The Copper-Rare Earth Systems

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Introduction

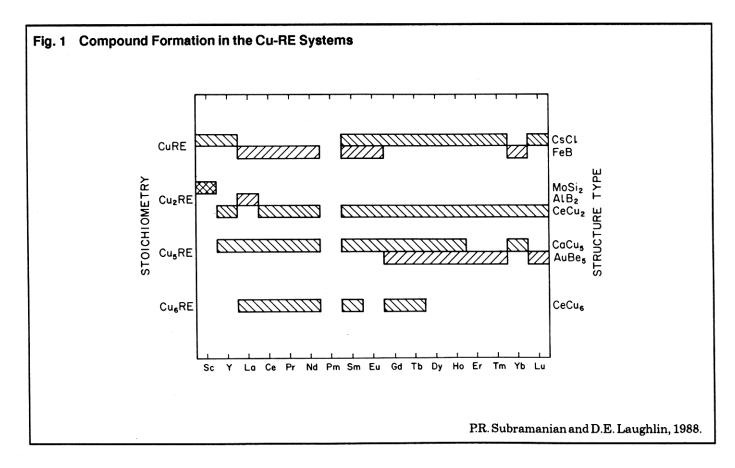
Rare earth (RE) intermetallic compounds exhibit a regular and systematic change of physical properties, including lattice parameters, melting temperatures, and thermodynamic variables [83Gsc1]. Such systematic variations have been reported for alloys of RE with many non-RE elements [71Gsc, 71Mcm, 82Gsc1, 83Gsc2, 84Gsc].

[83Car1] surveyed the behavior of the Cu-lanthanide alloys, giving particular attention to experimental results obtained for the Cu-Nd, Cu-Gd, and Cu-Dy systems. In addition, they compiled thermal, structural, and hardness data for Cu-RE compounds from selected sources. The present review provides a comprehensive discussion of the systematics of compounds that form in the binary Cu-RE alloy systems, primarily compound stoichiometries, crystal structures, and selected physical properties. This review supersedes

the work of [83Car1] and also serves as an introduction to the compilation and critical evaluation of Cu-RE phase diagrams. In this review, the term lanthanides refers to the elements from La to Lu, and the term rare earths (RE) refers to the lanthanides, together with Sc and Y.

Stoichiometry and Crystal Structures of Intermediate Phases

The nature of compound formation in the Cu-RE systems is summarized in Fig. 1. Only those stoichiometries for which crystal structures have been well established are included. Structural data are well established for at least four compound stoichiometries, although intermediate phases with more than seven different stoichiometries have been reported. Structural data for the various compound stoichiometries are listed in Table 1. In the following text, lanthanide elements to the left of Gd in the periodic table are



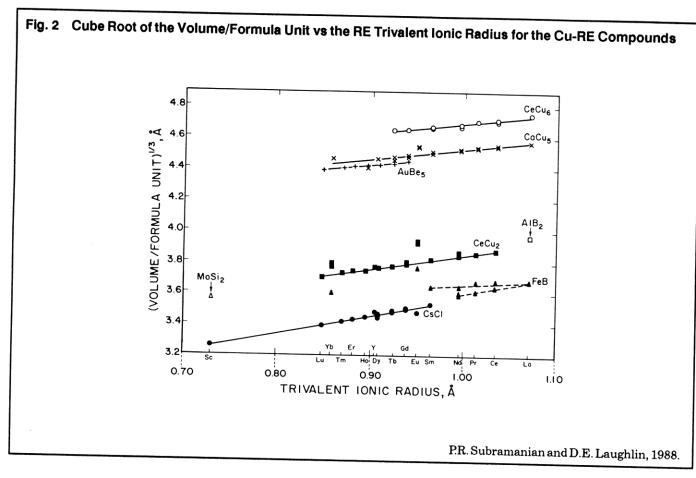


Table 1 Cu-RE Crystal Structure Data

Phase	Pearson	Space	Strukturbericht	Proto-
	symbol	group	designation	type
$CuRE$ Cu_2RE Cu_6RE Cu_6RE	cP2 oI12 hP3 tI6 hP6 cF24	Pnma Pm3m Imma P6/mmm I4/mmm P6/mmm F43m Pnma	$B27$ $B2$ $C32$ $C11_b$ $D2_d$	FeB CsCl CeCu ₂ AlB ₂ MoSi ₂ CaCu ₅ AuBe ₅ CeCu ₆

referred to as light, and the rest are referred to as heavy.

