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Phase Stability, Diffusion Kinetics and Their Applications (PSDK-III)

Critical Evaluation and Thermodynamic Modeling of the Mg-Mn, Al-Mn and Mg-Al-Mn Systems

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Abstract

A self-consistent thermodynamic description of the ternary Mg-Al-Mn system has been developed using the modified quasichemical model for the liquid phases, random solution model for the terminal solid solutions and the compound energy formalism for the intermediate solid solutions. The thermodynamic descriptions of the binary sub-systems are combined to calculate and assess the ternary Mg-Al-Mn system. Only one composition dependent ternary parameter has been used to describe the ternary liquid phase. All the available experimental phase diagram and thermodynamic information in the literature have been evaluated and compared with the current results. The optimized parameters of the present assessment reproduced the experimental data within the experimental error limit. The ternary database thus forms the basis for the design of experiments and the subsequent update with the availability of new experiments.

Introduction

Mg-based alloys are being used extensively in many industries for producing different parts and equipments, because of their better physical and mechanical properties compared to other metal alloys. Many different elements which include Al, Ca, Zn, Sr, Mn, Cu, Y etc. are alloyed with Mg to improve its properties for specific applications. A comprehensive and reliable thermodynamic database which includes these elements as constituents for Mg alloy system is thus an essential requirement for the better understanding of the system behavior. This can be utilized for the design of experiments, solidification and heat treatment process and for many other practical applications with significantly reduced amount of time and effort. The present study deals with the thermodynamic modeling, within the CALPHAD framework, of the Mg-Al-Mn system which is one of the most important parts of the desired multi-component Mg alloy database. It has been established for a long time that even a little amount of Mn in the order of less than 1 wt% has a very significant effect on the properties of commercial Mg alloys. The effect is attributed to the ability of Mn atoms to precipitate the impurity iron atoms which is the primary cause of corrosion in this type of alloys. The binary subsystems Mg-Mn, Al-Mn have been critically evaluated and modeled in the present study and the other subsystem Mg-Al has been taken form [1]. All these binary subsystems have been combined to calculate and model the ternary Mg-Al-Mn system. A self-consistent thermodynamic description of the ternary Mg-Al-Mn system has been developed using the modified quasichemical model for the liquid phases, random solution model for the terminal solid solutions and the compound energy formalism for the intermediate solid solution phases in each system.

Literature Review

Reliable experimental data for the Mg-Mn binary system is scarce. Many researchers investigated only the small Mg-rich corner of the system and there is no general agreement. Hashemi and Clark [2] provided a good discussion on the available experimental data on the Mg-Mn system. Very limited solid solubility of Mn in Mg and no evidence of solid solubility of Mg in Mn were confirmed. No experimental thermodynamic data on the binary could be found in the literature. Most recent experimental work reporting a monotectic reaction temperature in the phase diagram was performed by Gröbner et al. in 2005 [3]. All available published experimental data on the system are analyzed and only the reliable and consistent data set are compared with the present calculation.

Experimental data for the Al-Mn binay system investigated prior to 1987 were summarized by McAlister et al. [4]. Jansson [5] modeled the Al-Mn system thermodynamically based on the previous experimental results. Liu et al. [6-7] has modified some phase relations associated with the ε (HCP) phase based on their own experimental results. Okamoto [8] assessed the previous experimental results and proposed the most likely features of the system. Based on their own XRD, DTA, SEM and EDS experimental results on the Al-rich side of the Al-Mn system, Du et al. [9] modeled the Al-Mn system thermodynamically.

Several researchers investigated the phase equilibria in the ternary Mg-Al-Mn system for different composition and temperature ranges. Ohno and Schmid-Fetzer [10] critically evaluated the experimental data of Ageev et al. [11], Nelson et al. [12], Mirgalovskaya et al. [13], Siemensen [14-15] et al., Thorvaldsen et al. [16] and Beerwald et al. who studied the phase equilibria in the Mg-rich side of the ternary. They [10] also presented the thermodynamic modeling of the system with the parameters which were primarily optimized on the basis of the Mn solubility data of Beerwald et al., Nelson et al. [12] and Thorvaldsen et al. [16]. Du et al. [9] assessed the previous experimetnal investigations on the Al-rich part of the ternary system by Leemann [17], Hoffmann [18], Fahrenhorst et al. [19], Butchers et al. [20], Little et al. [21], Mondolfo , Butchers et al. [22], Wakeman et al. [23], Ohnishi et al. [24 - 25], Fun et al. [26] and Barlock et al. [27]. They [9] found the data of Fahrenhorst et al. [19], Butchers et al. [20], Wakeman et al. [23], Ohnishi et al. [24-25] and Barlock et al. [27] to be consistent. They presented the thermodynamic model for the ternary Mg-Al-Mn system for the entire composition range based on these consistent data. All the original sources of data were consulted and compared with the present assessment but not reported in detail here to avoid duplication. No experimental information on the Mn-rich side of the ternary Mg-Al-Mn phase diagram could be found in the literature.

Evaluation of the Experimental Data

The available experimental data are collected from the original source and evaluated critically. Only the reliable phase diagram and thermodynamic data sets are compared to the calculated values. Different factors have been considered in evaluating the experimental data and are described briefly in the following paragraphs.

Structural characterization of different phases (e.g. whether XRD was used to confirm the presence of a phase or not) is crucial to accept an experimental result especially if there exists a large number of metastable phases. (Example: Al-Mn system) [4].

Mn containing alloy samples were not available with high purity upto around 1960s. Thus the experimental results obtained before 1960s may have significant measurement errors and not used for comparison with the present work except for few of the consistent results.

The results that show evidence of attaining equilibrium (e.g. the time allowed for the equilibration) before taking the final reading is considered reliable. This is important for all the systems, especially for Al-Mn which shows very slow reaction to equilibrium [4].

When similar results have been produced by two independent experiments, carried out by different experimental set-ups and different environmental settings, these results are considered as consistent and reliable and thus were compared to the calculated values.

Usually it is assumed that undercooling is more significant than overheating [6]. Thus when considerable deviations were found between heating and cooling data in the same experiment, the heating data were preferred. Thus the heating data of the liquidus in the Al-rich side of the Al-Mn system were preferred in the assessment.

When a phase boundary of a temperature-composition phase diagram is found steep, the fixed composition techniques (such as thermal analyses) may give rise to large error because of the weak signals generated by indistinguishable change in ΔCp values. However, fixed temperature technique (such as diffusion couple method) should give more accurate results as discussed by Liu et al. [6].

