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The Cu-Ni-Pd (Copper-Nickel-Palladium) System

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Introduction

The Cu-Ni-Pd system was found to be an isomorphous system. A further investigation of the Cu-Ni-Pd system at less than 70 at.% Cu region indicated the presence of a ternary miscibility gap in the fcc γ phase.

Binary Systems

The Cu-Ni system [1991Nas] (Fig. 1) is a simple isomorphous system with a possible phase separation below ~300 °C.

The Cu-Pd system [Massalski2] (Fig. 2) is a simple isomorphous system at high temperatures. The fcc (Cu, Pd) γ phase, however, undergoes transformation below 600 °C to give two phases β and γ′ with congruent transformation temperatures of 598 and 508 °C, respectively. Between the two phases β and γ′ two long period superlattice phases γ″ with one dimensional (1D) and two dimensional (2D) antiphase domain structures exist. A eutectoid type reaction γ ↔ γ″ (2D) + β has been suggested to exist at ~400 °C.

The Ni-Pd system [1991Nas] (Fig. 3) is an isomorphous system with a solidus/liquidus minimum of 1237 °C at 45.4 at.% Pd. At ≤700 °C the experimental results suggest the possible existence of short range order/clustering in the fcc (Ni, Pd) γ phase.

Binary and Ternary Phases

The Cu-Ni, Cu-Pd, Ni-Pd, and Cu-Ni-Pd systems are isomorphous systems. No ternary phase has been reported in the Cu-Ni-Pd system. The structure data for all the binary phases are given in Table 1.

Ternary System

The Cu-Ni-Pd system was studied by [1951Nem] and [1965Rao] and was reported to be a ternary isomorphous system. Only at low Pd concentration, alloys showed the existence of two fcc phases with different lattice parameters [1965Rao]. A possible phase transformation was suggested on the basis of this observation.

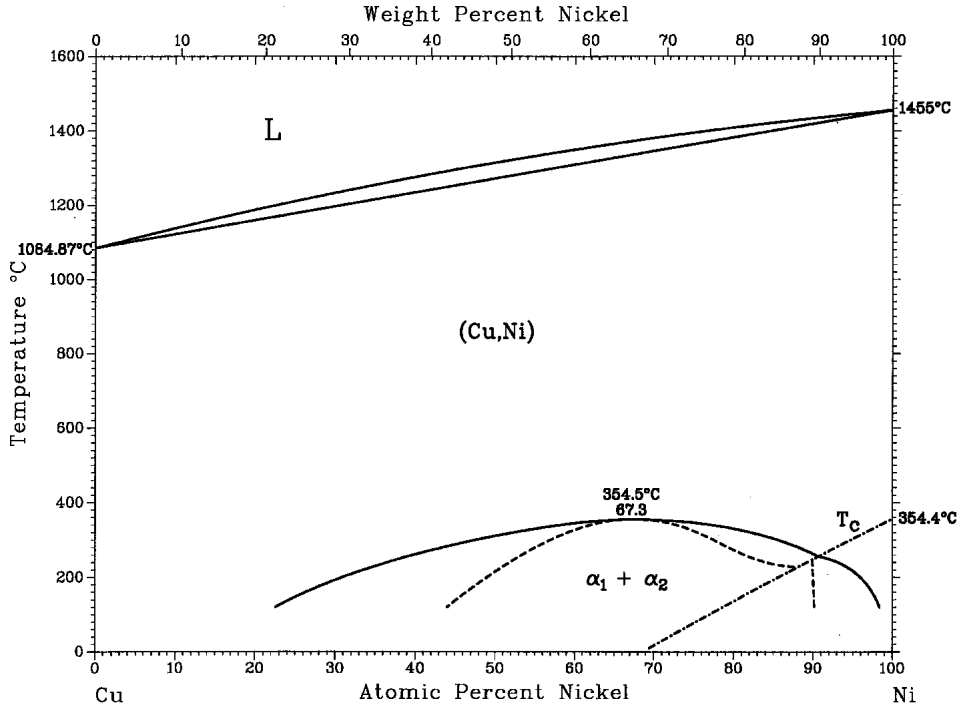

Fig. 1 Cu-Ni binary phase diagram [1991Nas]

