Beryllium – Copper – Nickel

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Introduction

Few experimental investigations of the phase equilibria of this system exist in the literature. The earliest study was by [1938Sla] who used thermal analysis and hardness measurements to study Cu rich alloys of up to 5 mass% Be and 3 mass% Ni producing 4 partial vertical sections. The work of [1941Iwa] was more comprehensive, studying phase equilibria up to 13 mass% Be by thermal and X-ray analyses, dilatometric and hardness measurements supplemented by microanalysis. They produced isopleths at 4 and 6 mass% Be, 3, 12 and 30 mass% Ni, plus a partial liquidus surface and a diagram showing the solubility of Be in the (Ni,Cu) phase. More recently, [1958Chz] reinvestigated the Cu rich corner of the phase diagram. Along with the quasibinary Cu-NiBe section, they gave solidus isotherms for 10 different temperatures between 850 and 1050°C and isopleths for 0.25 and 1 mass% Ni. However, the quasibinary section of [1958Chz] is in conflict with the liquidus surface of [1941Iwa] in that there is no maximum shown on the monovariant line corresponding to the L ⇌ (Ni) + β′ reaction. This conflict is yet to be resolved. The experimental work has been reviewed in [1973Saa, 1979Cha, 1979Dri]. Details of the experimental studies are given in Table 1. Studies of the mechanical and physical properties of alloys of the system have been made. Details are given in Table 4.

Binary Systems

The Be-Cu and Cu-Ni systems are taken from the MSIT evaluation program [2006Wat, 2002Leb], and the Be-Ni is accepted from [Mas2]. For the purposes of this assessment, the phase designated γ in the binary evaluation of Be-Cu [2006Wat] is designated here as β′.

Solid Phases

No ternary phases have been discovered in this system. Details of the binary and unary phases are given in Table 2. The CuBe and NiBe phases form a continuous series of solid solutions. The β phase was found to dissolve up to 2 mass% Ni [1941Iwa].

Quasibinary Systems

Following the work of [1958Chz], a quasibinary section exists between pure Cu and NiBe, having a simple eutectic form. Part of the diagram is shown in Fig. 1 taken [1979Cha]. However, this is not consistent with the liquidus surface of [1941Iwa] (see below). It is highly desirable that this conflict be resolved.

Invariant Equilibria

Only one invariant four-phase reaction has been found in the system. [1941Iwa, 1979Cha] reports a transition reaction occurring at 868°C, just above the (Cu) + L ⇌ β peritectic reaction in the Be-Cu system (863°C). An invariant reaction at 855°C was found by [1958Chz], but this is most probably the same reaction [1979Cha]. The data for the invariant reported by [1941Iwa, 1979Cha] are given in Table 3.

Liquidus Surface

Part of the liquidus surface is given in Fig. 2. This is taken from the review of [1979Cha] based on the work of [1941Iwa]. Owing to the presence of the Cu-NiBe quasibinary section, a maximum has been added speculatively where the L ⇌ (Ni) + β′ monovariant crosses the Cu-NiBe join. There must also be a minimum on the monovariant at some point to the Ni-side of the maximum. Alterations have been made to ensure consistency with the binary systems.

Isothermal Sections

Figures 3-5 show isothermal sections for 915, 820 and 500°C, resepectively, taken from [1958Chz]. It was necessary to adjust the phase boundaries to ensure compatibility with the accepted Be-Cu binary phase diagram.

Temperature – Composition Sections

Isopleths are shown in Figs. 6-9. They correspond to sections of constant Ni content of 3 and 12 mass%, and constant Be contents of 4 and 6 mass%. Minor changes have been made to make them consistent with the accepted binary phase diagrams. Owing to the very narrow width of the L+γ phase field in the Be-Cu binary system at 6 mass% Be (31 at.% Be), the gap between the liquidus and solidus at the right-hand edge of Fig. 9 (0% Ni) is very small. Also, as the assessed β phase composition in the β ⇌ (Cu) + β′ eutectoid at 31.4 at.% Be, this is very close to the locus of the phase boundaries separating the β, β + β′, (Ni,Cu) + β + β′ and (Ni,Cu) + β phase fields in the vertical section of the ternary (31.05 at.% Be). Making the vertical section agree with the binary phase diagram to within less than 0.5 at.% Be would have great consequences on the nature of the Ni rich phase equilibria within this section. Therefore, as the difference in the composition is so small at the binary edge it was decided not to alter these phase boundaries in the vertical section.

