The Cu-La (Copper-Lanthanum) System

63.546 amu 138.9055 amu

By D. J. Chakrabarti and D. E. Laughlin
Carnegie-Mellon University

Equilibrium Diagram

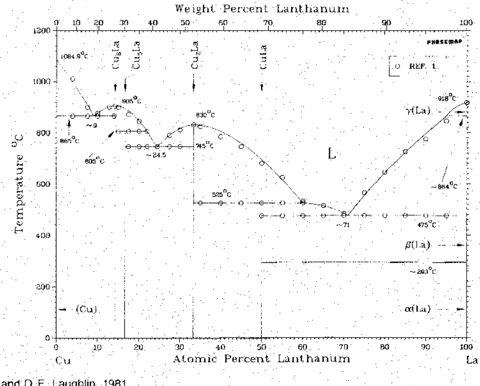
The Cu-La equilibrium diagram is given in Fig. 1. The equilibrium phases in the system include: (1) the liquid; (2) the face-centered cubic terminal solid solution based on Cu, with an insignificant solubility of La; (3) the stoichiometric compound Cu_6La, stable up to the congruent melting temperature at 905 °C; (4) the stoichiometric compound Cu_5La, stable up to the peritectic decomposition temperature at 805 °C; (5) the stoichiometric compound Cu_2La, stable up to the congruent melting temperature at 830 °C; (6) the stoichiometric compound CuLa, stable up to the peritectic decomposition temperature at 525 °C; (7) the hexagonal solid solution based on La, with insignificant terminal solubility of Cu, and stable up to the $(\alpha La) \rightleftarrows (\beta La)$ transition temperature at about 293 °C; (8) the face-centered cubic solid solution based on La, with insignificant terminal solubility of Cu, and stable between about 293 °C and the $(\beta La) \rightleftarrows (\gamma La)$ transition temperature at about 864 °C; and (9) the body-centered cubic solid solution based on La, with insignificant terminal solubility of Cu, and stable between about 864 °C and the melting temperature of La at 918 °C.

The Cu-La equilibrium diagram in Fig. 1 is derived from [1], based on differential thermal analysis (DTA), X-ray diffraction (single crystal and powder) and microscopic studies of alloys made from 99.999% Cu and 99.9% nominal purity La. The accuracy of the recorded temperature is ±5 °C.

Liquidus, Solidus and Solvus. The melting and the $\beta \rightarrow \gamma$ polymorphic transition temperatures of La obtained by [1] are 930 °C and 860 °C, respectively. The corresponding accepted values for La metal are 918 °C [2] and 864 °C [3]. The difference in the melting point (12 °C) is too high to correspond to the reported 0.1% impurity content in La. Assuming Clausius-Clapeyron approximation for dilute solutions with near zero terminal solubility, as in La with Cu, the initial slope at the melting temperature of La is approximately 19 °C per at.% Cu. Assuming ideal solution approximation is valid for 0.1% solute in La, there seems to be a discrepancy between the reported melting point and the thermodynamically compatible value. There are three eutectic, two peritectic and two congruent transformations in the system, detailed as follows:

- **Eutectic:** (1) the liquid of composition ~9.0 at.% La in equilibrium with (Cu) and Cu_6La at 865 °C, (2) the liquid of ~24.5 at.% La in equilibrium with Cu_5La and Cu_2La at 745 °C, and (3) the liquid of ~71 at.% La in equilibrium with CuLa and (βLa) at 475 °C.

Fig. 1 Cu-La Phase Diagram



D. J. Chakrabarti and D. E. Laughlin, 1981.

- **Peritectic:** (1) Cu_5La in equilibrium with Cu_6La and the liquid of ~22 at.% La at 805 °C, and (2) CuLa in equilibrium with Cu_2La and the liquid of ~60 at.% La at 525 °C.
- **Congruent:** (1) Cu_6La in equilibrium with liquid of the same composition at 905 °C, and (2) Cu_2La in equilibrium with liquid of the same composition at 830 °C.

There are two more three-phase equilibria in this system given below whose types are not known.

Type 1. The liquid of ~5 at.% La is in equilibrium with (βLa) and (γLa) at an invariant temperature not determined. Supposedly, this is close to 864 °C, the $\gamma \rightarrow \beta$ transformation temperature of La, because the solubility of Cu in La at this temperature is negligible. The characteristic transformation type will be either peritectic or metatectic, depending on whether the $\beta \rightarrow \gamma$ transition temperature of La is raised or lowered, respectively, by Cu addition, which is not known.

Type 2. CuLa is in equilibrium with (αLa) and (βLa) at an invariant temperature not determined. Supposedly, this is close to 293 °C, the $\beta \rightarrow \alpha$ transition temperature of La, because the solubility of Cu in La at this temperature is negligible. The characteristic transformation type will be either peritectoid or eutectoid, depending on whether the $\alpha \rightarrow \beta$ transition temperature of La is raised or lowered, respectively, by Cu addition, which is not known.

The terminal solubilities of Cu in La and La in Cu are negligible because lattice parameters of the pure metals do not change on alloying [1].

Intermetallic Compounds. There are four intermetallic compounds—i.e., CuLa, Cu_2La, Cu_5La and Cu_6La—all of which occur at stoichiometry without a report, to date, of any extended solid solubility. Whereas the first two compounds were reported early by [4], the identification of the last two evolved gradually through subsequent works. They were identified as Cu_3La and Cu_4La by [4], and as Cu_4La and Cu_6La by [5], until recently, when [1] confirmed them as Cu_5La and Cu_6La and rejected the occurrence of Cu_4La.

Based on X-ray and metallography, [6] identified earlier the occurrence of a phase with Cu_5La composition and suggested the possibility of another phase between (Cu) and Cu_5La. This was confirmed later by [5] through microscopy as Cu_6La. The occurrence of Cu_5La was confirmed by [1] by means of differential thermal analysis (DTA), X-ray and microscopy, who also established the compositions and temperatures at the other invariant points. Table 1 summarizes these results along with those from others. Considering the high accuracy of measurement and better purity of material used, results from [1] (shown underlined in Table 1) are accepted in constructing the equilibrium diagram.

The La used by [5] is given as 98% and that by [4] as 99.6%. However, the purity of La given by [4] is doubtful, in view of the low melting point (812 °C) reported. La, like rare-earth elements, is very reactive; thus, minor impurities may alter phase equilibria considerably [7]. Some of the early confusion with the Cu-rich compounds may be related to this effect. This appears to be the situation with [4], whose thermal analysis data indicate the congruent point at Cu_4La rather than at Cu_6La composition. However, the thermal data of [5] show an extension of the 725 °C isotherm up to Cu_5La composition that lend support, in disagreement with [Hansen], to the microscopic evidence for the occurrence of the Cu_5La rather than the Cu_4La compound as postulated.

Metastable Phase

The effect of rapid solidification on splat-cooled alloys of 33 to 100 at.% La was studied by [8]. The results are inclusive. The suspected amorphous phase near the eutectic composition, based on the X-ray indication of a broad intensity maximum, was identified later by electron microscopy to be microcrystalline and made up of crystals about 2.0 nm in diameter.

Table 1 Composition and Temperature at Invariant Points in Cu-La System(a)

Reaction	Phase I	Phase II	Phase III	Composition, at.% La I	Composition, at.% La II	Composition, at.% La III	Temperature, °C	References
Eutectic	(Cu)	L	Cu_6La	**~0**	**~9.0**	**14.3**	**865**	1
					7.4(b)?		851(b)?	4
					9.0		840	5
Congruent	Cu_6La	L	...	**~14.5**	**~14.5**	...	**905**	1
							902(b)?	4
Peritectic	Cu_6La	Cu_5La	L	**~14.5**	**16.7**	**~22**	**805**	1
							793(c)?	4
							~785(d)	5
Eutectic	Cu_5La	L	Cu_2La	**16.7**	**~24.5**	**33.3**	**745**	1
					27.3		742(c)	4
					~27.5		~725(d)	5
Congruent	Cu_2La	L	...	**33.3**	**33.3**	...	**830**	1
							834	4
Peritectic	Cu_2La	CuLa	L	**33.3**	**50**	**~60**	**525**	1
							551	4
Eutectic	CuLa	L	(βLa)	**50**	**~71**	**~100**	**475**	1
					73.8		468	4
Eutectoid/peritectoid	(αLa)	(βLa)	CuLa	...	...	...	**~293**	16
Peritectic/metatectic	(βLa)	(γLa)	L	...	...	...	**~864**	3

(a) Accepted values are shown in boldface type. (b) Reported for Cu_4La but supposedly belonging to Cu_6La. (c) Reported for Cu_3La, but supposedly belonging to Cu_5La. (d) Reported for Cu_4La, but supposedly belonging to Cu_5La.