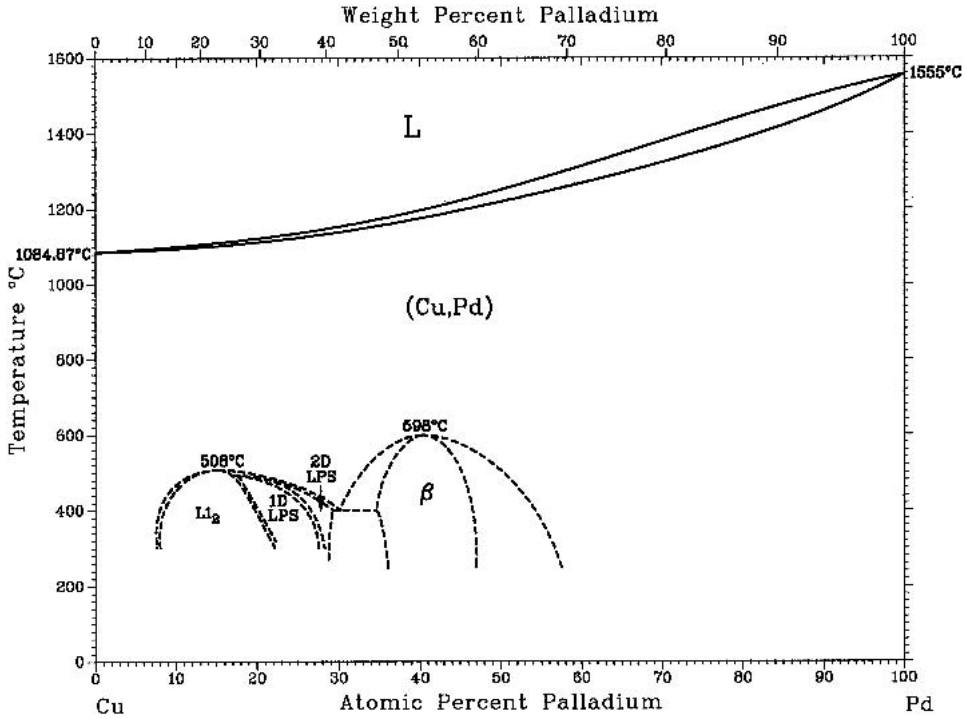

Fig. 2 Cu-Pd binary phase diagram [Massalski2]

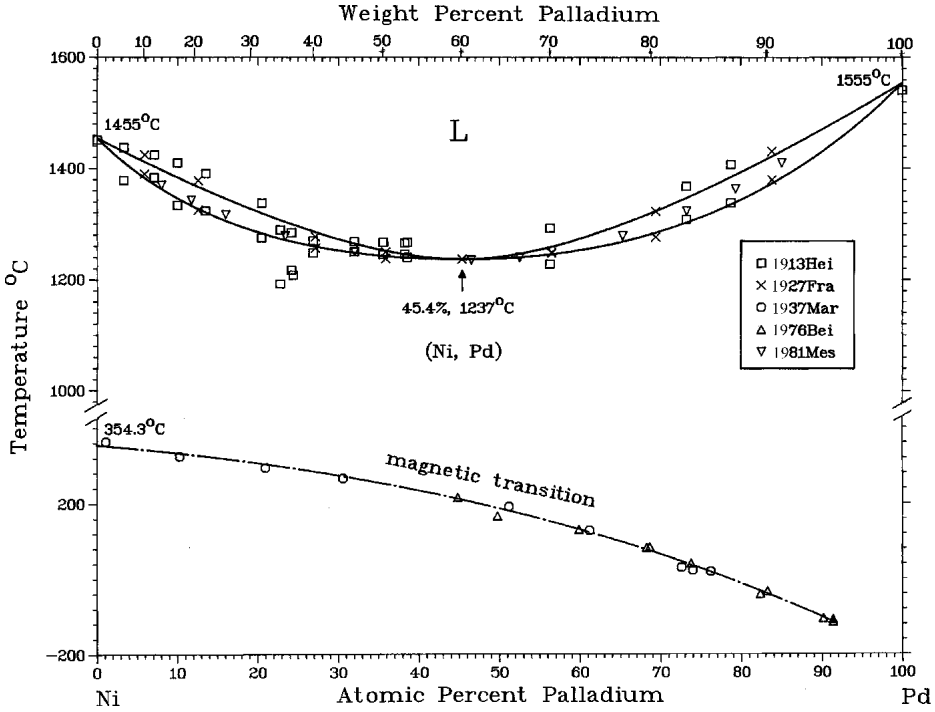

Fig. 3 Ni-Pd binary phase diagram [1991Nas]

Further study of the Cu-Ni-Pd system has been done by [1971Rau] at <70 at.% Cu concentration in the temperature range between 400 and 700 °C. The alloys were prepared by arc melting high purity metals (purity not quoted) under argon atmosphere. The alloys were sealed in evacuated quartz capsules and were homogenized at 900 °C and then annealed at different temperatures between 700 and 400 °C for 100-160 days. Only the x-ray diffraction (XRD) method was used for phase analysis of the annealed alloys.

