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## The Cu-Nb (Copper-Niobium) System

63.546 amu

92.9064 amu

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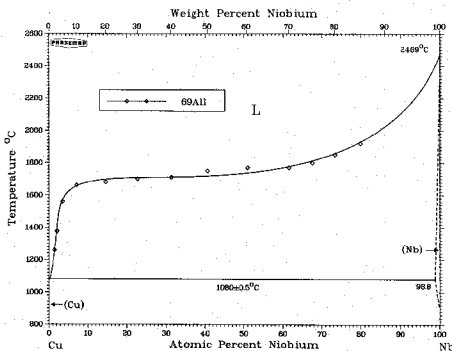
### Equilibrium Diagram

The Cu-Nb equilibrium diagram, with data from [69All] and [79Pet], is shown in Fig. 1. The equilibrium phases are: (1) the liquid; (2) the face-centered cubic terminal solid solution, based on Cu with limited solubility of Nb; and (3) the body-centered cubic terminal solid solution, based on Nb with limited solubility of Cu.

The Cu-Nb system is a typical example of a system in which the strong effect of compositional impurities in modifying the nature and extent of distribution of coexisting

phases is observed. The S-shaped, near-horizontal appearance of the liquidus in Fig. 1 indicates that the free-energy curve of the liquid is flat over a range of composition and temperature, and it implies that a miscibility gap may be observed. However, the miscibility gap does not appear in the equilibrium Cu-Nb diagram. It is well known that impurities from starting materials, or picked up during processing (or both), can influence the relative shape and positioning of the free-energy curves of the coexisting phases and, thus, the relative stability of the phases. Such an effect of impurities is encountered in this system.

Fig. 1 Cu-Nb Phase Diagram



Showing liquidus data of [69All] and 1080 °C isotherm from [79Pet].

D. J. Chakrabarti and D. E. Laughlin, 1982.

Fig. 2 Cu-Nb Phase Diagram

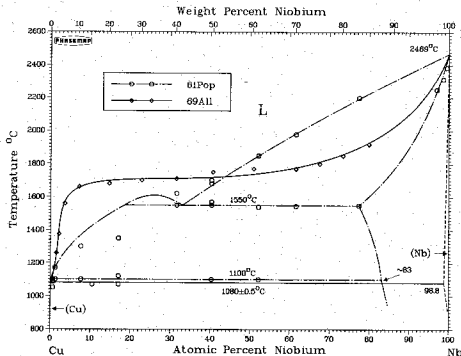


Diagram of [61Pop] superimposed on the accepted diagram shown in Fig. 1.

D.J. Chakrabarti and D.E. Laughlin, 1982.

In Fig. 2, the equilibrium diagram as proposed by [61Pop] is superimposed on the diagram of Fig. 1. The Nb used was of 99.5 wt.% purity, having the impurities 0.22 wt.% Ta, 0.1 wt.% Ti, 0.05 wt.% Fe, 0.05 wt.% Si, and 0.05 wt.% C. Both thermal analysis and optical measurement confirmed the existence of an invariant reaction at approximately 1550 °C in the midcomposition range. Based on this, a monotectic reaction with the liquid miscibility gap occurring somewhere between 25 and 42 wt.% Nb was postulated by [61Pop]. Although no direct metallographic evidence for the occurrence of the gap was obtained, their inference is supported by the recent findings of [78Ver], who studied the chill cast solidification behavior of Cu-Nb alloys. This study established that a monotectic reaction is induced by the presence of dissolved oxygen, and this is further assisted by rapid solidification of the melt. Using a 99.92+ wt.% purity Nb with the oxygen impurity picked up during melting from crucibles, it was demonstrated that liquid immiscibility occurred in 15 and 20 wt.% Nb alloys at oxygen levels of 2300 ppm on up, depending on the solidification rate. Occurrence of other impurities, such as 0.023 wt.% Zr, C, 0.01 wt.% Al, or 0.05 wt.% Y had no recognizable effect.

Similar effects of oxygen in causing liquid immiscibility were noticed earlier by [71Sch] in Cu-Nb alloys prepared from pressed bars of respective metal powders by arc melting. The phenomenon occurred in alloys of 10 to 40 wt.% Nb and was attributed to the relatively high oxygen content in the metal powders, because alloys made from bulk material using 99.9 wt.% nominal purity Nb were free from liquid immiscibility effects.

The Nb used by [61Pop] appears to be relatively free from oxygen, but its pick-up is likely during melting. Besides,

some of the other impurities present in the Nb can also have combined effects. For example, the presence of carbon is known to induce liquid immiscibility in Cu-Fe systems [63Kie]. Interestingly, the miscibility gap noticed by [78Ver] at 15 and 20 wt.% Nb is outside the composition range suggested by [61Pop]. Also, [78Ver] did not observe a gap to exist at 40 wt.% Nb. This lies within the gap according to [61Pop]. This further demonstrates the sensitivity of this system to the different impurities in determining the occurrence and location of the various phase fields.

