

The Cu-Hf (Copper-Hafnium) System

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Equilibrium Diagram

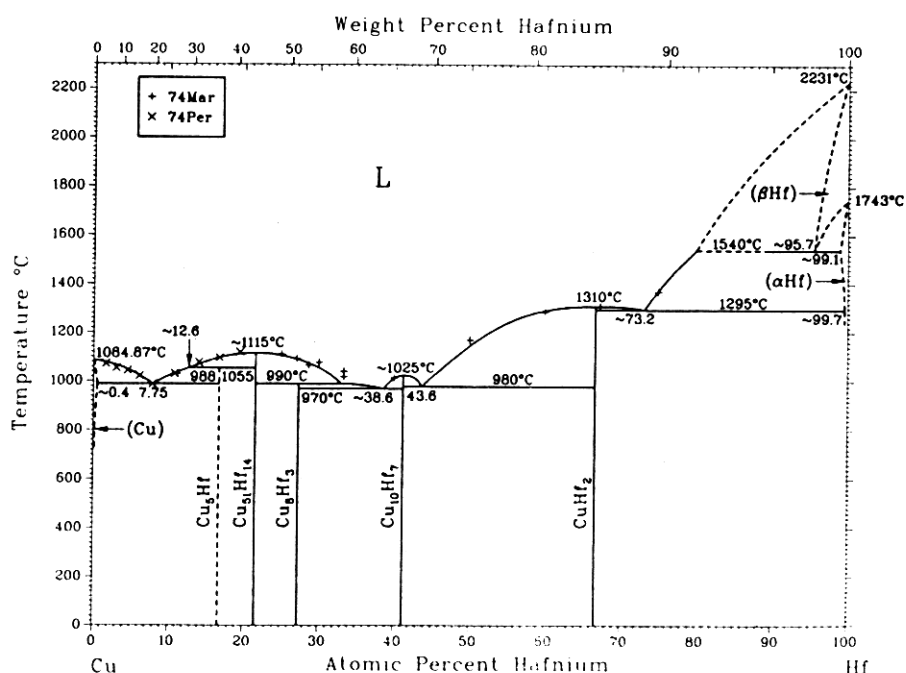
The assessed Cu-Hf equilibrium diagram, shown in Fig.1, consists of (1) the liquid, L; (2) the fcc terminal solid solution (Cu), with a maximum solid solubility of ~0.4 at.% Hf; (3) the intermediate phase Cu_5Hf , with an undetermined crystal structure and stable up to the peritectic melting temperature of 1055 °C; (4) the Ag_5I_4 -type hexagonal intermediate phase $\text{Cu}_5\text{Hf}_{14}$, stable up to the congruent melting point of ~1115 °C; (5) the orthorhombic phase Cu_8Hf_3 with a new prototype crystal structure, stable up to the peritectic temperature of 990 °C; (6) the orthorhombic $\text{Ni}_{10}\text{Zr}_7$ -type intermediate phase $\text{Cu}_{10}\text{Hf}_7$, stable up to the congruent melting temperature of ~1025 °C; (7) the tetragonal MoSi_2 -type intermediate phase CuHf_2 , stable up to the congruent melting temperature of 1310 °C. (8) the hexagonal Mg-type terminal solid solution, (αHf), stable up to 1743 °C and having a maximum solid solubility of ~0.9 at.% Cu at 1540 °C; (9) the cubic W-type terminal solid solution, (βHf), stable between 1540 °C and 2231 °C and having a maximum solid solubility of ~4.3 at.% Cu.