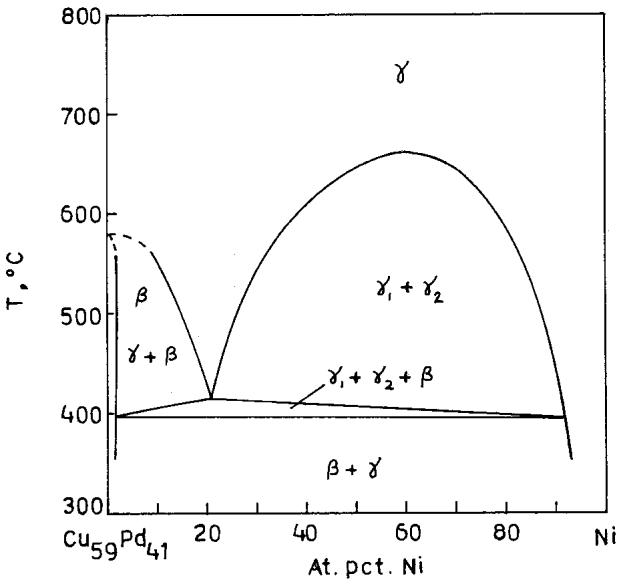

Fig. 4 The $Cu_{59}Pd_{41}$-Ni isopleth below 800 °C

β phase region and a β phase region were also observed.

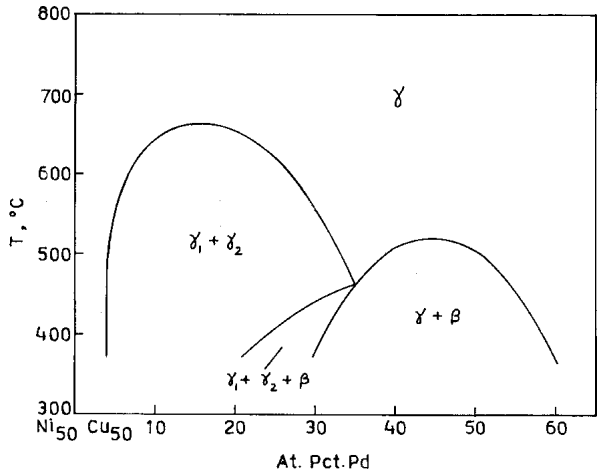

Fig. 5 The $Cu_{50}Ni_{50}Pd$ isopleth below 800 °C

Table 1 Structure Data for Binary Phases in the Cu-Ni-Pd System

Phase Designation	Composition	Pearson's Symbol	Space Group	Type	Lattice Parameter, nm	
					a	*c*
γ	(Cu, Ni), (Cu, Pd) (Ni, Pd), (Cu, Ni, Pd)	*cF*4	$Fm\bar{3}m$	Cu	…	…
γ′	Cu_3Pd	*cP*4	$Pm\bar{3}m$	Cu_3Au	0.3674	…
γ″	Cu_3Pd 1D-LPS	*tP*28	*P*4*mm*	Cu_3Pd	0.3701	2.5655
	2D LPS	…	…	…	…	…
β	CuPd	*cP*2	$Pm\bar{3}m$	CsCl	0.2958	…

[1971Rau] established two isopleths along the $Cu_{59}Pd_{41}$-Ni and $Cu_{50}Ni_{50}$-Pd lines (Fig. 4 and 5). The results indicate the existence of a ternary miscibility gap in the Cu-Ni-Pd system. The high temperature fcc γ solid solution phase gives a dome shaped ternary miscibility gap $\gamma \rightarrow (\gamma_1, \gamma_2)$ at 660 °C. The composition of the maximum of the γ_1 and γ_2 phase regions in the two isopleths are, however, quite far apart—at 24 at.% Cu and 16 at.% Pd in Fig. 4 and at 43 at.% Cu and 15 at.% Pd in Fig. 5. Hence, neither of them represents a true maximum of the $\gamma_1 + \gamma_2$ phase region. The maximum temperature of the two-phase region is expected to be higher than 660 °C. The presence of the three-phase equilibrium region $\gamma_1 + \gamma_2 + \beta$ was also established in the two isopleths. Figure 5 also shows a dome shaped $\gamma + \beta$ region with a maximum temperature of 520 °C at ~44 at.% Pd.

Six isothermal sections of the Cu-Ni-Pd system were established by [1971Rau] at 50 °C intervals between 400 and 650 °C (Fig. 6-11). The two high temperature isothermal sections at 600 and 650 °C show only $\gamma_1 + \gamma_2$ phase regions, which are more or less ellipse shaped, surrounded by the fcc γ phase region. Both γ_1 and γ_2 phases are of fcc structure, one with high Ni concentration (γ_1) and the other with high Cu concentration (γ_2). In the isothermal sections at 500 and 550 °C, besides the $\gamma_1 + \gamma_2$ phase region, a $\gamma + \beta$ phase region and a β phase region were also observed. The solubility of Ni in the β phase was found to be ≤2 at.% Ni. In the isothermal section at 400 °C a $\gamma_1 + \gamma_2 + \beta$ three-phase region was observed and at 450 °C the experimental data suggest the existence of a narrow three-phase region. The approximate location of the $\gamma_1 + \gamma_2 + \beta$ three-phase region at 450 °C has been drawn on the basis of single-phase and two-phase alloys.

