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Al-Ce-Cu (Aluminum-Cerium-Copper)

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The early experimental data on this system were reviewed/updated by [2004Ria] and [2007Rag]. Subsequently, the phase relationships in the Al-rich region were studied by [2007Bel] and reviewed by [2008Rag]. Recently, the phase equilibria in a wider range of composition were reported by [2009Yao] and assessed thermodynamically by [2009Bo].

Binary Systems

The Al-Ce phase diagram was reassessed thermodynamically by [2005Gao], using new experimental results as additional input. The intermediate phases in this system are: αCe_3Al ($D0_{19}$, Ni_3Sn-type hexagonal), βCe_3Al ($L1_2$, $AuCu_3$-type cubic), Ce_2Al (stable between 775 and 648 °C; Co_2Si-type orthorhombic?), CeAl (orthorhombic), $CeAl_2$ ($C15$, $MgCu_2$-type cubic), $\alpha CeAl_3$ (Ni_3Sn-type hexagonal), $\beta CeAl_3$ (stable between 1192 and 973 °C), $CeAl_4$ or βCe_3Al_{11} ($D1_3$, Al_4Ba-type tetragonal), and αCe_3Al_{11} (αLa_3Al_{11}-type orthorhombic). The Al-Cu phase diagram [1998Liu] depicts a number of intermediate phases: $CuAl_2$ (θ, $C16$-type tetragonal), CuAl (η_1, orthorhombic), CuAl (η_2, monoclinic), Cu_5Al_4(LT) (ζ_2, orthorhombic), ε_1(bcc), ε_2 ($B8_2$, Ni_2In-type hexagonal), Cu_3Al_2 (δ, rhombohedral), Cu_9Al_4(HT) (γ_0, $D8_2$, Cu_5Zn_8-type cubic), Cu_9Al_4(LT) (γ_1, $D8_3$-type cubic), and Cu_3Al (β, bcc). In the above, HT = high-temperature and LT = low-temperature. The Ce-Cu phase diagram [Massaslki2] has the following intermediate phases: Cu_6Ce (orthorhombic, space group *Pnma*), Cu_5Ce ($D2_d$, $CaCu_5$-type hexagonal), Cu_4Ce (orthorhombic, space group *Pnnm*), Cu_2Ce (orthorhombic, space group *Imma*), and CuCe ($B27$, FeB-type orthorhombic).

Ternary Compounds

Five ternary compounds known in this system were summarized by [2004Ria] and [2009Yao] (see Table 1). $Al_{12-x}Cu_xCe$ (τ_1) ($4.0 \le x \le 4.52$) has $ThMn_{12}$-type tetragonal structure. $Al_{17-x}Cu_xCe_2$ (τ_2) ($6.5 \le x \le 7.55$) is Th_2Zn_{17}-type rhombohedral. $Al_{13-x}Cu_xCe$ (τ_3) ($6.62 \le x \le 6.92$) is cubic with $NaZn_{13}$ as the prototype. $Al_{4-x}Cu_xCe$(τ_4) ($0.74 \le x \le 1.10$) is Al_4Ba-type tetragonal. AlCuCe (τ_5) is Fe_2P-type hexagonal. The designations τ_1, τ_2, etc. adopted here are those given by [2009Yao] and differ from those given by [2009Bo].

Table 1 Al-Ce-Cu crystal structure and lattice parameter data [2009Yao]

Phase	Composition, at.%	Pearson symbol	Space group	Prototype	Lattice parameter, nm
$Al_{12-x}Cu_xCe$ (τ_1) ($4.0 \le x \le 4.52$)	61.5-57.5 Al 30.8-34.8 Cu 7.7 Ce	*tI*26	*I*4/*mmm*	$Mn_{12}Th$	*a* = 0.88223 *c* = 0.51557
$Al_{17-x}Cu_xCe_2$ (τ_2) ($6.5 \le x \le 7.55$)	55.3-49.7 Al 34.2-39.7 Cu 10.5 Ce	*hR*57	$R\bar{3}m$	Th_2Zn_{17}	*a* = 0.89501 *c* = 1.30452
$Al_{13-x}Cu_xCe$ (τ_3) ($6.62 \le x \le 6.92$)	45.6-43.4 Al 47.3-49.4Cu 7.1 Ce	*cF*112	$Fm\bar{3}c$	$NaZn_{13}$	*a* = 1.18754
$Al_{4-x}Cu_xCe$ (τ_4) ($0.74 \le x \le 1.10$)	65.2-58 Al 14.8-22 Cu 20 Ce	*tI*10	*I*4/*mmm*	Al_4Ba	*a* = 0.42633 *c* = 1.06852
AlCuCe (τ_5)	33.3 Al 33.3 Cu 33.3 Ce	*hP*9	$P\bar{6}2m$	Fe_2P	*a* = 0.7176 *c* = 0.4201
$AlCu_2Ce_2$ (τ')	20 Al 40Cu 40 Ce	...	...	...	...