It is likely that more recent data reflect more accurate results. Thus, recently available data are preferred in the assessment. However, there are some cases where more recent data had to be discarded because of some other factors described above. For instance, in the Al-Mn system, Mn-solubility data in the Al-rich side reported by Drits et al. [28] in 1964 was discarded because of the probability of having impurities but the older data reported by Dix et al. [29] in 1933, Butcher et al. [22] in 1945, Fahrenhorst et al. [19] in 1940 and Obinata et al. [30] in 1953 were taken as reliable because of their mutual consistency.

Results and Discussions

The assessed Mg-Mn phase diagram, as shown in figure 1 is characterized by a wide miscibility gap in the liquid region. This is expected considering the homologous systems Li-Mn, Ca-Mn, Sr-Mn and Ba-Mn. The Mg-Mn system consists of a monotectic and peritectic reaction in the Mn-rich and Mg-rich side, respectively. The monotectic temperature as determined by the most recent experiments by Gröbner et al. [3] is reproduced in the calculation as shown in figure 1. In figure 2, the calculated diagram is compared with the experimental data of the Mg-rich side. The calculation is consistent with the solid solubility data of Drits et al. [31] and Petrov. et al [32] and the liquidus data of Petrov et al. [32].

The optimized Al-Mn phase diagram along with the experimental data from the literature has been shown in figure 3. It shows an overall good agreement between the calculated phase diagram with the accepted experimental data evaluated in this assessment throughout the entire composition region. The calculated solubility of Mn in Al shown in figure 4, has an excellent agreement with the mutually consistent experimental data of [19, 22, 29, 30]. The calculated Al-rich portion of the phase diagram are compared with the experimental heating and cooling data and shown in figures 5 and 6.

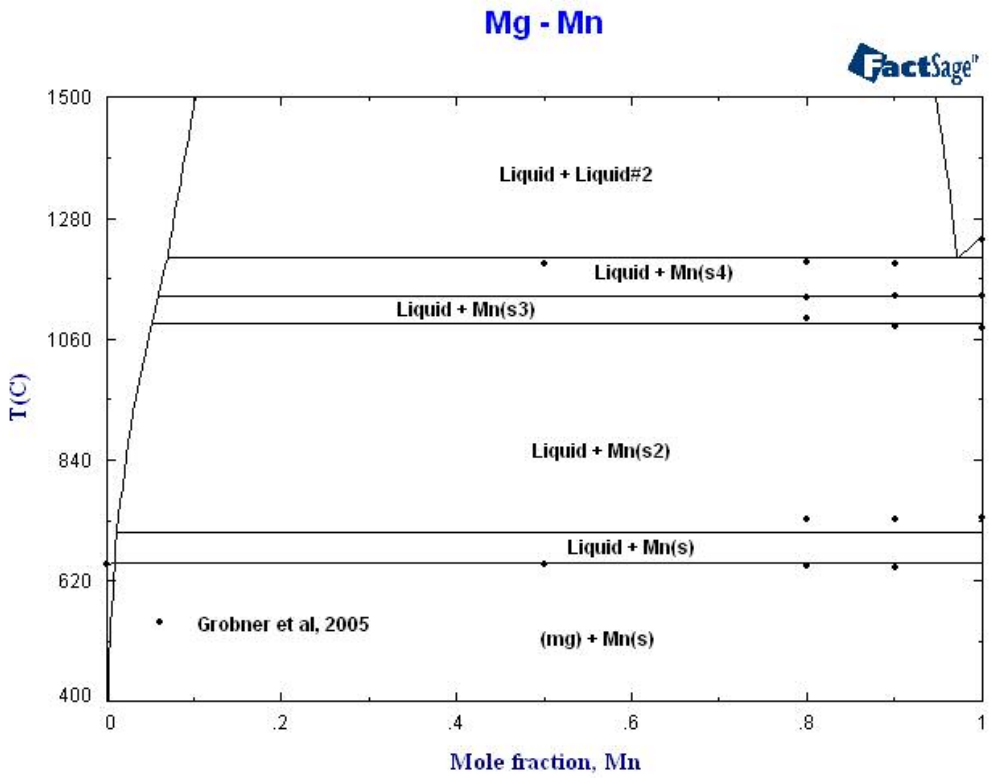

Fig1. Calculated Mg-Mn phase diagram compared with the experimental data of GrÖbner et al. [3].

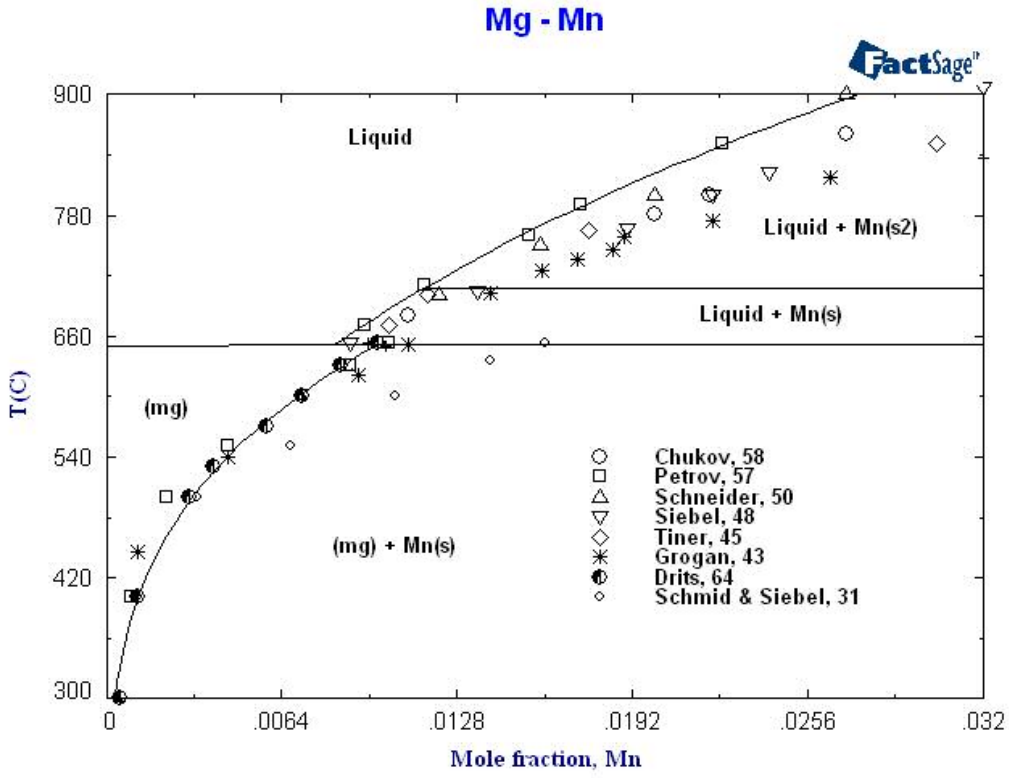

Fig2. Calculated Mg-rich region of the Mg-Mn phase diagram compared with the experimental data of [31-34] and the remaining data from [2].