Figure 12 shows the superimposed ellipse-like $\gamma_1 + \gamma_2$ phase region observed between 500 and 650 °C. The compositions of the two maximum points of the $\gamma_1 + \gamma_2$ phase regions (T = 660 °C) of the isopleths fall within the 650 °C curve. Since all the $\gamma_1 + \gamma_2$ phase regions are more or less ellipse-like, possibly the two 660 °C points also lie on an ellipse-like curve (dashed curve in Fig. 12). If the approximate long and short axes of the ellipse-like regions are drawn, the center point of the region turns out to be of composition 35 at.% Cu, 50 at.% Ni, and 15 at.% Pd. If the observed trend in Fig. 12 continues at temperatures higher than 650 °C, the maximum point for the $\gamma_1 + \gamma_2$ phase region is expected to be at the center of the ellipse-like regions, i.e., at ~35 at.% Cu and ~15 at.% Pd. [1971Rau] also suggested the maximum point to be at ~15 at.% Pd., and the expected maximum temperature is quoted to be ≤675 °C.

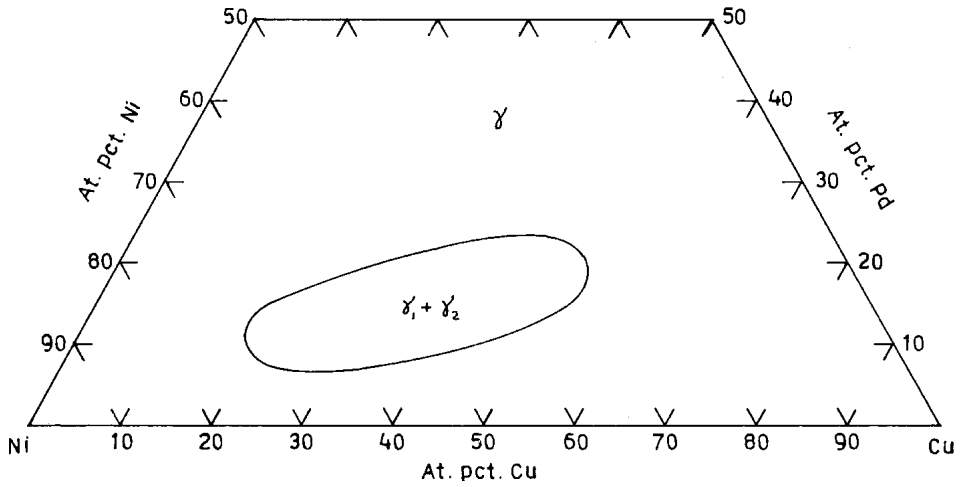

Fig. 6 The 650 °C isothermal section of the Cu-Ni-Pd system

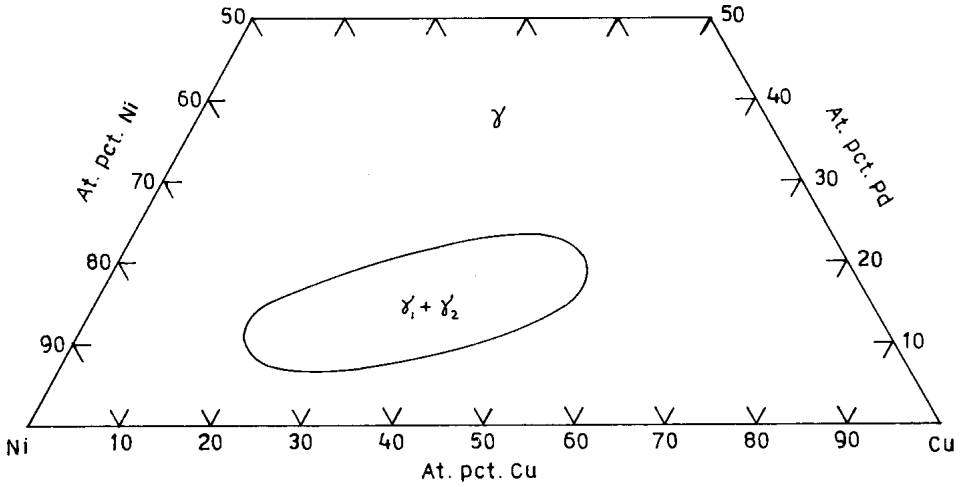

Fig. 7 The 600 °C isothermal section of the Cu-Ni-Pd system

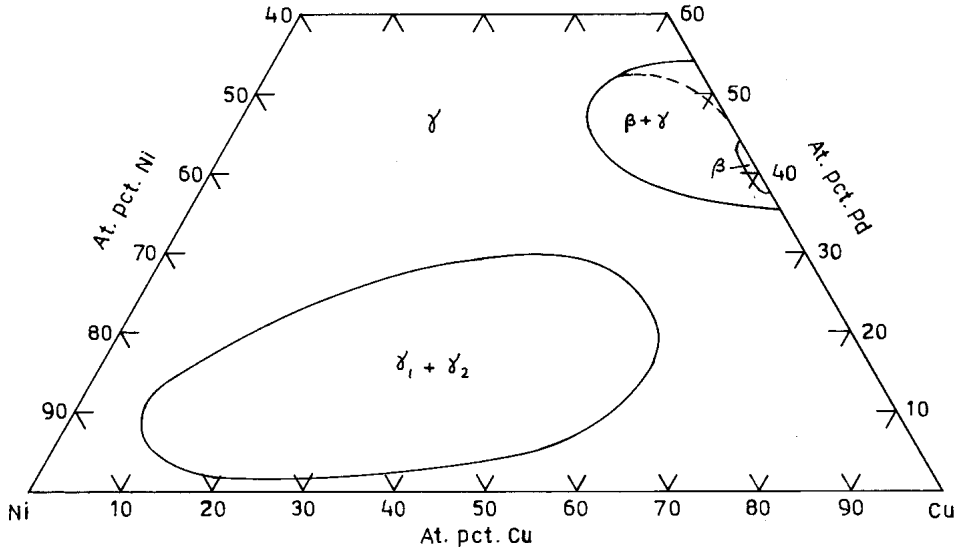

Fig. 8 The 550 °C isothermal section of the Cu-Ni-Pd system

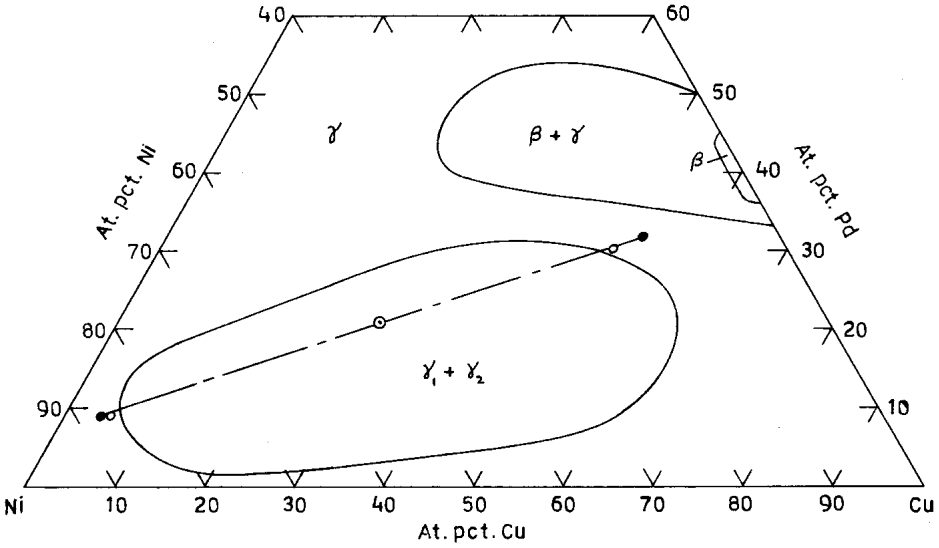

Fig. 9 The 500 °C isothermal section of the Cu-Ni-Pd system. ⊙ The alloy composition is $Cu_{29}Ni_{50}Pd_{21}$ [1981Mur]. ● The γ_1 and γ_2 phase compositions in equilibrium in this alloy were determined by the graphical method of [1981Mur]. ○ The reevaluated γ_1 and γ_2 phase compositions in the above alloy using the method of [1981Mur]

