Aluminium – Cerium – Copper

Peter Rogl, updated by Paola Riani, Pierre Perrot

Literature Data

No complete phase diagram exists for the Al-Ce-Cu system and information about the phase equilibria in the Al-rich part of the system is mainly based on the investigations by [1961Gla1, 1964Zar, 1991Yun]. The crystallographic characterization of the ternary compounds is due to [1961Gla2, 1963Zar, 1964Che, 1964Zar, 1968Dwi, 1976Bus, 1985Cor1, 1985Cor2], while interesting physical properties were reported by [1987Bau, 1988Fis, 1991Kim, 2000Jav] and structural properties by [1978Tak, 1985Rau, 1990Cor, 1996Moz]. Investigations on magnetic properties were made by [1973Oes, 1982Fel, 1992Bau, 1996Moz, 1998Jav, 1999Kon] and thermal effects studied by [2000Kon, 2001Che].
[1961Gla1] was the first to examine the phase relations in the Al-rich corner employing X-ray, metallographic and chemical analysis and micro-hardness measurements on a total of 130 alloys. Ce-rich specimens were prepared from 99.9 mass% pure Al, 98.6% pure Ce and 99.89% pure Cu by melting the constituents; Ce-poor specimens were prepared from a "hardener" alloy in Al_2O_3-crucibles under carnallite. All the alloys were annealed in vacuum at 500 and 400 ± 2°C for 120 or 240 h, respectively and were finally quenched in toluene. Lattice parameters were measured with a claimed precision of 0.01 pm on polished sample surfaces in a back-reflection camera at 400 and 500°C for three series of alloys with constant amounts of 1 mass% Ce, 5 mass% Ce and 5 mass% Cu, respectively. The plots of the unit cell dimensions versus concentration were used to establish the extension limits and vertices of the two- and three-phase equilibria of the (Al) solid solution. A series of successive crystallographic investigations [1961Gla2, 1963Zar, 1964Che, 1964Zar, 1990Cor, 1996Moz] confirmed and completed the description of the ternary compounds originally reported by [1961Gla1], with some changes in the composition and homogeneity fields of the intermediate phases. A more complete version of the phase equilibria in the Al-rich part of the 400°C isothermal section was presented in a review article by [1985Bod]. Similar preparation methods were employed by [1968Dwi, 1973Oes, 1982Fel, 1985Cor1, 1985Cor2]. [1991Yun] employed DTA and microstructural analysis to investigate the specimens prepared by melting the constituent metals and annealing them at 500°C for 240 h. The liquidus surface and a number of vertical sections in the Al-rich region have been constructed by [1991Yun]. The present evaluation updates and completes the evaluation made earlier by P. Rogl in the MSIT Evaluation Program [1991Rog].

Binary Systems

The present evaluation of ternary data is consistent with the description of the edge binary diagrams Al-Ce by [2000Oka], Al-Cu by [2003Gro] and Ce-Cu by [2002Per].

Solid Phases

Crystallographic data of all the binary and ternary compounds are listed in Table 1. On the basis of X-ray powder data for $\tau_1(CeCu_4Al_8)$, [1963Zar] and [1976Bus] agree on the existence of complete atomic order with Ce in the 2a sites, Cu in 8f and Al in the 8i and the 8j sites of space group *I4*/*mmm*. There is, however, a slight discrepancy in the unit cell dimensions reported by the two research groups possibly due to homogeneity differences. The existence of the τ_2 homogeneous range extending at 500°C from $Ce_2Cu_{6.5}Al_{10.5}$ to $Ce_2Cu_{7.3}Al_{9.7}$ was determined by [1963Zar]. From an analysis of the X-ray powder intensity data a partial atomic order was revealed for $Ce_2Cu_{6.5}Al_{10.5}$ with Ce in the 6c-sites, Cu in 9d, (10.5Cu+7.5Al) in 18 h, Al in 6c (0, 0, 0.097) and Al in the 18f sites of space group $R\bar{3}m$. Single crystal and powder X-ray intensity data for $\tau_4(CeCu_xAl_{4-x})$ ($0.75 \le x \le 1.00$) revealed Ce atoms in 2a, Al atoms in 4d and a statistical distribution of Cu and Al atoms in the 4e-positions (0, 0, 0.385(3)) [1964Zar]. A partially ordered structure for $CeCuAl_3$ and its conversion into the completely ordered $BaNiSn_3$ type has been described by [1995Hul]. According to [1996Moz] the refinement results of neutron powder diffraction

patterns show that the $CeCuAl_3$ compound does not crystallize as a disordered form of the $ThCr_2Si_2$ structure but belongs to the more ordered $BaNiSn_3$-type. Refinement of single crystal X-ray data of $\tau_3(CeCu_{6.5}Al_{6.5})$ confirmed isotypism with the $NaZn_{13}$ type and a statistical distribution of Cu, Al atoms in the 96i-sites (0, 0.1780(2), 0.1181(2)) of space group $Fm\bar{3}c$ with Ce in 8a and Cu in 8b. No indications for the existence of a homogeneous range were made by [1985Cor1, 1985Cor2], however, significantly larger cell parameters for a stoichiometry of "$CeCu_6Al_6$" were reported by [1982Fel].

Liquidus Surface

A projection of the liquidus surface was suggested by [1991Yun]. However it does not completely fit neither the vertical sections presented in the same work, nor the accepted binary diagrams, and therefore the liquidus projection is not reproduced in this evaluation. Figure 1 shows the primary crystallization domains in the Al-$CeAl_2$-$CuAl_2$ part of the diagram after [1991Yun] with some modifications made to comply with the accepted binary edge diagrams. The τ_1, $CeCu_4Al_8$ and τ_4,$CeCu_xAl_{4-x}$ compounds are considered as stoichiometric and melt congruently at 825 and 1230°C, respectively. The stoichiometry given for τ_4,$CeCu_xAl_{4-x}$ by [1991Yun] differs slightly from that proposed by [1964Zar]: τ_4,$CeCu_xAl_{4-x}$ (with $0.75 < x < 1$). Invariant equilibria and reaction scheme are presented in Table 2 and Fig. 2, respectively. However it has to be noted that phase compositions at invariant reactions given by [1991Yun] in a tabular presentation are not compatible with those shown in the diagram in the same publication. The values given in Table 2 in the present evaluation are estimated from the diagram given by [1991Yun] and should be considered as tentative.
For the τ_5,CeCuAl compound a peritectoid decomposition above 650°C was suggested by [2001Che], with the formation of $CeCu_{5-x}Al_x$, $CeAl_2$ and a new ternary phase with unknown structure corresponding to the Ce_2Cu_2Al composition.

Isothermal Sections

Figures 3 and 4 show the equilibria in the Al-rich region at 400 and 500°C. The phase field distribution at 400°C is mainly based on [1961Gla1] with small corrections made regarding to the position and homogeneity ranges of the binary and ternary phases. The two-phase equilibrium $\alpha Ce_3Al_{11} + \tau_4 CeCu_{0.75}Al_{3.25}$ as shown in Figs. 3 and 4 was also observed at 800°C by [1964Zar], whereas alloys with 20 at.% Ce and with 40 and 50 at.% Al at 800°C were reported to reveal a two-phased equilibrium between $CeCu_xAl_{4-x}$ and $CeCu_{5-x}Al_x$ ($CaCu_5$ type). The extended solid solution of Al in $CeCu_5$ with the $CaCu_5$ type structure is confirmed by [1978Tak], who claimed the existence of $CeCu_4Al$ and $CeCu_3Al_2$ with this structure, whilst an alloy "$CeCu_2Al_3$" was found to be multi-phase. There are, however, no details available concerning the extended solid solution $CeCu_{4-x}Al_x$ reported by [1985Bod].

