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Al-Ca-Mg (Aluminum-Calcium-Magnesium)

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Recently, [2007Rag] reported an update on this ternary system, which included a liquidus projection for the Mg-rich alloys from the results of [2005Suz] and two partial isothermal sections in the Ca-lean region at 500 and 400 °C from [2006Suz]. The present update will be limited to the new results reported by [2008Cao1], [2008Cao2] and [2009Jan]. [2009Jan] carried out a thermodynamic assessment of the entire composition range and compared the computed liquidus projection, several isothermal sections and vertical sections with their own and previously-reported experimental data.

Binary Systems

The Al-Ca system was experimentally reinvestigated by [2001Kev1] and assessed thermodynamically by [2001Kev2]. There are four intermediate phases in this system: Al_4Ca ($D1_3$, Al_4Ba-type tetragonal), Al_2Ca ($C15$, $MgCu_2$-type cubic), AlCa (or $Al_{14}Ca_{13}$; monoclinic, space group $C2/m$), and Al_3Ca_8 (Ca_8In_3-type triclinic, space group $P\bar{1}$). The Al-Mg phase diagram [1998Lia] has the following intermediate phases: Mg_2Al_3 (cubic, denoted β), ε or R (rhombohedral), and $Mg_{17}Al_{12}$ ($A12$, αMn-type cubic, denoted γ). The Ca-Mg phase diagram [1995Aga] has one intermediate phase Mg_2Ca ($C14$, $MgZn_2$-type hexagonal).

Ternary Phase Equilibria

Recently, [2008Cao1] combined the directional-solidification technique with thermodynamic computations to establish the saddle points on the monovariant liquidus lines near the Mg corner. The microstructures of several directionally solidified alloys in the near-solidification zone, the mushy zone, and the steady-state zone were characterized by optical and electron metallography. The saddle point maxima identified were: L + (Mg) + $C14$ and L + (Mg) + $C36$.

The composition of the $C36$ phase in three alloys measured by [2008Cao2] shows a significant variation of the Al and Mg content, with a smaller variation in the Ca content. The composition measured by [2009Jan] in two samples also shows a significant range for $C36$. The composition range among a total of five samples of [2008Cao2] and [2009Jan] put together is (in at.%): 44.9-59.8 Al, 26.6-30.9 Ca and 22.5-12.9 Mg. The $C36$ phase clearly lies below the Al_2Ca-Mg_2Ca join, is located closer to Al_2Ca than to Mg_2Ca and extends in the Ca-poor direction. [2008Cao2] combined their new experimental data with the previously-known results to develop a thermodynamic description for Mg-rich alloys. The computed liquidus projection near the Mg corner (not shown here) confirms the two saddle points found by [2008Cao1]. [2008Cao2] also computed a vertical section along the Al_2Ca-Mg_2Ca join.

The thermodynamic analysis of [2008Cao2] for Mg-rich alloys was extended to the entire composition range of the ternary system by [2009Jan]. With starting metals of 99.998% Al, 99.99% Ca, and 99.98% Mg, [2009Jan] melted four alloys in tantalum capsules and conducted differential thermal analysis or differential scanning calorimetry at heating/cooling rates of 1 and 5 °C per min. The phase equilibria were studied with scanning electron microscopy (back scattering electron imaging mode) and electron probe microanalysis. The measured compositions of the coexisting phases were listed.

In the thermodynamic description of [2009Jan], the binary interaction parameters were derived from the works of [2001Kev2] (Al-Ca), [1998Liu] (Al-Mg), and [1995Aga] (Ca-Mg). In the ternary system, the liquid, face-centered cubic (fcc), body centered cubic (bcc) and close packed hexagonal (cph) phases were modeled as substitutional solutions. The binary phases Al_2Ca, Mg_2Ca, Al_4Ca, and Al_3Ca_8 were modeled as line compounds with two sublattices to reflect the observed ternary solubilities. For the $Mg_{17}Al_{12}$ with a composition range as well as ternary solubility and for the ternary $C36$ phase with a homogeneity range, a three sublattice model was adopted.