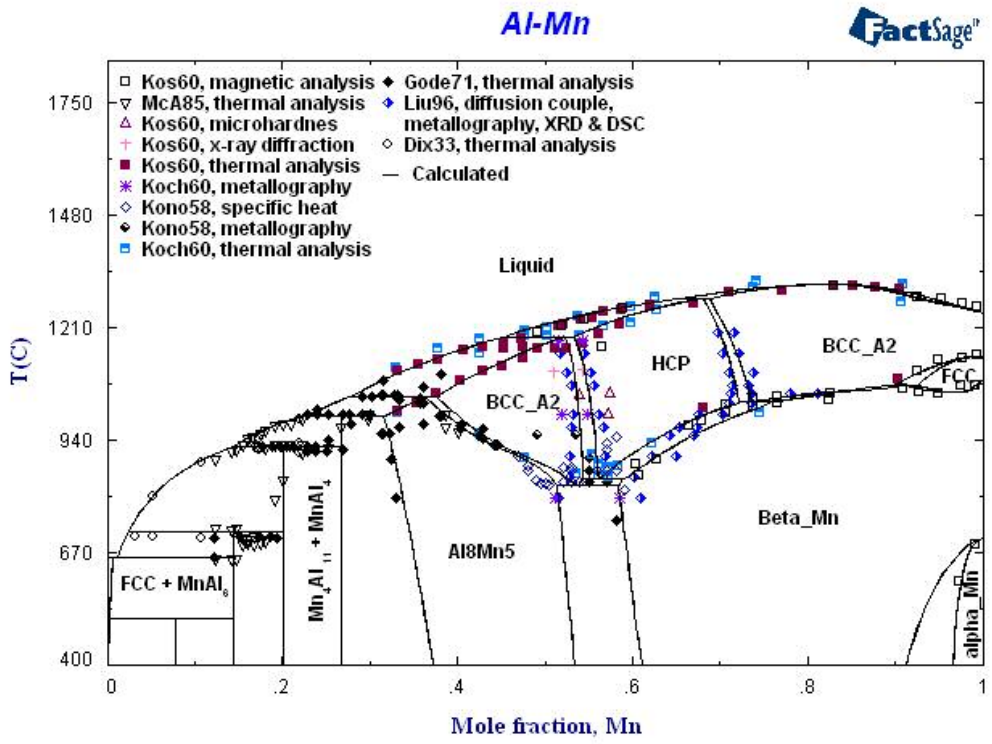

Fig3. Calculated Al-Mn phase diagram compared with the experimental data of [6, 29, 35-39]

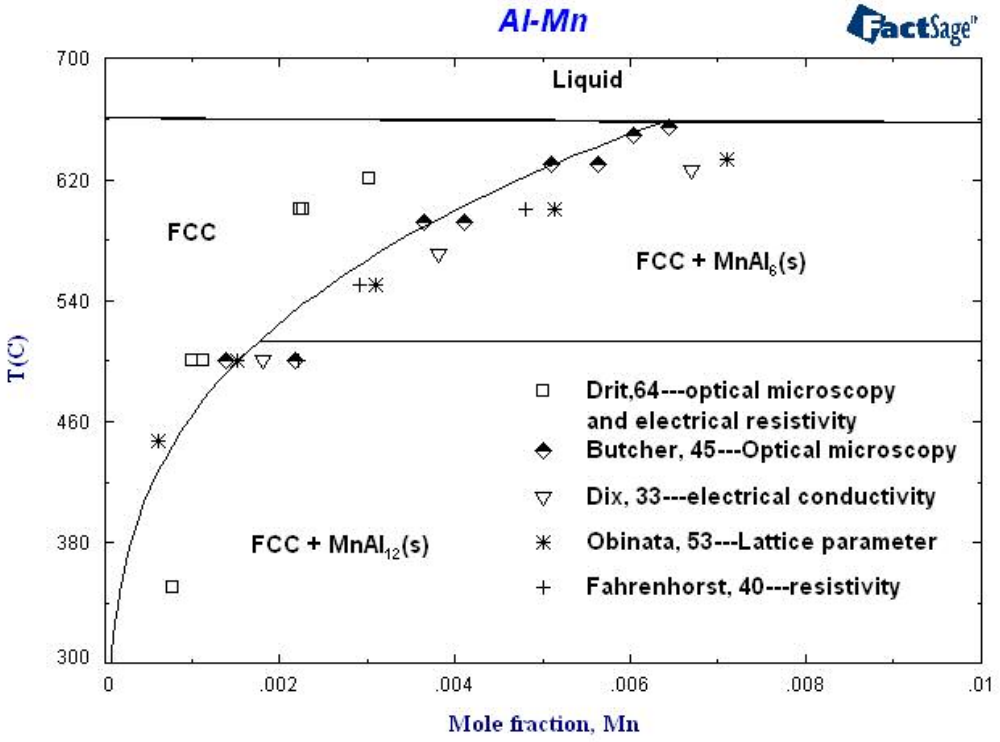

Fig4. Comparison of the calculated solubility of Mn in Al with the experimental data of [19, 22, 28-30].