Notes on Materials Properties and Applications

Be-Cu alloys are used as precipitation hardened high-strength alloys for low-temperature applications where small magnetic susceptibilities are required; such as in SQUID magnetometers and magnetic resonance imaging. Ni is added to limit grain growth and enhance mechanical properties further. On the other hand, “Cupronickel” has application where good corrosion resistance is required, and ternary additions improve mechanical properties and can give materials with heat resistant properties where high electrical conductivity is required.

This has led to much research on the mechanical behavior of Be-Cu-Ni alloys, and these are listed in Table 4. Of particular interest is the age hardening behavior of the material. [1972Gup] found, through microstructural and hardness studies of a Cu-30Ni-0.3Be alloy, the precipitation of G.P. zones at around 550°C.

[2005Coo] studied the origins of paramagnetism in a 0.4Be-Cu-1.95Ni (mass%) commercial alloy. Using a Quantum SQUID magnetometer, the magnetic susceptibility was found to follow the Curie-Weiss law between 4.75 and 300 K. The values for the effect Ni magnetic moments correspond to a lower Ni concentration for the material, which suggests that some of the Ni forms non-magnetic beryllides spread uniformly throughout the matrix.

References

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1938Sla]	Thermal analysis, microstructural studies and hardness measurements	Cu rich alloys
[1941Iwa]	Thermal, X-ray, hardness, dilatometric and microscopic analyses	Up to 13 mass% Be
[1958Chz]	Hardness and microstructural studies.	Cu rich alloys

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$(Ni_{1-x}Cu_x)$	*cF*4 $Fm\overline{3}m$ Cu		
(Ni) < 1455		*a* = 352.4	pure Ni at 25°C [2002Leb]. Dissolves 15 at.% Be at 1150°C [Mas2]
(Cu) < 1084.62		*a* = 361.46	dissolves 13.7 at.% Be at 863°C [2006Wat]
(βBe) 1289 - 1270	*cI*2 $Im\overline{3}m$ W	*a* = 255.15	HT, dissolves ~17 at.% Cu at 1199°C [2006Wat], 10 at.% Ni at 1338°C [Mas2]
(αBe) < 1270	*hP*2 $P6_3/mmc$ Mg	*a* = 228.59 *c* = 358.45	LT, at 25°C [Mas2] dissolves 9.5 at.% Cu at 1109°C [2006Wat], 4.5 at.% Ni at 1062°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β′, (Ni,Cu)Be	*cP*2 $Pm\bar{3}m$		
NiBe < 1605	CsCl	*a* = 260.4	25 at.% Ni at 1240°C to 51.6 at.% Ni at 1150°C [Mas2, V-C2]
CuBe < 933		*a* = 270.2 ± 0.3	46.2 to 49 at.% Be at 850°C [2006Wat]
γ, $NiBe_5$ < 1395	*cI*52 $I\bar{4}3m$ Ni_5Zn_{21}	*a* = 1527.6	11.5 at.% Ni at 1338°C, 19 at.% Ni at 1240°C [Mas2]
γ′, $NiBe_7$ < 1240	*cF*416 *F*23 γ-brass	*a* = 762.4	LT, 14 to 20 at.% Ni. [Mas2, V-C2]
δ, $Cu_{1-x}Be_{2+x}$ < 1219	*cF*24 $Fd\bar{3}m$ $CuMg_2$	*a* = 595.2 *a* = 589.9	*x* varies from 0.071 at 930°C to 0.455 at 1090°C at 66.7 at.% Be at 75 at.% Be [2006Wat]
β, Cu_2Be < 900	*cI*2 $Im\bar{3}m$ W	*a* = 281.0	24.5 to 41.7 at.% Be at 850°C [2006Wat]. Dissolves ~2 mass% Ni at 868°C [1979Cha]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Be	Cu	Ni
L + β′ ⇌ (Ni,Cu) + β	868	U_1	L	24.5	74.8	0.7
			β′	~51.5	~14.5	~34.0
			(Ni,Cu)	5.4	93.0	1.6
			β	~29.9	~68.5	~1.6
L ⇌ β′ + (Ni,Cu)	1030	e (max)?	L	~9.7	~80.6	~9.7