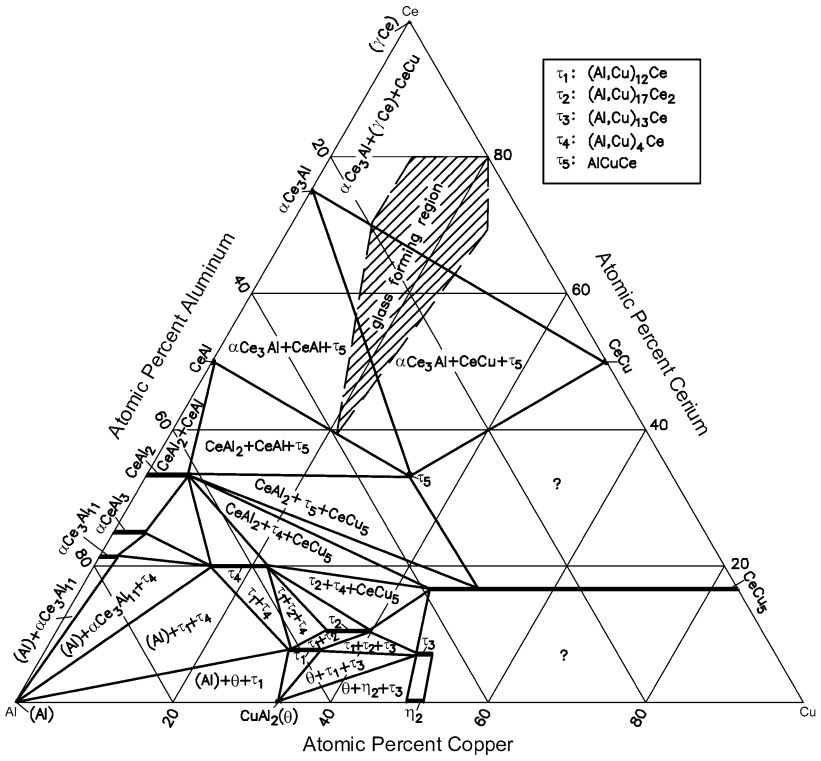

Fig. 1 Al-Ce-Cu isothermal section at 230 °C [2009Yao]. Narrow two-phase regions are omitted

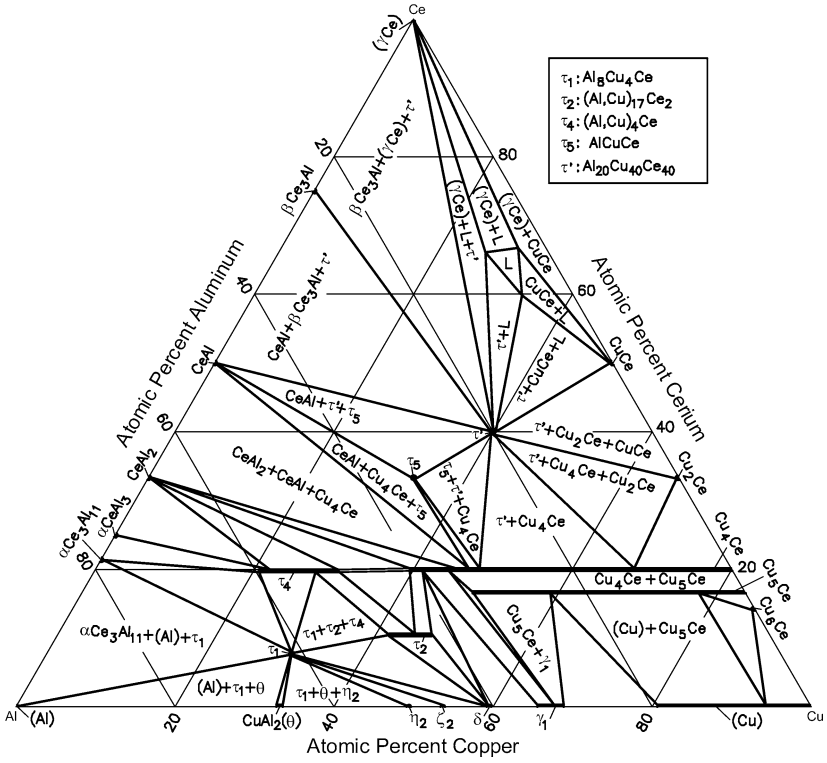

Fig. 2 Al-Ce-Cu computed isothermal section at 400 °C [2009Bo]. Narrow two-phase regions are omitted

