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The Cu-Ni-Y (Copper-Nickel-Yttrium) System

K.P. Gupta, The Indian Institute of Metals

Introduction

Only a very limited amount of work has been done on the Cu-Ni-Y system. One partial isothermal section at room temperature is available at Y ≤ 16.7 at.% Y. Phase transformations in CuY and $Cu_xNi_{1-x}Y$ alloys at low temperatures have been studied. Magnetic measurements on $Cu_xNi_{17-x}Y_2$ alloys and a hydrogen absorption study of a $Cu_{0.5}Ni_{2.5}Y$ alloy have been done.

Binary Systems

The Cu-Ni system [Massalski2] (Fig. 1) is a simple isomorphous system with a continuous liquid solution separated by a narrow two-phase region from a continuous solid solution. The face centered cubic (fcc) solid solution of Cu and Ni (γ), however, undergoes a short range order transformation at temperatures less than 300 °C.

The Cu-Y system [Massalski2] (Fig. 2) has five intermediate phases, $Cu_6Y(\eta)$, $Cu_4Y(\delta)$, $Cu_7Y_2(\theta)$, $Cu_2Y(\iota)$, and $CuY(\upsilon_1)$, of which the δ, ι, and υ_1 phases melt congruently at 975, 935, and 935 °C, respectively. The η and θ phases form through peritectic reactions $L + \delta \leftrightarrow \eta$ at 910 °C and $L + \delta \leftrightarrow \theta$ at 920 °C. Four eutectic reactions: $L \leftrightarrow \gamma + \eta$, $L \leftrightarrow \theta + \iota$, $L \leftrightarrow \iota + \upsilon_1$, and $L \leftrightarrow \gamma + \varepsilon$ occur at 860, 840, 830, and 770 °C, respectively. ε is the terminal solid solution (αY). A metastable phase of composition Cu_5Y was found to form through rapid quenching of a liquid alloy. The θ, ι, and υ_1 phases are of invariant compositions.

The Ni-Y system [1991Nas] (Fig. 3) has nine intermediate phases: $Ni_{17}Y_2(\zeta)$, $Ni_5Y(\omega)$, $Ni_4Y(\kappa)$, $Ni_7Y_2(\rho)$, $Ni_3Y(\pi)$, $Ni_2Y(\lambda)$, $NiY(\tau)$, $Ni_2Y_3(\psi)$, and $NiY_3(\xi)$. The $Ni_5Y(\omega)$ and $NiY(\tau)$ phases melt congruently at 1430 and 1070 °C, respectively. All the other phases form through peritectic reactions: $L + \omega \leftrightarrow \zeta$ at 1350 °C, $L + \omega \leftrightarrow \kappa$ at 1340 °C, $L + \kappa \leftrightarrow \rho$ at 1298 °C, $L + \rho \leftrightarrow \pi$ at 1237 °C, $L + \pi \leftrightarrow \lambda$ at 1106 °C, $L + \tau \leftrightarrow \psi$ at 820 °C, and $L + \varepsilon \leftrightarrow \xi$ at 902 °C, where ε is the terminal solid solution (Y). All the intermediate phases are of invariant compositions. Three eutectic reactions $L \leftrightarrow \zeta + \gamma$, $L \leftrightarrow \lambda + \tau$, and $L \leftrightarrow \psi + \xi$ occur at 1085, 950, and 805 °C, respectively.

Binary and Ternary Phases

In the three binary systems Cu-Ni, Cu-Y, and Ni-Y, there are 14 intermediate phases. No ternary intermediate phase has been reported in the Cu-Ni-Y system. The binary phases and their structure data are given in Table 1.