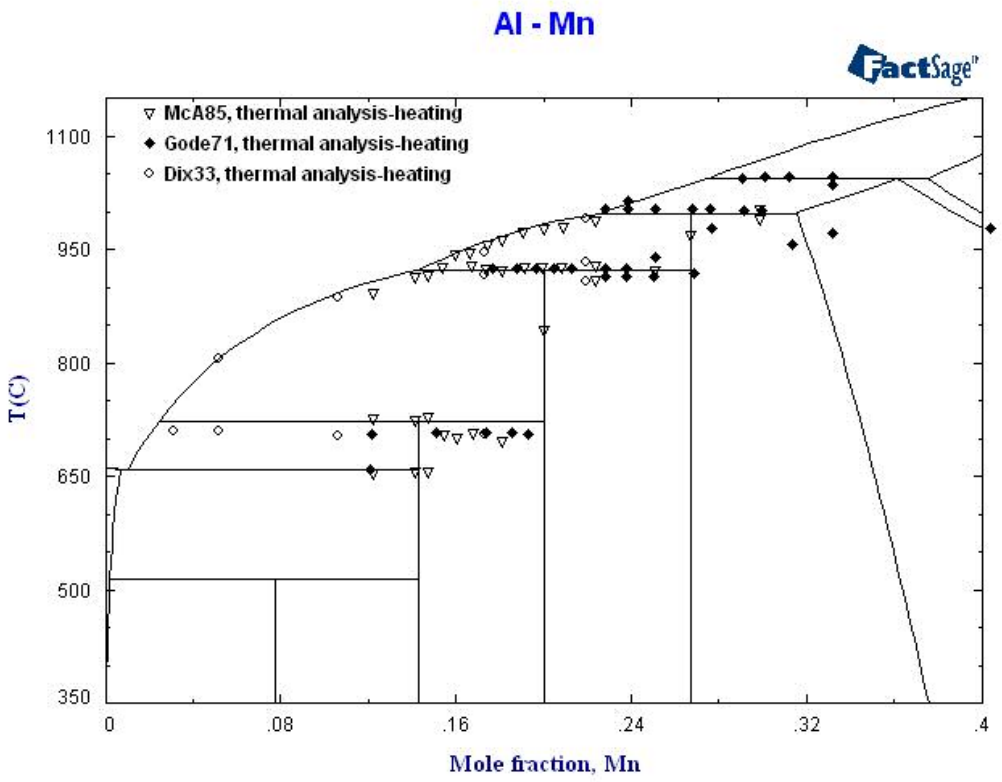

Fig5. Calculated Al-rich part of the phase diagram compared with the experimental heating data of [29, 38, 39].

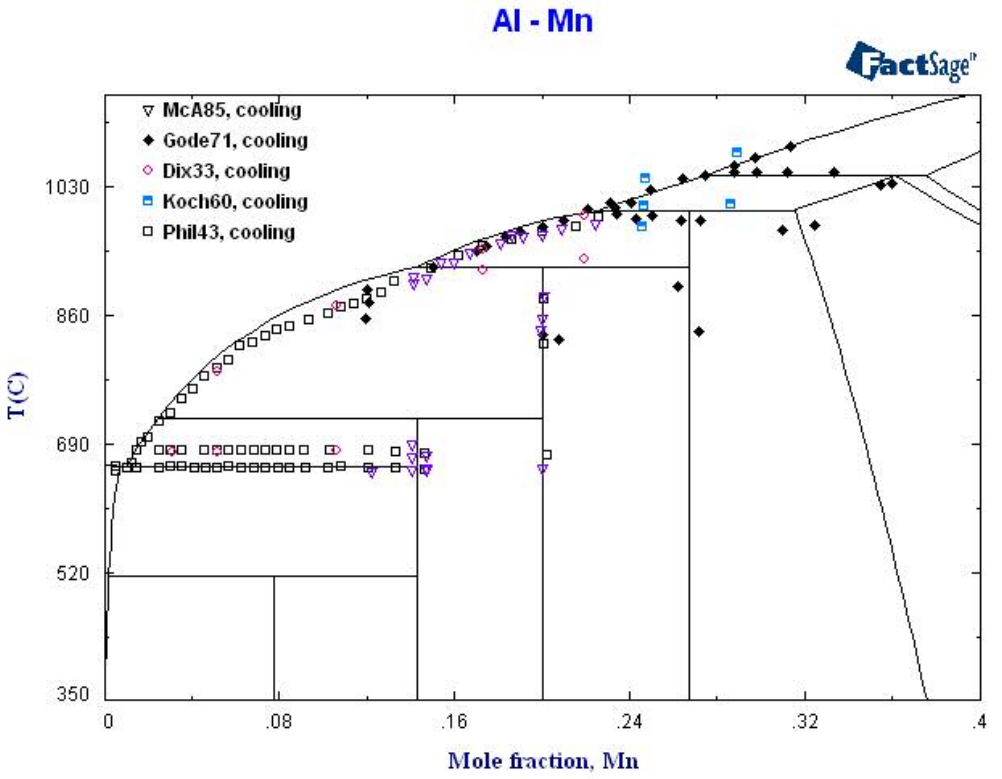

Fig6. Calculated Al-rich part of the phase diagram compared with experimental cooling data of [29, 37-40].

Figures 5 and 6 show that the calculated Al-rich portion of the phase diagram is more consistent with the heating than the cooling data as expected from the fact, that the undercooling effect is more prominent than the overheating effect [6]. The calculated thermodynamic properties of the Al-Mn liquid also have an excellent agreement with the measured values as shown in figures 7 and 8.

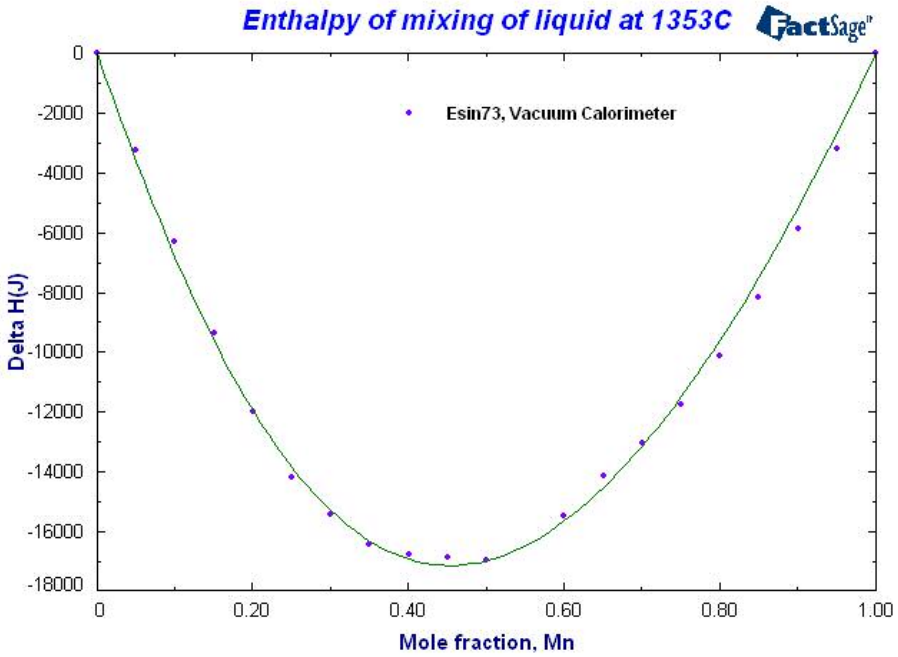

Fig7. Comparison of the calculated enthalpy of mixing of the liquid Al-Mn with experimental results of [41].

