.
The liquidus and solidus temperatures of the Cu-Mn-Ni phase diagram from [1912Par, 1913Par] were used by [1934Fis] to construct a ternary phase diagram in orthogonal coordinates. In the review by [1949Jae], the data of [1912Par, 1913Par] were reproduced without significant alteration. The changes consisted of drawing a tentative boundary outlining the part of the liquidus surface corresponding to the crystallization of the (δMn) rich phase.
[1951Zwi] studied the Mn rich part of the Cu-Mn-Ni phase diagram constructing partial isothermal sections at 1000, 700 and 500°C. The sections showed phase regions corresponding to existence of solid solutions based on the different allotropic forms of Mn. However, in the reviews of [1969Gue, 1979Cha, 1986Gup], the isothermal sections constructed by [1951Zwi] were found to be inconsistent with the reliable Mn-Ni binary phase diagram.
[1958Chj] reinvestigated the Cu-Mn-Ni phase diagram in the Cu rich region, up to 35 mass% Mn and 35 mass% Ni using X-ray diffraction, thermal analysis, microscopy and hardness measurement. [1958Chj] confirmed existence of the fcc solid solution immediately below the solidus surface. A partial vertical section Cu-MnNi and two partial isothermal sections at 350 and 450°C were constructed. The vertical section Cu-MnNi was found to be quasibinary on the Cu side. With increasing temperature, the (γMn,Ni,Cu)+MnNi phase field tends to narrow.
The existence of a continuous fcc solid solution immediately under the solidus surface in the Cu-Mn-Ni phase diagram was also reported by [1958Top].
To a certain extent, the existence of the quasibinary section Cu-MnNi, at least partially below the solidus surface, can be inferred from the results of [1962Gla]. In this study, microhardness measurement was conducted on alloys with compositions lying along sections of constant Cu contents of 95 and 90 at.%. The alloys had been annealed at 900, 700 and 500°C. Each of the microhardness curves showed a distinct minimum at the points where the Cu-MnNi section was crossed. Such features in the microhardness curves was interpreted by the authors [1962Gla] as evidence of Mn and Ni interaction in the (Cu) solid solution corresponding to the MnNi compound.
[1970Rol] studied effect of heat treatment on structure of alloys in the section Cu-MnNi using X-ray diffraction. Decomposition of the fcc solid solution at temperatures of about 350-370°C was observed. The decomposition was accompanied by the formation of the low-temperature modification of the MnNi compound. This can be interpreted as decrease in the solubility of MnNi in the fcc solid solution with decreasing temperature.
[1974Sch1, 1974Sch2] studied the equilibria between the liquid and solid phases in the Cu rich and Ni rich alloys of the Cu-Mn-Ni system at temperatures between the liquidus and solidus surfaces. The alloys were held isothermally at selected temperatures in the solid-liquid state and quenched into water. The compositions of the liquid and solid phases were then determined by local analysis of structure. In the review [1986Gup], data from [1974Sch1, 1974Sch2] were compared with those given in [1912Par, 1913Par]. It was found that the data from [1974Sch1, 1974Sch2] disagreed significantly from those of [1912Par, 1913Par] in the Ni corner of the phase diagram above 1300°C but were in agreement in the Cu corner of the phase diagram below 1100°C. In the opinion of [1986Gup], the data from [1974Sch1, 1974Sch2] were more reliable than those of [1912Par, 1913Par] because a better experimental method was used in the former work.