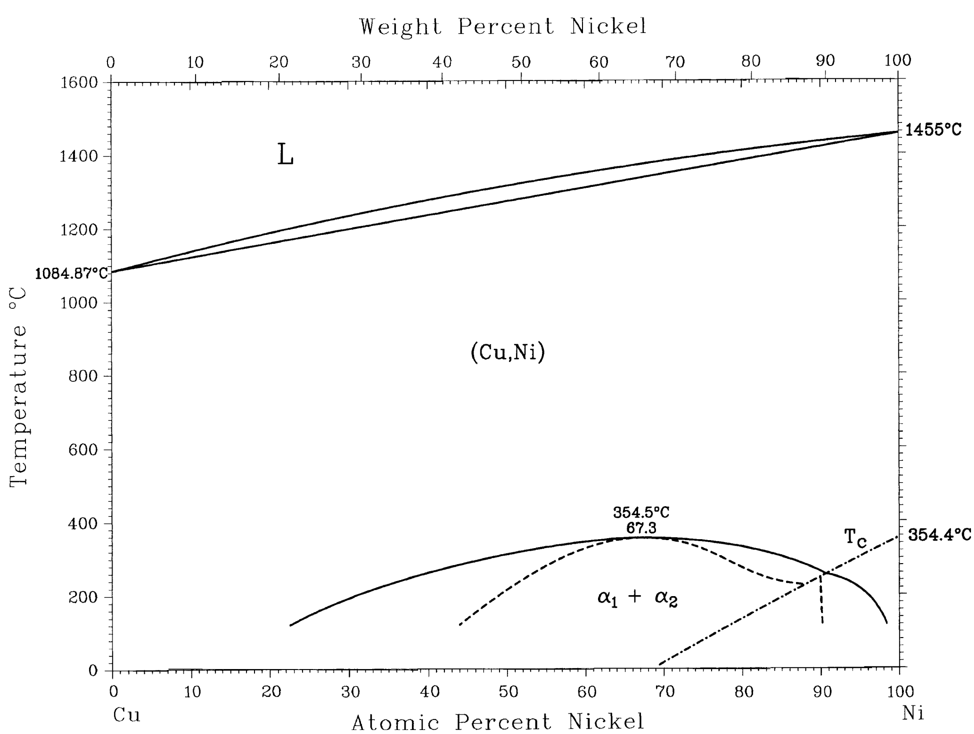

Fig. 1 Cu-Ni binary phase diagram

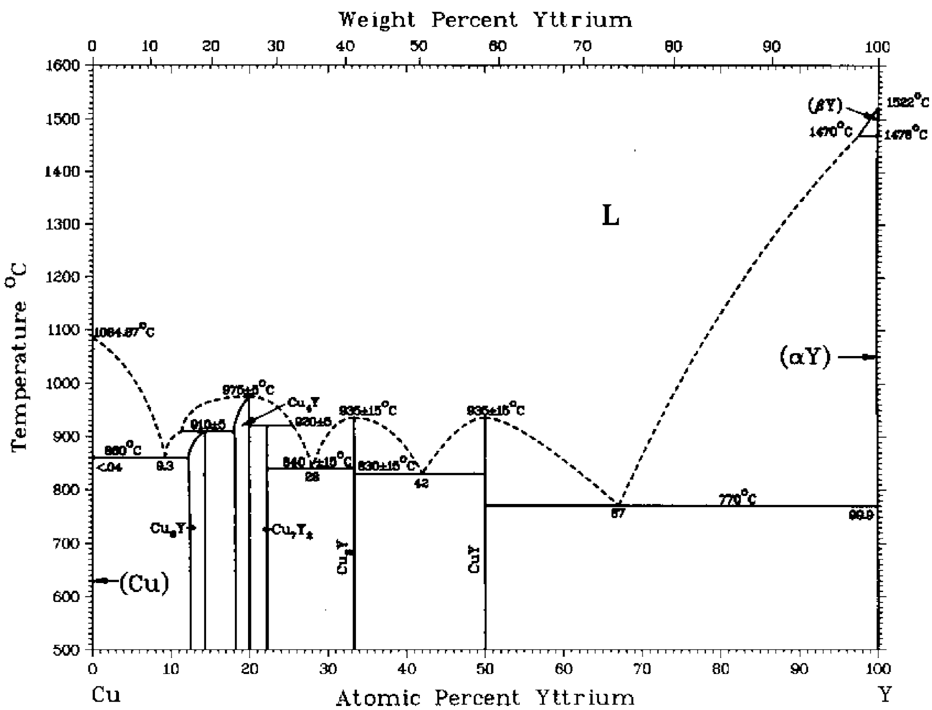

Fig. 2 Cu-Y binary phase diagram [Massalski2]

