

Al-Ce-Mg (Aluminum-Cerium-Magnesium)

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Cerium is the major constituent of mischmetal, which is an important additive to Mg-based alloys. In Al and Al-Mg alloys, the solubility of Ce is very limited, increasing the possibility of the formation of precipitates, which could improve high temperature strength. [1995Vil] summarized the limited data on the partial isothermal sections at 400 and 300 °C and the liquidus projection for compositions close to the Al-Mg side. The more recent results include those of [1989Odi], [1996Odi], [2002Gro], [2003Rok], and [2005Rok]. This review presents four vertical sections, a schematic computed liquidus projection close to the Al-Mg side and a full computed isothermal section at 400 °C.

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: $\alpha\text{Ce}_3\text{Al}$ ($D0_{19}$, Ni_3Sn -type hexagonal), $\beta\text{Ce}_3\text{Al}$ ($L1_2$, 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), αCeAl_3 (Ni_3Sn -type hexagonal), βCeAl_3 (stable between 1192 and 973 °C), CeAl_4 or $\beta\text{Ce}_3\text{Al}_{11}$ ($D1_3$, Al_4Ba -type tetragonal), and $\alpha\text{Ce}_3\text{Al}_{11}$ ($\alpha\text{La}_3\text{Al}_{11}$ -type orthorhombic). The Al-Mg phase diagram has the following intermediate phases: Mg_2Al_3 (cubic, denoted β), R or ε (rhombohedral), and $\text{Mg}_{17}\text{Al}_{12}$ ($A12$ -type cubic, denoted γ). The Ce-Mg phase diagram [Massalski2] depicts the following intermediate phases: CeMg ($B2$, CsCl -type cubic), CeMg_2 ($C15$, MgCu_2 -type cubic, stable between 750 and 615 °C), CeMg_3 ($D0_3$, BiF_3 -type cubic), $\text{Ce}_5\text{Mg}_{41}$ (tetragonal), and CeMg_{12} ($D2_b$, ThMn_{12} -type tetragonal).

Ternary Phase Equilibria

[1989Odi] reported an isothermal section for this system at 400 °C, depicting the ternary compound $\text{Al}_2\text{Mg}_{0.8}\text{Ce}_{0.2}$ (or $\text{Al}_{13}\text{CeMg}_6$ [2002Gro], denoted τ here), with the MgZn_2 -type hexagonal structure and lattice parameters of $a = 0.5531$ nm and $c = 0.8940$ nm. CeMg_2 dissolves about 45 at.% Al, with the lattice parameter a varying linearly from ~ 0.872 nm at 0% Al to ~ 0.815 nm at 45 at.% Al. The above observation of [1989Odi] may refer to a metastable state, as CeMg_2 is not stable at 400 °C. [2002Gro] have shown that the isomorphous $C15$ phases CeMg_2 and CeAl_2 form a continuous solid solution at 740 °C. CeMg dissolves 30 at.% Al, with a decreasing linearly from ~ 0.3883 nm at 0% Al to ~ 0.3831 nm at 30 at.% Al [1989Odi].

With starting metals of 99.8% Al, 99.98% Mg, and 99.9% Ce, [2002Gro] arc-melted four alloys with selected

compositions in the Ce-lean range. The alloys were annealed at 400 °C for 500 h and quenched in water. The phase equilibria were studied with differential thermal analysis (DTA) and x-ray powder diffraction. The liquidus temperatures deduced from the DTA arrests were found to be much higher than previously reported. The previous low DTA values were attributed to the other equilibria below the liquidus.

In the thermodynamic modeling, [2002Gro] described the liquid phase, (Al), (Ce), and (Mg) as substitutional solutions. The isomorphous phases CeAl_2 and CeMg_2 were rationalized as a continuous solid solution in the temperature range of 747–733 °C, with a miscibility gap below 733 °C. The third component solubility in CeMg and CeMg_{12} was taken into account. The other binary compounds and the ternary phase τ were treated as stoichiometric phases. Three vertical sections were computed along CeMg_2 - CeAl_2 , 30Al60Mg10Ce-100Al, and Ce_2Al -Mg joins respectively. In Fig. 1 and 2, the first two vertical sections are compared with the experimental data of [1989Odi], [1996Odi], and [2002Gro] as applicable. The CeMg_2 - CeAl_2 section (Fig. 1) depicts the miscibility gap that starts below 733 °C. The two experimental points shown on the gap boundary are from the isothermal section at 400 °C determined by [1989Odi]. As CeMg_2 forms peritectically and decomposes eutectoidally in the Ce-Mg binary system, the section in Fig. 1 does not have pseudobinary characteristics near the CeMg_2 end.