Similar effects of impurities on phase equilibria are manifested in the Cu-V system. The presence of interstitial impurities in V, such as C, O, and N, was found to decrease the monotectic temperature by more than 200 degrees and to double the terminal solid solubility at the V end. Impurities also increased the area of the miscibility gap. On the other hand, both the peritectic temperature and the terminal solid solubility based on Cu were affected very little by impurities [77All, 62Sav, 64Sav, 67Efi].

Apparently the effects of impurities on the phase stability of Cu-Nb alloys are similar to that on Cu-V alloys [81Smi]. Here also, the impurities tend to stabilize the miscibility gap, and the Nb end of the terminal solid solution field is considerably enlarged. Thus, the solid solubility of Cu in Nb at the peritectic temperature is ~12 wt.% (~17 at.%) as reported by [61Pop], compared to the accepted value of ~2 at.% by [69All]. The corresponding peritectic temperatures, on the other hand, are 1100 and 1090 °C, respectively, showing that it is less sensitive to impurity content. Likewise, the (Cu) terminal solid solubility results of [61Pop] are in reasonable agreement with those of [57Arg], who also reported a peritectic transformation.

Table 1 Proposed Transformation, Temperature, and Composition(a)

Reference	Temperature, °C	Liquid composition, at.% Nb	Reaction type
[61Pop]	1100	0.1	Peritectic
[71Sch]	1085 ± 5	...	Peritectic
[69All]	1090 ± 2	0.1	Peritectic
[57Arg]	1093	...	Peritectic
[79Pet]	1080 ± 0.5	0.2	Eutectic
[78Som]	...	0.3	Eutectic

(a) Accepted values taken from [79Pet].

Apparently, for Cu-rich alloys, the impurity concentration due to Nb is too diluted to have effects comparable in size to that of Nb-rich alloys.

**Liquidus and Solidus.** Both [61Pop] and [69All] determined the complete liquidus by using the thermal analysis method. For reasons described above, the liquidus as given by [61Pop] is incorrect. Unfortunately, [69All] did not report impurity specifications for the Nb and Cu used in their work. The liquidus determined by [71Sch] using 99.9 wt.% pure Nb supports qualitatively the work of [78Ver]. However, because of better consistency and considerably less scatter in the data of [69All] compared to those of [71Sch], the liquidus results from [69All] are accepted for the system. It is, however, possible that with the use of increased purity Nb, an upward revision of the liquidus in the temperature scale would occur. This is evidenced from the findings of [78Ver], who reported a liquidus temperature of slightly above 1730 °C for a 20 wt.% Nb alloy, which is nearly 40 °C higher than that of [69All].

The invariant solidus temperatures reported from different works are: 1090 ± 2 °C [69All], 1100 °C [61Pop], 1085 ± 5 °C [71Sch], 1093 °C [57Arg], 1080 ± 0.5 °C [79Pet], and 1067.5 °C [70Sin]. Because the fusion point of Cu is 1084.87 °C [81BAP], the data of [69All], [61Pop], [71Sch], and [57Arg] suggest a peritectic-type transformation, as shown in Fig. 3(a), whereas that of [79Pet] and [70Sin] show a eutectic type of transformation, as shown in Fig. 3(b). As discussed, the data from [61Pop] are affected by impurity contents in Nb. The purity of Nb used by [69All] and [57Arg] is not stated specifically, and the uncertainty in the invariant temperature reported by [71Sch] precludes any unique decision regarding the type of transformation. Thus, the validity of the peritectic transformation that the works of [69All], [61Pop], [71Sch], and [57Arg] suggest is open to debate.

In contrast, the Nb used by [79Pet] is of high purity (99.96 wt.%), and the results are based on thermal analysis utilizing both heating and cooling cycles, as well as on metallography and X-ray. Also, a transition from coarse to very fine (random) dispersion of Nb in Cu with increasing solidification rate of the melt was observed by [73Tsu] and [77Rob]. These fine precipitates appeared dendritic under the electron microscope [78Som], showing that they most likely formed during solidification and not by solid-phase transformation, as postulated earlier. A highly dispersed oriented microstructure was obtained by [78Som], by directional solidification of 1.5 wt.% Nb alloy, in which the liquid that solidified last was enriched in Nb. This suggests that the partition coefficient,  $k$ , is less than 1 for the solute. This was verified experimentally by the

Table 2 Solid Solubility of Nb in Cu

Temperature, °C	Composition, at.% Nb from reference				
	[61Pop]	[71Sch]	[57Arg]	[79Pet](a)	[72Rok]
1100	~1.14	...	...	...	...
1093	...	...	~1.1	...	...
1085	...	<0.7	...	...	...
1080	...	...	...	0.10	...
1050	...	...	~0.6	...	...
1000	~0.45	...	~0.35	...	...
900	...	...	...	...	0.11
800	...	...	~0.30	...	...
600	...	...	...	...	0.05
450	...	...	...	...	0.02
20	~0.2	...	...	...	...