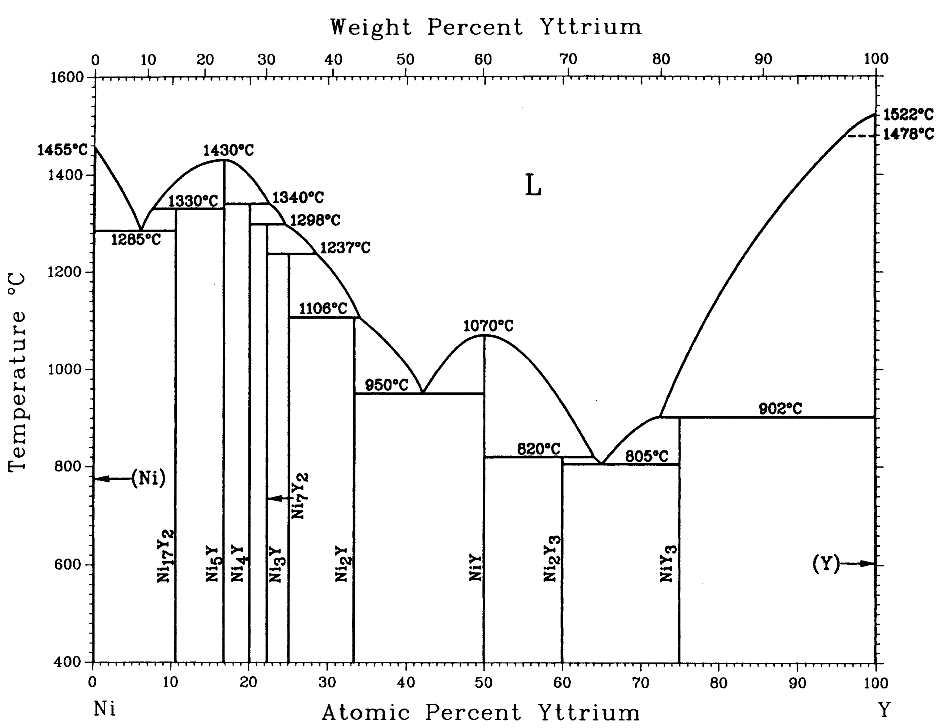

Fig. 3 Ni-Y binary phase diagram

Ternary System

The $Cu_xNi_{17-x}Y$ alloys have been studied by [1970Car]. Pure metals of purity at least of 99.9 mass% were used to prepare the alloys by levitation melting. The alloys sealed in evacuated Vycor capsules were annealed between 800 and 950 °C, the time of anneal was not mentioned. The annealed alloys were characterized by x-ray diffraction (XRD) and

Table 1 Binary phases of the Cu-Ni, Cu-Y, and Ni-Y systems and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameters, nm		
					a	***b***	***c***
γ	(Cu), (Ni), (Cu, Ni)	*cF*4	$Fm\bar{3}m$	Cu	···	···	···
α	(αY)	*hP*2	$P6_3/mmc$	Mg	···	···	···
β	(βY)	*cI*2	$Im\bar{3}m$	W	···	···	···
η	Cu_6Y	*h*	···	···	0.683	···	0.407
δ	Cu_4Y	*hp*6	$P6/mmm$?	$CaCu_5$?	0.4994	···	0.4113
ω	Cu_5Y (a)	*hp*6	$P6/mmm$	$CaCu_5$	0.5005	···	0.4097
θ	Cu_7Y_2	···	···	···	···	···	···
υ	Cu_2Y	*oI*12	*Imma*	$CaCu_2$	0.4305	0.6800	0.7315
υ_1	CuY	*cP*2	$Pm\bar{3}m$	CaCl	0.34775	···	···
υ_2	CuY (d)	*oP*8	*Pnma*	FeB	···	···	···
ζ	$Ni_{17}Y_2$	*hp*38	$P6_3/mmc$	Th2Ni117	0.8307	···	0.8040
ω	Ni_5Y	*hp*6	$P6/mmm$	$CaCu_5$	0.4883	···	0.3967
κ	Ni_4Y	···	···	···	···	···	···
ρ	Ni_7Y_2	*hR*18	$R\bar{3}m$	Gd_2Co_7	0.4924		3.667(b)
			$P6_3/mmc$	Ce_2Ni_7	0.4928	···	2.411(c)
π	Ni_3Y	*hR*12	$R\bar{3}m$	$PuNi_3$	0.5	···	0.430
λ	Ni_2Y	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.7181	···	···
τ	NiY	*op*8	*Pnma*	FeB	0.712	0.41	0.551
ψ	Ni_2Y_3	*tp*80	$P4_12_12$	Ni_2Y_3	0.7104	···	3.6597
ξ	NiY_3	*oP*16	*Pnma*	Fe_3C	0.692	0.447	0.636