In the review [1979Cha], the liquidus surface according to [1912Par, 1913Par] was accepted with a small amendment showing the existence of a narrow region relating to the primary crystallisation of (δMn). The isothermal section of the phase diagram at 350°C was presented after [1958Chj].
In the review [1979Dri], the liquidus and solidus surfaces of the Cu-Mn-Ni phase diagram after [1913Par] were accepted where it was assumed that there was a continuous solid solution between copper, nickel and the γ modification of manganese. Meanwhile, after [1951Zwi], [1979Dri] reported a face-centred tetragonal lattice for (γMn) and noted the existence of a narrow two-phase region of the (γMn,Ni,Cu) face-centred cubic solution and the face-centred tetragonal (γMn) solid solution near the Mn corner. In addition to this, [1979Dri] accepted from [1958Chj], the partial isothermal section of the phase diagram at 450°C (up to 50 mass% Mn and 50 mass% Ni) with the existence of a two-phase region comprising of the fcc (γMn,Ni,Cu) solid solution and the low-temperature modification η' of the compound MnNi.
As with other reviews [1979Cha, 1979Dri], the review [1980Bra] accepted the liquidus surface from [1913Par]. Also, a simplified view of the main phase fields in the system for solid state was presented. The fields corresponded to the homogeneous areas of the (γMn,Ni,Cu) fcc solid solution, with the phases on the base compounds $MnNi_3$, MnNi or one of the Mn modifications, except (γMn).
[1984Wea] presented the temperature-composition section Cu-MnNi of the phase diagram, but without description of the performed experiments and their results in detail. The section presented is reasonable, in general, taking into consideration the boundary binary systems, but on the MnNi side the exact position of the phase boundaries is not confirmed by any experimental work and, therefore, may be considered only as tentative.
In the review [1986Gup] the liquidus and solidus surfaces show isotherms accepted from [1912Par, 1913Par] with the addition of the monovariant line bounding the surface of the primary crystallization of (δMn) following [1979Cha]. The interaction between the fcc solid solution (γMn,Ni,Cu) and the MnNi based phase was characterized by the vertical section Cu-MnNi, taken mainly from [1958Chj] and solubility isotherms in (γMn,Ni,Cu) at 350 and 450°C after [1958Chj].
[1989Udo] studied phases formed in alloys along the section Cu-MnNi at temperatures between 450 and 600°C in the composition range 10-80 at.% Cu. The boundary between the phase regions of the (γMn,Ni,Cu) solid solution and (γMn,Ni,Cu)+MnNi was constructed.
More recently, [2003Mie] has performed a Calphad assessment on the ternary system using all available experimental phase equilibria and thermodynamic data. Despite introducing some simplifications into the study, the agreement between the assessed and experimental data is good.
Details of the investigations are given in Table 1.

Binary Systems

The binary systems are taken from the MSIT Evaluation Program [2002Leb, 2005Tur, 2006Wat].

Solid Phases

No ternary compounds were found in the Cu-Mn-Ni system. The unary and binary phases, including the fcc continuous solid solution (γMn,Ni,Cu), are listed in Table 2.

Quasibinary Systems

There is no true quasibinary section in this ternary system, although the Cu-MnNi section is considered to be a partial quasibinary system at temperatures below the solidus surface [1958Chj].

Liquidus, Solidus and Solvus Surfaces

Figure 1 shows the liquidus projection together with isotherms. It is constructed following [1986Gup] who, in their review of the system, modified the data of [1912Par, 1913Par] and considered the double saturation line connecting the invariant points of the (δMn) ⇌ L + (γMn,Cu) and (δMn) + L ⇌ (γMn,Ni) reactions in the Cu-Mn and Mn-Ni binary systems, respectively. The double saturation line divides the liquidus surface into two parts corresponding to the primary crystallization of the (γMn,Ni,Cu) and (δMn) solid solutions.

Figure 2 shows the projection of the solidus surface together with isotherms. It is constructed after [1986Gup] who used the data of [1912Par, 1913Par]. The projection is supplemented by lines connecting the critical points of the (δMn) ⇌ L + (γMn,Cu) and (δMn) + L ⇌ (γMn,Ni) transformations in the Cu-Mn and Mn-Ni binary systems. The lines correspond to the compositions of the (δMn) and (γMn,Ni,Cu) solid solutions in the monovariant ternary equilibrium with the liquid phase in the ternary system. The locations of these lines were not established experimentally and, therefore, the lines are shown dashed and are considered tentative.

Isothermal Sections

No full isothermal section of the Cu-Mn-Ni phase diagram has been constructed. [1958Chj] constructed the partial isotherms at 350 and 450°C of the solvus surface giving the solubility of the low-temperature modification of MnNi in the (γMn,Ni,Cu) solid solution. The isotherms are shown in Fig. 3 after [1986Gup] who used results of the experimental investigation of [1958Chj].

Temperature – Composition Sections

Figure 4 shows the Cu-MnNi partial vertical section of the Cu-Mn-Ni phase diagram. It is constructed after [1986Gup] who took into account a few consistent experimental studies. The section was corrected only slightly to be consistent with the solvus isotherms presented in Fig. 3 and the accepted version of the Mn-Ni binary phase diagram [2006Wat]. The version of the same section by [1984Wea] was not taken into account as it was thought to be unreliable. Actually, the section Cu-MnNi shown gives the extension of the (γMn,Ni,Cu) solid solution from the Cu corner and misses more complicated phase relations near the Mn-Ni side which could be expected in view of the Mn-Ni binary phase diagram.