The liquidus projection computed by [2009Jan] for the entire composition range is shown in Fig. 1. The features at the Mg corner agree with those found by [2008Cao2]. The phases of primary crystallization are marked. The liquidus lines depict four eutectic-type critical points (maxima) C_3 (526 °C), C_4 (518 °C), C_5 (476 °C), and C_6 (447 °C). Two peritectic type critical pints C_1 (833 °C) and C_2 (737 °C) are also seen. The $C36$ phase nucleates at the peritectic critical point C_1: L + $C14$ ↔ $C36$. The final solidification at the Mg and Al ends are through the ternary eutectic reactions E_1 and E_2. The computed invariant temperatures: U_1 (545 °C), U_2 (531 °C), U_3 (512 °C), U_4 (474 °C), U_5 (473 °C), U_6 (454 °C), U_7 (442.5 °C), E_1 (515 °C), E_2 (446 °C), E_3 (445 °C), E_4 (402 °C), and degenerate D (442.2 °C), agree well with the available experimental data.

Four isothermal sections at 600, 500, 400 and 300 °C computed by [2009Jan] are shown in Fig. 2-5. The agreement with the experimental data is satisfactory. The $C36$ phase is not stable at 400 and 300 °C (Fig. 4 and 5). Five vertical sections at 4, 8, 16, 20, and 38 mass% Al and a vertical section along the Al_2Ca-Mg_2Ca join were computed by [2009Jan]. Here, the vertical section at 4 mass% Al is given in Fig. 6. Two invariant horizontals are seen in Fig. 6, corresponding to the ternary eutectic reaction E_1 at 515 °C: L ↔ (Mg) + $C14$ + $C36$ and to the eutectoidal decomposition

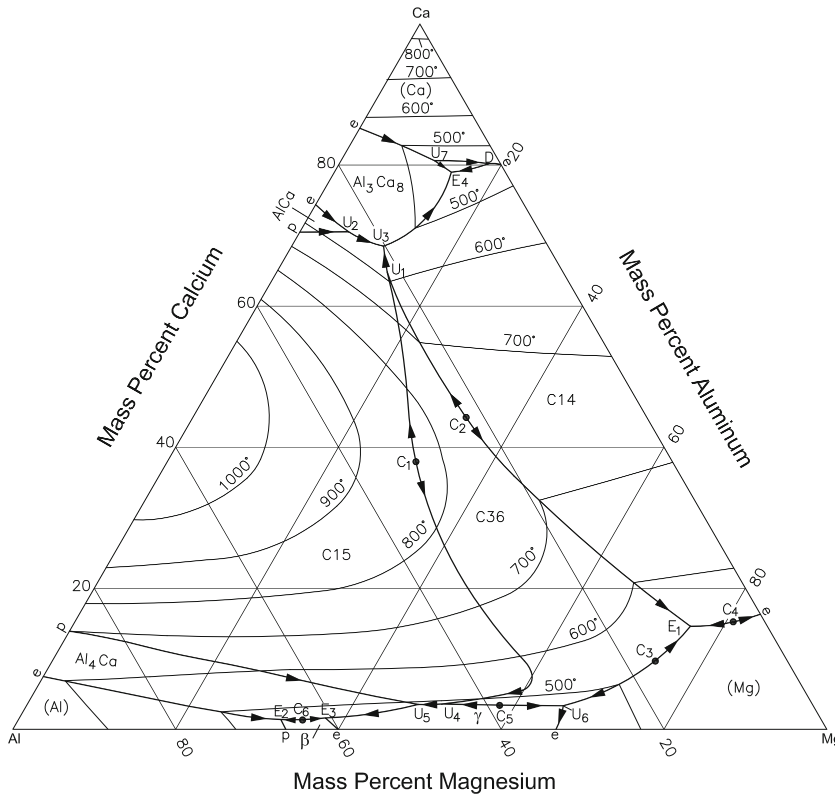

Fig. 1 Al-Ca-Mg computed liquidus projection [2009Jan]