Table 4: Investigations of the Be-Cu-Ni Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1932Mas]	Brinell hardness measurements	Mechanical properties with respect to tempering conditions
[1960Gla]	Microhardness measurement	Microhardness of solid solution.
[1972Gup]	Hardness measurement	Tempering properties of Cu-30Ni-0.3Be (mass%)
[1982Spa]	Yield strength and hardness measurement	Investigation of how mechanical properties vary with condition of material, tempering temperature.
[2005Coo]	SQUID magnetometry	Magnetic susceptibility of commercial alloy with composition 4Be-Cu-1.95Ni (mass%)

Fig. 1: Be-Cu-Ni. Part of the quasibinary section NiBe - Cu

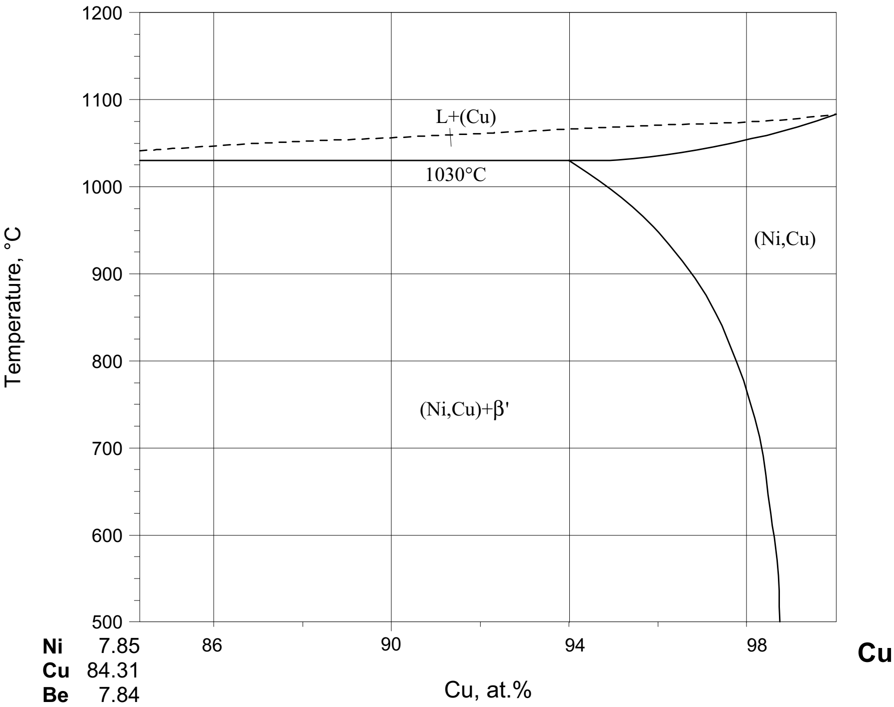

Fig. 2: Be-Cu-Ni. Part of the liquidus surface

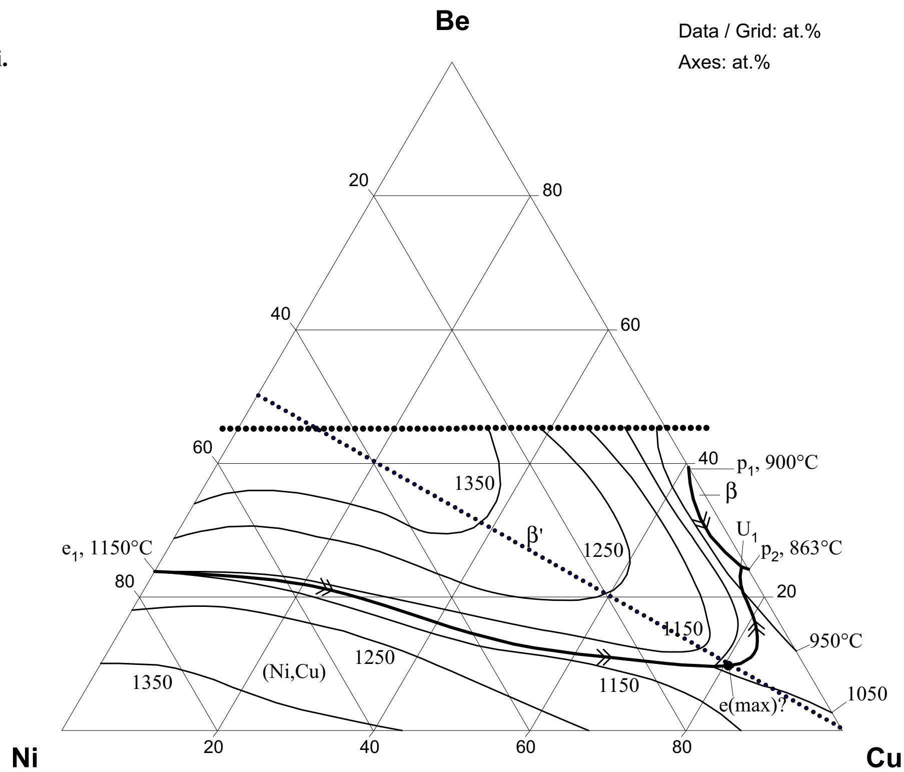

Fig. 3: Be-Cu-Ni.
Isothermal section at 915°C

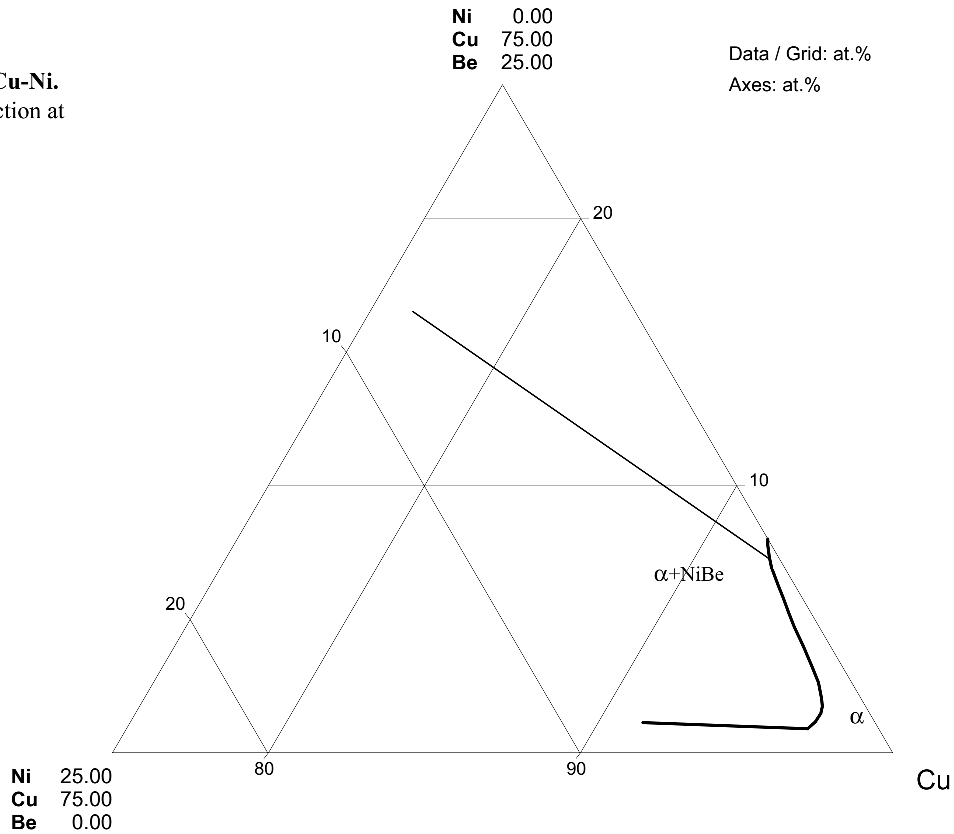