The ternary compound AlCuCe (τ_5) was found by [2001Che] to form through a ternary peritectic reaction between 600 and 650 °C. A new compound $AlCu_2Ce_2$ (unknown structure, denoted τ′ here and as E by [2009Hu]) was reported by [2001Che] and was included in the thermodynamic description by [2009Bo].

Ternary Phase Equilibria

With starting metals of >99.8% purity, [2009Yao] arc-melted 210 alloys under Ar atm. The samples were annealed at 230 °C for 5 months and quenched in iced water. The phase equilbria were studied with x-ray powder diffraction. The isothermal section at 230 °C constructed by [2009Yao] is shown in Fig. 1. The Cu-rich region was not investigated. The solubility of Al in $CeCu_5$ is 39.2 at.%. The solubility of Cu in αCe_3Al_{11}, $\alpha CeAl_3$ and $CeAl_2$ is 1.6, 3.6, and 5.3 at.% respectively. The ternary compounds τ_1 to τ_5 are present. The compound τ_5 is of fixed composition, whereas the other four compounds show a homogeneity range as indicated in Table 1.

In a related publication, [2009Hu] studied the phase structure of the as-cast, arc-melted alloys mainly with x-ray powder diffraction. The phase distribution in the arc-melted alloys was similar to that in Fig. 1, with the exception that the phase AlCeCu (τ_5) was not found, but τ' ($AlCu_2Ce_2$) was present. Earlier, [2006Zha] had reported that the bulk metallic glasses (BMG) form in the Ce-rich region of this ternary system, see Fig. 1. [2009Hu] confirmed that an alloy of composition $Al_{10}Ce_{70}Cu_{20}$ falling within this region forms a glass on suck-casting in a copper mold. They pointed out that the equilibrium phase αCe_3Al is present in all the phase fields covered by the glass forming region. The close-packed high coordination of the αCe_3Al-structure might be beneficial in glass forming [2009Hu].

In their thermodynamic description, [2009Bo] accepted the binary descriptions of Al-Cu by [2004Wit] and of Al-Ce by [2005Gao]. They reassessed the Ce-Cu system. The substitutional solution model was used for the liquid, fcc and bcc phases. A ternary interaction parameter was introduced for the liquid phase only. The binary phases Cu_5Ce and Cu_4Ce were modeled as $(Al,Cu)_xCe$ (x = 5 or 4), providing for Al solubility at constant Ce content. The ternary compounds τ_1, τ_5, and τ' were taken to be stoichiometric. The τ_2 and τ_4 phases were modeled providing for a range of homogeneity at constant Ce content. As the compound $Al_{13-x}Cu_xCe$ (τ_3) was not found at 400 °C and above, it was omitted from the thermodynamic description by [2009Bo].

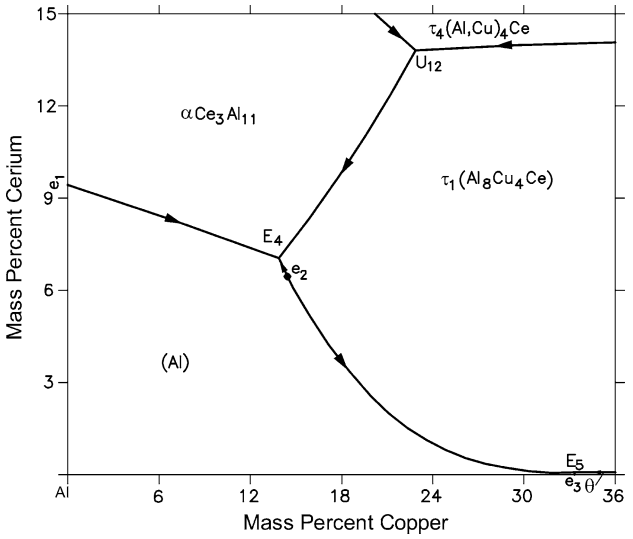

Fig. 3 Al-Ce-Cu computed liquidus projection for Al-rich alloys [2009Bo]