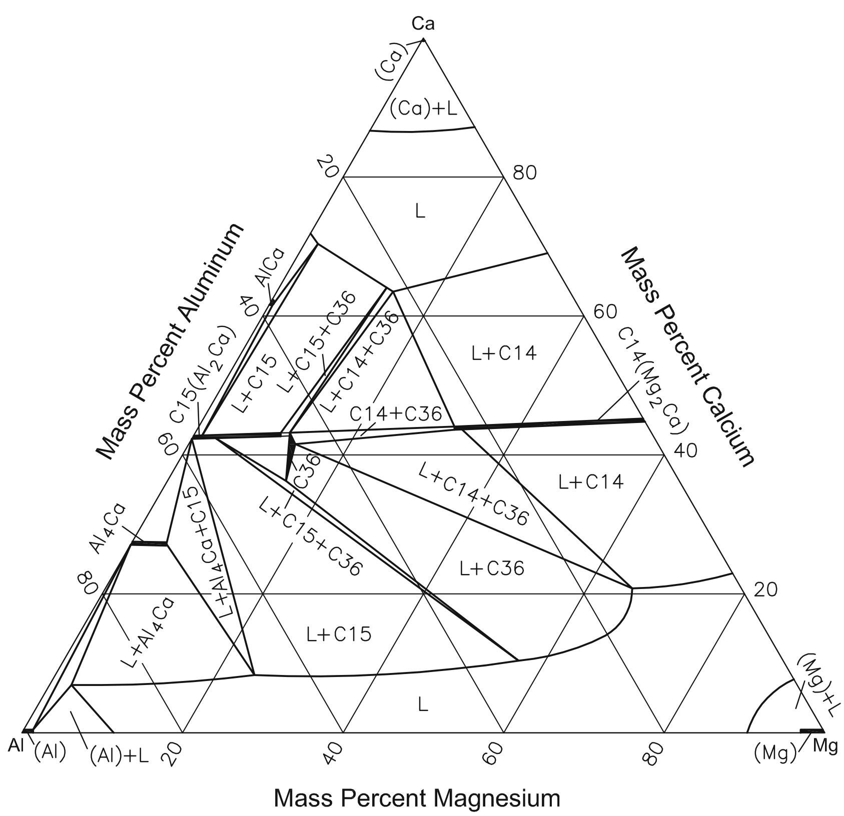

Fig. 2 Al-Ca-Mg computed isothermal section at 600 °C [2009Jan]

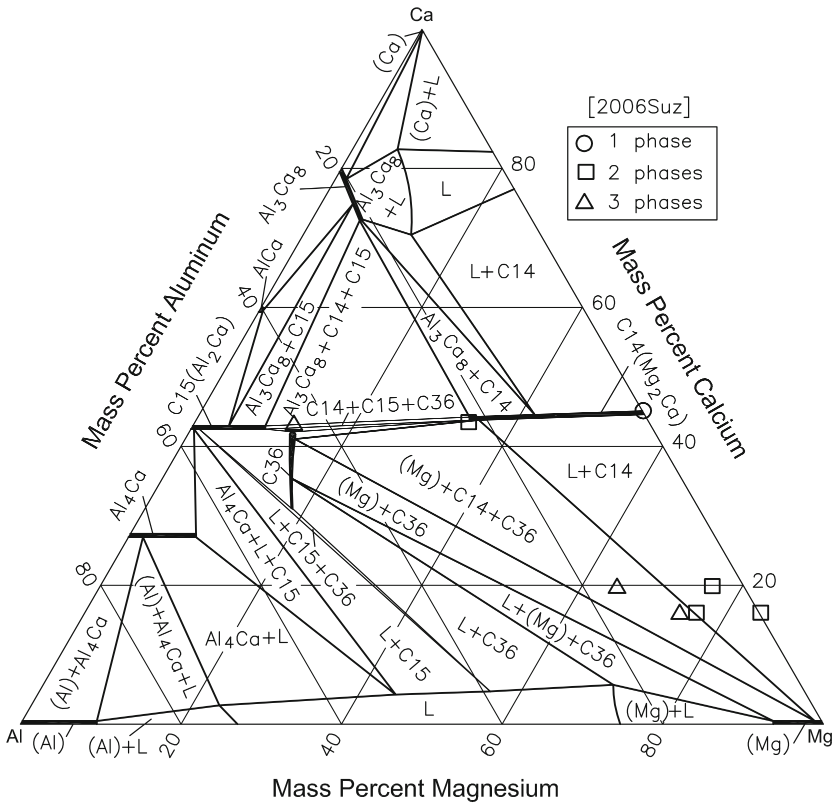

Fig. 3 Al-Ca-Mg computed isothermal section at 500 °C [2009Jan]