Notes on Materials Properties and Applications

Cu-Mn-Ni alloys are characterized, at certain compositions, by a low temperature coefficient of electrical resistivity combined with high values of electrical resistivity and are attractive for applications as resistor materials. Properties and structure of this kind of alloy are studied and described in [1941Ave1, 1941Ave2, 1949Sam, 1954Agl, 1961Die]. Other applications are highloaded springs working at high temperatures, non-magnetic bearings and gears and highloaded screws [1961Die, 1973Gro]. One of the advantages of using Cu-Mn-Ni alloys is their high corrosion resistance [1966Lah]. Investigations [1976Kho] have shown that the change in the thermoelectromotive force of Cu-Mn-Ni alloys has large limits depending on the Mn and Ni contents. In [1984Bey], electrical and magnetic properties of spin glasses of the Cu-Mn-Ni alloys are reported. [1989Don] studied the application of Cu-Mn-Ni alloys as thermally sensitive thermobimetals and calculated their linear thermal expansion coefficient over the full concentration range. The values obtained were presented in the form of isoproperty contours. [1990Wak] studied the application of the Cu-Mn-Ni alloys, eventually with small additions of other alloying elements, as dental materials. Cu-Mn alloys are well-known for their vibration and noise dampening properties. Investigations have been carried out to study the effects of adding Ni [2003Yin]. Ni was found to enlarge and broaden the characteristic twin-boundary damping peak. The aging behavior of Cu-Mn-Ni ternary alloys with 12 mass% Mn has been studied as a function of temperature and Ni content by [1991God], which was found to be due to vacancy and ordering reactions.
Details of some experimental works related to the Cu-Mn-Ni materials properties are given in Table 3.

Miscellaneous

In alloys containing about 25 - 60 at.% Cu, balance Mn and Ni by approximately even parts, very complicated phase transformations are observed during annealing at temperatures between 250 - 500°C. This is a result of solid solution decomposition [1972Fil1, 1972Fil2, 1973Gro, 1978Ron, 1982Mik]. The complicated phase transformations in the solid state were also observed in alloys with the Ni_3Mn composition with the addition of about 0.5-9.3 at.% Cu [1973Lot1, 1973Lot2, 1973Lot3, 1973Lot4, 1977Lot]. In [1975Bel, 1977Pop], the crystal structure and distribution of components present in vacuum deposited films have been studied. [1980Yok, 1987Tak] studied the interdiffusion in Cu rich alloys of the Cu-Mn-Ni system. The direct interdiffusion coefficients, $\tilde{D}^{Mn}_{NiNi}$ and $\tilde{D}^{Mn}_{CuCu}$, and the cross interdiffusion coefficients showed strong composition dependence. The Kirkendall effect was observed by [1980Yok] with the marker interface always moving towards the lower Ni concentration side. The deformation mechanism of single crystals of the Cu-MnNi section were studied by [1991Pol]. Using electron microscopy, XRD and neutron diffraction, they found that the strengthening mechanism was due to the drag of dislocations around the MnNi precipitate particles.

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

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1912Par]	Thermal analysis	Full composition range, liquidus and solidus
[1913Par]	Thermal analysis	Full composition range, liquidus and solidus
[1941Ave2]	XRD	Diffraction pattern of 2%Cu49%Mn49%Ni alloy quenched from 950°C
[1949Sam]	Dilatometry, electrical resistance	60Cu20Mn20Ni, up to 800°C
[1951Zwi]	X-ray and microstructural examination	Mn rich alloys at 500, 700 and 1000°C
[1958Chj]	X-ray diffraction, thermal analysis, microstructural examination and hardness measurement	Cu rich region, up to 35 mass% Mn and 35 mass%
[1958Top]	Microstructural examination, dilatometry, electrical resistivity and hardness measurement	Samples quenched from 950-850°C, tempered at 500, 400 and 300°C
[1962Gla]	Microhardness	Phase relations in alloys along sections of constant Cu of 95 and 90%, quenched from 500, 700 and 900°C
[1970Rol]	XRD	Alloys in the Cu-MnNi section
[1973Lot1] [1973Lot2] [1973Lot3] [1973Lot4]	Neutron diffraction, resistivity measurement	Ordering in Ni_3Mn-Cu