Temperature – Composition Sections

A number of vertical sections of the phase diagram, (Al)-τ_1,$CeCu_4Al_8$, (Al)-τ_4,$CeCuAl_4$, τ_1,$CeCu_4Al_8$-τ_4,$CeCuAl_4$ and τ_4,$CeCuAl_4$-$CeAl_2$, all showing a simple eutectic behavior were studied by [1991Yun]. They are shown in Figs. 5, 6, 7 and 8. The eutectic temperatures have been accepted as given by the authors. However, the positions of the eutectic e_5 (Fig. 5) and e_4 (Fig. 6) have been modified for the sake of coherence with crystallization domains shown in Fig. 1.

Notes on Materials Properties and Applications

[1961Gla1] reported on the microhardness of the (Al) solid solution; a microhardness of 200 MPa for a binary (Al - 1 mass% Ce) alloy is compared with 420 MPa for a ternary (Al - 1 mass % Ce - 6 mass % Cu) alloy. The microhardness of $CeCu_4Al_8$ was 3860 ± 100 MPa, and that of $CeCuAl_3$ was 3170 ± 100 MPa [1961Gla1]. From a magnetic analysis, CeCuAl exhibits a small value of susceptibility and does not order magnetically [1973Oes]. For the ternary compounds $CeCu_4Al_8$, $Ce_2Cu_7Al_{10}$ and $CeCu_{6.5}Al_{6.5}$ physical properties have been investigated by [1985Rau], such as electrical resistivity (30 mK to 400 K), thermoelectric power (1.5 to 400 K), low field a.c. susceptibility (117 Hz, 30 mK to 4.2 K, in fields up to

8 T) and the specific heat (from 100 mK to 4.2 K, 0-8 T) $CeCu_{6.5}Al_{6.5}$ shows a magnetic transition at 0.5 K, which displays spin-glass-like behavior although representing a periodic lattice of local moments [1985Rau].
"$CeCu_6Al_6$" ($NaZn_{13}$ type) was claimed to exhibit paramagnetic behavior of trivalent cerium down to 1.7 K [1982Fel]. [1996Shc] carried out L_{III} X-ray absorption (77 and 300 K) and magnetic susceptibility measurements on RCu_4Al_8 compounds finding peculiarities of the valence state of Ce and Yb in RCu_4Al_8. Finally [2000Kon] studied magnetic properties of $CeCu_{4+x}Al_{8-x}$ ($0 \le x \le 0.55$) by specific heat and electrical resistivity, ^{27}Al-NMR and ^{63}Cu-NQR measurements.
Spin fluctuations in the $Ce_2Cu_8Al_9$ phase have been studied by neutron scattering [1999Ooh].
[1996Aoy] carried out an NMR study on the heavy fermion material $CeCuAl_3$ and [1996Kon] studied by NMR the effect of high pressure on the heavy fermion anti-ferromagnet $CeCuAl_3$, up to 15 kbar. Subsequently [1999Kon] investigated magnetic properties of $CeCu_xAl_{4-x}$ for x = 0.8, 0.9, 1, 1.1, by magnetic susceptibility, high-held magnetization, specific heat and electrical resistivity measurements on single crystal samples.
Recent papers about magnetic properties of the RCuAl phases are the following.
[2000Jav] reported a comparative study of CeNiAl and CeCuAl with respect to crystal structure and specific heat: magnetic ordering below 5 K has been proposed for CeCuAl, the γ coefficient of the specific heat is ~150 $mJ \cdot mol^{-1}K^{-2}$, as obtained in the range 12-20 K. Subsequently the electrical resistivity and magnetization measurements, carried out by [2001Che], revealed the occurrence of antiferromagnetic ordering in CeCuAl below T_N = 5.2 K; moreover electronic structure has been investigated by core-level photoemission spectroscopy by [1993Sin].
Finally [2001Li] studied the effect of Ce addition on the hydrogen absorption of Al-32.2Cu (mass%) eutectic alloy melt. $CeCu_{6.5}Al_{6.5}$ was said to be stable in air but dissolves slowly in diluted acids [1985Cor1, 1985Cor2].

References

[1931Pre] Preston, G.D., "An X-ray Investigation of Some Copper-Aluminium Alloys", *Philos. Mag.*, **12**, 980-993 (1931) (Crys. Structure, Experimental, 11)

[1961Gla1] Gladyshevsky, E.I., Kolobnev, I.F., Zarechnyuk, O.S., "Aluminium-Rich Alloys in the Al-Ce-Cu System", *Russ. J. Inorg. Chem.*, **6**, 1075-1078 (1961), translated from *Zhur. Neorg. Khim.*, **6**, 2103 (1961) (Experimental, Equi. Diagram, 4)

[1961Gla2] Gladyshevsky, E.I., Kripyakevich, P.I., Teslyuk, M.Yu., Zarechnyuk O.S., Kuz'ma, Yu.B., "Crystal Structures of Some Intermetallic Compounds", *Sov. Phys. Crystallogr.,* **6**, 207-208 (1961) (Crys. Structure, 11)

[1963Zar] Zarechnyuk, O.S., Kripyakevich, P.I., "Crystal Structures of Ternary Compounds in the Systems Cerium - Transition Metal - Aluminium", *Sov. Phys. Crystallogr.*, **7**, 436-446 (1963) (Experimental, Crys. Structure, 9)

[1964Che] Cherkashin, E.E., Zarechnyuk, O.S., Kripyakevich, P.I., Kolobnev, I.F., "Crystal Structure of the Compounds in the Ce-Mn-Cu-Al System and in the Corresponding Ternary System", *Vopr. Teorii i Primeneniya Redkozem. Metal., Akad. Nauk SSSR*, 151-152 (1964) (Experimental, Crys. Structure, 8)

[1964Zar] Zarechnyuk, O.S., Kripyakevich, P.I., Gladyshevskij, E.I., "Ternary Intermetallic Compounds with a $BaAl_4$ Type Superlattice", *Sov. Phys. Crystallogr.*, **9**, 706-708 (1965), translated from *Kristallografiya,* **9**, 835-838 (1964) (Experimental, Crys. Structure, 6)

[1968Dwi] Dwight, A.E., Muller, M.H., Conner, Jr., R.A. Downey, J.W., Knott, H., "Ternary Compounds with the Fe_2P Type Structure", *Trans. AIME*, **242**, 2075-2080 (1968) (Experimental, Crys. Structure, 14)

[1973Oes] Österreicher, H., "Structural and Magnetic Studies on Rare Earth Compounds RNiAl and RCuAl", *J. Less-Common Met.*, **30**, 225-236 (1973) (Experimental, Crys. Structure, Magn. Prop., 21)

[1976Bus] Buschow, K.H.J., van Vucht, J.H.N., van den Hoogenhof, W.W., "Note on the Crystal Structure of the Ternary Rare Earth - 3d Transition Metal Compounds of the Type RT_4Al_8", *J. Less-Common Met.*, **50**, 145-150 (1976) (Crys. Structure, Experimental, 2)

[1978Tak] Takeshita, T., Malik, S.K., Wallace, W.E., "Crystal Structure of RCu_4Ag and RCu_4Al (R=Rare Earth) Intermetallic Compounds", *J. Solid State Chem.*, **23**, 225-229 (1978) (Experimental, Crys. Structure, 8)