There has been confusion with regard to the stoichiometries of some of the reported phases. Earlier

reviews of this system by [Hansen], [Elliott], and [Shunk] reported the existence of only Cu_2Hf and CuHf_2 . [67Wat] examined alloys from 0.6 to 33.3 at.% Hf by metallography and X-ray microanalysis and reported that the intermediate phase richest in Cu has the stoichiometry Cu_7Hf_2 . Subsequently, [74Mar] investigated the Cu-Hf system using X-ray, DTA and metallography. Fifteen alloys with compositions between 15 and 85 at.% Hf were prepared by arc melting appropriate amounts of 99.999% (not specified, presumably wt.%) pure Cu and 99.93% pure Hf. The authors reported the congruent formation of Cu_3Hf , Cu_3Hf_2 , and CuHf_2 at 1110, 1015, and 1310 °C, respectively, and the peritectic formation of Cu_5Hf_2 at 990 °C. Four eutectics were reported: Cu-Cu $_5\text{Hf}$ (950 °C, 6 at.% Hf), Cu_5Hf_2 - Cu_3Hf_2 (970 °C, 36.8 at.% Hf), Cu_3Hf_2 - CuHf_2 (980 °C, 43.6 at.% Hf), and CuHf_2 -(αHf) (1295 °C, 72.2 at.% Hf). [74Pie] studied the Hf-rich portion of the Cu-Hf system between 72.7 and 100 at.% Hf using DTA and metallography. The Hf used in their study contained 1.5 wt.% Zr and 200 ppm oxygen, which could have affected the results at the Hf-rich

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Fig. 1 Assessed Cu-Hf Phase Diagram



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Cu-Hf

end by depressing the melting point of Hf. [74Pie] proposed the eutectic decomposition of liquid Cu-Hf into (α Hf) and CuHf₂ at 1295 °C, which agrees with [74Mar], and the metatectic decomposition of (β Hf) into (α Hf) and L at 1540 °C. [74Per] established the Cu-rich end of the Cu-Hf system by DTA, metallography and electron microprobe analysis. They observed a terminal eutectic between (Cu) and Cu₅Hf at 7.75 at.% Hf and 980 °C, which is in disagreement with the data of [74Mar]. In addition, [74Per] reported the peritectic formation of Cu₅Hf at 1055 °C, and the congruent formation of Cu₄Hf at ~ 1130 °C. [74Per] identified the compositions of these phases with electron microprobe analysis. [75Bse] examined alloys from 20 to 70 at.% Hf using metallography and X-ray analysis, and reported the existence of compounds with

stoichiometries Cu₁₀Hf₇ and Cu₅₁Hf₁₄, with the structure types Ni₁₀Zr₇ and Ag₅₁Gd₁₄, respectively, and a peritectically formed phase with stoichiometry Cu_{0.72}Hf_{0.28}. Note that the Hf used in their work contained 3 wt.% Zr, but because [75Bse] observed that the Cu-Hf system is analogous to Cu-Zr, the effect of Zr may not be serious. It is clear that the phases designated Cu₃Hf and Cu₃Hf₂ by [74Mar] are identical to Cu₅₁Hf₁₄ and Cu₁₀Hf₇, respectively. Crystallographic analysis by [75Gab] confirmed the existence of Cu₅₁Hf₁₄ with the Ag₅₁Gd₁₄ structure. Moreover, [75Gab] have shown that the phase designated Cu₄Hf by [74Per] is correctly described by the formula Cu₅₁Hf₁₄. The phase observed by [75Bse] at 28 at.% Hf was subsequently assigned the correct formula Cu₈Hf₃ by [76Bse], who conducted a detailed crystal-

Table 1 Experimental Cu-Hf Liquidus Data

Reference	Composition, at.% Hf	Temperature °C	Reference	Composition, at.% Hf	Temperature °C
[74Mar]	0	1083	[74Per]	1.50	1072
	11.0	1030		2.90	1055
	25.0	1110		4.40	1045
	27.0	1093		6.00	1022
	28.6	1066		7.75	988
	30.0	1078		10.70	1031(a)
	33.3	1040		13.90	1078(a)
	33.3	1018		16.67	1096(a)
	40.0	1015		19.40	1120(a)
	50.0	1170			
	60.0	1286	[Melt]	0	1084.87
	67.3	1310		100	2231
	75.0	1370			

Note: Liquidus data presented as published.

(a) Average values from heating and cooling data.