Fig. 4: Be-Cu-Ni.
Isothermal section at 820°C

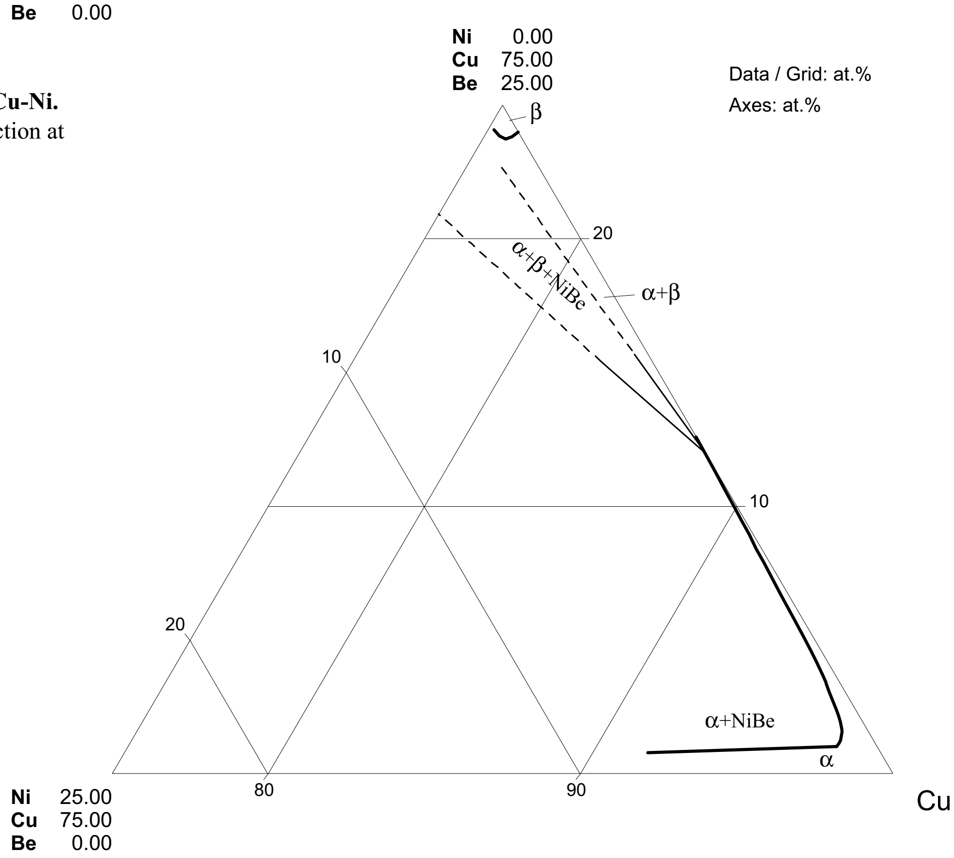

Fig. 5: Be-Cu-Ni.
Isothermal section at 500°C

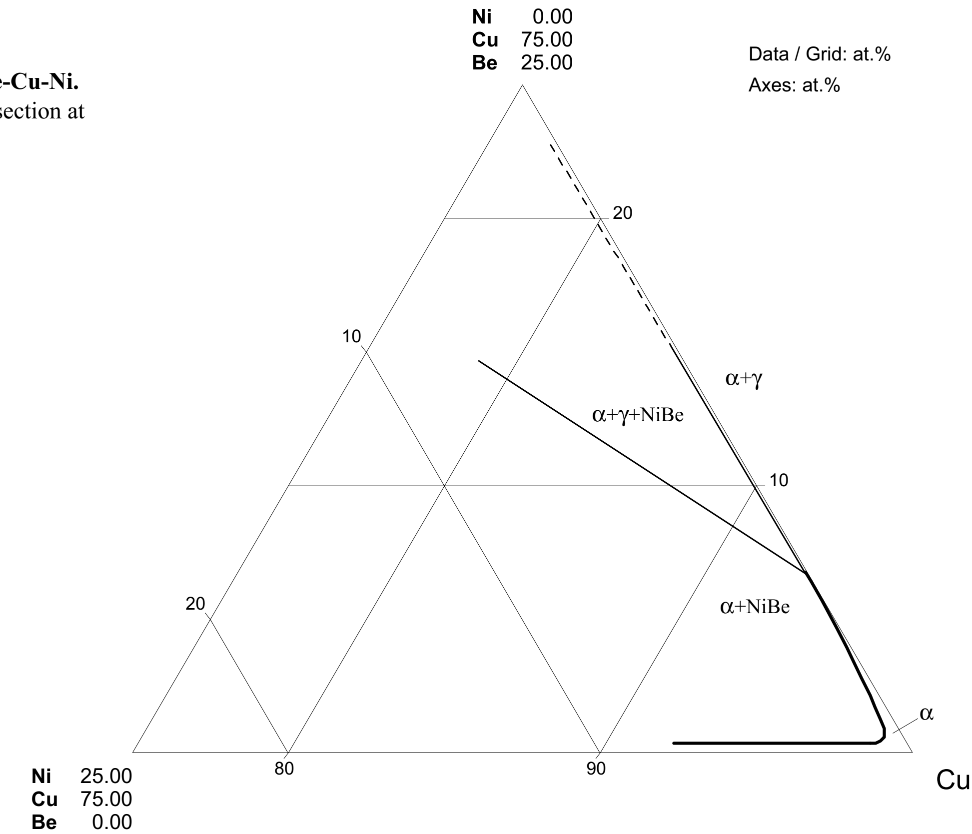

Fig. 6: Be-Cu-Ni.
Vertical section 96.76Cu3.24Ni - 48.96Be49.16Cu1.88 Ni

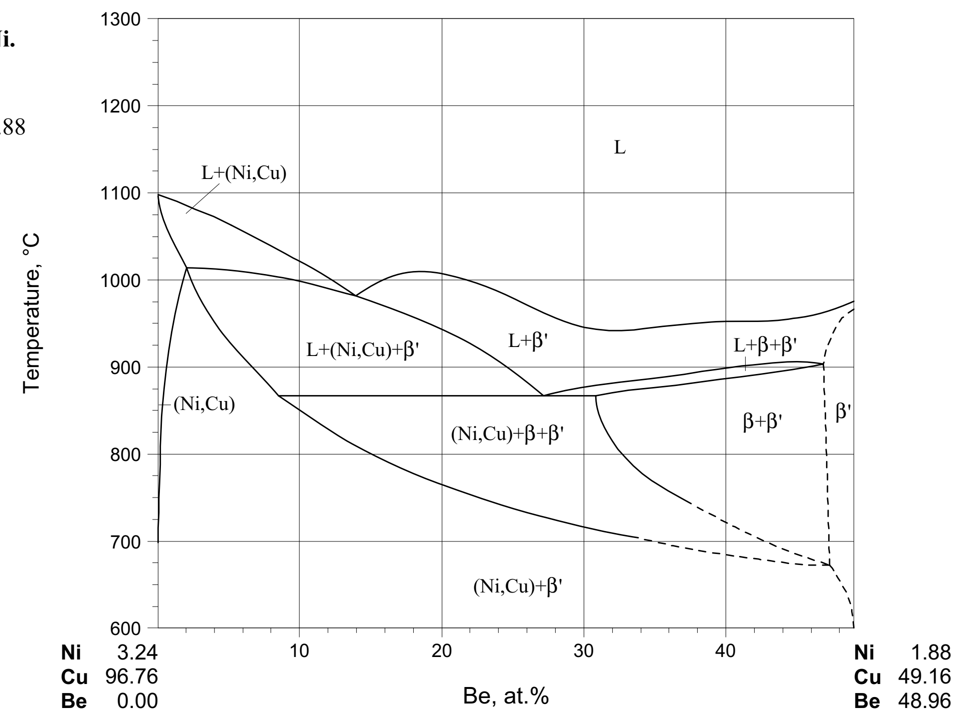