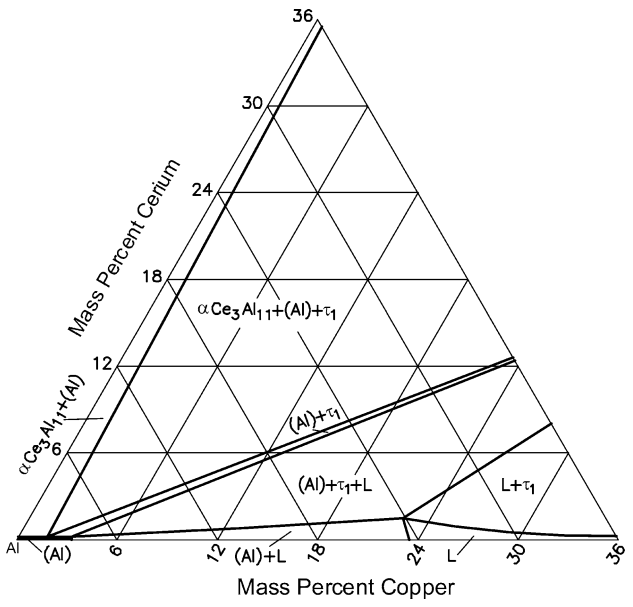

Fig. 4 Al-Ce-Cu computed isothermal section at 590 °C for Al-rich alloys [2009Bo]

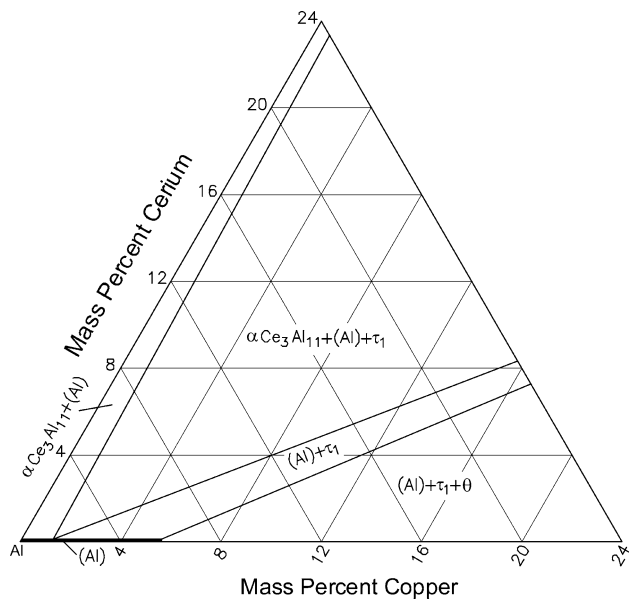

Fig. 5 Al-Ce-Cu computed isothermal section at 540 °C for Al-rich alloys [2009Bo]

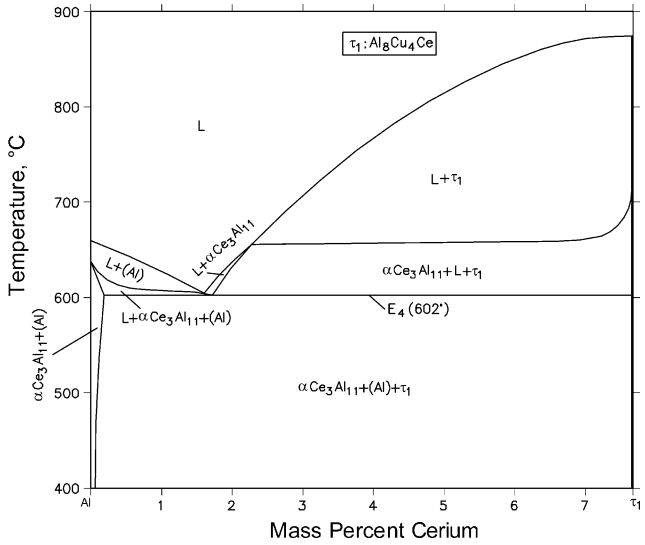

Fig. 6 Al-Ce-Cu computed vertical section along the Al-τ_1 join [2009Bo]