(a) Accepted values taken from [79Pet].

Table 3 Solid Solubility of Cu in Nb

Temperature, °C	Approximate composition, at.% Cu from reference				
	[61Pop]	[71Sch]	[62Sav], [64Sav], [67ER]	[69All]	[79Pet](a)
1100	~17	...	...	...	...
1090	...	...	...	~2	...
1085	...	≥3.6	...	...	...
1080	...	...	...	...	~1.2
1064-709	...	...	0.10	...	...
20	~4	...	...	...	...

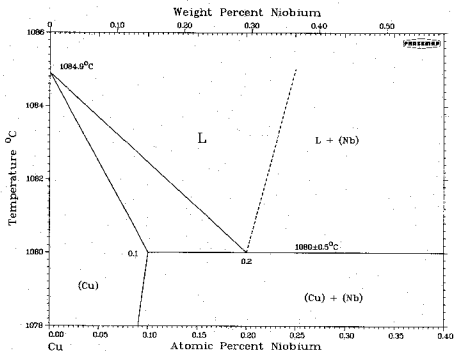
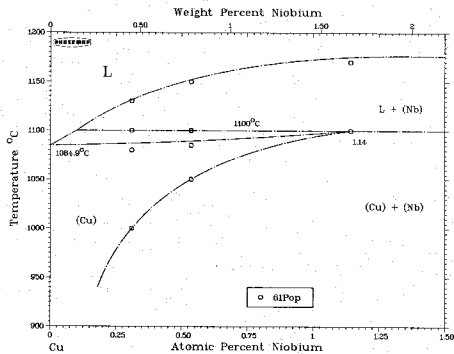
(a) Accepted values taken from [79Pet].

authors, who obtained  $k \sim 0.5$  with Cu-0.16 wt.% Nb and Cu-0.28 wt.% Nb melts. These findings support a eutectic rather than a peritectic transformation. Similarly, the solubility figures for Nb in Cu reported by [72Rok] are compatible with those of [79Pet] and at variance with those suggesting a peritectic reaction. The reported works of [78Som] and [72Rok] are of recent origin and are expected to have access to better grade Nb than possible in earlier times (e.g., [78Som] used 99.8 wt.% Nb). In view of these considerations, following [79Pet], the invariant temperature is taken at 1080 ± 0.5 °C, accepting a eutectic-type of transformation. The accepted composition of the eutectic is 0.3 wt.% (0.2 at.%) Nb, as reported by [79Pet]. The data of transformation temperature and the corresponding compositions of the liquid from various authors are shown in Table 1. Enlargements of the Cu-rich end of the phase diagram, showing a peritectic transformation [61Pop] and a eutectic transformation [79Pet], are shown in Fig. 3(a) and 3(b), respectively.

No compounds or intermediate phases occur in this system. Below 1080 °C, a wide two-phase field exists, consisting of an fcc terminal solution based on Cu and a bcc terminal solution based on Nb.

The results of the solubility of Nb in Cu, and Cu in Nb, from different authors are shown in Tables 2 and 3, respectively. The accepted values corresponding to the invariant temperature at 1080 °C are those due to [79Pet]. These values are considerably lower than the ones reported in relation to the peritectic reaction. The limiting solubility of Nb in Cu at ambient temperature is very small, as reported by [72Rok], whereas that for Cu in Nb is not accurately known.

Fig. 3 Possible Reactions in Cu-rich Cu-Nb Alloys



(a) Peritectic reaction, after [61Pop]; (b) Eutectic reaction, after [79Pet].

### Metastable Phase Equilibria

As discussed in "Equilibrium Diagram", a metastable liquid miscibility gap underlies the nearly flat liquidus in the midcomposition range of the Cu-Nb system. Oxygen has a strong effect in stabilizing this miscibility gap [78Ver]. Other interstitials, such as C and N, also are suspected to have similar effects. Solidification kinetics also have sig-

nificant effects, as demonstrated by [78Ver]—a higher rate of solidification of the melt favors the formation of the miscibility gap by suppressing the precipitation of the stable bcc Nb-terminal solid solution phase.

The impurities in Nb stabilize the Nb-base bcc phase ( $\beta$ ) and could be responsible for the peritectic transformation reported at the Cu-end of the phase diagram. This inference is consistent with a shallow or humped free-energy

Table 4 Crystal Structure

Phase	Approximate composition(a), at.% Nb	Pearson symbol	Space group	Prototype	Lattice parameter, nm a	Comment	Reference
(Cu) or $\alpha$	0	cF4	Fm3m	Cu	0.36147	b	[Landolt-Börnstein]
(Nb) or $\beta$	98.8-100	cI2	Im3m	W	0.3616 0.330307 0.330326 0.32986 $\pm 0.00001$	c d e f	[79Pet] [79Pet] [79Pet] [67Tay]

(a) From the phase diagram. (b) At 18 °C and 0% Nb. (c) Samples saturated with Nb and quenched from unspecified high temperatures. (d) Sample quenched from 1030 °C and containing 1.06 to 1.09 at.% Cu. (e) Sample quenched from 750 °C and containing 1.06 to 1.09 at.% Cu. (f) Zone-refined, degassed sample, 100% Nb; maximum total impurity 25 ppm, oxygen 9 ppm.

curve of the liquidus and the lowering of the  $\beta$  free-energy curve by means of impurities. A common tangent construction between the Cu-base fcc  $\alpha$ , the liquid, and the  $\beta$ -phase free-energy curves could then lead to a peritectic transformation with an extended solubility of Cu in Nb. Conversely, lowering the impurity level in Nb is commensurate with an upward shift of the  $\beta$  free-energy curve and, hence, would lead to a eutectic transformation with a reduced solubility of Cu in Nb.

### Crystal Structure and Lattice Parameters

The lattice parameter of bcc Nb metal is very sensitive to oxygen content, and decreases progressively even as the last traces of oxygen are removed. Earlier reported values are invariably high, due to high oxygen content in the metal. Using degassed and zone-refined Nb metal, the extrapolated oxygen-free lattice parameter value reported by [67Tay] is  $0.32986 \pm 0.00001$  nm, the lowest value reported so far. The corresponding lattice parameters for the bcc solid solution based on Nb are given in Table 4. Considering the possibility of the presence of oxygen in the prepared alloys, the small difference in the lattice parameters between the solid solution phase and elemental Nb is not very meaningful in determining the extent of solubility of Cu in the terminal solution. Also presented in Table 4 are the lattice parameter values for Cu and for the terminal solid solution based on Cu. The small difference between these two values is consistent with the very restricted solubility of Nb in the fcc terminal solid solution of Cu, as indicated in Fig. 1 and 3(b).

### Thermodynamics

The activity of Cu in the two-phase region bounded by the liquidus and the Nb-rich solidus, and between the temperature 1450 and 1750 K, was measured by [81Bai] by the Knudsen effusion method. Two alloys, of compositions 15 and 31 at.% Nb, were used to check the consistency of the results. Partial molar Gibbs energies,  $\Delta\bar{G}_{Cu}$ , derived from these experimental results when subjected to a linear least-squares fit, had the following expression [81Bai]:

$$\Delta\bar{G}_{Cu} = 2105 - 1.59 T \quad \text{J}\cdot\text{mol}^{-1}$$

It was found, however, that a nonlinear correlation of the above data with temperature was necessary for deriving the Gibbs energy function of the liquid,  $\Delta G_{Nb}$ , in order for the calculations to conform to a peritectic transformation at around the temperature and concentration suggested by [69All]. Modification in these calculations is called for,

Table 5 Thermodynamic Interaction Parameters in Cu-Nb System

Phase	$H^{XS}/X_{Cu}X_{Nb}$ (J/mol)	$S^{XS}/X_{Cu}X_{Nb}$ (J/mol·K)	Composition	Range Temperature, K
Liquid	111 294	41.84	$0 \leq X_{Cu} < 1$	$1200 \leq T \leq 2800$
bcc	46 024	0	$0 \leq X_{Cu} \leq 1$	$300 \leq T \leq 2800$
fcc	98 742	41.84	$0 \leq X_{Cu} \leq 1$	$300 \leq T \leq 1400$

From [78Kau].

because of the occurrence of a eutectic transformation and the related changes in the solubility limits.

Phase equilibria in the Cu-Nb system also was calculated by [78Kau], using the lattice stability values of Cu and Nb [78Kau, 70Kau] and the derived interaction parameter values for the different phases, on the basis of the experimental diagram of [69All]. These interaction parameter values for the excess functions of  $H$  and  $S$  are given in Table 5. No other thermodynamic data are available on this system.

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**Cu-Nb**  
**Cu-Rh**

Cu-Nb (continued)

**Provisional**

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