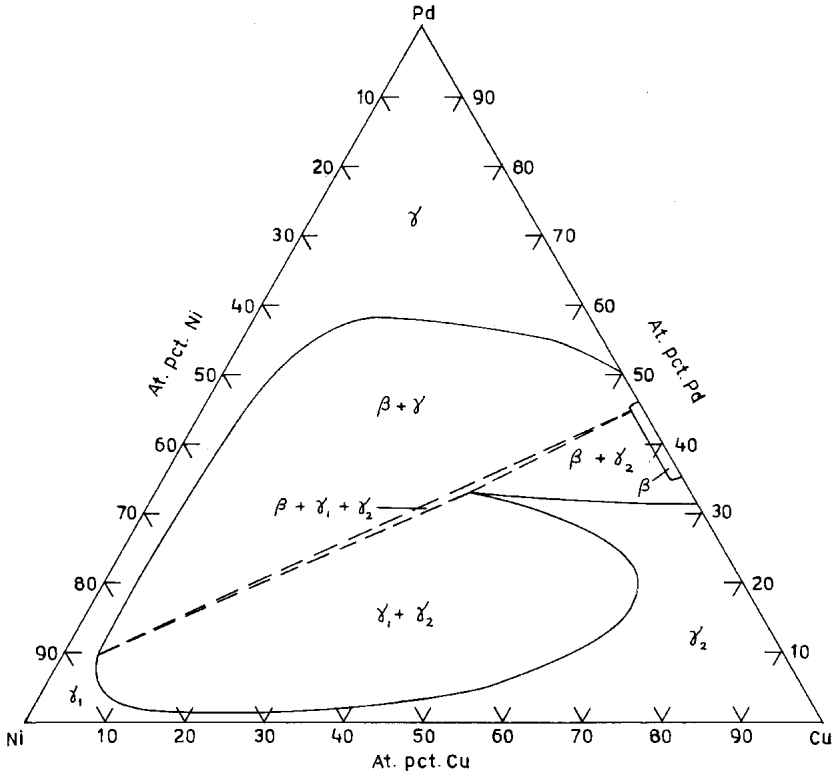

Fig. 10 The 450 °C isothermal section of the Cu-Ni-Pd system

Lattice parameters of the fcc γ phase were measured by [1971Rau] and isoparametric lines were plotted in the Cu-Ni-Pd diagram (Fig. 13). The lattice parameters are quoted to be in agreement with those reported by [1965Rao]. For the alloys annealed at T < 700 °C the lattice parameters of the γ_1, γ_2, and β phases were measured but since the compositions of the γ_1 and γ_2 phases are not known exactly, the variation of lattice parameters with composition of the phases cannot be plotted. The results, however, indicate that the variation of lattice parameters of the γ_1 and γ_2 phases are small. Some typical values of lattice parameters of the γ_1, γ_2 and β phases are given in Table 2.

Table 2 Lattice Parameters for the γ, γ_2, and β Phases in the Cu-Ni-Pd System

Alloy Composition, at.%	Annealing Temperature, °C	Number of Phases	Phase Designation	Lattice Parameter, nm*
57 Cu, 1 Ni, 42 Pd	400	One Phase	β	a = 0.2966
40 Cu, 40 Ni, 20 Pd	400	Two Phase	γ_1	a = 0.3547
			γ_2	a = 0.3709

* [1971Rau] gave lattice parameters in K_x units.