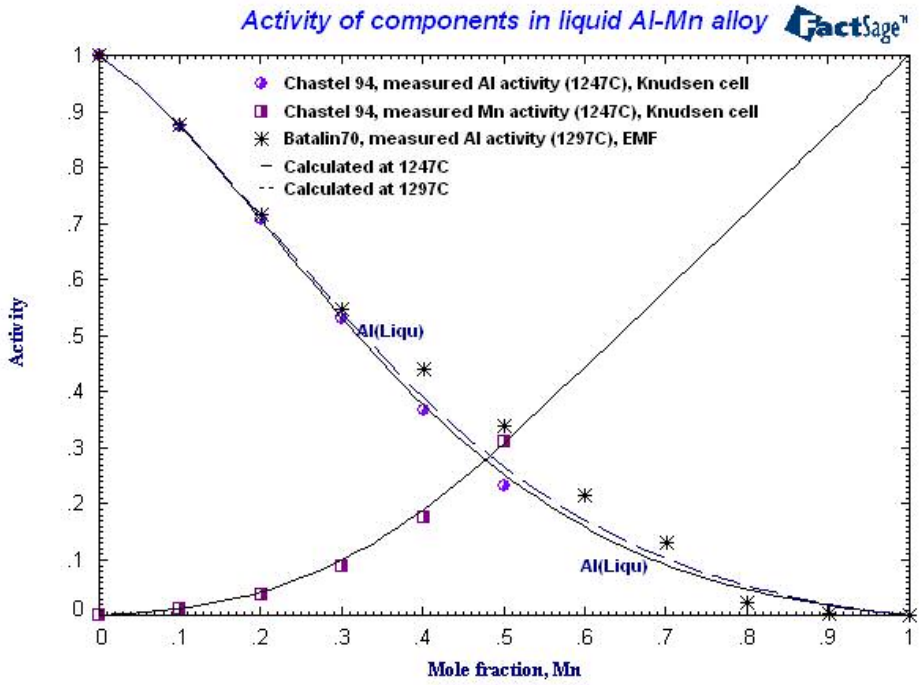

Fig8. Comparison of the calculated activity with experimentally measured values of [42, 43].

In the following paragraphs, the calculated Mg-Al-Mn ternary phase diagrams are compared to the reliable experimental results. Only one ternary interaction parameter was used to optimize the ternary liquid. The liquidus projection throughout the entire composition region of the ternary has been shown in figure 9.

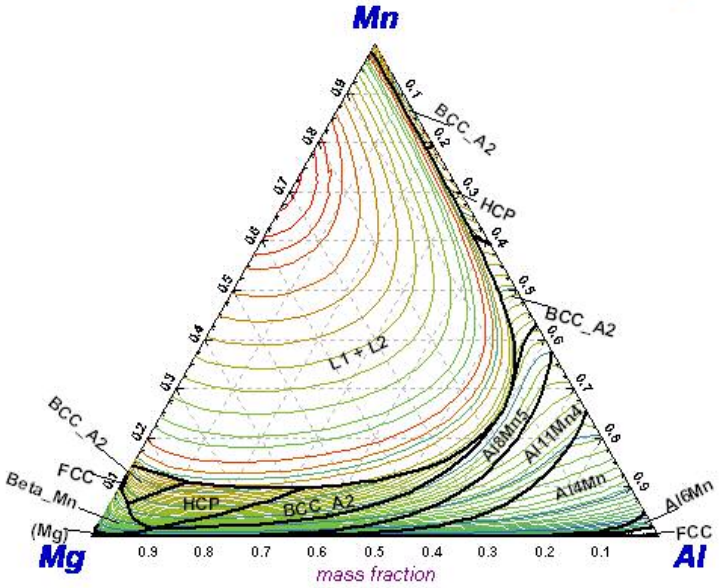

Fig9. Calculated liquidus projection of the Mg-Al-Mn ternary system showing the primary phase regions.

The liquidus projections on the two dimensional plane in figure 10 shows the primary crystallization fields in the Mg-rich corner. The experimental data of Thorvaldsen et al. [16] and Siemensen et al. [15] are compared with the current modeling results in this figure which show a reasonable consistency with the composition of the identified phases.

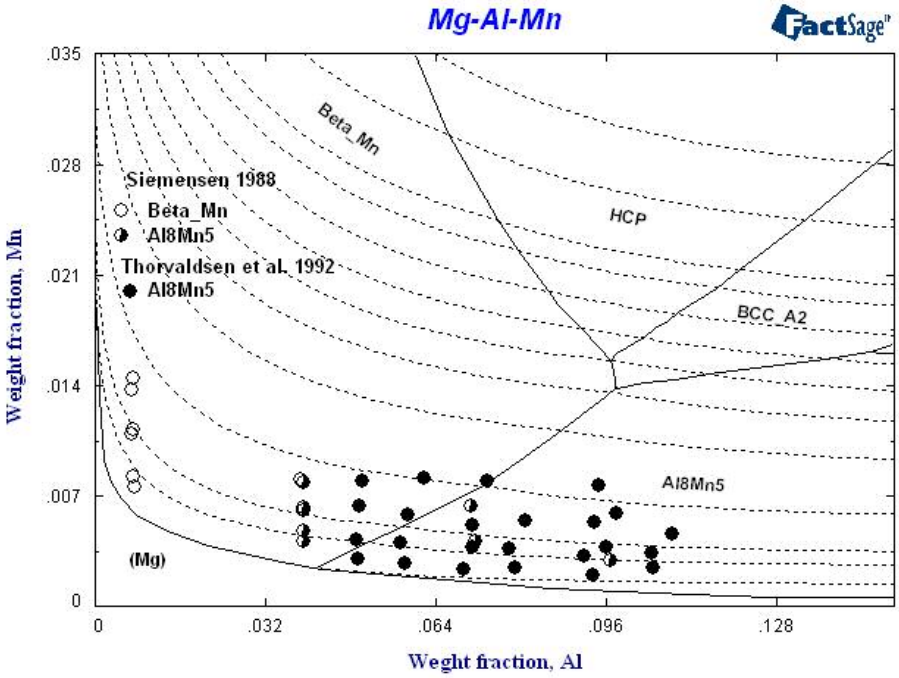

Fig10. Primary crystallization fields in the Mg-rich corner compared to the experimental data of [15, 16].

Several isothermal and two vertical sections have been calculated and compared with the experimental results shown in figures 11 through 13.