For the entire composition range, [2009Bo] computeded a liquidus projection and three isothermal sections at 650, 600, and 400 °C. As an example, the isothermal section at 400 °C is shown in Fig. 2. It depicts the ternary compounds τ_1, τ_2, τ_4, τ_5, and τ'. Except for Al-rich alloys, no experimental data are available for comparison with the computed diagrams. The computed liquidus projection for Al-rich alloys is shown in Fig. 3. The reactions are labeled as given by [2009Bo]. Satisfactory agreement was found between the computed invariant reaction temperatures and compositions and the experimental values reported by [2007Bel]. Two isothermal sections computed for Al-rich alloys at 590 and 540 °C are shown in Fig. 4 and 5. These are in satisfactory agreement with the phase distribution determined by [2007Bel], except that the solubility of Ce in the liquid at 590 °C is smaller in the computed section. Figure 6 shows the computed vertical section along the Al-τ_1 join. This section is not pseudobinary, as reported experimentally by [1991Yun] and [2006Bel]. The final solidification is through the ternary eutectic reaction (E_4) at 602 °C: $L \leftrightarrow (Al) + \alpha Ce_3Al_{11} + \tau_1$, corresponding to the invariant horizontal in Fig. 6.

References

1991Yun: L. Yunusov, I.N. Ganiev, and E.A. Shishkin, The Aluminum Rich Corner of the Al-Cu-Ce Phase Diagram, *Metally*, 1991, (3), p 200-203, in Russian; TR: *Russ. Metall.*, 1991, (3), p 197-200

1998Liu: X.J. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, Phase Equilibria in the Cu-Rich Portion of the Cu-Al Binary System, *J. Alloys Compd.*, 1998, **264**, p 201-208

2001Che: B. Chevalier and J.L. Bobet, On the Synthesis and Physical Properties of the Intermetallic CeCuAl, *Intermetallics*, 2001, **9**, p 835-838

2004Ria: P. Riani and P. Perrot, Aluminum-Cerium-Copper, *Light Metal Systems*, Landolt-Bornstein New Series IV: Physical Chemistry, Vol 11A1, 2004, p 181-195

2004Wit: V.T. Witusiewicz, U. Hecht, S.G. Fries, and S. Rex, The Ag-Al-Cu System. Part I: Reassessment of the Constituent Binaries on the Basis of New Experimental Data, *J. Alloys Compd.*, 2004, **385**, p 133-143

2005Gao: M.C. Gao, N. Unlu, G.J. Shiflet, M. Mihalkovic, and M. Widom, Reassessment of Al-Ce and Al-Nd Binary Systems Supported by Critical Experiments and First-Principles Energy Calculations, *Metall. Mater. Trans. A*, 2005, **36**, p 3269-3279

2006Bel: N.A. Belov, A.V. Khvan, and A.N. Alabin, Microstructure and Phase Composition of Al-Ce-Cu Alloys in the Al-Rich Corner, *Mater. Res. Forum*, 2006, **519-521**, p 395-400

2006Zha: B. Zhang, D.Q. Zhao, M.X. Pan, R.J. Wang, and W.H. Wang, Formation of Cerium Based Bulk Metallic Glasses, *Acta Mater.*, 2006, **54**, p 3025-3032

2007Bel: N.A. Belov and A.V. Khvan, The Ternary Al-Ce-Cu Phase Diagram in the Aluminum-Rich Corner, *Acta Mater.*, 2007, **55**. p 5473-5482

2007Rag: V. Raghavan, Al-Ce-Cu (Aluminum-Cerium-Copper), *J. Phase Equilb. Diffus.*, 2007, **28**(6), p 540-541

2008Rag: V. Raghavan, Al-Ce-Cu (Aluminum-Cerium-Copper), *J. Phase Equilb. Diffus.*, 2008, **29**(3), p 264-266

2009Bo: H. Bo, S. Jin, L.G. Zhang, X.M. Chen, H.M. Chen, L.B. Liu, F. Zheng, and Z.P. Jin, Thermodynamic Assessment of Al-Ce-Cu System, *J. Alloys Compd.*, 2009, **484**, p 286-295

2009Hu: X.D. Hu, H.Y. Zhou, J.B. Li, S.K. Pan, T. Wang, Q.R. Yao, L.B. Duan, and Y.C. Wang, Phase Composition of Arc-Melted Alloys in the Ternary System Ce-Al-Cu (Cu-Poor Portion), *Intermetallics*, 2009, **17**, p 775-779

2009Yao: Q.R. Yao, X.D. Hu, X.J. Chen, S.K. Pan, W. Zou, H.L. Wang, Y.C. Wang, P.P. Wang, F. Liu, Z.M. Wang, H.Y. Zhou, and C.Y. Tang, Phase Relations in the Cu-Poor Part of the Ce-Al-Cu System at 503 K, *J. Alloy Compd.*, 2009, **484**, p 86-89