Table 2 Special Points of the Assessed Cu-Hf Phase Diagram

Reaction	Compositions of the respective phases, at.% Hf			Temperature °C	Type
L↔(Cu).....		0.0		1084.87	Congruent point
L↔(Cu)+Cu ₅ Hf.....	7.75	~ 0.4	16.67	988	Eutectic
L+Cu ₅₁ Hf ₁₄ ↔Cu ₈ Hf.....	~ 12.6	21.54	16.67	1055	Peritectic
L↔Cu ₅₁ Hf ₁₄		21.54		~ 1115	Congruent point
L+Cu ₅₁ Hf ₁₄ ↔Cu ₈ Hf ₃	~ 33.0	21.54	27.27	990	Peritectic
L↔Cu ₈ Hf ₃ +Cu ₁₀ Hf ₇	~ 38.6	27.27	41.18	970	Eutectic
L↔Cu ₁₀ Hf ₇		41.18		~ 1025	Congruent point
L↔Cu ₁₀ Hf ₇ +CuHf ₂	~ 43.6	41.18	66.67	980	Eutectic
L↔CuHf ₂		66.67		1310	Congruent point
L↔CuHf ₂ +(αHf).....	~ 73.2	66.67	~ 99.7	1295	Eutectic
(βHf)↔L+(αHf).....	~ 95.7	~ 80.0	~ 99.1	1540	Metatectic
(βHf)↔Hf.....		100		1743	Congruent point
L↔(βHf).....		100		2231	Congruent point

lographic analysis of this phase. The existence of the phase denoted Cu₂Hf by [Elliott] has not been clearly established. [79Bse] proposed a Cu-Hf equilibrium diagram based on the data of [74Per] in the region 0 to 20 at.% Hf, those of [74Mar] in the region 20 to 67 at.% Hf, and those of [74Pie] in the region 67 to 100 at.% Hf.

The liquidus data of [74Mar] and [74Per] are listed in Table 1, where the melting points of elemental Cu and β Hf have been accepted from [Melt] as 1084.87 °C and 2231 °C, respectively. The assessed liquidus of the Cu-Hf system, shown in Fig. 1, has been derived primarily from thermodynamic calculations based on the data of [74Mar] and [74Per] (discussed under "Thermodynamic Modeling"). Liquidus data are not available for the region 76 to 100 at.% Hf, although the DTA study of [74Pie] indicated the occurrence of the metatectic reaction (β Hf) \leftrightarrow (Hf) + L at 1540 °C. This is shown in Fig. 1, where the liquidus between 80 and 100 at.% Hf is based on a simple interpolation between 1540 and 2231 °C. The (α \leftrightarrow β) transformation temperature of Hf has been accepted from [81Spe] as 1743 °C. Table 2 shows the compositions and temperatures of the various invariant reactions.

Table 3 Solid Solubility of Hf in (Cu)

Temperature, °C	Composition, at.% Hf	Reference	Method
500.....	0.02	[63Saa]	Metallography
600.....	0.03		
700.....	0.06		
800.....	0.09		
900.....	0.15		
965(a).....	0.31		
1000.....	0.24	[67Wat]	Electrical resistivity, metallography
1050.....	0.13		
600.....	0.04		
700.....	0.06		
800.....	0.10		
850.....	0.14		
900.....	0.19		
950.....	0.23		
970(a).....	0.34		
1000.....	0.29		
1050.....	0.15		

(a) Reported eutectic temperature.

Terminal Solid Solutions

[60Rei] reported a maximum solid solubility of 0.28 wt.% (0.1 at.%) Hf in Cu. [63Saa] studied the solid solubility of Hf in (Cu) by metallography, and observed a maximum solid solubility of 0.87 wt.% (0.31 at.%) Hf at the eutectic temperature, (reported as 965 °C). [67Wat] determined the solid solubility of Hf in (Cu) over the temperature range 600 to 950 °C by electrical resistivity measurements, and over the temperature range 970 °C to the melting point of Cu by metallography. The Hf used in their experiments was reportedly sponge Hf with 98 wt.% purity. [67Wat] observed a maximum solid solubility of 0.96 wt.% (0.34 at.%) Hf at the eutectic temperature of 970 °C, whereas [74Mar] reported a terminal solubility of 0.41 at.% Hf at the eutectic temperature. The solubility data of [63Saa] and [67Wat], listed in Table 3, are in good accord with one another. Although the bulk of the studies showed the Cu-rich terminal eutectic to lie between 950 °C and 970 °C, it has been accepted as 988 °C from [74Per], because this was based on thermal arrest data from at least 8 alloy compositions, and taken during both heating and cooling. The accepted maximum solid solubility of ~0.4 at.% Hf at 988 °C was obtained by extrapolation of the solubility data of [67Wat].

Only limited information is available on the solubility of Cu in (Hf). [74Pie] estimated the solubility in (α Hf) to be ~0.3 at.% Cu and ~0.9 at.% Cu at the invariant temperatures of 1295 °C and 1540 °C, respectively. The maximum solid solubility in (β Hf) was estimated by [74Pie] to be ~4.3 at.% Cu at the metatectic temperature of 1540 °C.

Crystal Structures and Lattice Parameters

Terminal Solutions

Lattice parameter data are not available for any of the terminal solid solutions. However, the lattice parameters of (Cu) and (α Hf) should not vary significantly from the respective elemental lattice parameters, because the terminal solubilities in (Cu) and (α Hf) are fairly restricted.

Cu₅Hf

No structural analysis has been performed on the Cu₅Hf phase; however, by analogy with the sys-

Table 4 Cu-Hf Crystal Structure Data

Phase	Composition(a), at.% Hf	Pearson symbol	Space group	Strukturbericht designation	Prototype	Comments	Reference
(Cu).....	0 to ~0.4	<i>cF4</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	A1	Cu	...	[King1]
Cu ₅ Hf ₁₄	21.54	<i>hP</i> 68	<i>P6</i> / <i>m</i>	...	Ag ₅ 1Gd ₁₄	...	[75Bse]
Cu ₈ Hf ₃	27.27	<i>oP</i> 44	<i>Pnma</i>	...	Cu ₈ Hf ₃	...	[76Bse]
Cu ₁₀ Hf ₇	41.18	<i>oC</i> 68	<i>Aba</i> 2	...	Ni ₁₀ Zr ₇	(b)	[75Bse]
CuHf ₂	66.67	<i>tI</i> 6	<i>I4</i> / <i>mmm</i>	C11 _b	MoSi ₂	...	[62Nev]
(α Hf).....	~99.1 to 100	<i>hP</i> 2	<i>P6</i> ₃ / <i>mmm</i> <i>c</i>	A3	Mg	< 1743 °C	[Massalski]
(β Hf).....	~95.7 to 100	<i>cI</i> 2	<i>Im</i> $\bar{3}$ <i>m</i>	A2	W	> 1743 °C	[Massalski]

(a) From the phase diagram. (b) Pearson symbol and space group from [Pearson3].

Cu-Hf

Table 5 Cu-Hf Lattice Parameter Data

Phase	Composition, at.% Hf	Lattice parameters, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
(Cu)	0	0.36146	25 °C	[Massalski]
Cu ₅₁ Hf ₁₄	21.54	1.11794	...	0.82457	(a)	[75Bee]
		1.1180	...	0.8235	(b)	[75Gab]
Cu ₈ Hf ₃	27.27	0.78113	0.99490	0.81014	(a)	[75Bee]
Cu ₁₀ Hf ₇	41.18	0.92654	0.92376	1.25872	(a)	[75Bee]
CuHf ₂	66.67	0.31695	...	1.11333	(c)	[62Nev]
		0.31643	...	1.11530	(c)	[79Ess]
(αHf)	100	0.31946	...	0.50511	25 °C	[Massalski]
(βHf)	100	0.3610	>1995 °C	[Massalski]

Note: Selected values are shown in boldface type.

(a) Alloy prepared from 99.99% (not specified, presumably wt.%) pure Cu and zone-refined Hf containing 3% Zr and <0.03% oxygen. (b) Alloy prepared from 99.999% (not specified, presumably wt.%) pure Cu and 99.9% pure Hf. (c) Alloy purity 99.9% or better.

Table 6 Enthalpy of Mixing of Liquid Cu-Hf Alloys

Composition, atomic fraction Hf	Enthalpy of mixing, J/mol
0.0095	790
0.0181	1 410
0.0263	1 990
0.0385	2 850
0.0475	3 480
0.1002	7 000
0.1480	10 140
0.1500	10 430
0.2998	17 210
0.3996	19 010
0.4002	19 210

Note: At 1373 K. From [82Kle].

tematics of the Cu-rare earth systems [88Sub], Cu₅Hf may be isotypic with either the hexagonal CaCu₅- or the cubic AuBe₅-type structure.

Cu₅₁Hf₁₄.

Preliminary analysis by [75Bse] indicated that Cu₅₁Hf₁₄ was isostructural with Ag_{3.6}Gd or Ag₅₁Gd₁₄, the structure of which was determined by [71Bai]. This was confirmed by the detailed crystallographic analysis of [75Gab]. Cu₅₁Hf₁₄ is hexagonal with the space group *P6/m*.

Cu₈Hf₃.

Cu₈Hf₃ was identified by [76Bse] as orthorhombic with the space group *Pnma*. The crystal structure of this phase consists of a stacking of atoms parallel to the (010) plane, with the stacking sequence repeated every four layers. The atoms in the four-fold positions are located on mirror planes at $y = 0.25$ and $y = 0.75$, while the atoms in the eight-fold positions at $y \sim 0$ and $y \sim 0.5$ form puckered layers between the mirror planes. This structure was not reported previously, and no other compounds are known to form with this structure.

Cu₁₀Hf₇.

The crystal structure of Cu₁₀Hf₇ was identified by [75Bse] as isostructural with Ni₁₀Zr₇. The structure is

base-centered orthorhombic with the space group *Aba2*.

CuHf₂.

CuHf₂ has the tetragonal MoSi₂-type structure with the space group *I4/mnm* [62Nev, 79Ess].

Table 4 summarizes the crystal structures and related parameters for the various phases. Lattice parameter data for the phases are listed in Table 5, where the data for the pure elements are from [King1] and [Massalski].

Thermodynamics

Thermodynamic Data.

[82Kle] determined the enthalpy of mixing of liquid Cu with solid Hf at 1373 K over the composition range 0.95 to 40.02 at.% Hf by high-temperature reaction calorimetry. The resulting enthalpies of mixing of liquid Cu-Hf alloys are listed in Table 6. In addition, [82Kle] determined the enthalpy of formation for each of the three congruently melting phases (designated Cu₄Hf, Cu₃Hf₂, and CuHf₂ by the authors) from heat content and heat of solution measurements. These values are listed in Table 7, along with the enthalpies obtained by thermodynamic modeling, described below.

Thermodynamic Modeling.

From liquid enthalpy of mixing data, [82Kle] concluded that the enthalpy interaction parameter for liquid Cu-Hf did not vary significantly with composition. The liquid enthalpy of mixing, therefore, was described by the relation:

$$\Delta_{\text{mix}}H(L) = -77\,800 X_{\text{Hf}}(1 - X_{\text{Hf}}) \text{ J/mol} \quad (\text{Eq 1})$$

Because no thermodynamic data are available for the Cu-Hf system, the experimental phase boundaries were combined with the limited thermodynamic data reported by [82Kle] to derive the excess entropy of the liquid and the Gibbs energy functions of the intermediate phases, as described in detail below.

In the present approach, the following assumptions were made: (1) the solid phases (Cu) and (αHf) have no significant solid solubilities; (2) the lattice stability

Table 7 Enthalpy of Formation Values for Cu-Hf Intermediate Phases

Phase	Enthalpy of formation, kJ/mol experimental, [82Kle]	present modeling
Cu ₅ Hf.....	...	-17.75
Cu ₅₁ Hf ₁₄	-13.65(a)	-45.54
Cu ₈ Hf ₃	-192.72
Cu ₁₀ Hf ₇	-12.64(b)	-4.15
CuHf ₂	-15.23	-56.12

Note: Standard states are pure solid Cu and pure solid α Hf.
(a) Phase designated "Cu₄Hf" by [82Kle]. (b) Phase designated "Cu₃Hf₂" by [82Kle].