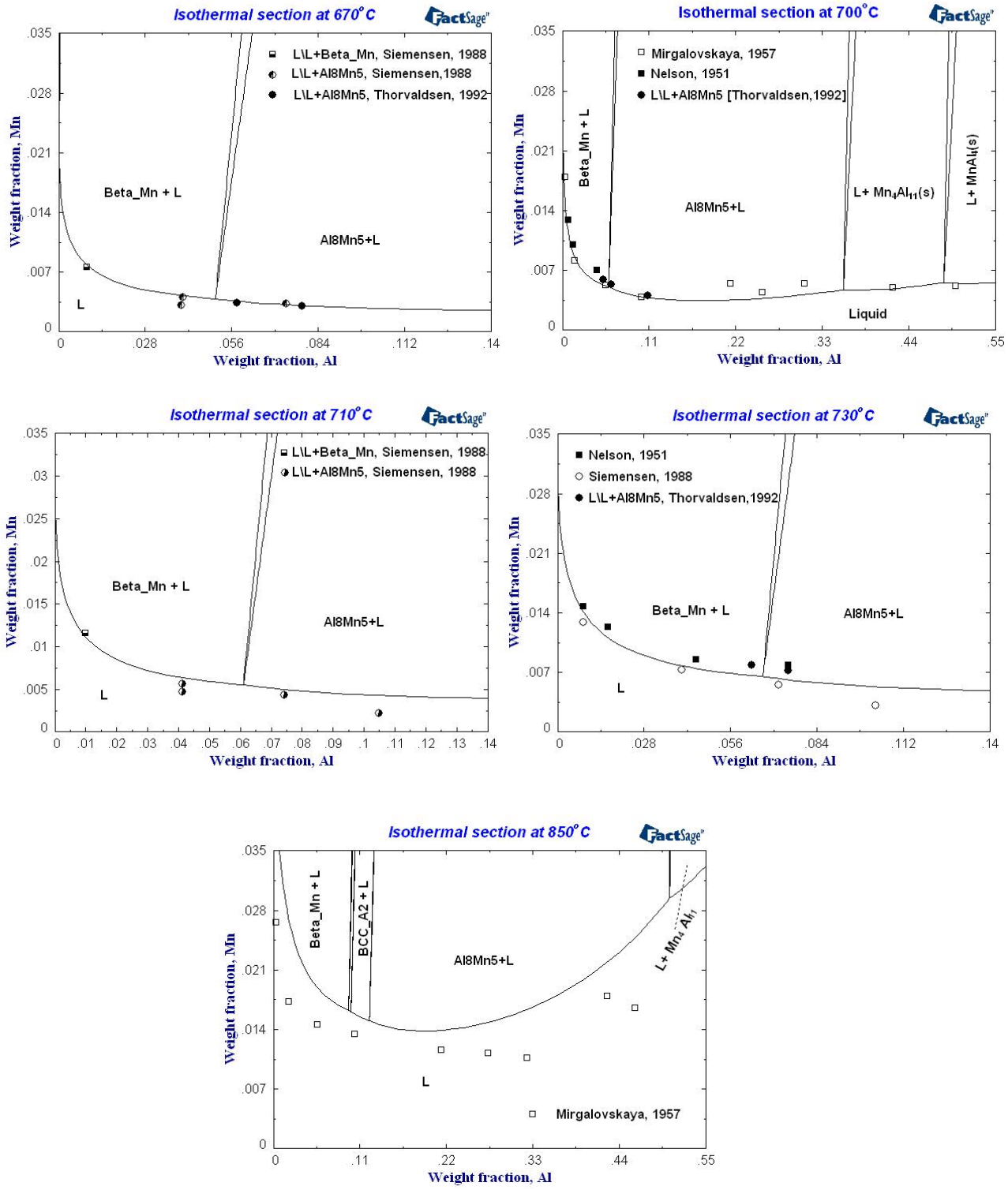

Fig11. Calculated isothermal sections of the Mg-Al-Mn system, compared with the experimental data of [12-16].

It can be seen from the above figures that all the reliable experimental results have been reproduced within the experimental uncertainty by the present modeling of the Mg-Al-Mn system. The identified phases of Ohnishi et al. [24] in figure 12 were also consistent with the two and three phase regions of the calculation qualitatively.

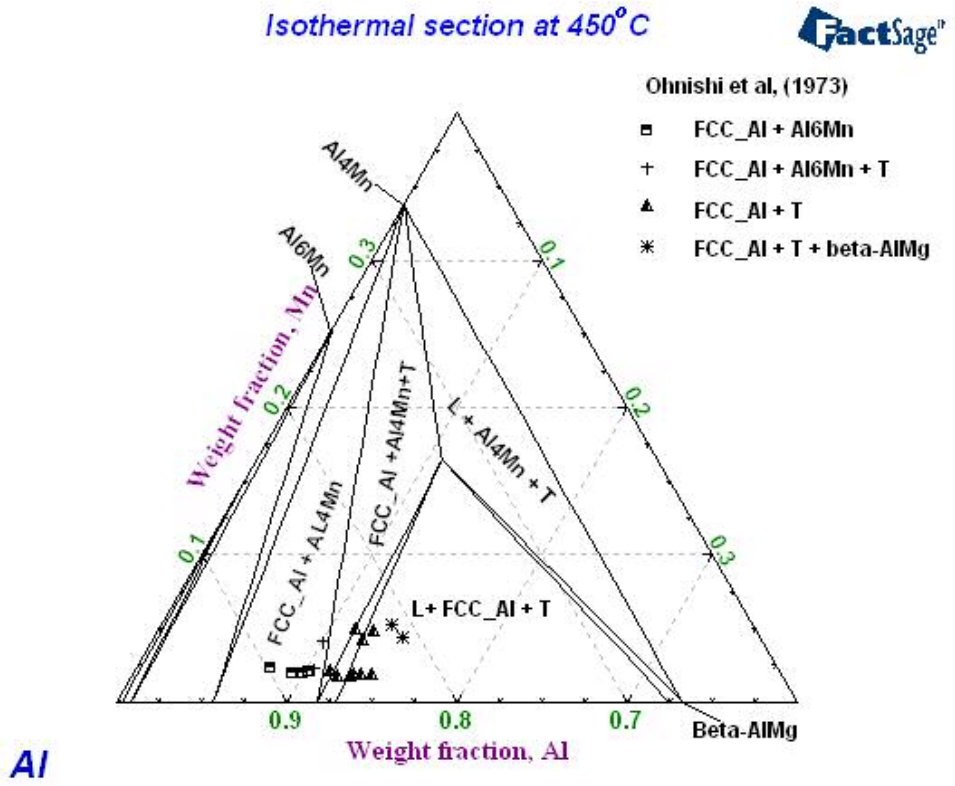

Fig12. Isothermal section at 450°C showing the ternary compound T and the other phases with the experimental data of [24].