(a) Metastable, produced by splat cooling
(b) At 1100 °C
(c) At 600 °C at low temperature

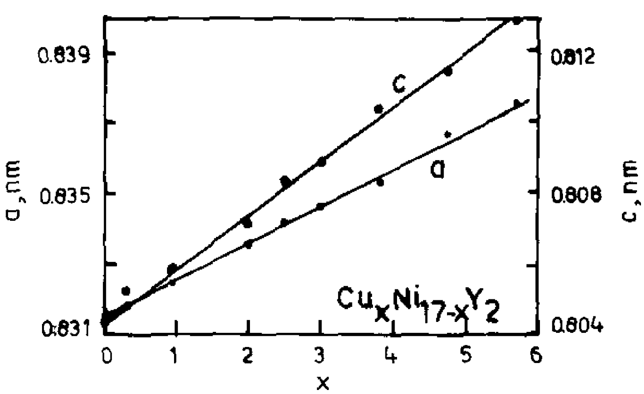

Fig. 4 Variation of lattice parameters of $Cu_xNi_{17-x}Y_2$ alloys as a function of x [1970Car]

magnetic measurements as a function of temperature were carried out using two Faraday balances which work between 4.2 K (∼−260 °C) to room temperature and from room temperature to 1000 °C. The lattice parameters of the $Cu_xNi_{17-x}Y_2$ alloys as a function of Cu content x are given in Fig. 4. Both c and a parameters were found to increase with x. Saturation magnetization (M_{sat}) and Curie temperature (T_c) of the $Cu_xNi_{19-x}Y_2$ alloys were measured and are shown in Fig. 5 as a function of x. T_c was found to decrease with increase in Cu content. M_{sat} was found to decrease linearly from $x = 0$ to $x = 2$ and then after a break at $x = 2$ again decrease linearly to $x = 4.5$. M_{sat}, however, did not go to zero even at $x = 5.0$. The change in magnetic properties

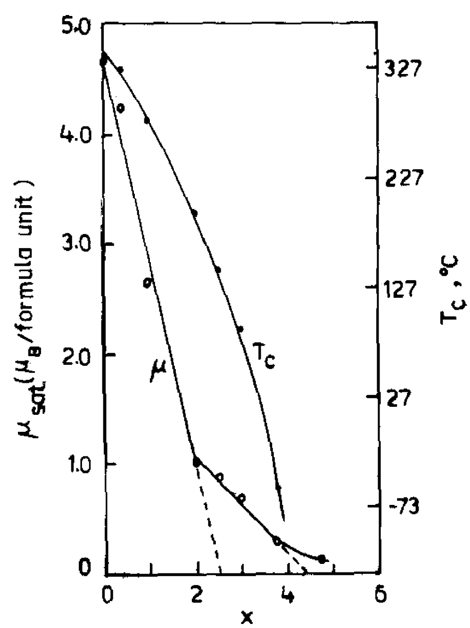

Fig. 5 Variation of M_{sat} and T_c as a function of x for the $Cu_xNi_{17-x}Y_2$ alloys [1970Car]

of the $Ni_{17}Y_2$ phase with addition of Cu was found to be similar to the addition of Cu to Ni.