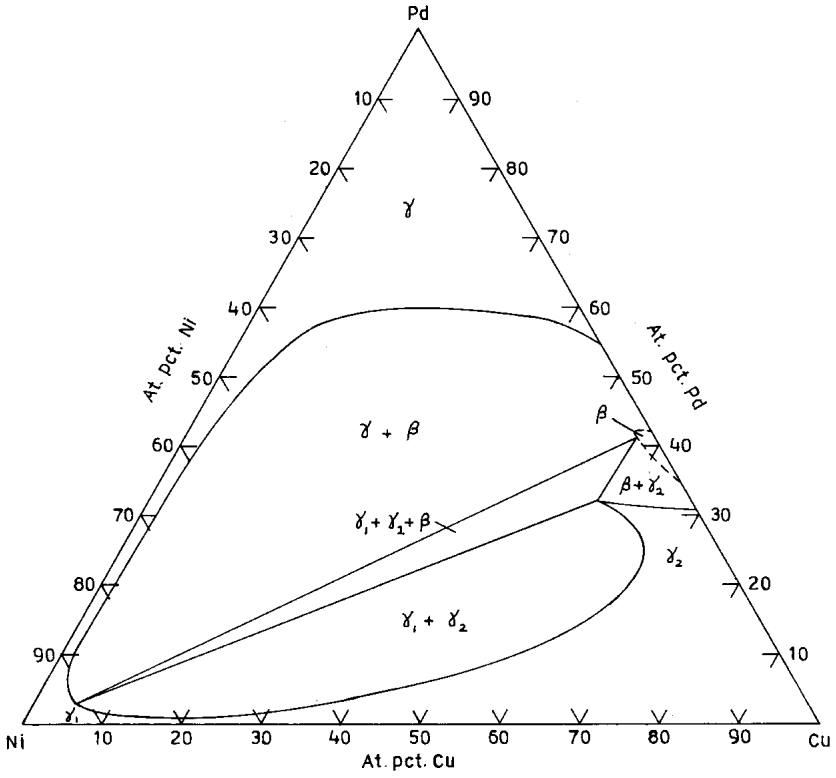

Fig. 11 The 400 °C isothermal section of the Cu-Ni-Pd system

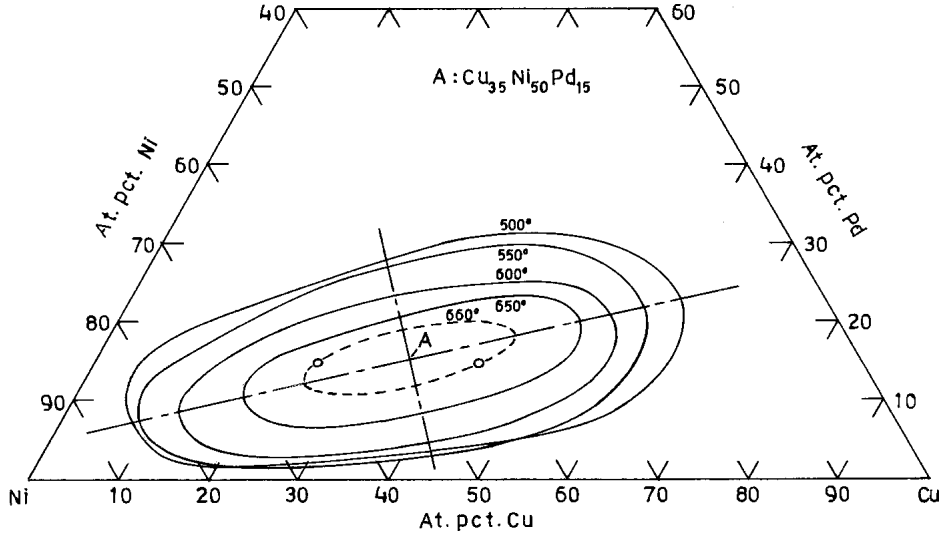

Fig. 12 The figure shows superimposition of the $\gamma_1 + \gamma_2$ phase regions experimentally determined at various temperatures between 500 and 650 °C. The dashed curve through the compositions of the maximum points of the $\gamma_1 + \gamma_2$ phase regions of Fig. 4 and 5 shows the expected $\gamma_1 + \gamma_2$ phase region at 660 °C. The dash-dot lines represent the approximate major and minor axes of the ellipse-like phase boundaries of the ($\gamma_1 + \gamma_2$) phase regions. Point A has a composition of $Cu_{35}Ni_{50}Pd_{15}$

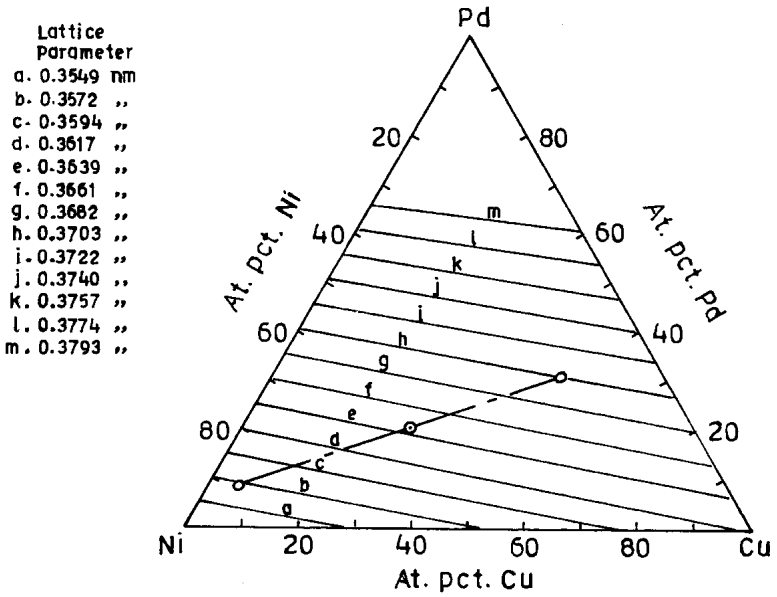

Fig. 13 Isoparametric lines in the Cu-Ni-Pd system [1971Rau]. The dash-dot line through the alloy composition of [1981Mur] ⊙ shows the reevaluated tie line for the phases in equilibrium.