[1982Fel] Felner, I., Nowik, I., "Magnetic Properties of RM_6Al_6 (R=Light Rare Earth, M = Cu, Mn, Fe)", *J. Phys. Chem. Solids*, **43**, 463-465 (1982) (Experimental, Crys. Structure, Magn. Prop., 4)

[1985Bod] Bodak, O.I., Gladyshevskij, E.I., *Ternary Systems with Rare Earth Metals*, Vyshcha Schola, Lviv, 79-80 (1985) (Review, Crys. Structure, Equi. Diagram, 3)

[1985Cor1] Cordier, G., Czech, E., Schäfer, H., "On the Knowledge of the Compounds $Ca_4Cd_5Al_3$, $CaAg_4Al_7$, $CaCu_{6.5}Al_{6.5}$, $SrAg_{6.5}Al_{6.5}$ and $CeCu_{6.5}Al_{6.5}$" (in German), *J. Less-Common Met.,* **108**, 225-239 (1985) (Experimental, Crys. Structure, 33)

[1985Cor2] Cordier, G., Czech, E., Schäfer, H., Woll, P., "Structural Characterization of New Ternary Compounds of Uranium and Cerium", *J. Less-Common Met.,* **110**, 327-330 (1985) (Experimental, Crys. Structure, 5)

[1985Mur] Murray, J.L., "The Aluminum-Copper System", *Int. Met. Rev.*, **30**(5), 211-233 (1985) (Equi. Diagram, Crys. Structure, Review, 230)

[1985Rau] Rauchschwalbe, U., Gottwick, U., Ahlheim, U., Mayer, H.M., Steglich, F., "Investigation of New Lanthanum-, Cerium- and Uranium-Based Ternary Intermetallics", *J. Less-Common Met.*, **111**, 265-275 (1985) (Experimental, Crys. Structure, 31)

[1987Bau] Bauer, E., Gratz, E., Pillmayr, N., "Heavy Fermion Behavior of the Nonmagnetic $CeCu_4Al$ Compound", *Solid State Commun.*, **62**(4), 271-274 (1987) (Magn. Prop., Experimental, 22)

[1988Fis] Fisk, Z., Thompson, J.D., Ott, H.R., "Heavy-Electrons: New Materials", *J. Magn. Magn. Mater.*, **76/77**, 637-641 (1988) (Crys. Structure, Experimental, 21)

[1988Gsc] Gschneidner Jr, K.A., Calderwood, F.W., "The Aluminum-Cerium (Al-Ce) System", *Bull. Alloy Phase Diagrams*, **9**(6), 669-672 (1988) (Review, 35)

[1989Mee] Meetsma, A., de Boer, J.L., van Smaalen S., "Refinement of the Crystal Structure of Tetragonal Al_2Cu", *J. Solid State Chem.*, **83**(2), 370-372 (1989) (Crys. Structure, Experimental, 17)

[1990Cor] Cordier, G., Doersam, G., Roehr, C., "New Ternary Representatives of $ThCr_2Si_2$- and of $CaZn_2Al_2$-Structure Types in the Systems A-T-X and RE-T-X (A = Calcium, Strontium, Barium; RE = Lanthanum, Cerium, Praseodymium; T = Copper, Silver, Gold and X = Aluminum, Gallium)" (in German), *J. Less-Common Met.,* **166**(1)**,** 115-124 (1990) (Crys. Structure, Experimental, 19)

[1990Vrt] Vrtis, M.L., Jorgensen, J.D., Hinks, D.G., "The Structural Phase Transition in the $RECu_6$ Compounds (RE = La,Ce,Pr,Nd)" *J. Solid State Chem.*, **84**, 93-101 (1990) (Crys. Structure, Experimental, 26)

[1991Ell] Ellner, M., Kolatschek, K., Predel, B., "On the Partial Atomic Volume and the Partial Molar Enthalpy of Aluminium in Some Phases with Cu and Cu_3Au Structures", *J. Less-Common Met.*, **170**, 171-184 (1991) (Experimental, Crys. Structure, 57)

[1991Kim] Kim, S.M., Buyers, W.J.L., Lin, H., Bauer, E., "Structure of the Heavy Electron Compounds Cerium-Copper-Aluminum $Ce(Cu_xAl_{1-x})_5$ and Cerium-Copper-Gallium $Ce(Cu_xGa_{1-x})_5$", *Z. Phys. B*, **84**(2), 201-203 (1991) (Crys. Structure, Experimental, 7)

[1991Rog] Rogl, P., "Aluminium - Cerium - Copper", MSIT Ternary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 10.17383.1.20, (1991) (Crys. Structure, Equi. Diagram, Assessment, 18)

[1991Yun] Yunusov, I., Ganiev, I. N., Shishkin, E. A., "Aluminum-Copper-Cerium Phase Diagram in the Aluminum-Rich Corner" (in Russian), *Izv. Akad. Nauk SSSR, Met.*, (**3**), 200-203 (1991) (Assessment, Equi. Diagram, 4)

[1992Bau] Bauer, E., "Anomalous Properties of Ce-Cu-Based Compounds", *J. Magn. Magn. Mater.*, **108**(1-3), 27-30 (1992) (Electr. Prop., Experimental, 19)

[1993Sin] Singhal, R.K., Saini, N.L., Garg, K.B., Kanski, J., Ilver, L., Nilsson, P.O., Kumar, R., Gupta, L.C., "Study of some Cerium Intermetallics by Core-Level Photoemission", *J. Phys.: Condens. Matter*, **5**, 4013-4020 (1993) (Experimental, Electr. Prop., 23)

[1994Mur] Murray, J.L., "Al-Cu (Aluminum-Copper)", in "*Phase Diagrams of Binary Copper Alloys*", Subramanian, P.R., Chakrabati, D.T., Laughlin D.E. (Eds.), ASM International, Materials Park, OH, 1994, 18-42, (Equi. Diagram, Review, 226)

[1994Sub] Subramanian, P.R., Laughlin, D.E., "Ce-Cu (Cerium-Copper)", in "*Phase Diagrams of Binary Copper Alloys*", Subramanian, P.R., Chakrabarti, D.J., Laughlin, D.E. (Eds.), ASM International 10, 127-133 (1994) (Equi. Diagram, Review, 29)

[1995Hul] Hulliger, F., "On Rare Earth Gold Aluminides $LnAuAl_3$ and Related Compounds", *J. Alloys Compd.*, **218**, 255-258 (1995) (Crys. Stucture, Magn. Prop., 14)

[1996Aoy] Aoyama, S., Ido, H., Nishioka, T., Kontani, M., "NMR Studies on Heavy Fermion Materials $CeCuAl_3$ and $CeCuGa_3$", *Czech. J. Phys.*, **46**, 2069-2070 (1996) (Experimental, 4)

[1996Goe] Goedecke, T., Sommer, F., "Solidification Behaviour of the Al_2Cu Phase", *Z. Metallkd.,* **87**(7), 581-586 (1996) (Equi. Diagram, Crys. Structure, 8)

[1996Kon] Kontani, M., Sugihara, N., Murase, K., Mori, N., "High Pressure NMR of Heavy Fermion Antiferromagnets $CeAl_2$ and $CeCuAl_3$", *Czech. J. Phys.*, **46**, 2067-2068 (1996) (Experimental, Phys. Prop., 4)

[1996Moz] Moze, O., Buschow, K.H.J., "Crystall Structure of $CeCuAl_3$ and its Influence on Magnetic Properties", *J. Alloys Compd.*, **245**, 112-115 (1996) (Crys. Structure, Experimental, Magn. Prop., 9)