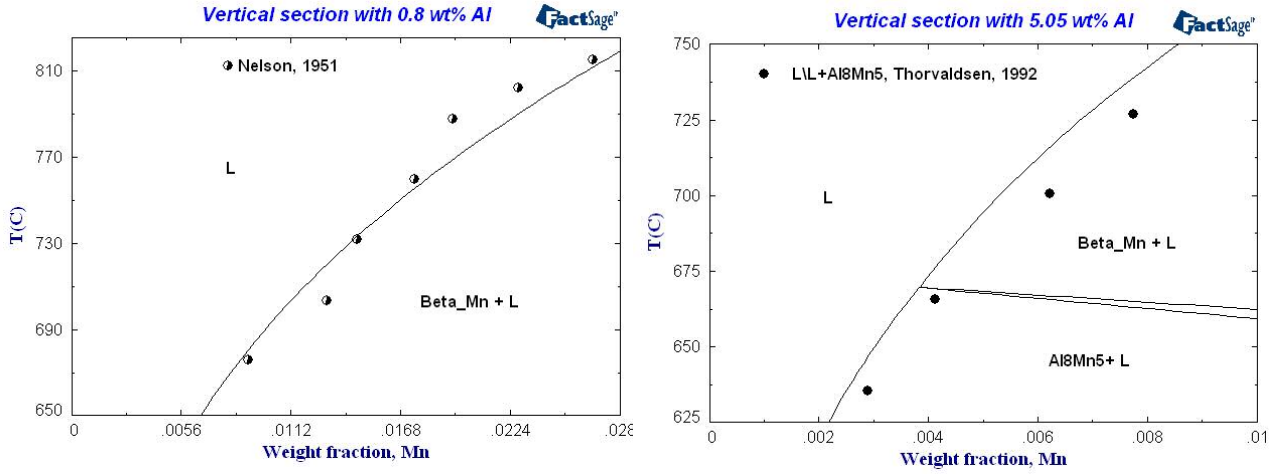

Fig13. Calculated vertical sections with fixed Al composition compared with the experimental data of [12, 16].

Choice of the Modified Quasichemical Model for the Liquid Phase

Choosing the appropriate model is one of the most important steps in the well known CALPHAD approach in thermodynamic modeling. The general idea is to adopt a model which is physically realistic and best represents the thermodynamic behavior of the phase in question both in the lower order and higher order system environment. For example, the short range ordering in the liquid phase may not exist in a specific lower order system but can exist in other binary or higher order systems. Thus, one representative model which can handle this kind of phenomenon effectively is necessary to remain consistent with the other systems in a mulcomponent Mg-alloy database. Modified quasichemical model is one of those existing models that can serve the purpose very well. Modified quasichemical model is, actually, a modification of the quasichemical model of Fowler and Guggenheim [44] and the modifications are proposed by [45]. The major advantage of the proposed model is that it allows choosing freely the composition of the maximum short range ordering in the liquid in the binary system and it is physically realistic. It also offers greater flexibility in optimizing the parameters for the binary systems, especially for those, which show a large degree of short range ordering in liquid [45]. Successful application of this model for the optimization of numerous binary and higher order systems by the researchers provides the basis for choosing the model for optimizing the Mg-Al-Mn system as a part of developing a multicomponent database.

Conclusion

The calculation of the phase diagram and thermodynamic properties shows a good overall agreement with the accepted experimental values. The model thus has the capacity to reproduce the phase diagram and thermodynamic properties of the Mg-Al, Mg-Mn, Al-Mn and Mg-Al-Mn systems. The main contribution of this work is the application of modified quasichemical model to describe the liquid phases in these systems. This thermodynamic model of the Mg-Al-Mn system can be combined with the multicomponent Mg-alloy database and used to extrapolate and calculate the higher order systems.

References

[1] M. Aljarrah, Thermodynamic Modeling and Experimental Investigation of the Mg-Al-Ca-Sr System, Ph.D. thesis, Concordia University, Montreal, Quebec, Canada, 2008

[2] A. Hashemi and J. Clark, the Mg-Mn (Magnesium-Manganese) System, Bulletin of Alloy Phase Diagrams, Voll. 6 (No. 2), 1985, p 160-164

[3] J. Gröbner, D Mirkovic, M. Ohno and R. Schmid-Fetzer, Experimental Investigation and Thermodynamic Calculation of Binary Mg-Mn Phase Equilibria, Journal of Phase Equilibria and Diffusion, Vol. 26 (No. 3), 2005, p 234-239

[4] A. McAlister and J. Murray, the (Al-Mn) Aluminum-Manganese System, Bulletin of Alloy Phase Diagrams, Vol. 8 (No. 5), 1987, p 438-447

[5] A. Jansson, A Thermodynamic Evaluation of the Al-Mn System, Metallurgical Transactions A, Vol. 23A, 1991, p 2953-2962

[6] X. Liu, R. Kainuma, H. Ohtani and K. Ishida, Phase Equilibria in the Mn-rich Portion of the Binary System Mn-Al, Journal of Alloys and Compounds, Vol. 235, 1996, p 256-261

[7] X. Liu, R. Kainuma and K. Ishida, Thermodynamic Assessment of the Aluminum-Manganese (Al-Mn) Binary Phase Diagram, Journal of Phase Equilibria, Vol. 20 (No. 1), 1999,