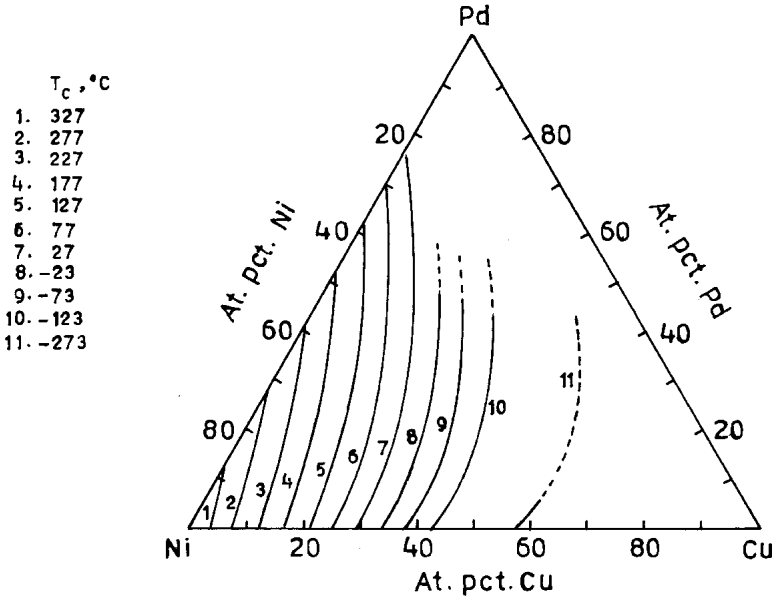

Fig. 14 Iso-Curie temperature lines in the Cu-Ni-Pd system [1981Mur]

A thermomagnetic study of the Cu-Ni-Pd system was made by [1981Mur]. Alloys were melted in a Tammann furnace under argon atmosphere using high purity metals (Cu of 99.98, Ni of 99.95 and Pd of 99.9 mass% purity) and cast in an iron mold. For magnetic measurements small cylindrical specimens were fabricated from homogenized (1000 °C/24 h) ingots, reannealed at 1000 °C for 2 h, water quenched, and magnetic moments (M) were measured as a function of temperature (T). The Curie temperatures (T_C) of the alloys were determined from the M versus T plots using the inflection point method and iso-Curie temperature lines were drawn in the Cu-Ni-Pd diagram (Fig. 14).

From the lattice parameter data of [1971Rau] (Fig. 13) and the Curie temperature data (Fig. 14), an attempt was made by [1981Mur] to determine the tie line for an alloy with 29 at.% Cu and 21 at.% Pd annealed at 500 °C for 168 h. The measured lattice parameters of the γ_1 and γ_2 phases were found to be $a_{\gamma_1} = 0.3564$ nm and $a_{\gamma_2} = 0.3703$ nm and of the two phases only the γ_1 phase is ferromagnetic with $T_C = 287$ °C whereas the γ_2 phase is paramagnetic.

Since the isoparametric lines of [1971Rau] and the iso-Curie temperature lines of [1981Mur] are more or less normal to each other, these data for the chosen alloy give uniquely the composition of the γ_1 phase ($Cu_4Ni_{87}Pd_9$). A line joining the γ_1 phase composition and the gross alloy composition on the isoparametric diagram of [1971Rau] gives the tie line which on extension to the isoparametric line corresponding to the lattice parameter of the γ_2 phase gives the composition of the γ_2 phase ($Cu_{53}Ni_{15}Pd_{32}$). When these compositions of the γ_1 and γ_2 phases are plotted in the isothermal section of 500 °C, the γ_2 phase is found to be reasonably far from the $\gamma_1 + \gamma_2$ phase boundary. This discrepancy is due to the fact that [1981Mur] determined lattice parameters in nm units and used them directly on the isoparametric line diagram of [1971Rau] in which Kx units were used. After representing lattice parameters in nm units in Fig. 13 and applying the same procedure, the γ_1 and γ_2 phase compositions turn out to be $Cu_5Ni_{86}Pd_9$ and $Cu_{50}Ni_{19}Pd_{31}$. These data have been plotted in Fig. 9 and show agreement with the phase boundaries of the $\gamma_1 + \gamma_2$ region. Thus, the graphical method may be used in this case quite effectively to determine tie lines in the $\gamma_1 + \gamma_2$ phase region.

An alloy with 29 at.% Cu and 21 at.% Pd was used for a study of spinodal decomposition of the γ phase. A transmission electron microscopic (TEM) study was made with an alloy quenched from high temperature and then annealed at 500 °C for 8 h. A TEM micrograph of (100) plane of this sample showed a modulated structure along the ⟨100⟩ direction, which suggested spinodal decomposition of the quenched alloy during the early stages of decomposition of the γ phase. Electron diffraction also showed satellite spots around the 200 diffraction spot, which resulted from periodic composition fluctuation. From the separation of the satellite spots the wavelength of composition fluctuation has been estimated to be ~6.5 nm.

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Cu-Ni-Pd evaluation contributed by **K.P. Gupta,** The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector-V, Calcutta, 70009, India. Literature searched through 1993. Dr. Gupta is the Alloy Phase Diagram Program Co-Category Editor for ternary nickel alloys.