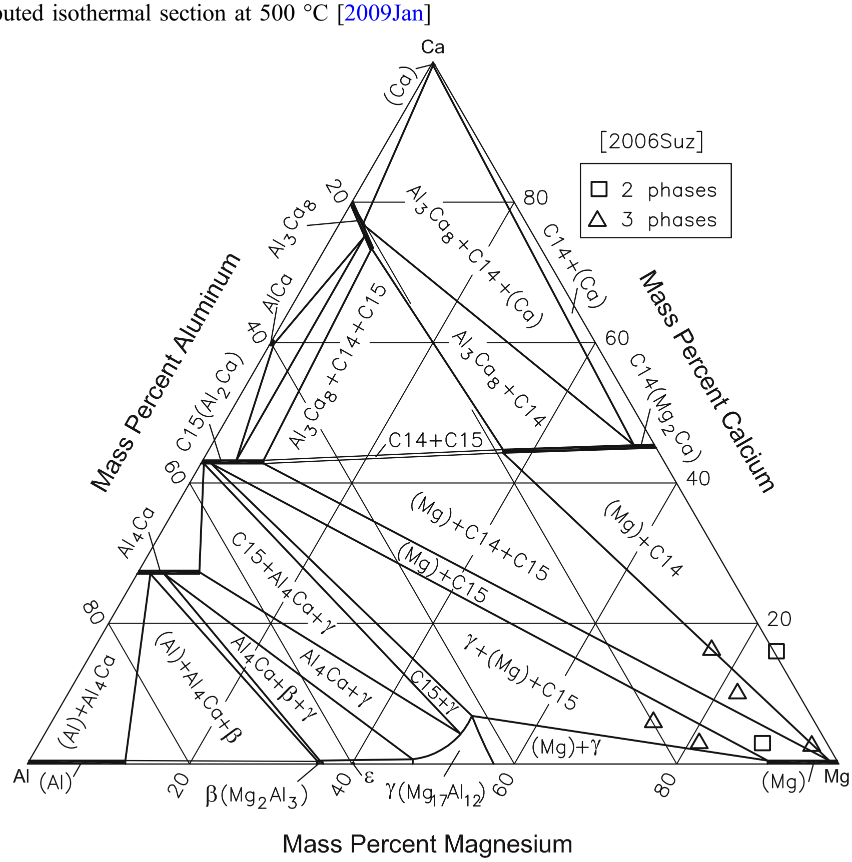

Fig. 4 Al-Ca-Mg computed isothermal section at 400 °C [2009Jan]

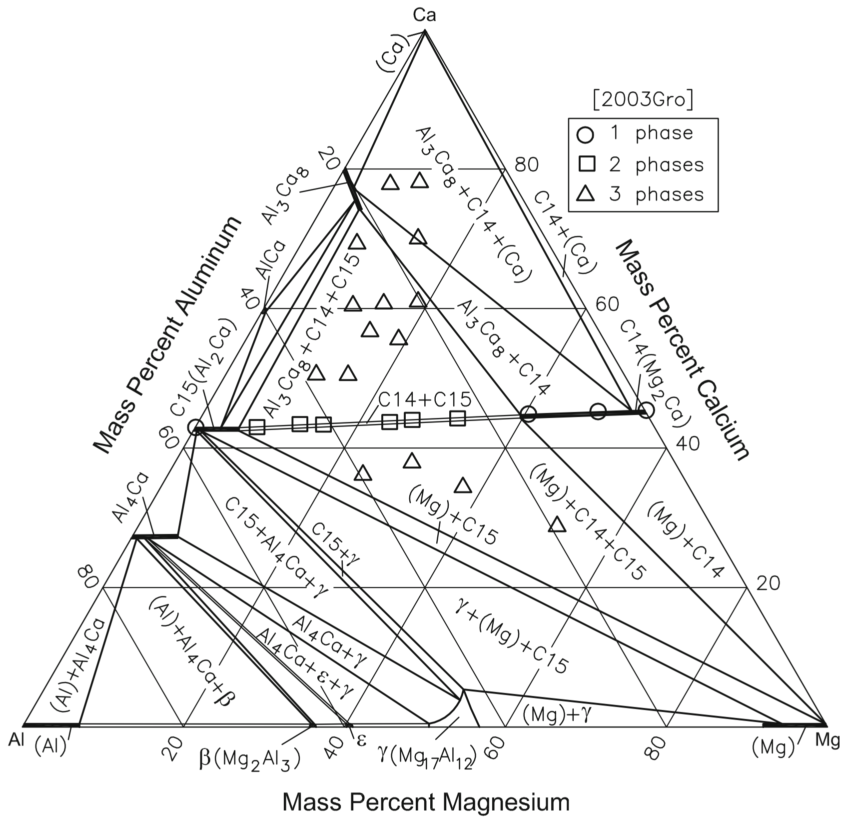

Fig. 5 Al-Ca-Mg computed isothermal section at 300 °C [2009Jan]

