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

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The experimental data on this system were reviewed recently by [2004Ria] and [2007Rag]. This update pertains to the new results reported by [2006Bel, 2007Bel], clarifying the phase relationships in the Al-rich region during solidification and in the solid state.

Binary Systems

The Al-Ce phase diagram was recently 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_3La_{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) ($\gamma_0, D8_2$, Cu_5Zn_8-type cubic), Cu_9Al_4(LT) ($\gamma_1, D8_3$-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 Phase Equilibria

In Al-rich alloys, two ternary phases have been reported: Al_8CeCu_4 (denoted $\tau_1, D2_b$, $ThMn_{12}$-type tetragonal), and Al_4CuCe (or Al_3CuCe, denoted τ_2). There is no general agreement about the ternary existence of Al_3CuCe. [2007Bel] argued that it was a solid solution based $CeAl_4$, with the Al_4Ba-type of structure with Cu substituting for Al. $CeAl_4$ or βCe_3Al_{11} has the Al_4Ba-type structure, but it is not stable below ~1000 °C. [2004Ria] discussed this aspect and concluded that Al_3CuCe has the $BaNiSn_3$-type of ordered structure. The isothermal section reviewed by [2004Ria] at 400 °C shows αCe_3Al_{11} with the orthorhombic structure to coexist with the ordered tetragonal structure of Al_3CuCe.

With starting metals of 99.99% Al, 99.9% Ce, and 99.9% Cu, [2007Bel] melted in a resistance furnace about 60 ternary alloys containing up to 16 mass% Ce and 35 mass% Cu. The alloys were annealed at 590 or 540 °C for 3 or 10 h and quenched in water. The phase equillibria were studied with optical and scanning electron microscopy, x-ray powder diffraction, electron probe microanalysis, and differential scanning calorimetry at heating/cooling rates of 5 °C per min.

[2007Bel] constructed for Al-rich alloys the liquidus and solidus projections, three isothermal sections at 590, 540, and 200 °C and five vertical sections along the Al-τ_1 join, at 20 and 14 mass% Cu and at 12 and 5 mass% Ce, respectively. The pseudobinary nature of the Al-τ_1 join earlier determined by [1991Yun] was confirmed by [2002Bel, 2007Bel], except that the eutectic temperature on this join was reported to be 610 °C, higher by 35 °C than that reported by [1991Yun]. Moreover, [2007Bel] did not find a pseudobinary section along the Al-τ_2 join as reported by [1991Yun]. They concluded that a separate phase labeled Al_4CuCe (or Al_3CuCe) did not exist, but only a solid solution based $CeAl_4$. As discussed above, $CeAl_4$ (Al_4Ba-type tetragonal) is not stable below 1000 °C, even though the addition of Cu could have a stabilizing effect on the tetragonal structure. This contradiction needs to be resolved by more detailed experiments on the effect of progressive Cu addition to $CeAl_4$.

The liquidus projection is shown in Fig. 1 [2007Bel]. The primary phases of crystallization are (Al), $CuAl_2$, $CeAl_4$, and Al_8CeCu_4 (τ_1). The eutectic temperature and composition on the Al-τ_1 pseudobinary section are 610 °C and 14Cu-7Ce in mass%. In the Al-$CuAl_2$-τ_1 region, the final solidification is through the ternary eutectic reaction E_1 at 545 °C. In the Al-$AlCe_4$-τ_1 region, the solidification is complete through E_2 at ~605 °C. Three isothermal sections for the Al-rich region at 590, 540, and 200 °C constructed by [2007Bel] are shown in Fig. 2-4. Two vertical sections at

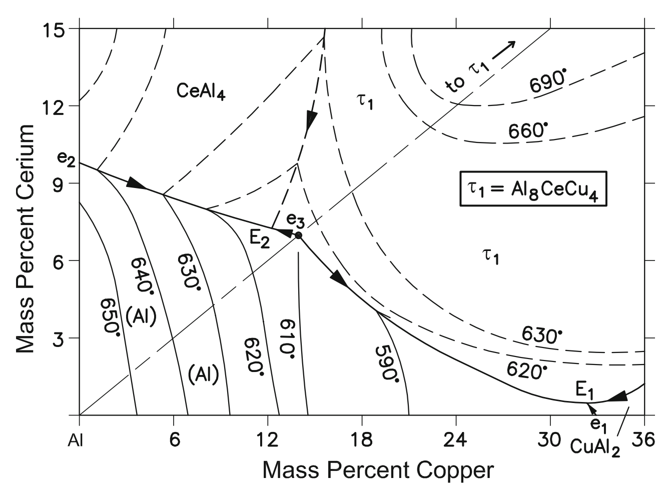

Fig. 1 Al-Ce-Cu liquidus projection for Al-rich alloys [2007Bel]

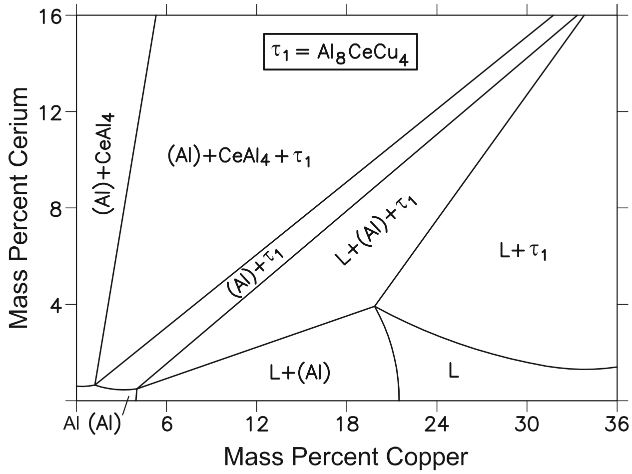

Fig. 2 Al-Ce-Cu isothermal section at 590 °C for Al-rich alloys [2007Bel]

