JPEDAV (2007) 28:450–452
DOI: 10.1007/s11669-007-9137-3
1547-7037 ©ASM International

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

V. Raghavan

The early literature on this ternary system, which includes the work of [1958Cat], is summarized by [1995Vil], who presented partial isothermal sections for Mg-rich alloys at 400, 370, and 290 °C. A number of recent publications [1995Nin, 2001Ozt, 2003Ame, 2003Gro, 2003Ozt, 2003Tka, 2004Zho, 2005Isl, 2005Par, 2005Suz, 2005Zho, 2006Suz, 2007Alj] have appeared on this system with focus on Mg-rich alloys.

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 (*C*15, $MgCu_2$-type cubic), AlCa (or $Al_{14}Ca_{13}$; monoclinic, space group *C*2/*m*), and Al_3Ca_8 (Ca_8In_3-type triclinic, space group $P\bar{1}$). The Al-Mg phase diagram [2003Cze, Massalski2] has the following intermediate phases: Mg_2Al_3 (cubic, denoted β), ε or R (rhombohedral), and $Mg_{17}Al_{12}$ (*A*12, αMn-type cubic, denoted γ). The Ca-Mg phase diagram [1995Aga] has one intermediate phase Mg_2Ca (*C*14, $MgZn_2$-type hexagonal). A thermodynamic reassessment of this system was reported recently by [2006Zho].

Ternary Phases

There are several reports on the existence of a *C*36, $MgNi_2$-type hexagonal ternary phase along the Al_2Ca-Mg_2Ca join [2003Ame, 2005Suz, 2005Zho, 2006Suz]. [2003Ame] found a homogeneity range from $CaAl_{1.34}Mg_{0.66}$ to $CaAl_{0.93}Mg_{1.07}$ and the corresponding lattice parameter ranges of a = 0.5835-0.5935 nm and c = 1.8897-1.9258 nm. However, [2006Suz] reported a stoichiometry close to $CaAl_{1.33}Mg_{0.67}$. The existence of the *C*36 phase appears to be established and the absence of this ternary phase in the earlier reports is probably due to the difficulty of distinguishing the x-ray patterns of the *C*14 and *C*36 phases. The existence of a second ternary phase Al_2(Mg, Ca) with Mg concentration range of 17.5-22.5 at.% was reported by [2005Zho]. This phase needs confirmation.

The Liquidus Surface

Calculated liquidus projections for the entire composition range of this ternary system presented by [2003Gro] and [2005Isl] are in agreement, but both calculations ignored the existence of the ternary *C*36 phase. Partial experimental liquidus projections for Mg-rich alloys were presented by [2003Tka] and [2005Suz]. The primary crystallization of the *C*36 phase was not reported by [2003Tka]. The partial projection from [2005Suz] is shown in Fig. 1. The phases of primary crystallization in the Mg-rich alloys are (Mg), γ, *C*14, and *C*36. Among the computed liquidus projections [2001Ozt, 2003Gro, 2003Ozt, 2004Zho, 2005Isl], only the projection by [2004Zho] shows a primary field of the *C*36 phase.

Figure 2 and 3 show the partial isothermal sections at 500 and 400 °C determined by [2006Suz]. At 500 °C (Fig. 2), the *C*36 phase forms tie-lines with *C*14 (Mg_2Ca), *C*15 (Al_2Ca),

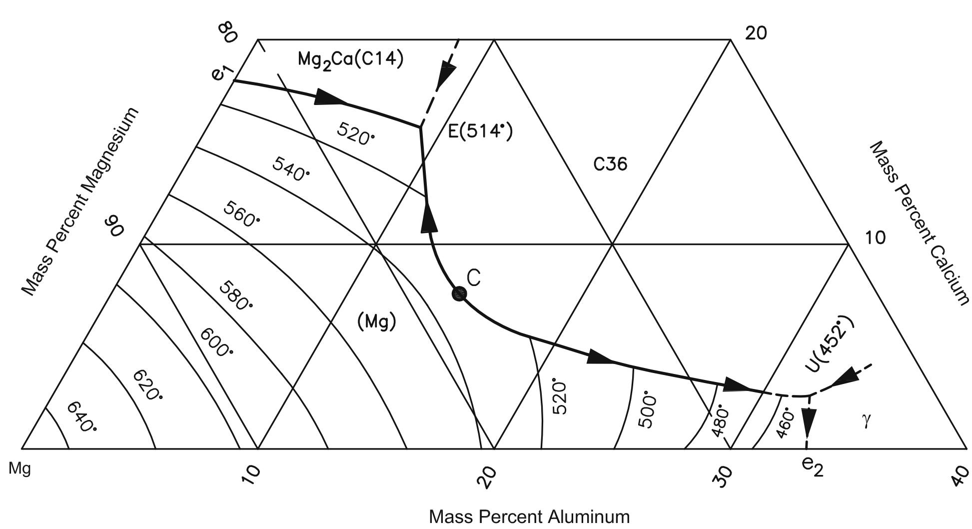

Fig. 1 Al-Ca-Mg partial liquidus projection [2005Suz]

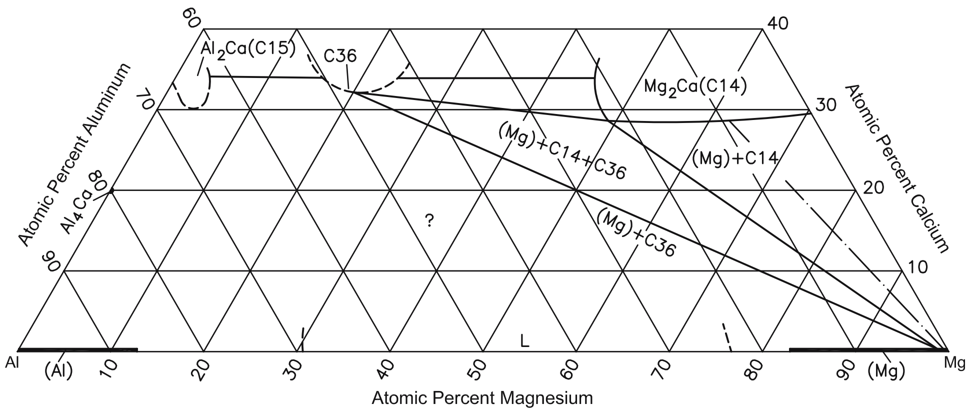

Fig. 2 Al-Ca-Mg partial isothermal section at 500 °C [2006Suz]

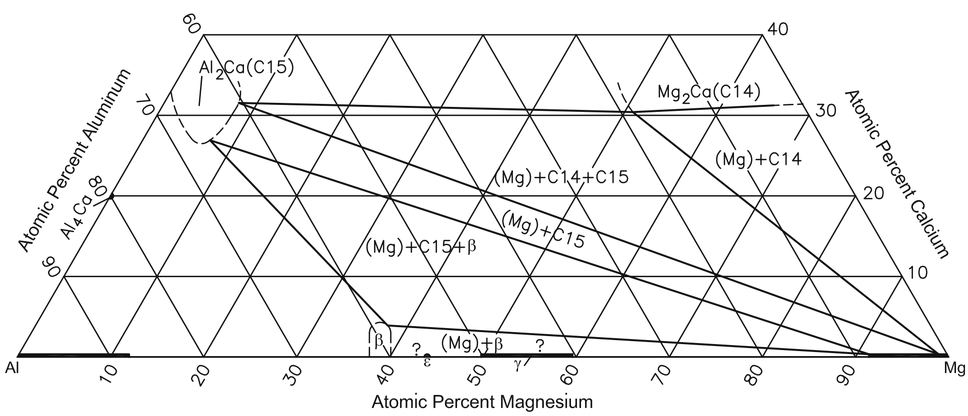

Fig. 3 Al-Ca-Mg partial isothermal section at 400 °C [2006Suz]

and (Mg). A three-phase field of (Mg) + *C*14 + *C*36 was identified by [2006Suz]. At 400 °C (Fig. 3), the *C*36 phase is not stable. (Mg) forms tie-lines with *C*14, *C*15, and Mg_2Al_3(β) phases. Three-phase fields of (Mg) + *C*14 + *C*15 and (Mg) + *C*15 + β were identified. A narrow three-phase field of (ε + β + γ) is probably present along the Al-Mg side.

Very recently, [2007Alj] carried out an experimental investigation of this system, using 21 ternary alloys covering the entire composition range. The phase equilibria were studied with differential scanning calorimetry, x-ray powder diffraction, and metallography. The results were compared with vertical sections computed from the thermodynamic description of [2005Isl]. The *C*36 phase was not found in the experiments of [2007Alj] and was not included in the thermodynamic description of [2005Isl]. The comparison of the DSC data with the computed liquidus showed agreement in some cases, but discrepancies were found in other cases.

References

1958Cat: J.A. Catterall and R.J. Pleasance, The Constitution of Mg-Rich Mg-Al-Ca Alloys, *J. Inst. Metals (London)*, 1958, **86**, p 189-192

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

1995Nin: R. Ninomiya, T. Ojiro, and K. Kubota, Improved Heat Resistance of Mg-Al Alloys by the Ca Addition, *Acta Metall. Mater.*, 1995, **43**, p 669-674

1995Vil: P. Villars, A. Prince, and H. Okamoto, Al-Ca-Mg, *Handbook of Ternary Alloy Phase Diagrams*, Vol. 3, ASM International, Materials Park, OH, 1995, p 2928-2929

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

2001Ozt: K. Ozturk, Y. Zhong, and Z.K. Liu, Computational Thermodynamics and Experimental Investigation of Mg-Al-Ca Alloys, *Magnesium Technology 2001*, J. Hryn, Ed., Minerals Metals Materials Soc., Warrendale, PA, 2001, p 113-117

2003Ame: S. Amerioun, S.I. Simak, and U. Haussermann, Laves-Phase Structural Changes in the System $CaAl_{2-x}Mg_x$, *Inorg. Chem.*, 2003, **42**(5), p 1467-1474

2003Cze: T. Czeppe, W. Zakulski, and E. Bielanska, Study of the Thermal Stability of Phases in the Mg-Al System, *J. Phase Equilibria*, 2003, **24**(3), p 249-254

2003Gro: J. Grobner, D. Kevorkov, 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

2003Ozt: K. Ozturk, Y. Zhong, A.A. Luo, and Z.K. Liu, Creep Resistant Mg-Al-Ca Alloys: Computational Thermodynamics and Experimental Investigation, *JOM*, 2003, **55**(11), p 40-44

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. Ceramics*, 2003, **42**(5-6), p 268-273

2004Zho: Y. Zhong, A.A. Luo, J.O. Sofo, and Z.K. Liu, Laves Phases in Mg-Al-Ca Alloys, *Magnesium Technology 2004*, A.A. Luo, Ed., Miner. Metals Mater. Soc., Warrendale, PA, 2004, p 317-323

2005Isl: F. Islam and M. Medraj, Thermodynamic Modeling of the Mg-Al-Ca System, *Can. Metall. Q.*, 2005, **44**(4), p 523-535

2005Par: M.A. Parvez, X. Wang, E. Essadiqi, and M. Medraj, Experimental Investigation of the Equilibria in Mg-Al-(Ca,Sr) Systems, *Magnesium Technology 2005*, N.R. Neelameggham, H.I. Kaplan, and B.R. Powell, Ed., Miner. Metals Mater. Soc., Warrendale, PA, 2005, p 179-184

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

2005Zho: Y. Zhong, A. Luo, J.F. Nie, J.O. Sofo, and Z.K. Liu, New Phases in Mg-Al-Ca System, *Magnesium Technology 2005*, N.R. Neelameggham, H.I. Kaplan, and B.R. Powell, Ed., Miner. Metals Mater. Soc., Warrendale, PA, 2005, p 185-190

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

2006Zho: Y. Zhong, K. Ozturk, and J.O. Sofo, Contribution of First-Principles Energetics to the Ca-Mg Thermodynamic Modeling, *J. Alloys Compd.*, 2006, **420**, p 98-106

2007Alj: M. Aljarrah, M. Medraj, X. Wang, E. Essadiqi, A. Muntasar, and G. Denes, Experimental Investigation of the Mg-Al-Ca System, *J. Alloys Compd.*, 2007, **436**, p 131-141