

# Al-Mg-Zn (Aluminum-Magnesium-Zinc)

V. Raghavan

[1986Des] and [1993Pet] reviewed the experimental results on this system. [1995Vil] presented liquidus projections from a number of sources, partial isothermal sections at 460, 440, 400, 350, 300, 250, 223, and 200 °C, full isothermal sections at 335 and 25 °C and 55 vertical sections! [1997Lia] made their own evaluation of the experimental data and presented assessed isothermal sections at 335 and 25 °C and a liquidus projection. They used their evaluated data in the thermodynamic assessment of the system. [1998Lia1] performed new experiments and used the new results in conjunction with the literature data to compute the phase equilibria.

## Binary Systems

The Al-Mg phase diagram [1998Lia2, 2003Cze] has the following intermediate phases.  $Mg_2Al_3$  or  $Mg_5Al_8$  (denoted  $\beta$ ) is cubic, space group  $Fd\bar{3}m$  with  $a = 2.8239$  nm. The other phases are: R or  $\epsilon$  (rhombohedral) and  $Mg_{17}Al_{12}$  ( $A12$ ,  $\alpha$  Mn-type cubic, denoted  $\gamma$ ). The Al-Zn phase diagram [1993Che] contains no intermediate phases. A miscibility gap occurs in the Al-based face centered cubic (fcc) solid solution below 351 °C, where the fcc phase splits into (Al)' and (Al)". The monotectoid reaction  $(Al)'' \leftrightarrow (Al)' + (Zn)$  follows at 277 °C. The Mg-Zn phase diagram [1992Aga, Massalski2] depicts the following intermediate phases:  $Mg_7Zn_3$  ( $D7_b$ ,  $Ta_3B_4$ -type orthorhombic),  $MgZn$ ,  $Mg_2Zn_3$  (or  $Mg_4Zn_7$ , monoclinic),  $MgZn_2$  ( $C14$ -type hexagonal), and  $Mg_2Zn_{11}$  ( $D8_c$ -type cubic). Using the specific heat measurements of the liquid phase, [1998Lia1] refined the description of the Mg-Zn system.

## Ternary Phases

There are two established ternary phases in this system. The T phase (denoted  $\tau$  by [1998Lia1]) with the nominal composition  $(Al,Zn)_{49}Mg_{32}$  is cubic (space group  $Im\bar{3}$ ). [1997Lia] used this semistoichiometric approximation for the T phase, even though the Mg content is also known to vary by a few percent. [1998Lia1] took into account the variation in Mg content in the thermodynamic modeling. The  $\phi$  phase has the nominal formula  $Al_2Mg_5Zn_2$  or  $(Al,Zn)_5Mg_6$ , with the composition variation of 18-29 at. % Al, 28-17 at. % Zn and 53-55 at. % Mg [1997Don]. It has an orthorhombic structure with possible space group of  $Pbc2_1$  or  $Pbcm$  and lattice parameters of  $a = 0.8979$  nm,  $b = 1.6988$  nm and  $c = 1.934$  nm [1997Don]. The occurrence of a third ternary phase close to the Mg-Zn boundary [1961Cla] has not been confirmed.

## Computed Ternary Phase Equilibria

[1997Lia] made their own evaluation of the experimental data and presented an assessed liquidus projection based mainly on the work of [1913Ege], [1936Kos1], [1936Kos2], [1936Kos3], and [1961Cla], an isothermal section at 335 °C based on [1936Kos1], [1936Kos2], [1936Kos3], [1937Fin], [1943Lit1], [1943Lit2], and [1961Cla]. An isothermal section at 25 °C was also presented, assuming that the  $\phi$  phase is stable at room temperature.

In the thermodynamic modeling of [1997Lia], the liquid phase and the face-centered cubic (fcc) and close-packed hexagonal (cph) solid solutions were treated as random

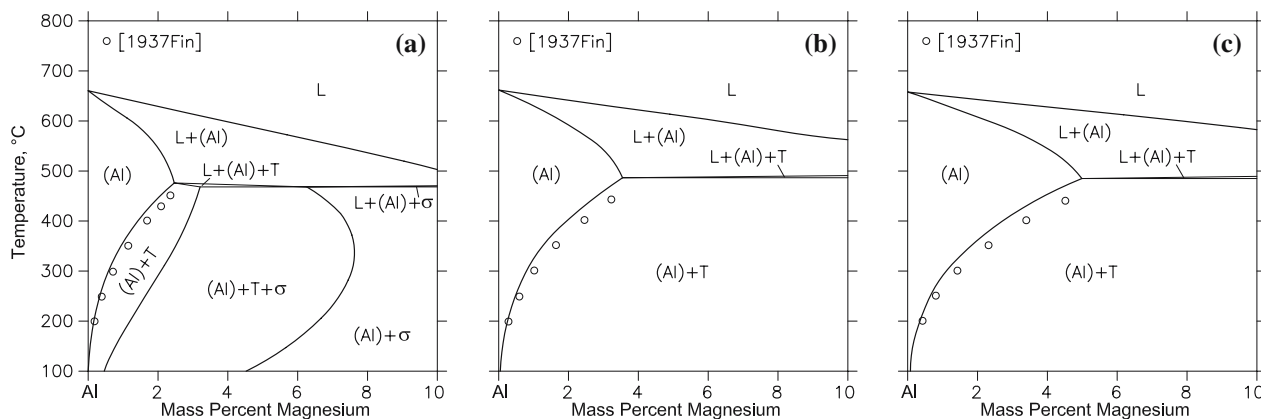
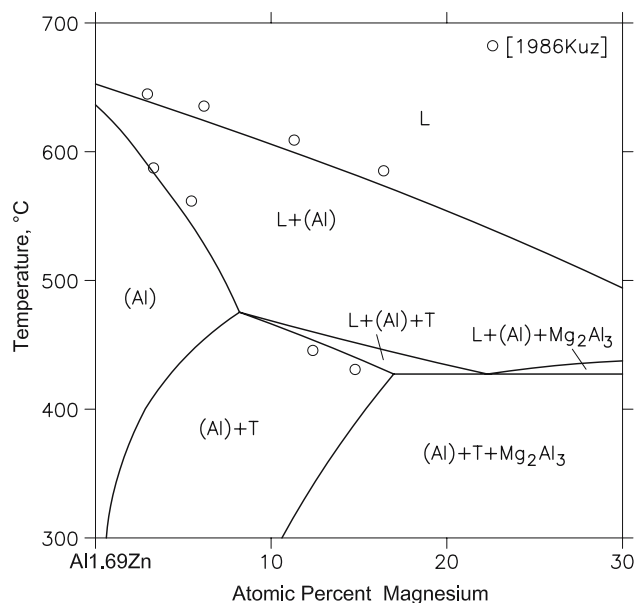
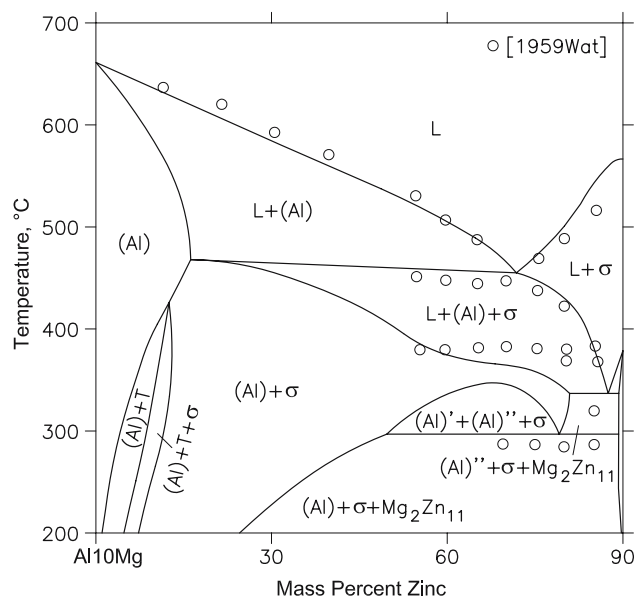


Fig. 1 Al-Mg-Zn computed vertical sections along (a) Al-MgZn<sub>2</sub>, (b) Al-MgZn, and Al-Mg<sub>2</sub>Zn joins [1997Lia]

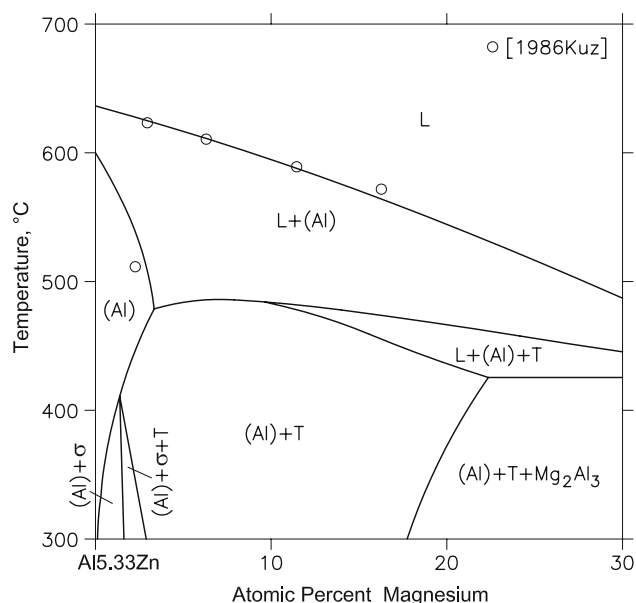
## Section II: Phase Diagram Evaluations



**Fig. 2** Al-Mg-Zn computed vertical section at 1.69 at. % Zn [1997Lia]



**Fig. 4** Al-Mg-Zn computed vertical section at 10 mass % Mg [1997Lia]



**Fig. 3** Al-Mg-Zn computed vertical section at 5.33 at. % Zn [1997Lia]

solutions with a single lattice. The  $\phi$  phase was approximated to a stoichiometric compound:  $\text{Al}_2\text{Mg}_5\text{Zn}_2$ . The T phase was modeled as a semistoichiometric compound:  $(\text{Al,Zn})_{49}\text{Mg}_{32}$ . The Al solubility in  $\text{MgZn}_2$  was taken into account. All other binary phases were assumed to have negligible solubility for the third component. Their own assessed phase diagram data were used by [1997Lia] in the optimization. In addition, the vapor pressure of Zn over liquid alloys measured by [1960Koz] and [1971Luk] and

the activity of Mg in liquid alloys measured by [1974Pog] were inputs. The optimized interaction parameters were listed.

A number of vertical sections were computed by [1997Lia] and compared with the experimental data of [1937Fin], [1986Kuz] and [1959Wat] (Fig. 1-4). The agreement is generally good. In addition, [1997Lia] computed a liquidus projection and three isothermal sections at 400, 335 and 25 °C for the entire composition range. Some discrepancies exist between the invariant equilibria calculated by [1997Lia] and those in their own assessed data. The limitations arise from the assumptions made in the modeling such as a semistoichiometric T phase and negligible solubility of the third component in the binary phases. [1997Lia] concluded that more experimental data are needed for this ternary system over a wider range of composition and temperature.

With starting metals of 99.99% Al, 99.99% Mg and 99.9% Zn, [1998Lia1] induction-melted 34 ternary alloys under He atm. The samples were annealed at 335 °C for 19 days and cooled to room temperature in 10 min. The phase equilibria were studied by X-ray diffraction, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The compositions of the co-existing phases were determined by electron probe microanalysis (EPMA) and listed. In the thermodynamic optimization, the new data were used in conjunction with the constitutional, thermochemical and crystallographic information from the literature.

The (Al), (Mg) and (Zn) solid solutions and the liquid phase were modeled as substitutional solutions. The ternary interaction parameters were introduced for the liquid phase but neglected in the case of solid solutions which have limited solubility. In the binary phases, the third component solubility was taken into account. The T phase was modeled

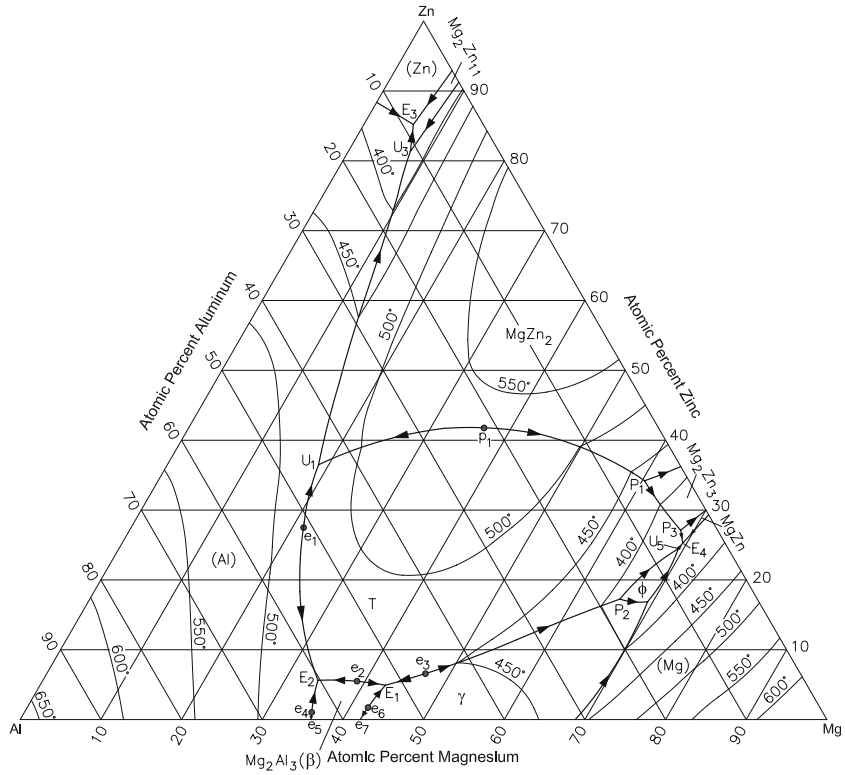


Fig. 5 Al-Mg-Zn computed liquidus projection [1998Lia1]

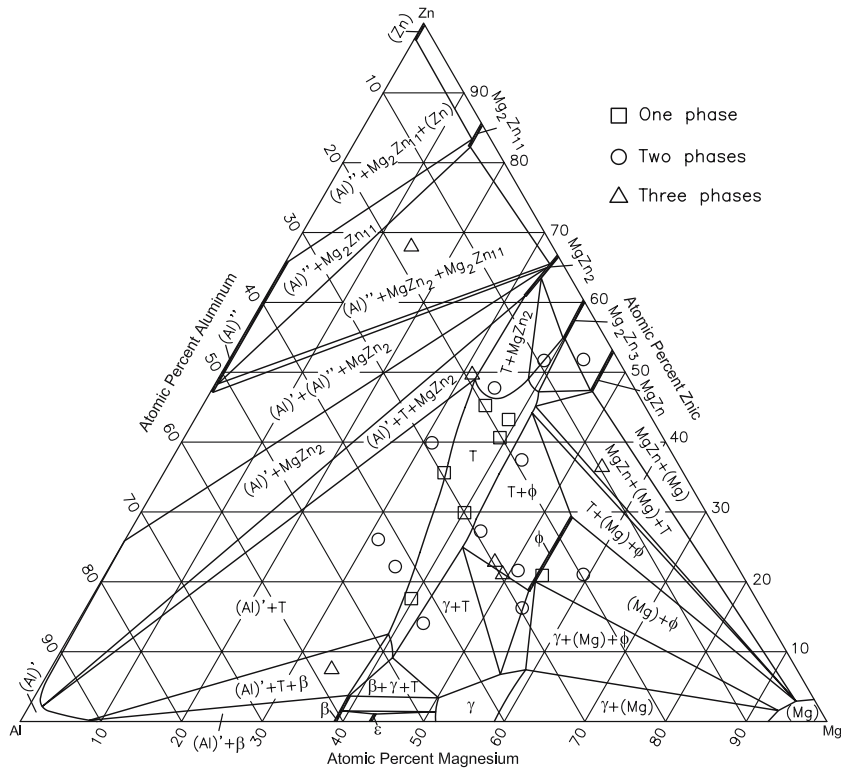
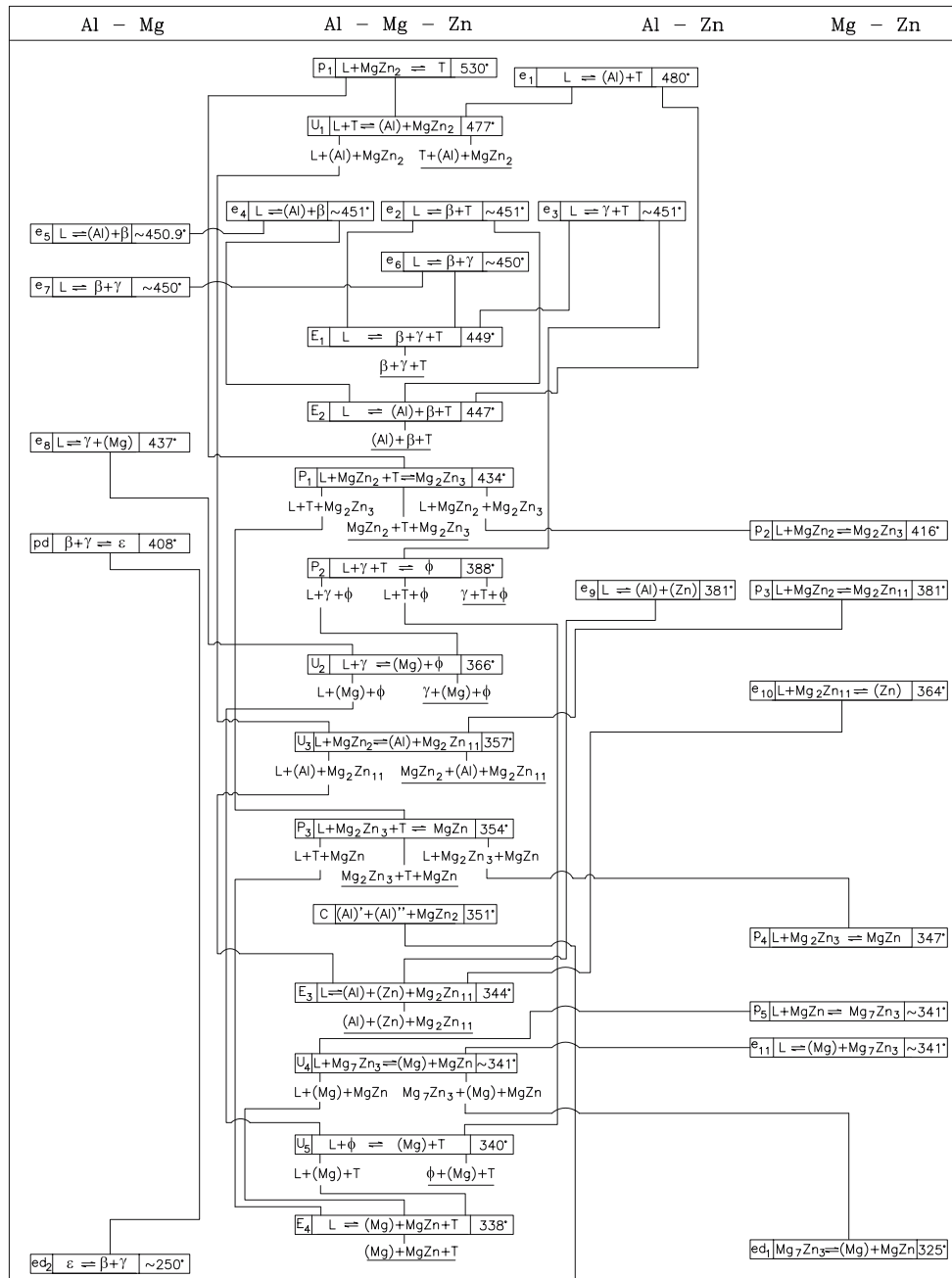


Fig. 6 Al-Mg-Zn computed isothermal section at 335 °C [1998Lia1]

## Section II: Phase Diagram Evaluations

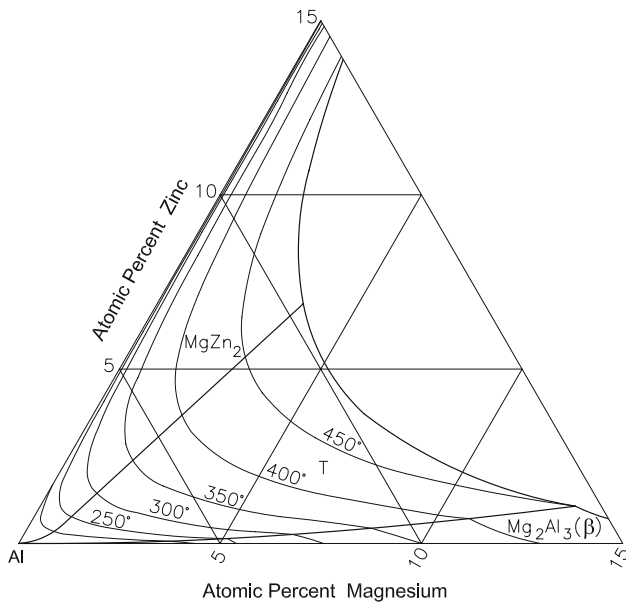


**Fig. 7** Al-Mg-Zn reaction sequence during solidification

as  $Mg_{26}(Mg,Al)_6(Al,Mg,Zn)_{48}Al_1$  [1998Lia1]. The variation in the Mg content obtained from the EPMA measurements was used in the optimization. The  $\phi$  phase was modeled as  $Mg_6(Al,Zn)_5$ , which provides for the small observed variation of Al and Zn at constant Mg content. The optimized interaction parameters were listed.

The liquidus projection computed by [1998Lia1] is shown in Fig. 5. The phases of primary crystallization are marked in the figure. The computed compositions and temperatures of the invariant reactions were listed by [1998Lia1]. The transition reaction  $L + Mg_7Zn_3 \leftrightarrow (Mg) +$

$MgZn$  (labeled  $U_4$  in Fig. 7) occurs too close to the Mg-Zn side and is not indicated in Fig. 5. The computed isothermal section at 335 °C (Fig. 6) is compared with the new data obtained by [1998Lia1]. The three-phase field of  $(MgZn + (Mg) + Mg_7Zn_3)$  is too close to the Mg-Zn boundary to be seen in Fig. 6. The reaction sequence in Fig. 7 is consistent with the liquid-solid reactions in Fig. 5 and the triangulations in Fig. 6. The underlined three-phase equilibria in Fig. 7 are stable at 335 °C. The computed solvus of (Al) is shown in Fig. 8 [1998Lia1]. Three regions corresponding to the equilibrium of (Al) with  $MgZn_2$ , T and  $Mg_2Al_3$  ( $\beta$ )



**Fig. 8** Al-Mg-Zn solvus of the (Al) solid solution [1998Lia1]

respectively are seen. The partial liquidus projection and the (Al) solvus computed by [2002Mur] are in agreement with the above. [1998Lia1] also computed three vertical sections at 20 at. % Al, 36 at. % Mg and 20 at. % Zn. These are in satisfactory agreement with their DTA/DSC data. [1997Lia] computed constant-temperature contours on the liquidus and solidus surfaces of (Al) and found good agreement with the experimental results of [1979Sti].

Among the other recent phase diagram studies, [1994Dro] explained the occurrence of local melting of the T and  $MgZn_2$  phases, using published phase diagrams. [2000Kra] studied the shift in the phase boundaries near the Al corner with different cooling rates during solidification. [2004Liu] made a thermodynamic analysis to predict the alloy compositions of this system, which are amenable to semisolid metal processing. [2005Alv] used the vertical section at 5.3 at. % Zn (see Fig. 3) to predict microstructures of Al-anodes used for cathodic protection. [2006Ohn] studied the phase equilibria and solidification of Mg-rich alloys of this system, using three alloys with Al up to 9.4 mass % and Zn up to 1.7 mass %. A partial liquidus surface computed for alloys up to 30 mass % each of Al and Zn was compared with the present and the previous experimental results. Vertical sections computed at 5, 10, 15, 20, 25, and 30 mass % Zn and at Al:Zn ratio of 1:1 were compared with the experimental data in the literature.

## References

- 1913Ege:** G. Eger, Study of the Constitution of Ternary Magnesium-Aluminum-Zinc Alloys, *Z. Metallkd.*, 1913, **4**, p 29-128, in German
- 1936Kos1:** W. Koster and W. Wolf, The Aluminum-Magnesium-Zinc Ternary System. I. The Al- $Al_2Mg_3Zn_3$ - $MgZn_2$ -Zn Region, *Z. Metallkd.*, 1936, **28**, p 155-158, in German
- 1936Kos2:** W. Koster and W. Dullenkopf, The Aluminum-Magnesium-Zinc Ternary System. II. The Al- $Al_3Mg_4$ - $Al_2Mg_3Zn_3$ -Al Region, *Z. Metallkd.*, 1936, **28**, p 309-312, in German
- 1936Kos3:** W. Koster and W. Dullenkopf, The Aluminum-Magnesium-Zinc Ternary System. II. The Mg- $Al_3Mg_4$ - $Al_2Mg_3Zn_3$ - $MgZn_2$ -Mg Region, *Z. Metallkd.*, 1936, **28**, p 363-367, in German
- 1937Fin:** W.L. Fink and L.A. Willey, Equilibrium Relations in Aluminum-Magnesium-Zinc Alloys of High Purity, *Trans. AIME*, 1937, **124**, p 78-109
- 1943Lit1:** A.T. Little, G.V. Raynor, and W. Hume-Rothery, The Constitution of Magnesium-Manganese-Zinc-Aluminum Alloys in the Range 0-5 Percent Mg, 0-2 Percent Mn, and 0-8 Percent Zn: III. 500 °C and 400 °C Isothermals, *J. Inst. Metals (London)*, 1943, **69**, p 423-440
- 1943Lit2:** A.T. Little, G.V. Raynor, and W. Hume-Rothery, The Constitution of Magnesium-Manganese-Zinc-Aluminum Alloys in the Range 0-5 Percent Mg, 0-2 Percent Mn and 0-8 Percent Zn. IV. The Equilibrium Diagram below 400 °C, *J. Inst. Metals (London)*, 1943, **69**, p 467-484
- 1959Wat:** H. Watanabe, Investigation of the Phase Diagram of the System Al-Zn-Mg, *Nippon Kinzoku Gakkaishi*, 1959, **23**(5), p 285-288, in Japanese
- 1960Koz:** Z. Kozuka, J. Moriyama, and I. Kushima, *J. Electrochem. Soc. Jpn.*, 1960, **28**, p 298-301, cited in [1998Lia1]
- 1961Cla:** J.B. Clark, Phase Relations in the Magnesium-Rich Region of the Mg-Al-Zn Phase Diagram, *Trans. Amer. Soc. Metals*, 1961, **53**, p 295-306
- 1971Luk:** E.E. Lukashenko and A.A. Pogodayev, Thermodynamics of Melts with Aluminum, Magnesium and Zinc, *Zhur. Fiz. Khim.*, 1971, **45**(8), p 2085-2087, in Russian; TR: *Russ. J. Phys. Chem.*, 1971, **45**(8), p 1182-1184
- 1974Pog:** A.M. Pogodaev and E.E. Lukashenko, Thermodynamic Study of Aluminum-Magnesium-Zinc Melts, *Izv. Akad. Nauk SSSR Metall.*, 1974, (6), p 90-92, in Russian
- 1979Sti:** W. Stiller and H. Hoffmeister, Determination of Liquid/Solid Phase Equilibria of Aluminum-Magnesium-Zinc Alloys, *Z. Metallkd.*, 1979, **70**(12), p 817-824, in German
- 1986Des:** N.U. Deshpande, K.K. Ray, and A.K. Mallik, The Aluminum-Magnesium-Zinc System, *J. Alloy Phase Diagrams*, 1986, **2**(2), p 108-130
- 1986Kuz:** G.M. Kuznetsov, A.D. Barsukov, G.B. Krivosheeva, and E.G. Dieva, Study of the Phase Equilibria in Alloys of the System Al-Zn-Mg, *Metally*, 1986, (4), p 198-200, in Russian; TR: *Russ. Metall.*, 1986, (4), p 203-205
- 1992Aga:** R. Agarwal, S.G. Fries, H.L. Lukas, G. Petzow, F. Sommer, T.G. Chart, and G. Effenberg, Assessment of the Mg-Zn System, *Z. Metallkd.*, 1992, **83**(4), p 216-223
- 1993Che:** S.L. Chen and Y.A. Chang, A Thermodynamic Analysis of the Al-Zn System and Phase Diagram Calculation, *CALPHAD*, 1993, **17**(2), p 113-124
- 1993Pet:** D.A. Petro, Aluminum-Magnesium-Zinc, *Ternary Alloys*, Vol 7, G. Petzow, G. Effenberg, Ed., VCH Verlagsgesellschaft, Weinheim Germany, 1993, pp 57-71
- 1994Dro:** P.E. Droenen and N. Ryum, Local Melting in Al-Mg-Zn Alloys, *Metall. Mater. Trans. A*, 1994, **25**, p 521-530
- 1995Vil:** P. Villars, A. Prince, and H. Okamoto, Al-Mg-Zn, *Handbook of Ternary Alloy Phase Diagrams*, ASM International, Materials Park, OH, 1995, **4**, p 3933-3985
- 1997Don:** P. Donnadieu, A. Quivy, T. Tarfa, P. Ochin, A. Dezellus, M.G. Harmelin, P. Liang, H.L. Lukas, H.J. Seifert, F. Aldinger, and G. Effenberg, On the Crystal Structure and Solubility Range of the Ternary  $\phi$  Phase in the Mg-Al-Zn System, *Z. Metallkd.*, 1997, **88**(12), p 911-916

## Section II: Phase Diagram Evaluations

- 1997Lia:** H. Liang, S.L. Chen, and Y.A. Chang, A Thermodynamic Description of the Al-Mg-Zn System, *Metall. Mater. Trans. A*, 1997, **28A**, p 1725-1734
- 1998Lia1:** P. Liang, T. Tarfa, J.A. Robinson, S. Wagner, P. Ochin, M.G. Harmelin, H.J. 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
- 1998Lia2:** P. Liang, H.L. Su, P. Donnadieu, M.G. Harmelin, A. Quivy, P. Ochin, G. Effenberg, H.J. Seifert, H.L. Lukas, and F. Aldinger, Experimental Investigation and Thermodynamic Calculation of the Central Part of the Mg-Al Phase Diagram, *Z. Metallkd.*, 1998, **89**(8), p 536-540
- 2000Kra:** T. Kraft, The Influence of Kinetic Effects on the Equilibrium Phase Diagram During Solidification-Aluminum-Rich Corner of the Quaternary System Al-Cu-Mg-Zn, *Z. Metallkd.*, 2000, **91**(3), p 221-226
- 2002Mur:** J.L. Murray, Thermodynamic Modeling of the Al-Cu-Mg-Zn System in the Aluminum Corner, *CALPHAD and Alloy Thermodynamics*, P.E.A. Turchi, A. Gonis, and R.D. Shull, Ed., Miner. Met. Mater. Soc., Warrendale PA, 2002, pp 165-175
- 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
- 2004Liu:** Y.Q. Liu, A. Das, and Z. Fan, Thermodynamic Predictions of Mg-Al-M (M = Zn, Mn, Si) Alloy Compositions Amenable to Semisolid Metal Processing, *Mater. Sci. Technol.*, 2004, **20**, p 35-41
- 2005Alv:** O. Alvarez, C. Gonzalez, G. Aramburo, R. Herrera, and J.A. Juarez-Islas, Characterization and Prediction of Microstructure in Al-Zn-Mg Alloys, *Mater. Sci. Eng. A*, 2005, **A402**, p 320-324
- 2006Ohn:** M. Ohno, D. Mirkovic, and R. Schmid-Fetzer, Phase Equilibria and Solidification of Mg-Rich Mg-Al-Zn Alloys, *Mater. Sci. Eng. A*, 2006, **A421**, p 328-337