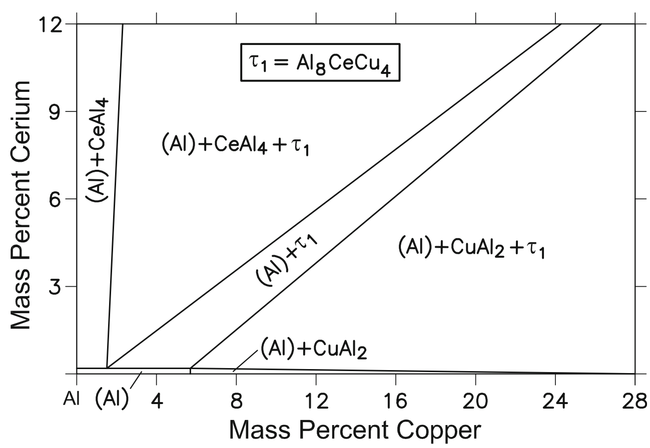

Fig. 3 Al-Ce-Cu isothermal section at 540 °C for Al-rich alloys [2007Bel]

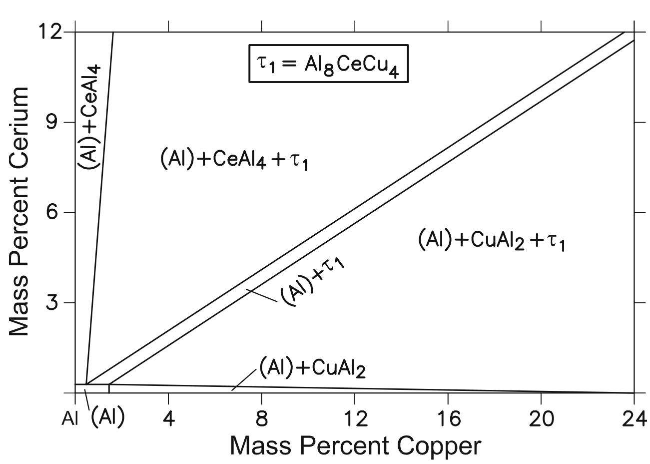

Fig. 4 Al-Ce-Cu isothermal section at 200 °C for Al-rich alloys [2007Bel]

12 and 5 mass% Ce, respectively, are given in Fig. 5 and 6. The invariant horizontals corresponding to E_2 occur with a temperature difference of about 10 °C in the two figures, though they should be at the same temperature. For reasons discussed earlier, the above results of [2007Bel] may be considered tentative. [2007Bel] pointed out that alloy compositions near the pseudobinary eutectic point (e_3 in Fig. 1) have a small solidification range and, therefore, possess better heat cracking resistance.

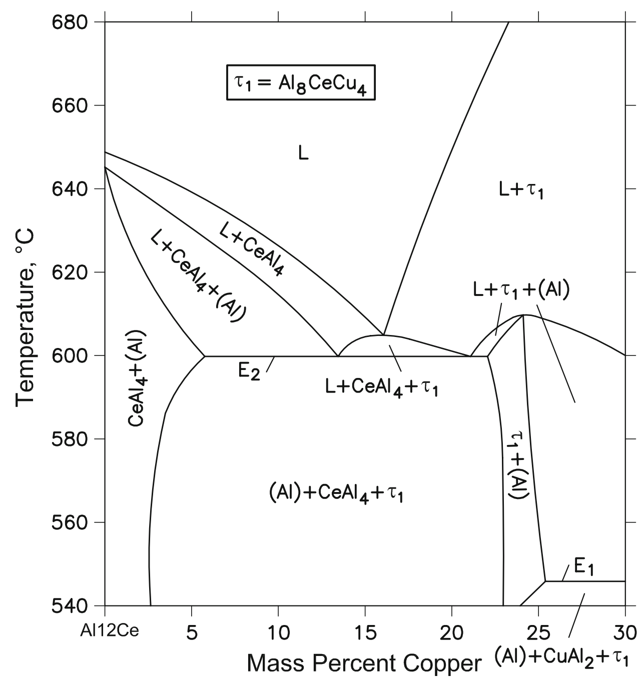

Fig. 5 Al-Ce-Cu vertical section at 12 mass% Ce [2007Bel]

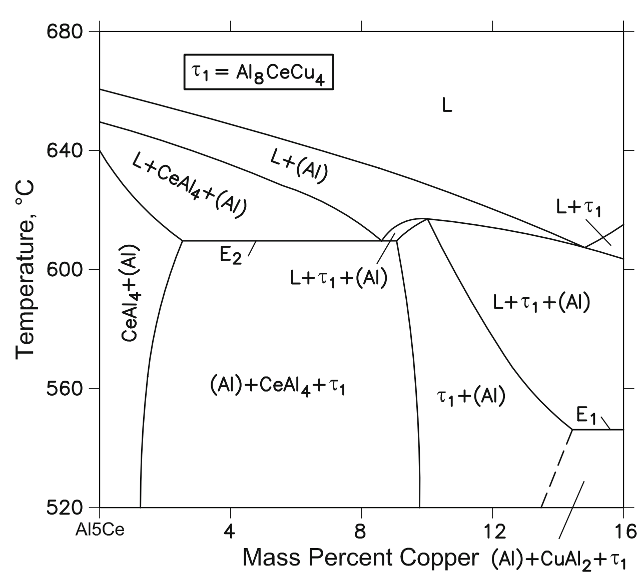

Fig. 6 Al-Ce-Cu vertical section at 5 mass% Ce [2007Bel]

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