[1975Dwi] studied Cu-Ni-Y alloys at the $Cu_xNi_{5-x}Y$ compositions. Arc melted alloys, prepared with 99.9 mass% pure metals, were annealed at 800 °C. The time of annealing was not mentioned. The annealed alloys were characterized by XRD only. The $CaCu_5$ type crystal structure was found to extend from Ni_5Y to Cu_4NiY composition. The alloys beyond this copper content were not of $CaCu_5$ type hexagonal structure, but were reported to have a cubic structure. The accepted Cu-Y binary diagram shows the Cu_5Y composition to be a two-phase region between the Cu_4Y and Cu_6Y phases. Thus, no Cu_5Y phase exists as a stable phase in the Cu-Y binary. Since the crystal structures of both Cu_4Y and Cu_6Y are not well known, the cubic phase mentioned by [1995Dwi] cannot be compared with either of these two stable phases. It is, however, possible that the phase with cubic structure may be a ternary phase. This has to be established by proper experimentation. The lattice parameters of the $Cu_xNi_{5-x}Y$ alloys has been measured by [1995Dwi] and is shown in Fig. 6. The increase in both *a* and *c* parameters of the hexagonal phase probably indicates random substitution rather than substitution of Cu at preferential sites in the $CaCu_5$ type structure.

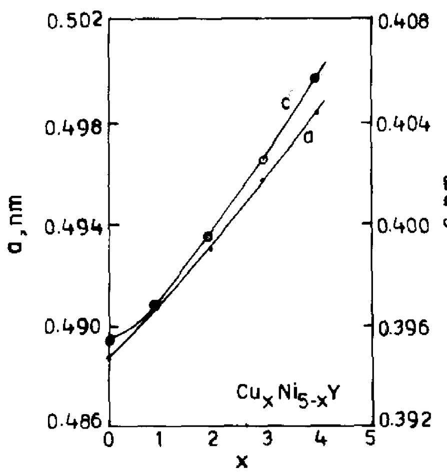

Fig. 6 Variation of lattice parameters of $Cu_xNi_{5-x}Y$ alloys as a function of *x* [1975Dwi]

[1985Zhe] investigated the Cu-Ni-Y system near the Cu-Ni side with alloys having Y contents ≤16.9 at.% Y. The alloys, prepared with 99.999 mass% pure Cu and Ni and 99.9 mass% pure Y, were melted in alumina crucibles under argon atmosphere. The alloys were annealed at 900 °C for 672 h and cooled to room temperature at the rate of 20 °C/h. Only XRD was used for phase analysis of the annealed alloys. Before taking XRD patterns the alloy powders were annealed at 500 °C for 72 h and cooled to room temperature at the rate of 10 °C/h. The partial isothermal section of the Cu-Ni-Y system at room temperature is given in Fig. 7.

The partial isothermal section at room temperature (Fig. 7) shows extension of the Ni_5Y phase to the Cu_5Y composition. The $Ni_{17}Y_2$ phase (ζ) was found to extend to ~35 at.% Cu, which is in good agreement with the lattice parameter data of [1970Car]. A three-phase equilibrium region $\gamma + \zeta + \omega$ was found to exist. At the higher Cu side, a three-phase equilibrium region $\gamma + \omega + \eta$ was found. The Cu_6Y phase (η) was found to extend into the ternary to ~5 at.% Ni. The ω phase composition of the three phase region $\gamma + \omega + \eta$ agrees well with the composition Cu_4NiY where [1975Dwi] found the $CaCu_5$ phase to exist. Since the Cu_5Y phase does not exist in the accepted Cu-Y binary as a stable phase the ω phase region cannot extend to Cu_5Y composition. Hence, the Ni_5Y-Cu_5Y line is shown by dashed line in Fig. 7 beyond the ω phase composition of the three phase region $\gamma + \omega + \eta$. The copper side of the Ni_5Y-Cu_5Y line should be redetermined. The maximum solubility of Y in the γ phase was found to be <1.5 at.% Y.