[1996Shc] Shcherba, I.D., Koterlyn, M.D., Kushnir, A.P., Kutjanskyj, R.R., Synjushko, V.G., Tsybukh, Y.D., Yatsyk, B.M., Margolych, I.I., "Peculiarities of the Valence State of Ce and Yb in RM_4Al_8 (R = Rare Earth; M = Cr, Mn, Fe, Cu)", *J. Magn. Magn. Mater.*, **157-158**, 688-689 (1996) (Magn. Prop., Experimental, 4)

[1998Jav] Javorsky, P., Havela, L., Sechovsky, V., Michor, H., Jurek, K., "Magnetic Behavior of RCuAl Compounds", *J. Alloys Compd.*, **264**, 38-42 (1998) (Crys. Structure, Experimental, 15)

[1998Liu] Liu, X.J., Ohnuma, I., Kainuma R., Ishida, K., "Phase Equilibria in the Cu-rich Portion of the Cu-Al Binary System", *J. Alloys Compd.*, **264**(1-2), 201-208 (1998) (Equi. Diagram, Crys. Structure, 25)

[1999Kon] Kontani, M., Motoyama, G., Nishioka T., Murase, K., "Magnetic Properties of $CeCu_xAl_{4-x}$ and $CeCu_xGa_{4-x}$ Single Crystals", *Physica B*, **261**, 24-25 (1999) (Crys. Structure, Experimental, Magn. Prop., 7)

[1999Ooh] Oohara, Y., Kubota, M., Yoshizawa, H., Itoh, S., Nishioka, T., Kontani, M., "Spin Fluctuations in $Ce_2Cu_8Al_9$ and $U_2Cu_8Al_9$", *J. Phys. Chem. Solids*, **60**(8-9), 1197-1198 (1999) (Magn. Prop., Experimental, 4)

[2000Jav] Javorsky, P., Chernyavsky, A., Sechovsky, V., "Valence Fluctuator CeNiAl Versus Ce(3+) State in CeCuAl", *Physica B*, **281-282**, 71-72 (2000) (Crys. Structure, Experimental, Thermodyn., 6)

[2000Kon] Kontani, M., Hamada, M., Mizukoshi, T., Mukai, H., "NMR/NQR and Specific Heat Studies on the $ThMn_{12}$-Type $CeCu_{4+x}Al_{8-x}$ System", *Physica B*, **284-288**, 1267-1268 (2000) (Crys. Structure, Experimental, Magn. Prop., Thermodyn., 6)

[2000Oka] Okamoto, H., Desk Handbook, in "*Phase Diagrams for Binary Alloys*", ASM International, Materials Park, OH, 2000 (Experimental, Equi. Diagram)

[2001Che] Chevalier, B., Bobet, J.-L., "On the Synthesis and Physical Properties of the Intermetallics CeCuAl", *Intermetallics*, **9**, 835-838 (2001) (Crys. Structure, Electr. Prop., Experimental, Phys. Prop., 9)

[2001Li] Li, W.H., Bian, X.F., Li, H.Y., Duan, Y.F., "Interaction Between Rare Earth Ce and Hydrogen in Al-Cu Eutectic Alloy Melt", *Acta Metall. Sin.*, **37**(8), 825-828 (2001)

[2002Gul] Gulay, L.D., Harbrecht, B., "The Crystal Structures of the ζ_1 and ζ_2 Phases in the Al-Cu System", Abstr. VIII Int. Conf. "*Crystal Chemistry of Intermetallic Compounds*", September 2002, Lviv, P139, 73 (2002) (Crys. Structure, Experimental, 5)

[2002Per] Perrot, P., Ferro, R., "Ce-Cu (Cerium-Copper)", MSIT Binary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 20.16303.1.20, (2003) (Equi. Diagram, Assessment, 25)