CuRE

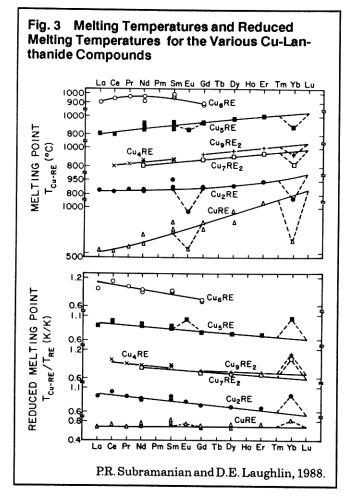
CuRE is the most RE-rich intermediate phase that forms in the Cu-RE systems; it has two modifications, the orthorhombic-FeB structure and the cubic-CsCl structure. The light lanthanide CuRE phases crystallize with the FeB structure. Almost all of the heavy lanthanide CuRE phases crystallize with the cubic CsCl structure, with the exception of CuYb, which forms with the FeB structure. Both structures have been reported for CuSm [65Dwi, 65Wal] and CuEu [66Mor, 76Mie]. The CsCl structure is also the prototype for the CuSc and CuY phases [65Dwi].

Cu₂RE

The orthorhombic CeCu2 structure is the prototype for all of the Cu2RE intermediate phases, except where RE is La or Sc. Cu2La and Cu2Sc form with the hexagonal AlB2 and the tetragonal MoSi2 structures, respectively [63Sto, 67Dwi].

Cu₅RE

The light lanthanides form Cu₅RE compounds with the hexagonal CaCu₅ structure, whereas the heavy lanthanides form Cu₅Re compounds with the cubic AuBe₅ structure. Cu₅Yb is an exception and crystallizes with the CaCu₅ structure [67Pal]. Both structural forms have been reported for Cu₅Gd [59Wer,



69Bus], Cu5Tb [69Bus, 71Bus], Cu5Dy [69Bus, 82Fra], and Cu5Ho [61Dwi, 69Bus]. For both Cu5Gd [83Car3] and Cu5Dy [82Fra], the hexagonal type is stable at high temperatures, and the cubic type is stable at low temperatures. Cu5Tb and Cu5Ho are expected to follow the same pattern. However, [71Bus] indicated that Cu5Gd, Cu5Tb, and Cu5Y could be obtained as single crystals only after splat cooling. [81Cha] concluded that Cu5Y is a metastable phase, and Cu6Y and Cu4Y are the equilibrium phases in the composition region near Cu5Y stoichiometry. Cu5Sc has not been reported.

Cu₆RE

Cu₆RE crystallizes with the orthorhombic CeCu₆ structure and has been reported for the light lanthanides from La to Sm [70Bus1]. Of the heavy lanthanides, only Gd and Tb form phases with the Cu₆RE stoichiometry.

Other Stoichiometries Reported

Cu₇RE₂

The existence of the intermediate phase Cu7RE2 has been reported for the Cu-Nd [83Car2], Cu-Gd

[83Car3], Cu-Dy [82Fra], and Cu-Yb [71Ian] systems. For all of these compounds, the stoichiometry was derived only on the basis of thermal effects, and no structural data were reported. In addition, the phases Cu7Nd2, Cu7Gd2, and Cu7Dy2 appear to exist only at elevated temperatures and within a very limited temperature range [83Car1].

Cu₄RE

Compounds with the Cu4RE stoichiometry have been reported for RE = Ce, Pr, Nd, Sm, Gd, and Y. Of these. Cu4Ce and Cu4Pr were found to crystallize with an orthorhombic structure [64Rhi, 79Pop]. [83Car2] could obtain Cu4Nd only after prolonged annealing, and concluded from single crystal studies that Cu4Nd forms with a fcc sub-structure. The existence of Cu4Nd was also reported by [84Lak], who did not provide any structural data. However, [61Gsc] proposed that the stoichiometry of the Cu4RE compound is actually Cu_{4.8}RE_{1.2}, and that it has a hexagonal CaCu₅ structure. [81Cha] accepted the equilibrium existence of Cu4Y with a hexagonal CaCu5 prototype structure. This contradicts [71Bus], who indicated that the hexagonal CaCu5 structure could not be observed for compounds with the Cu4RE stoichiometry. Cu4Sc was reported by [70Sav] and [78Mar], but no structural details were given.

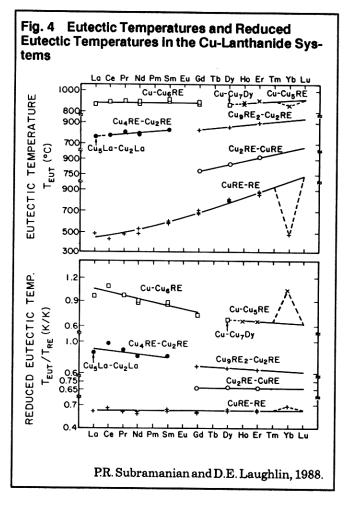
Cu₉RE₂

The congruent formation of Cu₉RE₂ phases was reported for the Cu-Gd [83Car3], Cu-Dy [82Fra], and Cu-Yb [71Ian] systems. These phases were identified on the basis of thermal analysis and microscopy, and were found to crystallize with a tetragonal symmetry. [70Bus2] reported the occurrence of two compounds, Cu_x Er and Cu_y Er, in the vicinity of 80 at.% Cu and at about the same composition as Cu_7 RE2 and Cu_9 RE2.