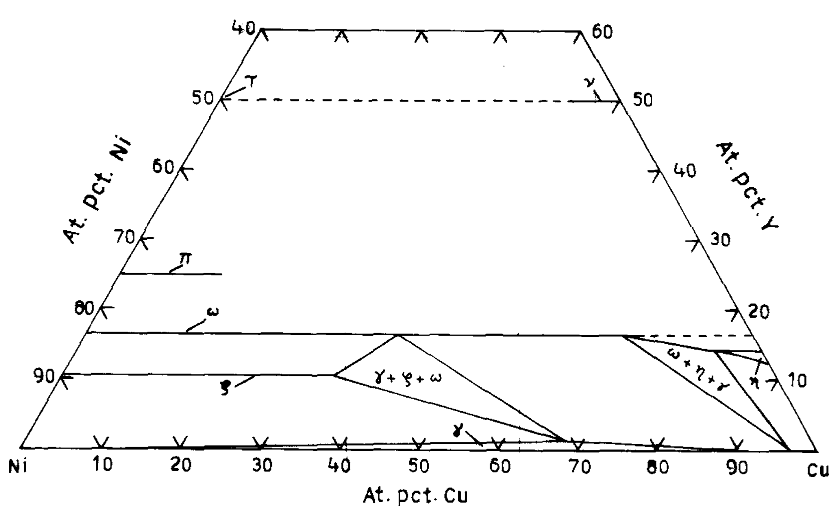

Fig. 7 A partial isothermal section of Cu-Ni-Y system (for Y ≤ 16.7 at.% Y) at 20 °C [1985Zhe]. The figure also shows the regions of υ and π phases and a probable extension of the τ phase region

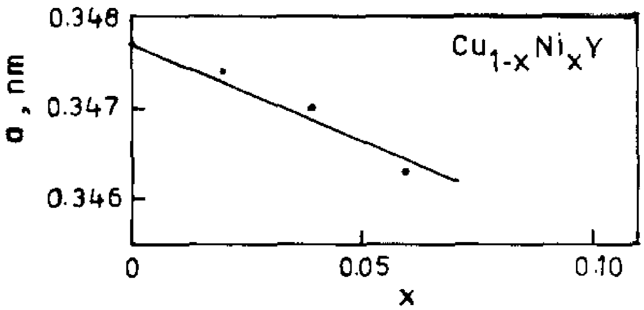

Fig. 8 Variation of lattice parameter of $Cu_xNi_{1-x}Y$ alloys as a function of x [1988Kad]

[1988Kad] studied structural transformation of CuY and $Cu_{1-x}Ni_xY$ alloys with $x \le 0.11$. The alloys were arc melted under argon atmosphere using 99.999 mass% pure Cu, 99.99 mass% pure Ni, and 99.9 mass% pure Y. The alloys were annealed at 800 °C for 1 week. The alloys were characterized by XRD, thermal expansion, and electrical resistivity measurement. Electrical resistivity and thermal expansion measurements of CuY alloy were carried out between liquid He and 800 K (527 °C). They showed the CsCl type CuY alloy undergoes a phase transition starting at T_L = 120 K (−153 °C) and ending at ~60 K (−213 °C). The phase transition takes place through discrete jumps. On heating, the CuY alloys from the liquid He temperature (4.2 K) to higher temperatures, the low temperature phase remained stable to T_H = 510 °C and complete transformation to CsCl type structure occurred above 690 °C. The phase transition of CsCl type CuY phase to low temperature phase is associated with a large hysteresis and involves a volume expansion of ~1.5%. The x-ray diffraction pattern of the low temperature phase (CuY alloy first cooled to liquid He temperature, heated to room temperature and then filed to prepare powder for XRD work) showed that it is similar to the diffraction pattern of the NdCu phase which is of FeB type structure. Pressure dependence of transformation of the CuY phase showed that with increase in pressure T_L decreased and vanished at ~4 K bar pressure, i.e., the CsCl type structure remained stable down to 4.2 K. On replacing Cu by Ni, the $Cu_{1-x}Ni_xY$ alloys were found to be single phase CsCl type CuY phase to x = 0.11. The lattice parameter of the $Cu_{1-x}Ni_xY$ alloys were found to decrease linearly with increase in x (Fig. 8). The $Cu_{1-x}Ni_xY$ alloys with x to 0.11 were also found to transform to the low temperature FeB type structure. The T_L and T_H temperatures for the $Cu_{1-x}Ni_xY$ increased with increase in Ni content x (Fig. 9). The difference in transformation temperatures, $\Delta T = T_H - T_L$, was found to decrease with increase in Ni content x. The CsCl type CuY phase was found stable at room temperature to at least x = 0.11. Since NiY phase is also of FeB type structure, it is possible that solid solution of NiY and CuY (FeB type) may form a continuous solid solution region.