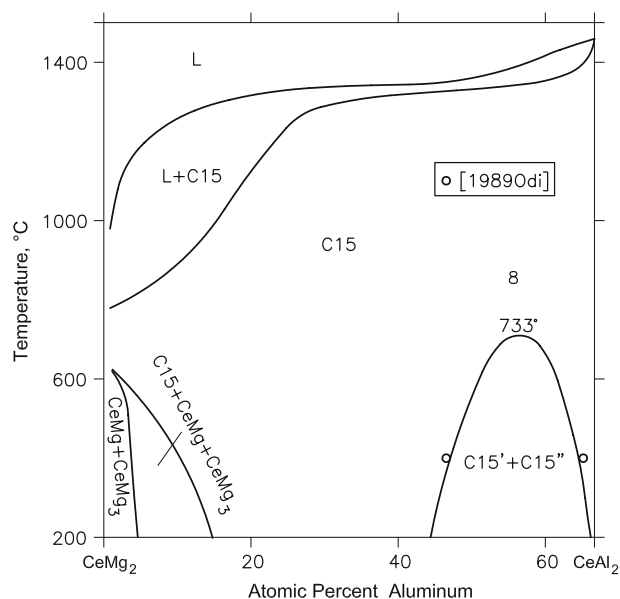


Fig. 1 Al-Ce-Mg computed vertical section along the CeMg_2 - CeAl_2 join [2002Gro]

Section II: Phase Diagram Evaluations

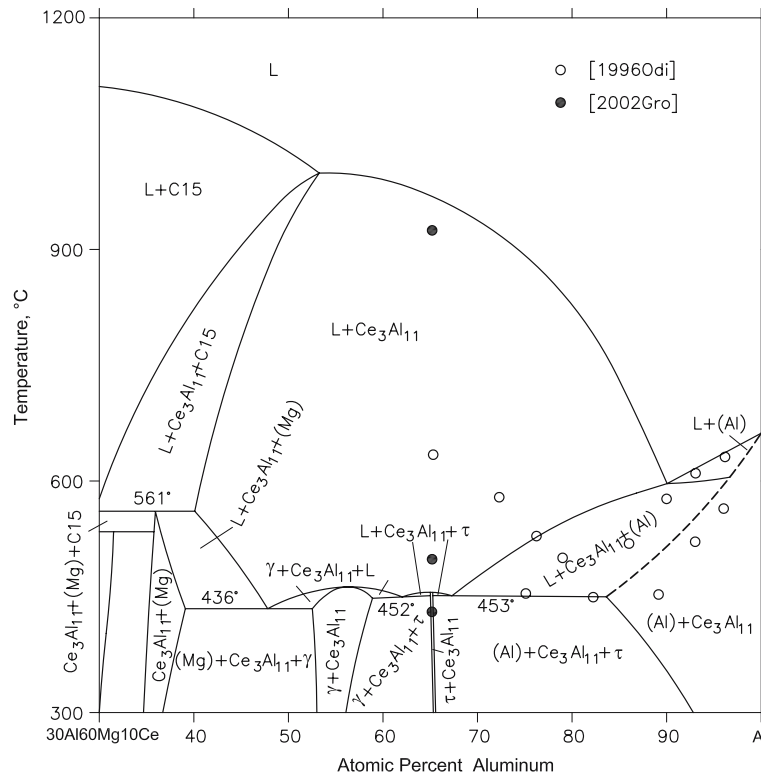


Fig. 2 Al-Ce-Mg computed vertical section along the Al-30Al60Mg10Ce join [2002Gro]

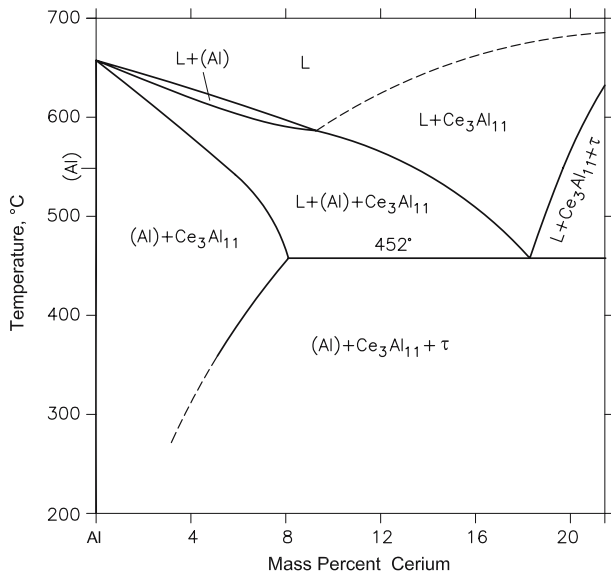


Fig. 3 Al-Ce-Mg partial vertical section along the (Al)- τ join [2005Rok]

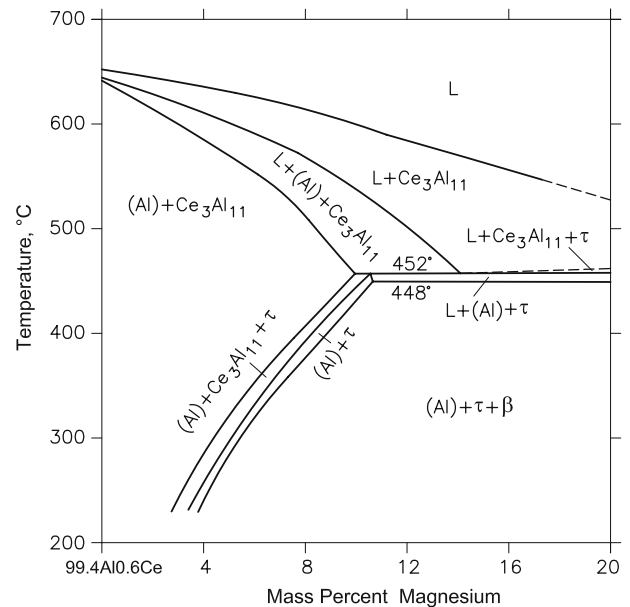


Fig. 4 Al-Ce-Mg vertical section at 0.6 mass% Ce [2005Rok]

With starting metals of 99.99% Al, 99.96% Mg and 99.85% Ce, [2003Rok] and [2005Rok] melted up to 25 ternary alloys in an electrical resistance furnace with protection from a salt flux. DTA was performed at a

heating/cooling rate of 3 °C/min. The phase equilibria were studied using an optical microscope and a scanning electron microscope equipped with energy-dispersive x-ray analyzer. The results were used by [2005Rok] to construct two

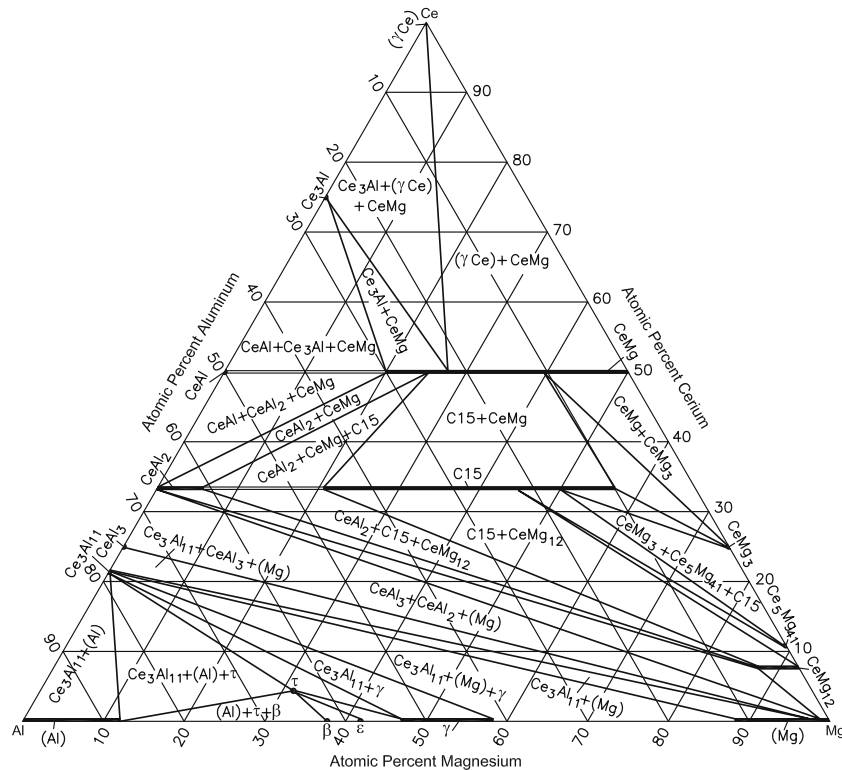


Fig. 5 Al-Ce-Mg computed isothermal section at 400°C [2002Gro]. Thin two-phase regions are omitted

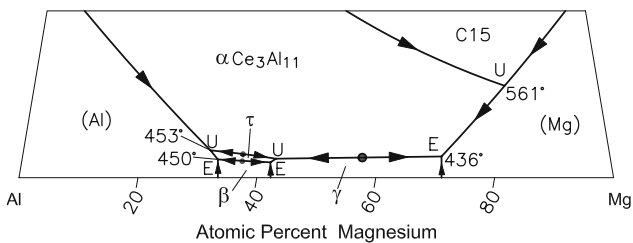


Fig. 6 Al-Ce-Mg computed partial liquidus projection shown schematically near the Al-Mg side [2002Gro]

vertical sections along the Al- τ join (Fig. 3) and at a constant Ce content of 0.6 mass% (Fig. 4). The invariant horizontal at 452 °C corresponding to the four-phase U-type reaction $L + \text{Ce}_3\text{Al}_{11} \leftrightarrow (\text{Al}) + \tau$ is seen in Fig. 3 and 4. This is in agreement with the U-reaction computed by [2002Gro] at 453 °C

Figure 5 shows the computed isothermal section at 400 °C from [2002Gro]. CeMg dissolves up to 30 at.% Al, confirming the result of [1989Odi]. The C15 phase occurs only in the ternary region separated from the extension of the CeAl₂ phase. Figure 6 shows schematically the computed partial liquidus projection near the Al-Mg side [2002Gro].

References

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