Crystal Structures and Lattice Parameters

The experimental values for the lattice parameters of the compounds Cu_6La, Cu_5La, Cu_2La and CuLa are given in Table 2, whereas the accepted values, along with the structure types, are listed in Table 3. The lattice parameter values in Table 3 are taken from [1], in view of the use of high purity La (99.9%) and because of accurate results that correspond closely with earlier values. Also shown in Table 3 are the corresponding data for the α, β and γ polymorphic forms of La.

Cu_6La has an orthorhombic $CeCu_6$-type structure that is stable at high temperatures. Structural details for the low temperature modification are not known. Attempts to identify the structure for the as-cast or annealed alloy by [1], or for annealed alloys of varying Cu content by [9], were not successful and showed that it was not of the $CeCu_6$ type. Several Cu_6R compounds, where R is Ce, Pr, Nd, Sm or Th, have the $CeCu_6$-type structure [9]. The same structure type was found by [1] to occur with Cu_6La only on quenching from high temperature. Crushing the quenched alloy destroyed the high temperature form, as did annealing. DTA could not detect the polymorphic transformation temperature, probably because of the low thermal effect or the proximity to the melting temperature, and hence it is not known.

Cu_5La belongs to the hexagonal $CaCu_5$-type structure. The different lattice parameters given by [1], [6], [9], [10] and [11] are given in Table 2.

The crystal structure of Cu_2La was mistaken for orthorhombic $CeCu_2$ prototype by [12], in analogy with many Cu_2R compounds (R stands for rare-earth elements). [13] confirmed the structure to be hexagonal isotopic with AlB_2. Attempts to obtain $CeCu_2$-type modification in Cu_2La by quenching the alloy from 740 °C by [13], or by varying the composition around Cu_2La followed by casting or annealing at 500 °C by [14], were not successful. The La used by [13] and [14] were of 99+% and 99.5 to 99.9% purity, respectively. The lattice parameters obtained by [13], [14] and [1] are shown in Table 2.

CuLa is orthorhombic, isotypic with BFe structure [15], with lattice parameters from [15] and [1] given in Table 2.

The low temperature form of La is given as double hexagonal [16], the intermediate temperature form, βLa, as face-centered cubic [3] and the high temperature modification, γLa, as body-centered cubic [16], with lattice parameters as shown in Table 3.

Table 2 Experimental Lattice Parameter Values

Phase	Crystal structure	Lattice parameters, nm a	b	c	References
Cu_6La	Orthorhombic	0.8165(a)	0.5148(a)	1.023(a)	1
Cu_5La	Hexagonal	0.5092	···	0.4086	10
		0.5159	···	0.4108	6
		0.5184	···	0.4112	11
		0.5186(b)	···	0.4110(b)	9
		0.5187(c)	···	0.4109(c)	1
Cu_2La	Hexagonal	0.4348	···	0.3818	14
		0.4346 ±0.0005	···	0.3807 ±0.0005	13
		0.4345	···	0.3819	1
CuLa	Orthorhombic	0.7532	0.4625	0.5711	15
		0.7543	0.4616	0.5724	1

(a) For quenched single crystal. (b) Arc-melted and annealed 700 °C for 3 weeks. (c) Annealed 350 °C for 1 week.