Since Ni_3Y phase has been found a good hydrogen storage material, [1984Bur] investigated what effect replacement of Ni by other transition elements has on the hydrogen

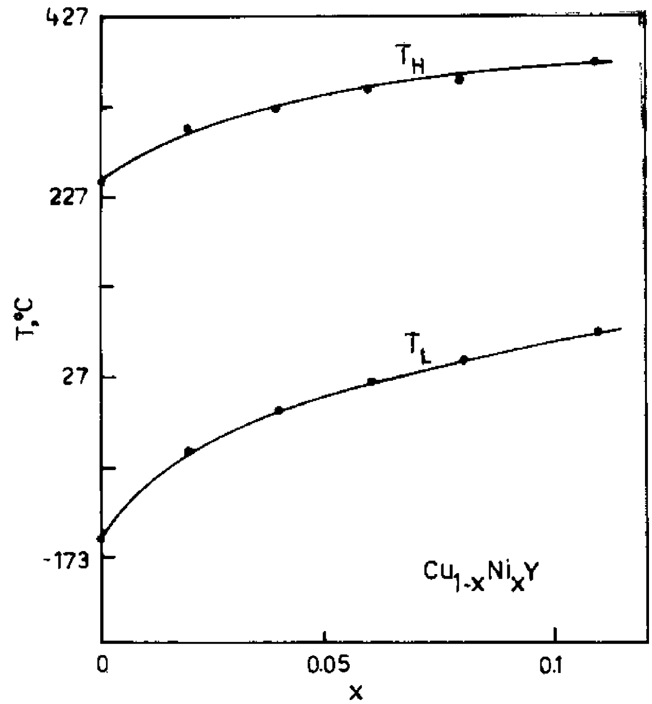

Fig. 9 The transformation temperature T_L of the low temperature phase and T_H the high temperature phase of the $Cu_xNi_{1-x}Y$ alloys [1988Kad]

storage property of Ni_3Y. $M_{0.5}Ni_{2.5}Y$ alloys with M = Cr, Mn, Fe, Co, and Cu were investigated. The $Cu_{0.5}Ni_{2.5}Y$ alloy was prepared by arc melting pure metals, Y of 99.9 mass% purity and Cu and Ni of 99.9 mass% purity, annealed at 497 °C for 250 h and characterized by XRD. The $Cu_{0.5}Ni_{2.5}Y$ alloy was found to be single phase with the same crystal structure as the Ni_3Y phase (Ni_3Pu type structure) and the lattice parameters were found to be a = 0.5003 nm and c = 2.451 nm. Hydrogenation was carried out between 0 and 100 °C temperatures at pressures ≤6 MPa. The hydride phase produced was not pyrophoric. At 5 MPa and 293 K (20 °C) the $Cu_{0.5}Ni_{2.5}Y$ alloy was found to absorb 4.1 at. H/formula unit of the phase, only slightly lower than the Ni_3Y phase (4.5 at. H/formula unit). The crystal structure of the hydride phase was the same as the Ni_3Pu type structure of Ni_3Y phase and the lattice parameters of the hydride $Cu_{0.5}Ni_{2.5}YH_{2.3}$ were found to be a = 0.5080 nm and c = 2.680 nm. The decomposition of the hydride was found to start at ~350 K (77 °C) and is completed by 408 K (135 °C).

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# indicates presence of phase diagram.

Cu-Ni-Y evaluation contributed by **K.P. Gupta**, The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1996. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary nickel alloys.