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1974Sch1] [1974Sch2]	Isothermal annealing and microprobe analysis	Liquidus and solidus
[1977Lot]	Neutron diffraction, resistivity measurement	Ordering in Ni_3(Mn,Cu) with Cu from 0.45 to 9.29 at.%. Samples tempered at 900°C.
[1978Ron]	XRD, metallography, mechanical property measurement	kinetics of ordering
[1982Mik]	XRD, optical and electron microscopy, hardness measurement	Cu-20Mn-20Ni and Cu-30Mn-30Ni (mass%) aged at 250-450°C
[1984Wea]	XRD, dilatometry, metallography, DTA, hardness measurement	Cu-MnNi quasibinary section
[1989Udo]	XRD	Cu-MnNi quasibinary section, 400-800°C
[2003Mie]	Calphad assessment	Phases considered limited to liquid, (γMn,Ni,Cu), η, ε and ζ phases

Table 2: Crystallographic Data of Solid Phases

Phases/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γMn,Ni,Cu) < 1455	*cF*4 $Fm\bar{3}m$ Cu	*a* = 361.46 *a* = 386.26 *a* = 352.40	continuous ternary solid solution [1979Cha, 1986Gup] pure Cu at 25°C [Mas2] pure Mn at 1097°C [1991Gok] pure Ni at 25°C [1991Gok]
(δMn) 1246 - 1138	*cI*2 $Im\bar{3}m$ W	*a* = 308.13	dissolves up to 6 at.% Ni and 12.5 at.% Cu pure Mn at 1137°C [1991Gok]
(βMn) 1100 - 586	*cP*20 $P4_132$ βMn	*a* = 631.52 *a* = 636.96	dissolves up to 18 at.% Ni pure Mn at room temperature [1991Gok] at 15 at.% Ni, room temperature [1991Gok]
(αMn) < 727	*cI*58 $I\bar{4}3m$ αMn	*a* = 891.39	dissolves up to 9 at.% Ni pure Mn, room temperature [1991Gok]
η, MnNi 911 - 675	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 297.7	45-52 at.% Ni at 50 at.% Ni, 750°C [1991Gok]

Phases/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η', MnNi 775 - 620	*tP*4 *P*4/*mmm* AuCu	 *a* = 373.1 *c* = 363.2	47-55.5 at.% Ni at 50 at.% Ni, room temperature [1991Gok]
η'', MnNi < 480	*t*** ?	-	~46-54 at.% Ni [1991Gok]
γ', $MnNi_3$ < 520	*cP*4 $Pm\overline{3}m$ $AuCu_3$	 *a* = 358.9	71-85 at.% Ni at 75 at.% Ni, room temperature [1991Gok]
ϕ, Mn_3Ni < 430	*t**	*a* = 369.8 *c* = 369.2	[1991Gok]
ε, Mn_2Ni 720 - 560	-	-	31.5-35.5 at.% Ni [1991Gok]
ζ, $MnNi_2$ 710 - 580	*t***	-	64-68.5 at.% Ni [1991Gok]
ζ', $MnNi_2$ < 440	*t***	-	~66.7-73 at.% Ni [1991Gok]
Cu_5Mn ≲ 400	-	-	at ~14-18 at.% Mn [Mas2]
Cu_3Mn ≲ 450	-	-	at ~23-27 at.% Mn [Mas2]

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

Reference	Method/Experimental Technique	Type of Property
[1941Ave1, 1941Ave2]	Not specified	Resistivity and EMF with respect to temperature. Workability of alloys at 500°C
[1949Sam]	Rockwell hardness measurement	Softening and hardening characteristics during heat treatment
[1954Agl]	Resistivity measurement	Electrical resistivity
[1961Die]	Resistivity, mechanical property measurement.	Temperature coefficient of resistivity, tensile strength and hardness.
[1962Gla]	Microhardness measurement	Microhardness of alloys along sections of constant Cu of 95 and 90%, quenched from 500, 700 and 900°C
[1966Lah]	Combination of stress and ammonia environment. Mechanical property tests.	Stress-corrosion cracking properties. Tensile strength, elongation and hardness.
[1972Fil1]	Double bridge	Resistivity with respect to temperature

Reference	Method/Experimental Technique	Type of Property
[1972Fil2]	Dilatometry, electrical and magnetic measurement	Electrical and magnetic properties, ordering.
[1975Bel]	XRD, vacuum deposition	Structure of thin films
[1976Kho]	Thermoelectromotive force measurement, resistivity	Electrical properties
[1977Pop]	XRD, vacuum deposition	Structure of thin films
[1978Ron]	Mechanical property measurement	Tensile strength, hardness
[1980Yok]	Diffusion couples	Interdiffusion and cross interdiffusion
[1984Bey]	Induction method, 4-point method, vibrational magnetometer	Dynamic magnetic susceptibility, resistivity, magnetization.
[1984Wea]	Hardness measurement	Hardness of MnNi-Cu quasibinary alloys with aging time at 450°C
[1987Tak]	Diffusion couples	Interdiffusion in Cu rich alloys
[1990Wak]	Hardness measurement	Hardness of 30Cu-40Mn-30Ni (mass%) experimental dental alloy
[1991God]	Dilatometry, resistivity measurement	Aging behavior
[1991Pol]	XRD, EM, neutron diffraction	Structure and deformation mechanisms
[2003Yin]	DMA	Young’s modulus, damping capacity

Fig. 1: Cu-Mn-Ni. Projection of the liquidus surface

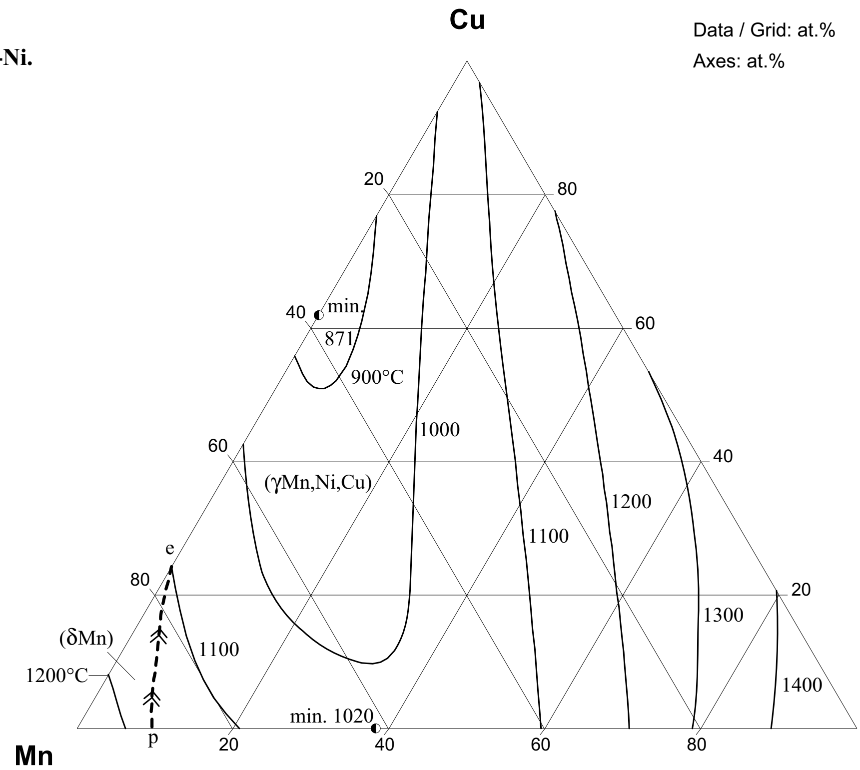

Fig. 2: Cu-Mn-Ni. Projection of the solidus surface

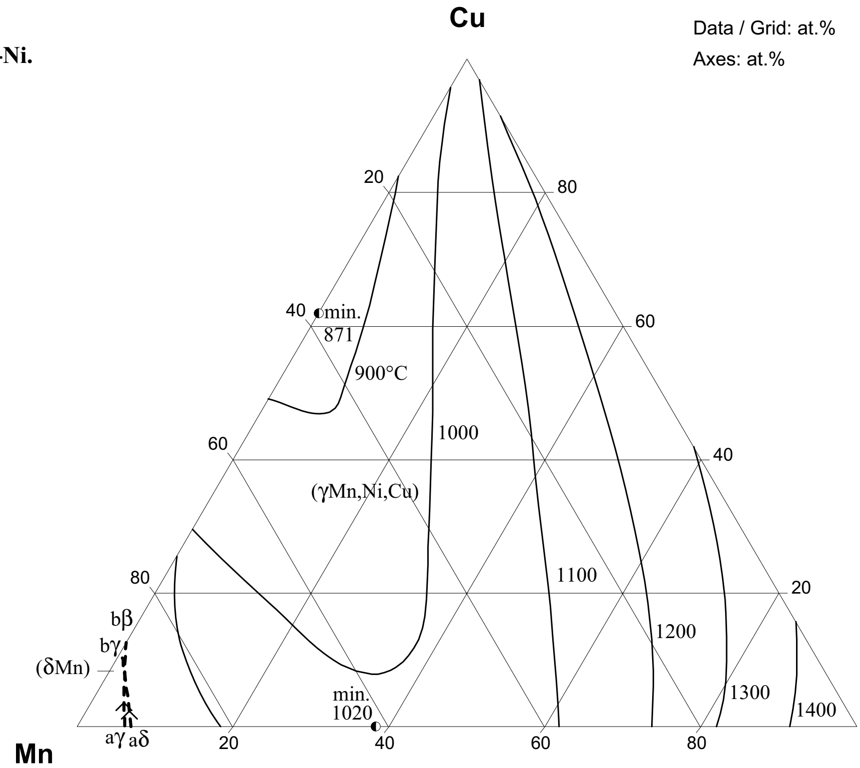

Fig. 3: Cu-Mn-Ni. Partial isotherms at 350 and 450°C of the (Cu,γMn,Ni) solvus surface

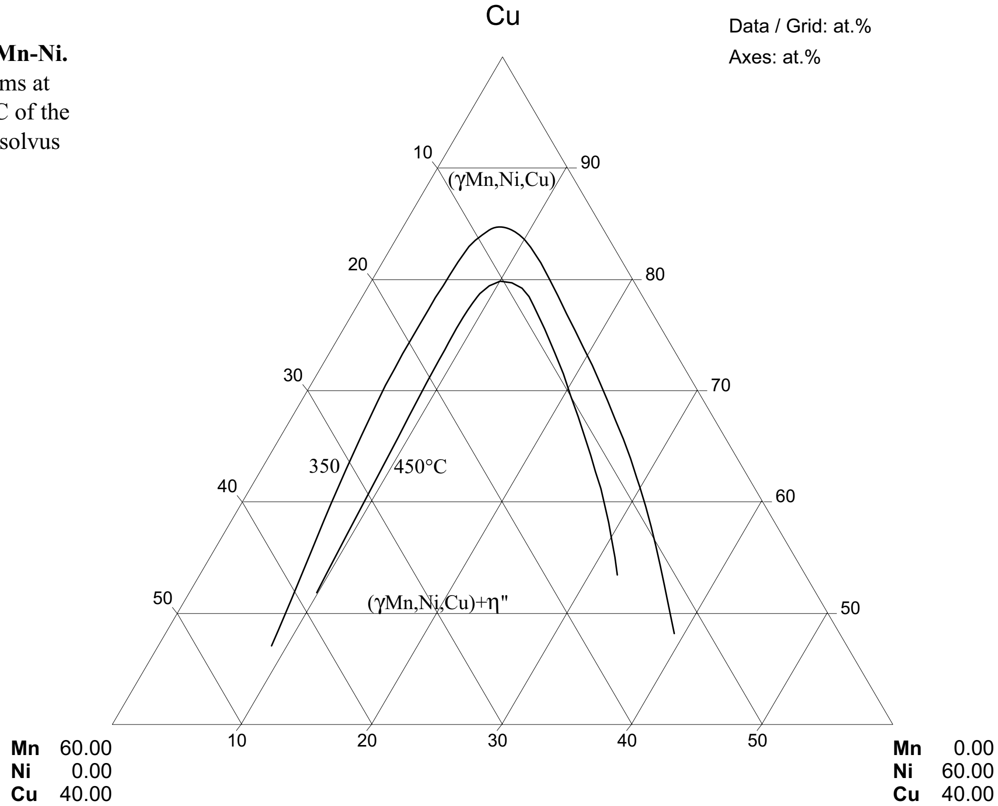

Fig. 4: Cu-Mn-Ni. Partial vertical section MnNi-Cu