Table 3 Crystal Structures

Phase	Approximate composition (a), at.% La	Pearson symbol	Prototype	Space group	Lattice parameters, nm a	b	c	Comments
(Cu)	···	$cF4$	Cu	$Fm3m$	0.36147	···	···	At 18 °C, 0% La. From [Landolt-Börnstein].
Cu_6La	14.3	$oP28$(b)	$CeCu_6$	$Pnma$	0.8165	0.5148	1.023	From [1]; structure stable at high temperatures. Low temperature structure not known.
Cu_5La	16.6	$hP6$	$CaCu_5$	$P6/mmm$	0.5187	···	0.4109	From [1].
Cu_2La	33.3	$hP3$	AlB_2	$P6/mmm$	0.4345	···	0.3819	From [1].
CuLa	50	$oP8$	BFe	$Pnma$	0.7543	0.4616	0.5724	From [1].
(αLa)	···	$hP4$	αLa	$P6_3/mmc$	0.3770	···	1.2137	100% La. From [16]. Room temperature values. Length of c-axis doubled, i.e., ($abac$) rather than (ab).
(βLa)	···	$cF4$	Cu	$Fm3m$	0.53058	···	···	100% La. From [17]. Surface impurities stabilize the form below $T_{\alpha\text{-}\beta}$ at 293 °C.
(γLa)	···	$cI2$	W	$Im3m$	0.426	···	···	100% La. From [16].

(a) From the phase diagram. (b) From [1].

Thermodynamics

No thermodynamic data are available for this system. To estimate change of melting and $\beta \rightarrow \gamma$ transition temperatures of (La) by the Clausius-Clapeyron approximation, the enthalpy-difference values used are 6.2 kJ/g·at and 3.1 kJ/g·at, respectively [Hultgren, Elements].

Cited References

1. S. Cirafici, A. Palenzona, *J. Less-Common Met.*, *53*(N2), p 199–203 (1977).
2. *Bull. Alloy Phase Diagrams*, *2*(1), p 146 (1981), quoting melting points of elements.

3. F. H. Spedding, A. H. Daane and K. W. Herrmann, *J. Met.*, *9*, p 895 (1957).
4. G. Canneri, *Metallurgia Ital.*, *23*, p 813–815 (1931).
5. R. Vogel and T. Heumann, *Z. Metallkunde*, *35*, p 29–42 (1943).
6. H. Nowotny, *Z. Metallkunde*, *34*, 247–253 (1942).
7. K. A. Gschneidner, Jr., *Rare Earth Alloys*, D. Van Nostrand Co. Inc., Princeton, NJ, p 155, 159–160 (1961).
8. J. Favaron, M. E. de la Cruz, P. Esquinazi and F. de la Cruz, *Phys. Rev. B*, *21*(7), p 2804–2808 (1980).
9. K. H. J. Buschow and A. S. Vander Goot, *Acta Cryst.*, *27B*, p 1085–1088 (1971).
10. W. Haucke, *Z. Anorg. Chem.*, *244*, p 17–22 (1940).
11. A. E. Dwight, *Trans. ASM*, *53*, p 479–500 (1961).
12. H. Bommer and E. Krose, *Z. Anorg. Allg. Chem.*, *252*, p 62 (1943); quoted by [7].
13. A. R. Storm and K. E. Benson, *Acta Cryst.*, *16*, p 701–702 (1963).
14. A. Iandelli, A. Palenzona, *J. Less-Common Met.*, *15*, p 273 (1968).
15. A. E. Dwight, R. A. Conner, Jr. and J. W. Downey, Proc. 5th Rare Earth Research Conf., Session M, 1965, Iowa State Univ., Ames, Iowa, Legvold Publ., p 35 (1965).
16. F. H. Spedding, A. H. Daane and K. W. Herrmann, *Acta Cryst.*, *9*, p 559 (1956); F. H. Spedding, J. J. Hanak and A. H. Daane, *J. Less-Common Met.*, *3*, p 110 (1961).
17. H. H. Hill and F. H. Ellinger, *J. Less-Common Met.*, *23*, p 92 (1971).

Cu-La evaluation contributed by **D. J. Chakrabarti** and **D. E. Laughlin**, Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213, USA. Work was supported by the International Copper Research Association, Inc. (INCRA) and the Department of Energy through the Joint Program on Critical Compilations of Physical and Chemical Data, coordinated through the Office of Standard Reference Data (OSRD), National Bureau of Standards. Literature searched through 1980. Prof. Laughlin is the ASM/NBS Data Program's Category Editor for binary copper alloys.