Cu₇RE

[71Bus] gave lattice parameter data for Cu7Gd, Cu7Tb, Cu7Dy, and Cu7Y, and observed that these compounds crystallize with a structure closely related to hexagonal CaCu5-type. These phases, however, were reported to be stable only at elevated temperatures. [81Cha] concluded that Cu7Y does not exist as a distinct compound, but lies within the phase field of the Cu6Y compound.

In addition to these stoichiometries, researchers have reported Cu₁₃RE compounds with the cubic NaZn₁₃ structure for RE = La and Pr [81Blo]. These compounds, however, have been observed only in splat cooled alloys and therefore are likely to be metastable. [84All] reported the formation of Cu_{3.6}Ce with a hexagonal Ag_{3.6}Gd-type structure. This compound was not reported for any of the other Cu-RE systems, although its stoichiometry is very close to that of Cu₇RE₂ (RE = Nd, Gd, Dy, and Yb). Compounds with the Ag_{3.6}Gd-type structure are known to form in the RE-Au [71Mcm] and RE-Ag [70Mcm] systems.



Physical Properties of the Intermediate Phases

The systematics of the Cu-RE intermediate phases were evaluated in terms of two variables, the volume contraction and the melting points of the intermediate phases and eutectic temperatures. Deviations from ideal behavior are usually expected for systems containing Eu and Yb, (because these elements are divalent in their standard states [69Gsc1]), and occasionally for systems containing Ce and Sm [82Gsc2]. The details of the evaluations are given below.

Volume Contraction

The nature of the volume contraction in the Cu-RE intermetallic compounds can be examined by observing the variation in the lattice parameters or other related parameters as one progresses across the RE series. Lattice parameter variation can be examined either as a function of the RE atomic number or as a function of the RE trivalent ionic radius. [79Ian] observed that there usually exists a linear correlation with the lattice parameter and other related data. Moreover, [79Ian] indicated that the cube root of the unit formula volume (V_u) provides a convenient representation of the lat-

tice parameters, because of its relative insensitivity to experimental errors. In the present study, the variation of the cube root of V_u was therefore evaluated as a function of the trivalent ionic radii of the RE component for Cu-RE intermetallic compounds with the stoichiometries CuRE, Cu₂RE, Cu₅RE, and Cu₆RE. The results are shown in Fig. 2, where data from all of the sources are included. Data points corresponding to isostoichiometric compounds having the same structure fall essentially in a straight line. The results are summarized below.

CuRE

The FeB structure is reported for RE = La, Ce, Pr, Nd, Sm, and Eu. Two conflicting sets of lattice parameter data have been reported for RE = Ce, Pr, and Nd; plots of the cube root of V_u of these compounds fall in two distinct lines, with the larger values for Pr and Nd corresponding to data from [65Wal] and the smaller values corresponding to data from [65Dwi]. For Ce, the larger value corresponds to data from [61Lar]. Eu and Yb are exceptions, showing substantially larger values for V_u , which indicates that these elements show divalent behavior in their respective compounds. Values for CuRE compounds with the CsCl structure increase linearly with increasing ionic radii. The values for the elements Sc and Y do not form exceptions and lie on the same line as those for the CuRE compounds with the CsCl structure. The data point for CuEu with the CsCl structure shows a deviation in the direction opposite that expected for divalent behavior and therefore is questionable.

Cu₂RE

All of the Cu₂RE compounds, except Sc and La, crystallize with the CeCu₂ structure, and the plot of the cube root of $V_{\mathcal{U}}$ of the Cu₂RE phases shows a linear decrease from Ce to Lu, with the expected exceptions for Eu and Yb.

Cu₅RE

Cu5RE compounds form with either the hexagonal CaCu5 structure or the cubic AuBe5 structure. Cu5Gd, Cu5Tb, and Cu5Ho reportedly crystallize in both forms. Again, a regular linear trend is observable with increasing ionic radii, with exceptions noted in the cases of Eu and Yb. The data point for Cu5Ho with the hexagonal CaCu5 structure is unusually low and does not fit in with the general trend.

Cu₆RE

Cu₆RE compounds with the CeCu₆ crystal structure exist for RE = Ce, Pr, Nd, Sm, Gd, and Tb. The values of the cube root of V_u for these compounds increase linearly with increasing rare earth ionic radii.