[2003Gro] Groebner, J., "Al-Cu (Aluminium-Copper)", MSIT Binary Evaluation Program, in *MSIT Workplace,* Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart, to be published, (2003) (Equi. Diagram, Assessment, 68)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	a = 361.46	at 25°C [Mas2], 0 to 19.7 at.% Al [Mas2] 0 to 0.1 at.% Ce at 876°C [1994Sub]
$Cu_{1-x}Al_x$		a = 361.52 a = 365.36	[1991Ell], x = 0, quenched from 600°C [1991Ell], x = 0.152, quenched from 600°C
(Al) < 660.45	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2], 0 to 2.48 at.% Cu [Mas2]
(δCe) 798-726	*cI*2 $Im\bar{3}m$ W	a = 412	0 to 0.55 at.% Cu at 708°C [1994Sub] 0 to 2.5 at.% Al at 720°C [2000Oka]
(γCe) 726-61	*cF*4 $Fm\bar{3}m$ Cu	a = 510.10	0 to 0.37 at.% Cu at 708°C [1994Sub]
(βCe) 61-(-177)	*hP*4 $P6_3/mmc$ αLa	a = 308.10 c = 1185.7	at 24°C [1994Sub]
(αCe) < -177	*cF*4 $Fm\bar{3}m$ Cu	a = 485	at –196°C [1994Sub]
β, Cu_3Al(h) 1049-559	*cI*2 $Im\bar{3}m$ W	a = 295.64	70.6 to 82 at.% Cu [1985Mur][1998Liu] at 672°C in β + (Cu) alloy
α_2, $Cu_{1-x}Al_x$ < 363	 $TiAl_3$ Long period super-lattice	 a = 366.8 c = 368.0	$0.22 \le x \le 0.235$ [Mas2, 1985Mur] 76.5 to 78.0 at.% Cu at 76.4 at.% Cu (subcell only)
γ_0, $Cu_{1-x}Al_x$ $Cu_{\sim 2}Al$ 1037-800	*cI*52 $I\bar{4}3m$ Cu_5Zn_8		$0.31 \le x \le 0.402$ [Mas2], $0.32 \le x \le 0.38$ [1998Liu]
γ_1, Cu_9Al_4 < 890	*cP*52 $P\bar{4}3m$ Cu_9Al_4	 a = 870.23 a = 870.68	62 to 68 at.% Cu [Mas2, 1998Liu]; powder and single crystal [V-C2] from single crystal [V-C]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ, $Cu_{1-x}Al_x$ < 686	*hR** $R\bar{3}m$	a = 1226 c = 1511	0.381 ≤ x ≤ 0.407 [Mas2, 1985Mur] 59.3 to 61.9 at.% Cu at x = 0.389 [V-C]
ε_1, $Cu_{1-x}Al_x$ 958-848	Cubic?	-	0.379 ≤ x ≤ 0.406 59.4 to 62.1 at.% Cu [Mas2, 1985Mur]
ε_2, $Cu_{2-x}Al$ 850-560	*hP*6 *P6₃/mmc* Ni_2In	a = 414.6 c = 506.3	0.47 ≤ x ≤ 0.78; 55.0 to 61.1 at.% Cu [Mas2, 1985Mur, V-C2] NiAs type in [Mas2, 1994Mur]
ζ_1, ~$Cu_{47.8}Al_{35.5}$(h) 590-530	*oF*88 - 4.7 *Fmm2* $Cu_{47.8}Al_{35.5}$	a = 812 b = 1419.85 c = 999.28	55.2 to 57 at.% Cu [Mas2, 1994Mur] structure: [2002Gul]
ζ_2, $Cu_{11.5}Al_9$(r) < 570	*oI*24 - 3.5 *Imm2* $Cu_{11.5}Al_9$	a = 409.72 b = 703.13 c = 997.93	55.2 to 56.3 at.% Cu [Mas2, 1985Mur] structure: [2002Gul]
η_1, CuAl(h) 624-560	*o**32	a = 408.7 b = 1200 c = 863.5	49.8 to 52.4 at.% Cu [V-C2, Mas2, 1985Mur] Pearson symbol: [1931Pre]
η_2, CuAl(r) < 560	*mC*20 *C2/m* CuAl(r)	a = 1206.6 b = 410.5 c = 691.3 β = 55.04°	49.8 to 52.3 at.% Cu [V-C2]
θ, $CuAl_2$ < 591	*tI*12 *I4/mcm* $CuAl_2$	a = 606.7 c = 487.7	32.05 to 32.6 at.% Cu at 549°C 32.4 to 32.8 at.% Cu at 250°C [1996Goe] single crystal [V-C2, 1989Mee]
CeCu < 516	*oP*8 *Pnma* FeB	a = 737.0 b = 462.3 c = 564.8	[1994Sub]
$CeCu_2$ < 817	*oI*12 *Imma* $CeCu_2$	a = 442.9 b = 706.1 c = 747.4	[1994Sub]
$CeCu_{4-x}Al_x$ $CeCu_4$ < 796	*oP*20 *Pnnm* $CeCu_4$	a = 458 b = 810 c = 935	0 ≤ x ≤ 2 [1985Bod] at x = 0 [1994Sub]
$CeCu_{5-x}Al_x$	*hP*6 *P6/mmm* $CaCu_5$	a = 525.1 c = 417.3	0 ≤ x ≤ 2.1 [1978Tak] at x = 2 [2001Che]
$CeCu_5$ < 798		a = 514.8 c = 410.8	at x = 0 [Mas2, 1994Sub]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βCeCu$_6$	*oP*28	*a* = 810.88	at 22°C [1990Vrt]
938 - (-43)	*Pnma*	*b* = 510.04	
	βCeCu$_6$	*c* = 1016.21	
		a = 810.09	at -23°C [1990Vrt]
		b = 509.78	
		c = 1015.48	
αCeCu$_6$	*mP*28	*a* = 509.5	at -73°C [1990Vrt]
< -43	*P2$_1$/c*	*b* = 1014.66	
	αLaCu$_6$	*c* = 809.31	
		β = 90.485°	
		a = 508.92	at -173°C [1990Vrt]
		b = 1013.26	
		c = 807.89	
		β = 91.148°	
		a = 508.41	at -263°C [1990Vrt]
		b = 1012.79	
		c = 807.31	
		β = 91.442°	
αCe$_3$Al$_{11}$	*oI*28	*a* = 439.5	[1988Gsc]
<1020	*Immm*	*b* = 1302.	
	αLa$_3$Al$_{11}$	*c* = 1009	
βCe$_3$Al$_{11}$	*tI*10	*a* = 437.7	[1988Gsc]
1235-1020	*I4/mmm*	*c* = 1008	
	BaAl$_4$		
CeAl$_3$	*hP*8	*a* = 654.7	[1988Gsc]
<1135	*P6$_3$/mmc*	*c* = 461.0	
	Ni$_3$Sn		
CeAl$_2$	*cF*24	*a* = 806.1	[1988Gsc]. Dissolves Al$_2$Cu.
<1480	*Fd$\bar{3}$m*		Al$_2$Ce$_{1-x}$Cu$_x$ ($0 < x < 0.1$) [1991Yun]
	Cu$_2$Mg		
CeAl	*oC*16	*a* = 926.9	[1988Gsc]
<845	*Cmc2* or *Cmcm*	*b* = 768.0	
	CeAl	*c* = 576.1	
βCe$_3$Al	*cP*4	*a* = 498.9	[1988Gsc]
655-250	*Pm$\bar{3}$m*		
	AuCu$_3$		
αCe$_3$Al	*hP*8	*a* = 704.2	[1988Gsc]
< 250	*P6$_3$/mmc*	*c* = 545.1	
	Ni$_3$Sn		
*τ$_1$, CeCu$_4$Al$_8$	*tI*26	*a* = 884	[1963Zar], [1964Che]
< 925	*I4/mmm*	*c* = 517	
	ThMn$_{12}$	*a* = 882.9	[1976Bus]
		c = 515.7	
		a = 885	[1985Rau], [1961Gla2]
		c = 518	

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
*τ_2,$Ce_2Cu_xAl_{17-x}$	*hR*57		6.5 ≤ *x* ≤ 7.3 [1963Zar]
	$R\bar{3}m$	*a* = 898	at *x* = 6.5 [1963Zar]
	Th_2Zn_{17}	*c* = 1307	
		a = 897	at *x* = 7.0 [1985Rau]
		c = 1306	
		a = 896	at *x* = 7.3 [1963Zar, 1964Che]
		c = 1304	
*τ_3,$CeCu_{6.5}Al_{6.5}$	*cF*112	*a* = 1182.2 ± 0.04	[1985Cor1, 1985Cor2]
	$Fm\bar{3}c$	*a* = 1180	[1985Rau]
	$NaZn_{13}$	*a* = 1187	[1982Fel]
*τ_4,$CeCu_xAl_{4-x}$	*tI*10		0.75 ≤ *x* ≤ 1 [1964Zar]
	I4/mmm	*a* = 427	at *x* = 0.75 [1964Zar]
	$BaAl_4$	*c* = 1075	
		a = 425	at *x* = 1.0 [1964Zar]
		c = 1065	
	I4mm	*a* = 425.693	at *x* = 0 neutron diffraction data [1996Moz]
	$BaNiSn_3$	*c* = 1063.414	
*τ_5,CeCuAl	*hP*9	*a* = 717.6	[1968Dwi]
	$P\bar{6}_3m$	*c* = 419.8	
	Fe_2P	*a* = 717.9	[1973Oes]
		c = 420.1	

Table 2: Invariant Equilibria

Reaction	Type	*T* [°C]	Phase	Composition (at.%)		
				Al	Ce	Cu
L + $CeAl_2$ ⇌ Ce_3Al_{11}	p_1	1235	L	78.7	21.3	0
			$CeAl_2$	66.7	33.3	0
			Ce_3Al_{11}	78.6	21.4	0
L ⇌ $CeAl_2$ + τ_4,$CeCu_xAl_{4-x}$	e_1	1220	L	66.7	20.0	13.3
			$CeAl_2$	66.7	30.1	3.2
			τ_4	66.6	16.7	16.7
L + $CeAl_2$ ⇌ Ce_3Al_{11} + τ_4,$CeCu_xAl_{4-x}$	U_1	1150	L	77.0	18.0	5.0
			$CeAl_2$	66.7	33.3	0
			Ce_3Al_{11}	21.4	78.6	0
			τ_4	66.6	16.7	16.7
L ⇌ τ_1,$CeCu_4Al_8$ + τ_4,$CeCu_xAl_{4-x}$	e_2	850	L	62.1	8.7	29.2
			τ_1	61.5	7.7	30.8
			τ_4	66.6	16.7	16.7
L ⇌ (Al) + Ce_3Al_{11}	e_3	640	L	96.0	4.0	0
			(Al)	100	0	0
			Ce_3Al_{11}	21.4	78.6	0

Reaction	Type	T [°C]	Phase	Composition (at.%)		
				Al	Ce	Cu
$L \rightleftharpoons (Al) + \tau_4,CeCu_xAl_{4-x}$	e_4	595	L	96.0	2.0	2.0
			(Al)	98.4	0.8	0.8
			τ_4	66.6	16.7	16.7
$L + \eta_1,CuAl \rightleftharpoons \theta,CuAl_2$	p_2	591	L	67.8	0	32.2
			η_1	50.2	0	49.8
			$\theta,CuAl_2$	67.2	0	32.8
$L \rightleftharpoons (Al) + \tau_1,CeCu_4Al_8$	e_5	585	L	90.0	2.0	8.0
			(Al)	98.9	0.4	1.5
			τ_1	61.5	7.7	30.8
$L + \eta_1,CuAl \rightleftharpoons \theta,CuAl_2 + \tau_1,CeCu_4Al_8$	U_2	584	L	73.0	1.5	25.5
			η_1	50.2	0	49.8
			θ	67.2	0	32.8
			τ_1	61.5	7.7	30.8
$L \rightleftharpoons (Al) + Ce_3Al_{11} + \tau_4,CeCu_xAl_{4-x}$	E_1	560	L	95.0	3.5	1.5
			(Al)	100	0	0
			Ce_3Al_{11}	21.4	78.6	0
			τ_4	66.6	16.7	16.7
$L \rightleftharpoons (Al) + \theta,CuAl_2$	e_6	548.2	L	82.9	0	17.1
			(Al)	97.5	0	2.5
			$\theta,CuAl_2$	68.1	0	31.9
$L \rightleftharpoons (Al) + \tau_1,CeCu_4Al_8 + \tau_4,CeCu_xAl_{4-x}$	E_2	545	L	92.0	2.0	6.0
			(Al)	97.5	0	2.5
			τ_1	61.5	7.7	30.8
			τ_4	66.6	16.7	16.7
$L \rightleftharpoons (Al) + \theta,CuAl_2 + \tau_1,CeCu_4Al_8$	E_3	541	L	83.8	1.1	15.1
			(Al)	97.5	0	2.5
			θ	68.1	0	31.9
			τ_1	61.5	7.7	30.8

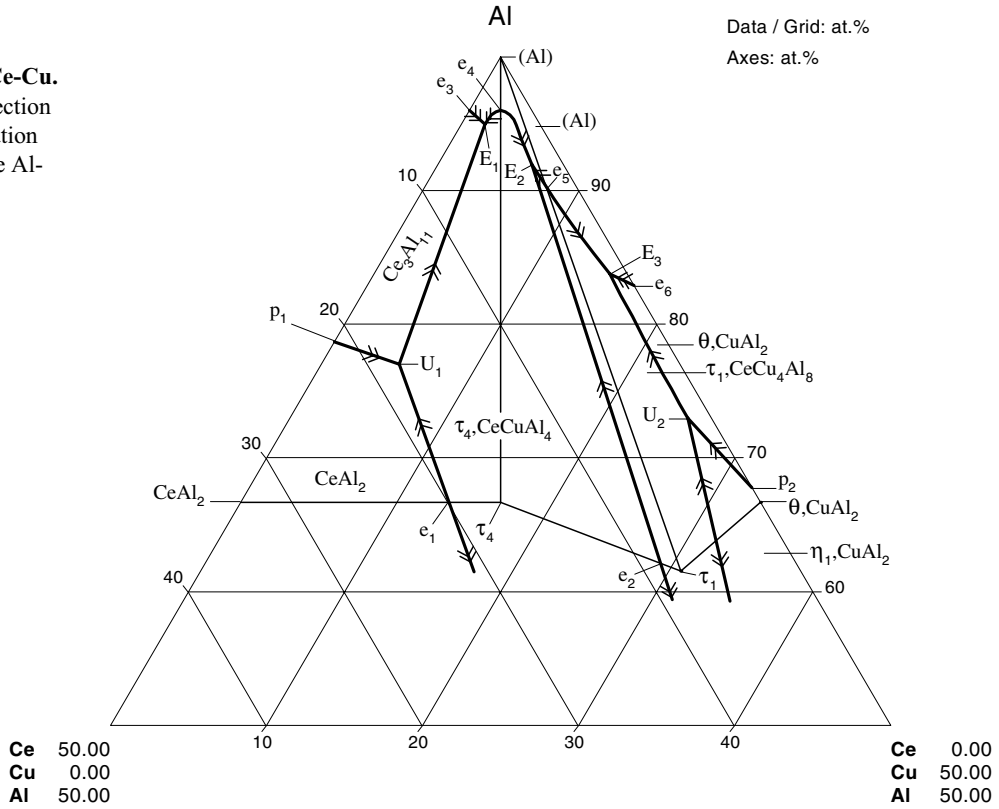

Fig. 1: Al-Ce-Cu. Liquidus projection and crystallisation domains of the Al-rich part

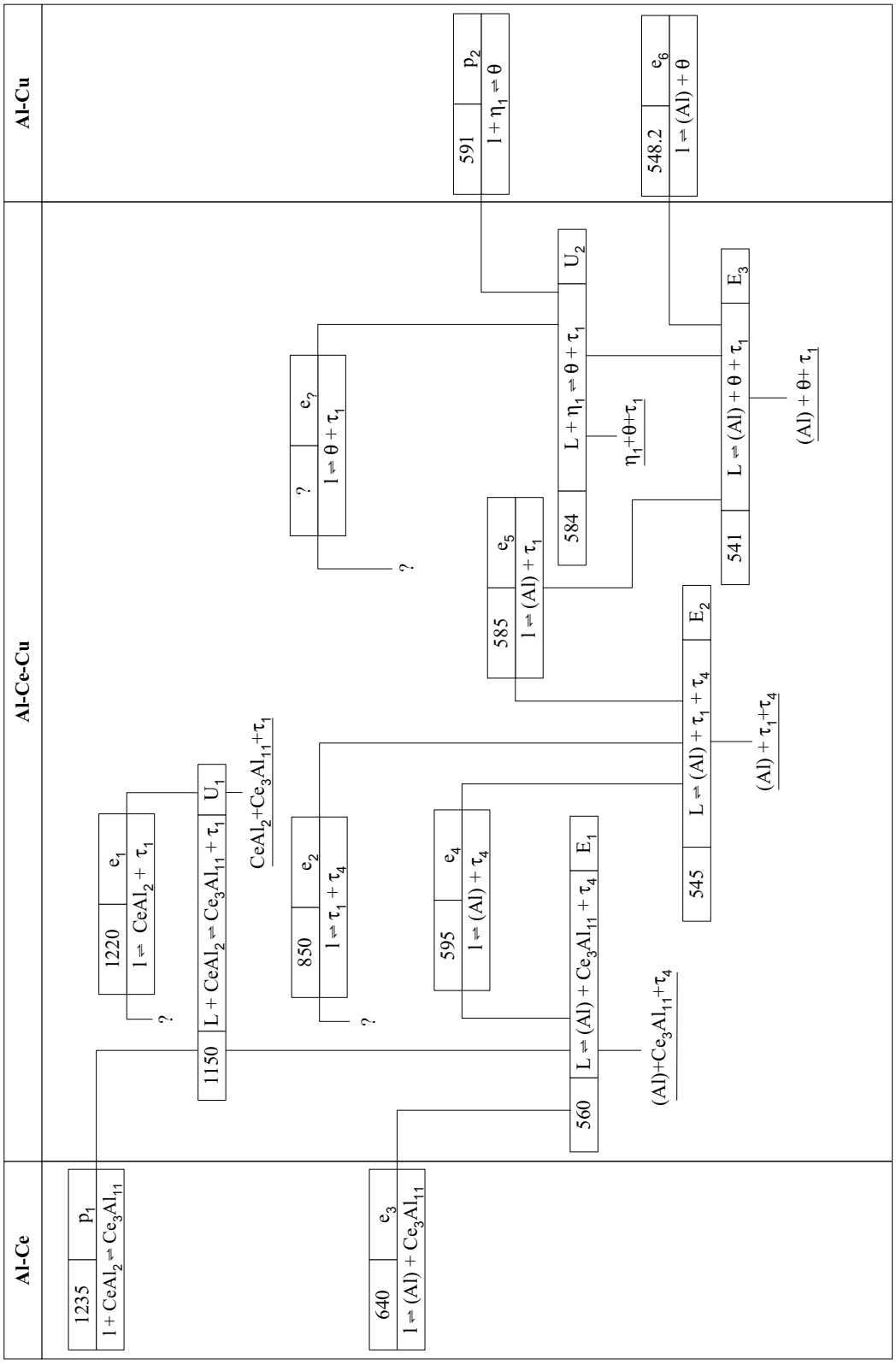

Fig. 2: Al-Ce-Cu. Partial reaction scheme

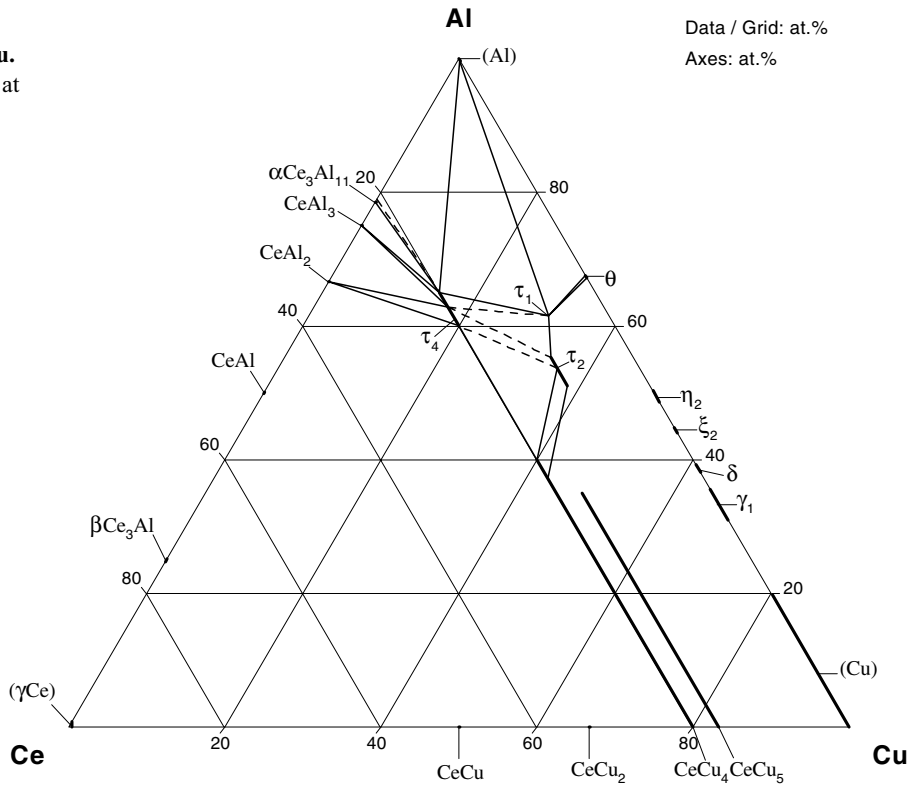

Fig. 3: Al-Ce-Cu. Isothermal section at 400°C

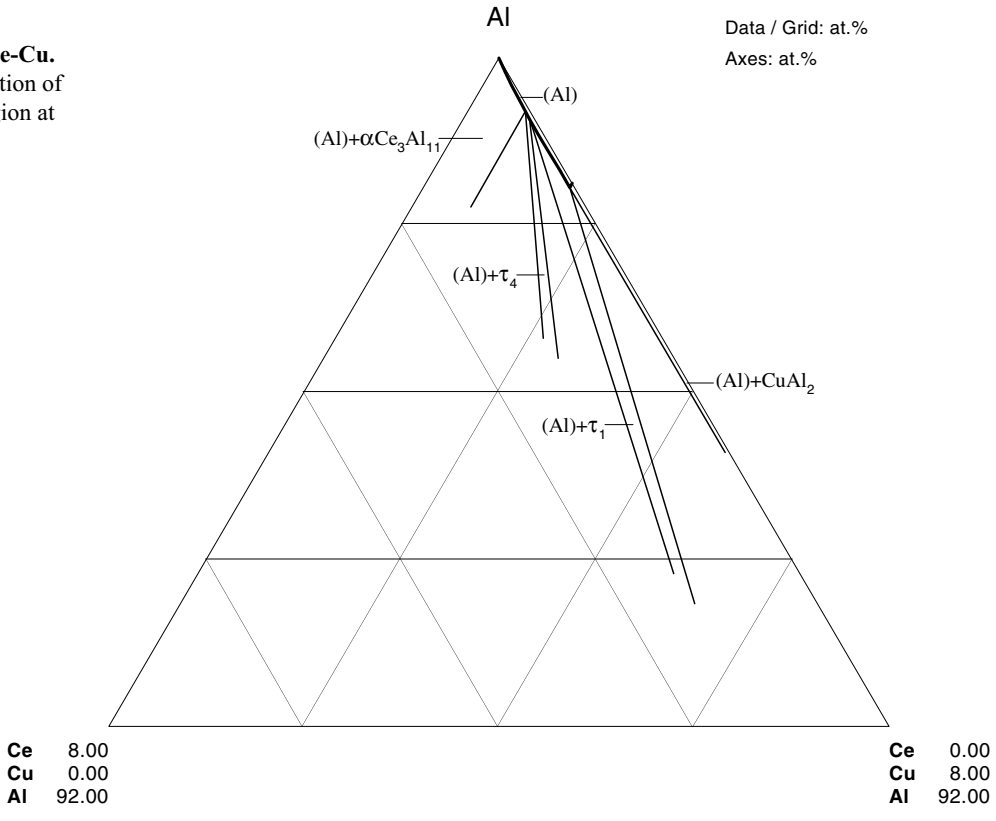

Fig. 4: Al-Ce-Cu. Isothermal section of the Al-rich region at 500°C

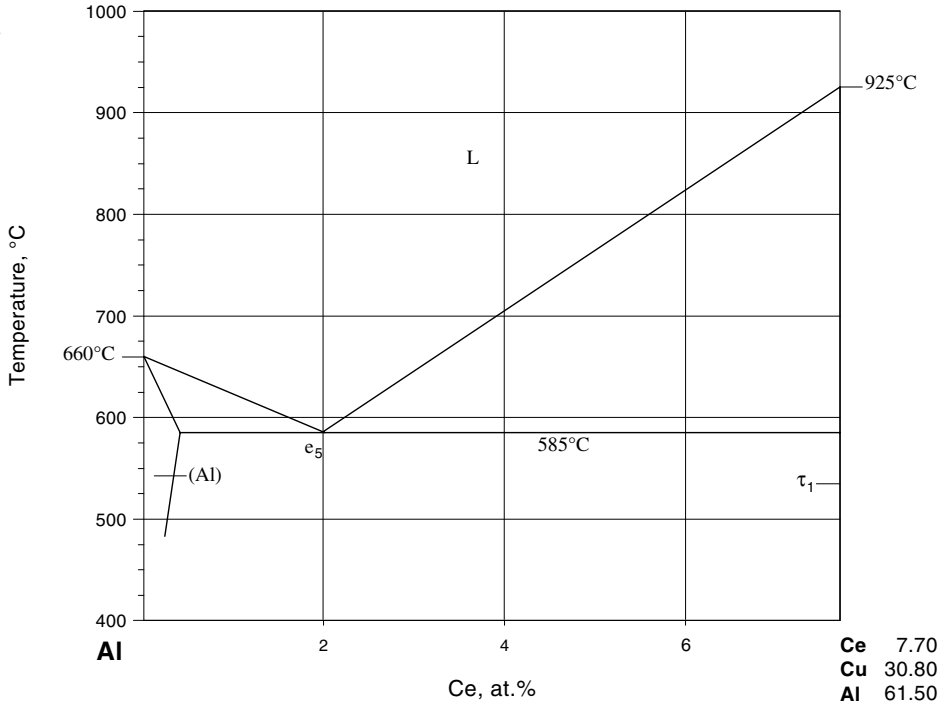