parameters for Cu and β Hf, given in Table 7, are derived from the enthalpies of fusion as well as the melting points of the respective elements. The lattice stability parameter for α Hf is derived from that of β Hf as well as from the enthalpy and temperature of the $\alpha \leftrightarrow \beta$ transformation; and (3) all of the intermediate phases are line compounds, i.e., the phases show negligible homogeneity ranges. The enthalpy of mixing function in (Eq. 1) was combined with the (Cu)/(Cu) + L liquidus data from [74Per] in the composition range 0 to 7.75 at.% Hf and the L/L + (β Hf) datum from [74Mar] at 75 at.% Hf to derive the following function for the excess entropy of the liquid phase:

$$S^{\text{ex}}(L) = X_{\text{Hf}}(1 - X_{\text{Hf}})(83.009 + 248.426 X_{\text{Hf}} - 596.531 X_{\text{Hf}}^2 + 328.495 X_{\text{Hf}}^3) \text{ J/mol}\cdot\text{K} \quad (\text{Eq. 2})$$

The enthalpy and excess entropy functions for the liquid were then utilized in conjunction with the experimental liquidus temperatures from [74Per] in the composition range 7.75 to 19.4 at.% Hf and from [74Mar] in the composition range 11 to 66.67 at.% Hf to derive the Gibbs energy of formation values for the phases Cu₅Hf, Cu₅₁Hf₁₄, Cu₈Hf₃, Cu₁₀Hf₇, and CuHf₂. Table 8 lists the values of the various thermodynamic properties. Comparison of the calculated enthalpy of mixing values with the experimental data of [82Kle], shown in Table 7, indicates a complete lack of agreement. Moreover, the calculated enthalpy for Cu₈Hf₃ shows an unreasonably large exothermic value in comparison with the data for the other intermediate phases. This could be explained by the lack of experimental data for the Cu₈Hf₃/Cu₈Hf₃ + L liquidus boundary. Nevertheless, the calculated Gibbs energies for the intermediate phases should be regarded only as fitting parameters, not as actual thermodynamic quantities.

Liquidus boundaries, evaluated from the expressions in Table 8, are shown as solid lines in Fig. 1. Liquidus boundary calculations were not successful for the Hf-rich end of the diagram, primarily because of the scarcity of experimental liquidus and thermodynamic data within the composition range 75 to 100 at.% Hf. Moreover, the solidus and solvus boundaries for (β Hf) are not known within reasonable confidence levels. Therefore, the present evaluators consider the Hf-rich

Table 8 Cu-Hf Thermodynamic Properties

Lattice stability parameters for Cu(a)	
$G^0(\text{Cu}, L) = 0$	
$G^0(\text{Cu}, \text{Fcc}) = -13\,054 + 9.613\,T$	
Lattice stability parameters for Hf(b)	
$G^0(\text{Hf}, L) = 0$	
$G^0(\text{Hf}, \text{bcc}) = -23\,390 + 9.341\,T$	
$G^0(\text{Hf}, \text{cph}) = -29\,300 + 12.272\,T$	
Integral molar Gibbs energies(c)	
$G^{\text{ex}}(L) = X(1 - X)[-77\,800 - T(83.009 + 248.426\,X - 596.531\,X^2 + 328.495\,X^3)]$	
$\Delta_f G(\text{Cu}_5\text{Hf}) = -33\,512 - 2.137\,T$	
$\Delta_f G(\text{Cu}_{51}\text{Hf}_{14}) = -62\,089 + 11.983\,T$	
$\Delta_f G(\text{Cu}_8\text{Hf}_3) = -210\,207 + 126.04\,T$	
$\Delta_f G(\text{Cu}_{10}\text{Hf}_7) = -23\,890 - 27.682\,T$	
$\Delta_f G(\text{CuHf}_2) = -80\,005 + 16.393\,T$	

Note: Gibbs energies are expressed in J/mol, and T is in K. X is the atomic fraction of Hf. Mol refers to the atom as the elementary entity. Standard states are pure liquid Cu and pure liquid Hf.
(a) From [Hultgren, E]. (b) From [83Cha]. (c) From the present modeling.

end of the Cu-Hf phase diagram tentative and in need of further experimental research.

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- * Indicates key paper.
Indicates presence of a phase diagram.

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