p 45-56
[8] H. Okamoto, Al-Mn (Aluminum-Manganese), Journal of Phase Equilibria, Vol. 18 (No. 4), 1997, p 398-399.
[9] Y. Du, J. Wang, J. Zhao, J. Schuster, F. Weitzer, R. Schmid-Fetzer, M. Ohno, H. Xu, Z. Liu, S. Shang and W. Zhang, Reassessment of the Al-Mn System and A Thermodynamic Description of the Al-Mg-Mn System, Int. J. Mat. Res., Vol. 98 (No. 9), 2007, p 855-871.
[10] M. Ohno and R. Schmid-Fetzer, Thermodynamic Assessment of Mg-Al-Mn Phase Equilibria, Focusing on Mg-rich Alloys, Z. Metallkd, Vol. 96 (No. 8), 2005, p 857-869
[11] N. Ageev, I. Kornilov and A. Khlapova, Magnesium-rich Alloys of the System Magnesium-Aluminum-Manganese. Izvest. Sektora Fiz.-Khim. Anal., Vol.16 (No. 4), 1948, p 130-43.
[12] B. Nelson, Equilibrium relations in Magnesium-Aluminum-Manganese Alloys, Journal of Metals, Vol. 3(Trans.), 1951, p 797-799
[13] M. Mirgalovskaya, L. Matkova, and E. Komova, System Magnesium-Aluminum-Manganese, Trudy Inst. Met. im. A. A. Baikova , (No. 2), 1957, p 139-48
[14] C. Simensen, B. Oberlaender, J. Svalestuen and A. Thorvaldsen, The phase diagram for magnesium-aluminum-manganese above 650^{o}C**,** Zeitschrift fuer Metallkunde (1988), Vol. 79 (No. 11), p 696-699
[15]. C. Simensen, B. Oberlaender, J. Svalestuen and A. Thorvaldsen, Determination of the Equilibrium Phases in Molten Magnesium-4% Aluminum-Manganese Alloys**,** Zeitschrift fuer Metallkunde (1988), Vol. 79 (No. 8), p 537-540
[16] A. Thorvaldsen and C. Aliravci, Solubility of Manganese in Liquid Mg-Al Alloys, Adv. Prod. Light Met. Met. Matrix Comp., Proc. Int. Symp., 1992, p 277-287
[17] W. Leemann, and H. Hanemann, The System Aluminum-Magnesium-Manganese, Aluminium-Arch, 1938, p 9-10
[18] W. Hofmann, R.Ovrddot. Ontgenographic Methods in the Investigation of Aluminum Alloys, Aluminium, Vol. 20, 1938, p 865-872
[19] E. Fahrenhorst and W. Hofmann, The Solubility of Manganese in Aluminum Containing up to 2% Magnesium, Metallwissenschaft, Vol. 19, 1940, p 891-893
[20] E. Butchers, G. Raynor and W. Hume-Rothery, The Constitution of Magnesium-Manganese-Zinc-Aluminum Alloys in the Range 0-5 Per Cent Magnesium, 0-2 Per Cent Manganese, 0-8 Per Cent Zinc. I. The Liquidus, Journal of the Institute of Metals, Vol. 69 (No. 942), 1943, p 209-228
[21] A. Little, G. Raynor and W. Hume-Rothery, The Constitution of Mg-Mn-Zn-Al Alloys in the Range Mg 0-5, Mn 0-2 and Zn 0-8%. III. The 500^{o} and 400^{o} Isothermals, Journal of the Institute of Metals, Vol. 69 (PT 10, No. 952), 1943, p 423-40
[22] E. Butchers and W. Hume-Rothery, The Solubility of Mn in Al, Journal of the Institute of Metals, Vol. 71 (No. 985), 1945, p 87-91
[23] D. Wakeman and G. Raynor, The Constitution of Aluminum-Manganese-Magnesium and Aluminum-Manganese-Silver Alloys, with Special Reference to Ternary-Compound Formation, Journal of the Institute of Metals, Vol. 75 (No. 1148), 1948, p 131-150
[24] T. Ohnishi, Y. Nakatani and K. Shimizu, Phase Diagram in the Aluminum- Rich Side of the Aluminum-Magnesium-Manganese-Chromium Quaternary System, Keikinzoku, Vol. 23 (No. 10), 1973, p 437-443
[25] T. Ohnishi, Y. Nakatani and K. Shimizu, Phase Diagrams and Ternary Compounds of Aluminum-Magnesium-Chromium and Aluminum-Magnesium-Manganese Systems in the Aluminum-Rich Corner, Keikinzoku, Vol. 23 (No. 5), 1973, p 202-209

[26] H. Fun, H. Lin, T. Jen and B. Yip, T-phase $Al_{18}Mg_3Mn_2$**,** Acta Crystallographica, C50 (5), 1994, p 551-553
[27] J. Barlock and L. Mondolfo, Structure of Some Aluminum-Iron-Magnesium-Manganese-Silicon Alloys, Zeitschrift fuer Metallkunde, Vol. 66 (No. 10), 1975, p 605-611
[28] M. Drits, E. Kadaner, E. Padezhnova and N. Bochvar, Determination of the Limits of Mutual Solubility of Manganese and Cadmium in Solid Aluminum, Zhurnal Neorganicheskoi Khimii
[29] E. Dix, W. Fink and L.Willey, Equilibrium Relations in Aluminum-Manganese Alloys of High Purity. II, Trans. Am. Inst. Mining Met. Eng., Vol. 104, 1933, p 335-352
[30] I. Obinata, K. Yamaji, and E. Hata, Subcooled Aluminum-Manganese Alloys. I, Nippon Kinzoku Gakkaishi, Vol. 17, 1953, p 496-501
[31] M. Drits, Z. Sviderskaya and L.Rokhlin, Solid Solubility of Mn in Mg, Izv. Nauka, 1964, p 272-278
[32] D. Petrov, M. Mirgalovskaya, I. Strelnikova and E. Komova, The Constitution Diagram for the Magnesium-Manganese System, Trans. Inst. Met. A.A.Baikova, Vol 1, 1958, p 142-143
[33] E. Schmid and G. Siebel, Determination of Solid Solubility of Mn in Mg by X-Ray Analysis, Metallwirtschaft, Vol 10 (No.49), 1931, p 923-925
[34] J. Grogan and J. Haughton, Alloys of Magnesium. Part XIV. The Constitution of the Magnesium Rich Alloys of Magnesium and Manganese, J. Inst. Met., Vol 69, 1943, p 241-248
[35] W. Koster and E.Wachtel, Constitution and Magnetic Properties of Aluminum-Manganese Alloys with More Than 25 At. % Mn, Zeitschrift fuer Metallkunde, Vol. 51, 1960, p 271-280
[36] H. Kono, On the Ferromagnetic Phase in Manganese-Aluminum System, Journal of the Physical Society of Japan, Vol. 13 (No.12), 1958, p 1444-1451
[37] A. Koch, P. Hokkeling, M.Steeg and K. Vos, New Material for Permanent Magnets on a Base of Mn and Al, J. Appl. Phys., Vol. 31(No. 5), 1960, p 75S-77S
[38] T. Goedecke and W. Koester, Constitution of the Aluminum-Manganese System, Zeitschrift fuer Metallkunde, Vol. 62(No. 10), 1971, p 727-32
[39] J.Murray, A. McAlister, R. Schaefer, L. Bendersky, F. Biancaniello and D. Moffat, Stable and Metastable Phase Equilibria in the Al-Mn System, Metall. Trans., Vol. 18A, 1987, p 385-392
[40] H. Phillips, The Constitution of Alloys of Aluminum with Manganese, Silicon and Iron. I.-The Binary System: Aluminum-Manganese. II.-The Ternary Systems: Aluminum-Manganese-Silicon and Aluminum-Manganese-Iron, J. Inst. Met., Vol. 69, 1943, p 275-350
[41] Y.Esin, N. Bobrov, M. Petrushevski and P. Geld, Concentration Variation of the Enthalpies of Formation of Manganese-Aluminum Melts at 1626 K, Russ. J. Phys. Chem., Vol. 47, 1973, p 1103-1105
[42] R.Chastel, M. Saito and C. Bergman, Thermodynamic Investigation on $Al_{1-x}Mn_x$ Melts by Knudsen Cell Mass Spectrometry, Journal of Alloys and Compounds, Vol. 205, 1994, p 39-43
[43] G. Batalin, E. Beloboradova, B. Stukalo and A. Chekhovskii, Thermodynamic Properties of Molten Alloys of Aluminum with Manganese, Sov. Prog. Chem., Vol. 38, 1972, p 83-84
[44] R. Fowler and E. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, United Kingdom, 1939, p 350-366
[45] A. Pelton, S. