

The Cu-Rh (Copper-Rhodium) System

63.546 amu

102.9055 amu

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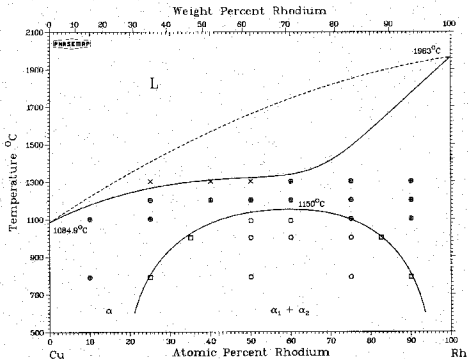
Equilibrium Diagram

The equilibrium phases in the Cu-Rh system are: (1) the liquid; and (2) the face-centered cubic phase that forms a continuous solid solution between Cu and Rh at high temperature, and decomposes at lower temperatures into two

face-centered-cubic solid solution phases, one rich in Cu and the other rich in Rh.

Liquidus, Solidus and Solvus. The provisionally evaluated equilibrium diagram of the Cu-Rh system is shown in Fig. 1 and is derived primarily from the work of [71Rau], based on microstructural and X-ray investigations. Be-

Fig. 1 Cu-Rh Phase Diagram



x = fusion point by metallurgy; \oplus = single phase in X-ray and microscopy; \circ = two phase in X-ray and microscopy; \square = two phase in X-ray. From [71Rau].

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cause no thermal analysis measurements were made, the liquidus is not determined.

The system is characterized by the presence of an isomorphous solid across the entire diagram in the temperature regions immediately below the solidus. The solidus determined by the incipient fusion technique appears nearly flat between approximately 25 and 50 at.% Rh. This would imply a shallow free-energy versus composition curve of the solid in corresponding composition and temperature ranges and a tendency toward formation of a miscibility gap at lower temperatures.

A single-phase continuous solid solution field exists between the components below the solidus. At still lower temperatures, the phase field enters into a wide miscibility gap wherein it separates into two equilibrium isostructural phases, one of which is rich in Cu and the other in Rh. The critical temperature and composition of the gap are 1150 °C and 60 at.% Rh, according to [71Rau].

The likelihood of the existence of a miscibility gap in the solid state was indicated in an earlier work by [64Luo]. They obtained a continuous single-phase metastable solid solution by rapid solidification of the melt over the entire composition range. On subsequent annealing of two of these alloys, 50 and 75 at.% Rh at 600 °C, the single-phase fcc structure separated into two equilibrium fcc phases of different lattice parameters, as observed by X-ray diffraction. This suggested the existence of either a miscibility gap conforming to the findings of [71Rau], or two fcc terminal solid solutions, as suggested in an earlier work by [35Svy].

Based on thermal, microstructural, X-ray, and hardness results, [35Svy] postulated a limited solid solubility of the components with approximately 0 to 20 and 90 to 100 at.% Rh, respectively, and a peritectic reaction at about 1100 °C. Possibility of nonattainment of equilibrium in their work because of insufficient annealing was pointed out by [Hansen]. In light of the findings of [71Rau], it appears that the lack of equilibrium and/or unspecified impurities in the alloy might have resulted in greater stabilization of the liquid phase and perhaps also of the miscibility gap, giving rise to the truncation of the gap by the peritectic invariant. The material purity specified by both [71Rau] and [64Luo] was 99.9% or better for both Cu and Rh, whereas the same is not known for [35Svy].

[64Luo] reported good correspondence of the phase boundary composition, namely 18.5 and 90.8 at.% Rh, estimated from the lattice parameters of their samples annealed at 600 and 800 °C, with the values of 20 and 90 at.% Rh at 800 °C from [35Svy]. However, they were not explicit regarding the temperature at which the lattice parameters were measured.

The miscibility gap boundary given by [71Rau] has been modified slightly in this evaluation in order to include, inside the gap, the compositions for which the X-ray showed a two-phase structure. This appears reasonable because X-ray is not sensitive to the presence of small amounts of a second phase. A microstructural study would have been more definitive but is not reported. The gap boundaries at 800 °C, according to [71Rau], are approximately at 25 and 90 at.% Rh.

A maximum in the microhardness was observed at 60 at.% Rh for alloys quenched from the single-phase region. Both X-ray and metallography confirmed the alloys to be single

Table 1 Crystal Structure And Lattice Parameter of Cu-Rh Alloys

Approximate composition, at.% Rh	Lattice parameter, nm		Comments
	Equilibrium phase(a)	Metastable phase(b)	
0(Cu)	0.36147	...	At 18 °C from [Landolt-Börnstein]
10	0.3625	0.3639	Metastable phase normal cooled
25	0.3655	0.3675	...
35	...	0.3697	...
40	0.3683
50	0.3710	0.3727	...
60	0.3734	0.3747	...
70	...	0.3765	...
75	0.3755
85	...	0.3787	...
90	0.3775	...	At 22.6 °C from [63Ros]
100(Rh)	0.38032

Note: Crystal structure for Cu and Rh and for all the alloys is fcc, $cF4$, Cu prototype, and space group $Fm\bar{3}m$. (a) From [71Rau] unless noted. (b) From [64Luo].

phase [76Vis]. The existence of ordered structures at 25, 50, and 75 at.% Rh suggested by [35Svy] is not correct. The thermal arrest at about 1300 °C, observed by the same authors on some alloys in the midcomposition range, apparently corresponds to the flat solidus existing in that region.

Metastable Phase

The existence of a metastable single-phase continuous solid solution between Cu and Rh was established by [64Luo], based on rapid solidification of the alloys from the melt. This is in agreement with the generally accepted conditions for mutual solubility of metals in the solid state, which Cu and Rh satisfy. Transition to equilibrium phases occurred when the samples were heated at 600 °C for seven to ten days.

Crystal Structure and Lattice Parameter

The Cu-Rh alloys in the solid state have an fcc structure. The lattice parameter varies linearly with composition within the limits of experimental error, for alloys quenched from high temperature (~1200 °C) that retained the single-phase structure. On the other hand, the lattice parameter versus composition plot for the metastable single-phase alloys shows positive deviation from linearity. The increment in the lattice parameter (from linearity) in the latter situation is apparently a consequence of increased quenched-in vacancies in these alloys due to their rapid solidification from a much higher temperature (i.e., melt). The results are presented in Table 1.

Thermodynamics

No experimental thermodynamic data are available on the Cu-Rh system. Thermodynamic interaction parameters for the liquid (L and L') and the fcc phases (A and A') were derived from the experimental phase diagram data by [80Ove] and by [79Les], on the basis of regular and subregular solution models, respectively. The results are

Table 2 Thermodynamic Interaction Parameters in Cu-Rh System

Thermodynamic model	Interaction parameter, J/mol					Experimental points (a)	References
	L	Liquid	L'	A	fcc		
Regular solution	20 092	22 604	...	$x_L = 0.25, x_{cr} = 0.63$ at $T = 1673; T_{cr} = 1373$ $(x_{cr} = 0.5)$ (b)	[80Ovc]
Subregular solution	8 414	19 799	...	14 609	11 051	$x_L = 0.3, x_{cr} = 0.75$ at $T = 1673; T_{cr} = 1373$ $x_{cr} = 0.65$	[79Les]

(a) Composition, x , in at.% Rh, temperature, T , in K. Subscripts l = liquid; α = fcc; cr, α = critical point in α . (b) Assumed value.

presented in Table 2. Experimental data used in the calculation also are shown in the table.

The inadequacy of the regular solution model in this system is evident in the derived phase diagram based on the above interaction parameters (L and A), because the resultant miscibility gap is symmetrical and the critical composition is at $\alpha = 50$ at.% Rh, contrary to the apparent asymmetry in the experimental diagram. In the subregular solution approximation by [79Les], additional composition-dependent terms were added to the excess free-energy expression to skew the symmetrical $x(1-x)$ composition dependence of the interaction energy in the regular solution model, so that:

$$G^{XS}(x) = x(1-x)[W_K + x \cdot W_K']$$

where $W_K = L$ or A and $W_K' = L'$ or A' . No temperature dependence of the interaction energy was assumed, similar to the requirements in a regular solution model.

The lattice stability parameters for Cu and Rh for the relevant phases, liquid and fcc, are presented in Table 3 from [78Kau, 70Kau].

Cited References

35Svy: O. E. Svyagintsev and B. K. Brunovskiy, *Izv. Sektora Platiny*, 12, p 37-66 (1935), as cited by [Hansen].

Table 3 Lattice Stability Values for Cu and Rh

Metal	Free energy difference, J/mol	Temperature, K	Reference
Cu... $^{\circ}G^L - ^{\circ}G^{fcc} = 13\ 054 - 9.623 T$		$T > 300$	[78Kau]
Rh... $^{\circ}G^L - ^{\circ}G^{fcc} = 18\ 763 - 8.372 T$		$T = 2240$	[70Kau]

63Ros: R. G. Rose and W. Hume-Rothery, *J. Less-Common Met.*, 5, p 258-270 (1963).

64Luo: H. L. Luo and P. Duwez, *J. Less-Common Met.*, 6, p 248-249 (1964).

70Kau: I. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*, Academic Press, p 69 (1970).

71Rau: Ch. J. Raub, E. Roschel, D. Menzel and M. Gadhof, *Metall.*, 25(7), p 761-762 (1971).

76Vis: K. Viswanathan, H. R. Khan and Ch. J. Raub, *J. Phys. Chem. Sol.*, 37, p 431-432 (1976).

78Kau: I. Kaufman, *Calphad*, 2(2), p 117-146 (1978).

79Les: A. G. Lesnik, V. V. Nemoshkalenko and A. A. Ovcharenko, *Akad. Nauk Ukr. SSR, Metallofiz.*, 75, p 20-31 (1979) in Russian.

80Ove: A. A. Ovcharenko, *Fiz. Metall. Metalloved.*, 49(5), p 1013-1020 (1980) in Russian; translated as *Phys. Met. Metall.*, 49(5), p 96-102 (1980).

81BAP: *Bulletin of Alloy Phase Diagrams*, 2(1), p 146 (1981) for melting points of elements with corrections to conform to the 1968 temperature scale.