Fig. 5: Al-Ce-Cu. The Al - τ_1 quasibinary section

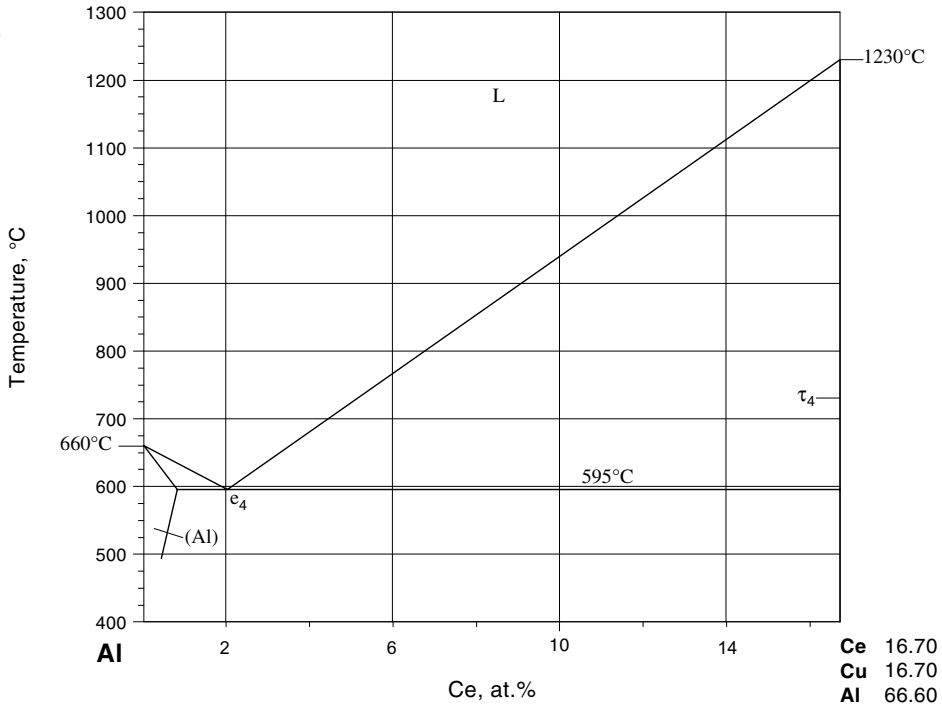

Fig. 6: Al-Ce-Cu. The Al - τ_4 quasibinary section

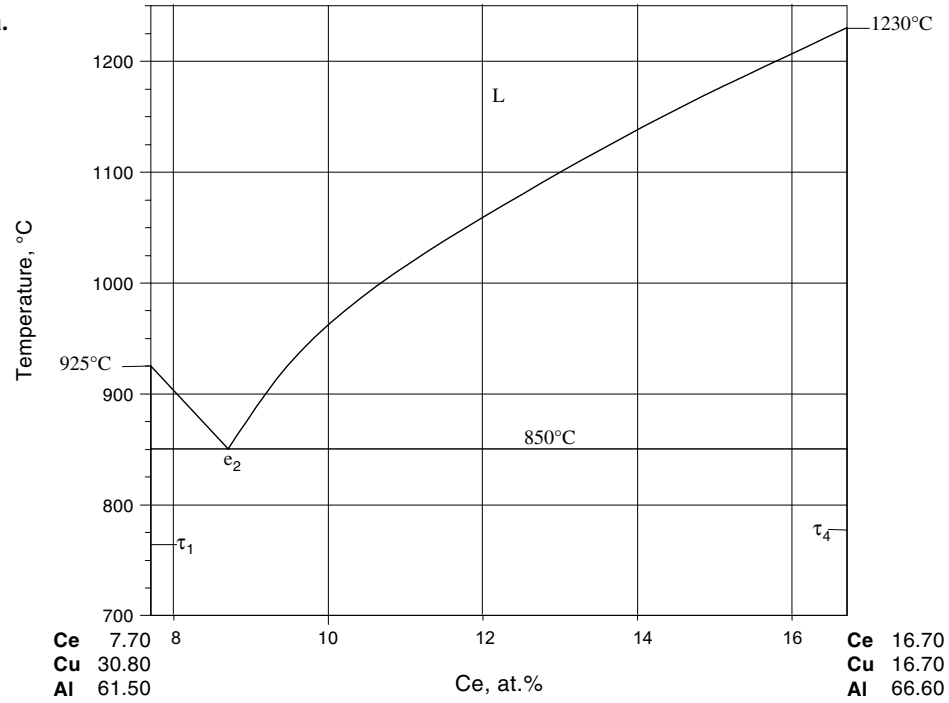

Fig. 7: Al-Ce-Cu. The τ_1 - τ_4 quasibinary section

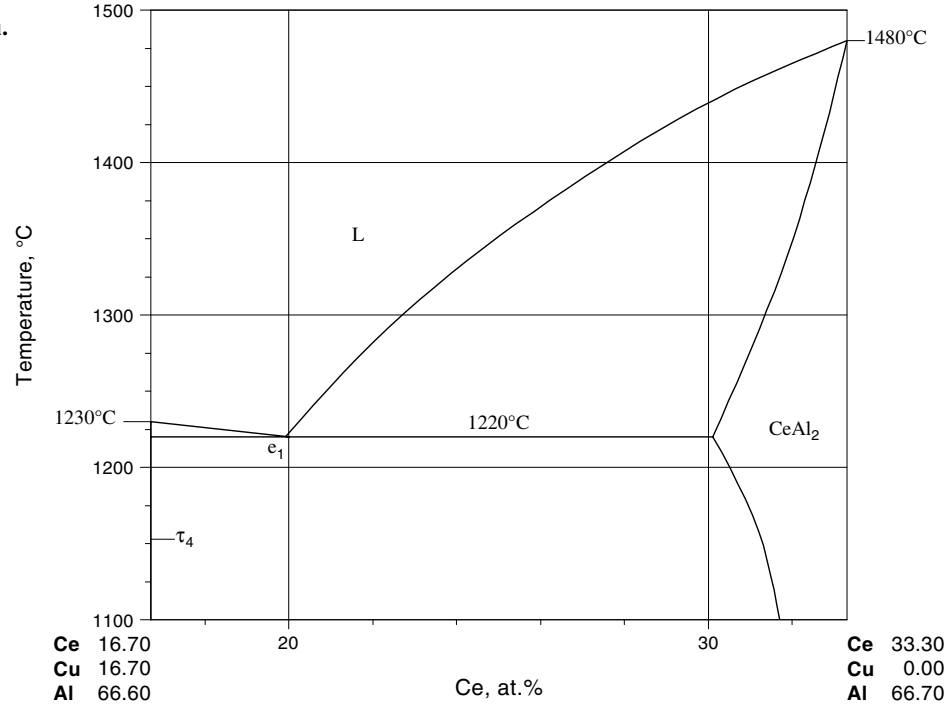

Fig. 8: Al-Ce-Cu. The τ_4 - $CeAl_2$ quasibinary section