Fig. 7: Be-Cu-Ni.
Vertical section
87.13Cu12.87Ni -
43.67Be48.29Cu8.04

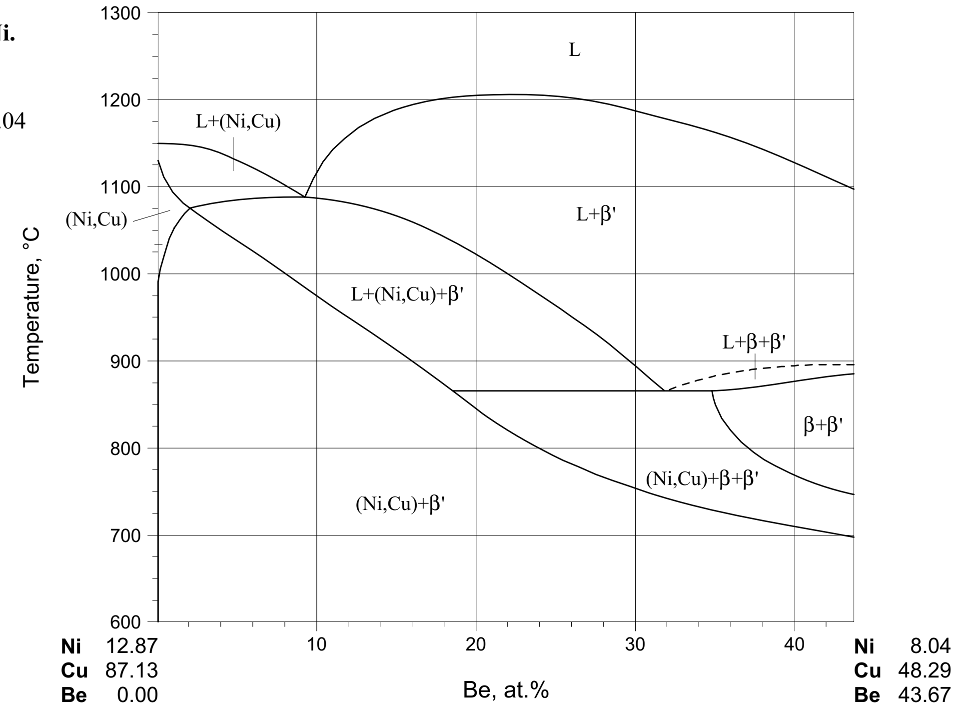

Fig. 8: Be-Cu-Ni.
Vertical section
21.35Be78.65Ni -
22.71Be77.29Cu

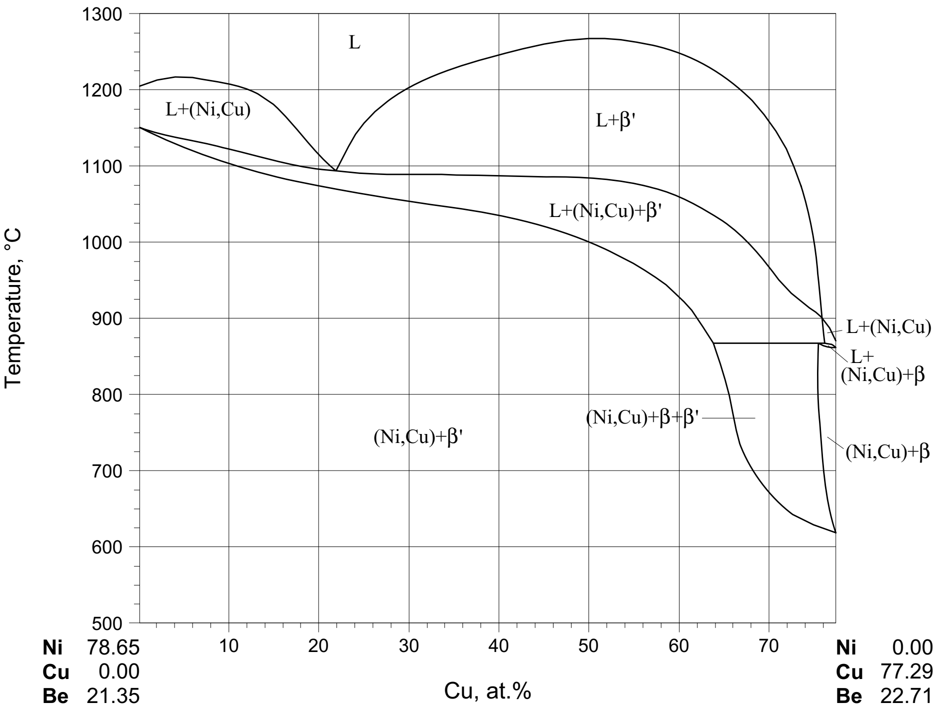

Fig. 9: Be-Cu-Ni. Vertical section 29.37Be70.63Ni - 31.04Be68.96Cu