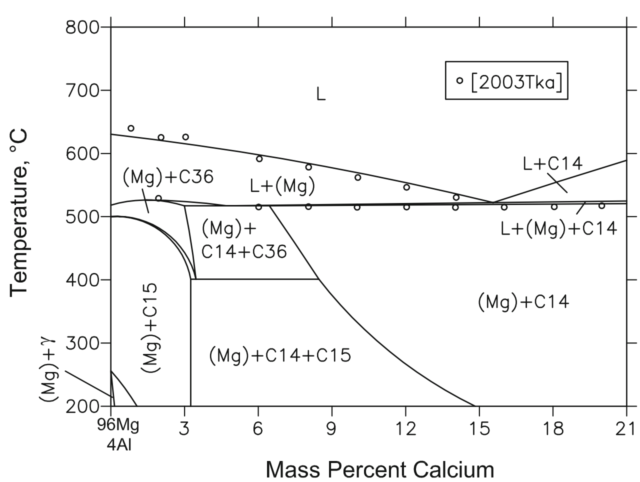

Fig. 6 Al-Ca-Mg computed vertical section at 4 mass% Al [2009Jan]

of $C36$ at 400.3 °C: $C36 \leftrightarrow (Mg) + C14 + C15$. The sections close to the Al_2Ca-Mg_2Ca join computed by [2008Cao2] and [2009Jan] (not shown here) depict some differences, probably arising from the homogeneity range of the $C36$ phase used by the authors. A more detailed investigation of the homogeneity region of $C36$ is needed to refine this section.

References

1995Aga: R. Agarwal, J.J. Lee, H.L. Lukas, and F. Sommer, Calorimetric Measurements and Thermodynamic Optimization of the Ca-Mg System, *Z. Metallkd.*, 1995, **86**(2), p 103-108

1998Lia: P. Liang, T. Tarfa, J.A. Robinson, S. Wagner, P. Ochin, M.G. Harmelin, H.O. Seifert, H.L. Lukas, and F. Aldinger, Experimental Investigation and Thermodynamic Calculation of the Al-Mg-Zn System, *Thermochim. Acta*, 1998, **314**, p 87-110

2001Kev1: D. Kevorkov and R. Schmid-Fetzer, The Al-Ca System, Part 1: Experimental Investigation of Phase Equilibria and Crystal Structures, *Z. Metallkd.*, 2001, **92**(8), p 946-952

2001Kev2: D. Kevorkov, R. Schmid-Fetzer, A. Pisch, F. Hodaj, and C. Colinet, The Al-Ca System, Part 2: Calorimetric Measurements and Thermodynamic Assessment, *Z. Metallkd.*, 2001, **92**(8), p 953-958

2003Gro: J. Grobner, D. Kevarkov, I. Chumak, and R. Schmid-Fetzer, Experimental Investigation and Thermodynamic Calculation of Ternary Al-Ca-Mg Phase Equilibria, *Z. Metallkd.*, 2003, **94**(9), p 976-982

2003Tka: V.G. Tkachenko, V.G. Khoruzhaya, K.A. Meleshevich, M.V. Karpets, and V.V. Frizel, Phase Equilibria in the Mg-Al-Ca System (Region 50-100 mass% Mg), *Porosh. Metall.*, 2003, (5-6), p 59-65, in Russian; TR: *Powder Metall. Met. Ceram.*, 2003, **42**(5-6), p 268-273

2005Suz: A. Suzuki, N.D. Saddock, J.W. Jones, and T.M. Pollock, Solidification Paths and Eutectic Intermetallic Phases in Mg-Al-Ca Ternary Alloys, *Acta Mater.*, 2005, **53**, p 2823-2834

2006Suz: A. Suzuki, N.D. Saddock, J.W. Jones, and T.M. Pollock, Phase Equilibria in the Mg-Al-Ca Ternary System at 773 and 673 K, *Metall. Mater. Trans. A*, 2006, **37A**, p 975-983

2007Rag: V. Raghavan, Al-Ca-Mg (Aluminum-Calcium-Magnesium), *J. Phase Equilb. Diffus.*, 2007, **28**(5), p 450-452

2008Cao1: H. Cao, C. Zhang, J. Zhu, G. Cao, S. Kou, R. Schmid-Fetzer, and Y.A. Chang, A Computational/Directional Solidification Method to Establish Saddle Points on the Mg-Al-Ca Liquidus, *Scr. Mater.*, 2008, **58**, p 397-400

2008Cao2: H. Cao, C. Zhang, J. Zhu, G. Cao, S. Kou, R. Schmid-Fetzer, and Y.A. Chang, Experiments Coupled with Modeling to Establish the Mg-Rich Phase Equilibria of Mg-Al-Ca, *Acta Mater.*, 2008, **56**, p 5245-5254

2009Jan: A. Janz, J. Grobner, H. Cao, J. Zhu, Y.A. Chang, and R. Schmid-Fetzer, Thermodynamic Modeling of the Mg-Al-Ca System, *Acta Mater.*, 2009, **57**, p 682-694