[69Gsc2] suggested that the lanthanide contraction can be correlated with heats of formation of the Cu-RE compounds. However, because of the very limited experimental information available on the heats of formation of the Cu-RE compounds, such correlations have not been attempted in the present study.

Melting Temperatures

Intermediate Phases

Melting temperatures have been reported for Cu-RE intermediate phases with the following stoichiometries: CuRE, Cu2RE, Cu7RE2, Cu4RE, Cu9RE2, Cu5RE, and Cu6RE. Figure 3 shows the variation of both melting temperatures and reduced melting temperatures for the various Cu-lanthanide compounds. Plots of the reduced melting point (i.e., the ratio of the melting point of the compound to that of the pure lanthanide) are included in Fig. 3, because [69Gsc2] observed that these plots show a linear decrease with increasing atomic number. In most instances the melting temperatures show a smooth increase with increasing atomic number. Deviations occur for Yb, melting temperatures of whose phases lie below the smooth curves. Such deviations are expected, because the divalent state of Yb produces weaker bonding in the solid state. The melting point data for Cu₄RE, Cu₇RE₂, and Cu₉RE₂ are plotted on a common scale in Fig. 3, where melting temperature data for Er correspond to CuxEr and CuyEr with the compositions 79 and 81 at.% Cu, respectively [70Bus2]. CuxEr decomposes by a peritectic reaction, whereas CuyEr melts congruently at a slightly higher temperature. The data for these compounds are included in the plots for Cu7RE2 and Cu9RE2 because their compositions lie very close to the stoichiometries of Cu7RE2 (77.8 at.% Cu) and Cu₉RE₂ (81.8 at.% Cu). The data for CuxEr and CuyEr lie very close to the extrapolated curves for Cu7RE2 and Cu9RE2, respectively. It is therefore likely that the compounds Cu_xEr and Cu_yEr correspond to the stoichiometries Cu7Er2 and Cu9Er2. respectively. Reduced melting points decrease linearly as a function of atomic number and agree with the observations of [69Gsc2] (with the expected deviations for Yb, and in some cases for Ce and Sm).

Eutectics

Eutectic melting points are observed in the following two-phase regions: Cu-Cu₆RE, Cu-Cu₅RE, Cu-Cu₇Dy, Cu₉RE₂-Cu₂RE, Cu₅La-Cu₂La, Cu₄RE-Cu₂RE, Cu₂ RE-CuRE, and CuRE-RE. The variation of the eutectic temperature (T_e) and the reduced eutectic temperature (T_e/T_{RE}) were evaluated for the lanthanides from La to Lu. The results from all of the available data are plotted in Fig. 4. The plots of the eutectic temperature show an overall smooth variation with increasing atomic number. Some data points, however, deviate from the systematic behavior. Of these deviations, that for Yb is expected. The eutectic temperature for Cu-CuCe is about 25 °C below the curve for CuRE-RE eutectics. Minor deviations are observed for the Cu4Pr-Cu2Pr, Cu4Nd-Cu2Nd, Cu-Cu₆Pr, and Cu-Cu₆Sm eutectics. Compounds of Pr. Nd, and Sm are not expected to show anomalous behavior, and therefore, the data for Pr. Nd. and Sm are suspect. Otherwise the plots for the reduced eutectic temperature show a linear trend with increasing atomic number, and are in accord with the expected behavior.

Conclusions

It has been shown that the lattice parameters and melting temperatures of the Cu-lanthanide intermetallic compounds show a systematic variation across the lanthanide series from La to Lu. Anomalies have been observed for Eu and Yb, because these elements show divalent characteristics in their respective compounds. For a first approximation, therefore, the accepted lattice parameters and melting temperatures for the Cu-RE compounds are those for which there exist no significant deviations from the general trend. A more critical evaluation involves taking into account other factors, such as purity of the constituent elements, experimental techniques, evidence of equilibration, etc. These factors are considered in the evaluations of the individual Cu-RE systems.

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Cu-RE evaluation contributed by PR. Subramanian, Materials Science Division, Universal Energy Systems, Incorporated, 4401 Dayton-Xenia Road, Dayton, Ohio 45435 and D.E. Laughlin, Department of Metallurgical Engineering and Materials Science, 3325 Science Hall, Carnegie Mellon University, Schenley Park, Pittsburgh, PA 15213. Work was supported by the International Copper Research Association, Inc. (INCRA), ASM INTERNATIONAL, and the Department of Energy through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data (OSRD). Bibliographic search was provided in part by ASM, and in part by K.A. Gschneidner, Jr., Director, and F.W. Calderwood, Rare-earth Information Center, Ames Laboratory, Iowa State University, Ames, IA, which is gratefully acknowledged. Literature searched through 1983. Professor Laughlin is the ASM/NBS Category Editor for binary copper alloys.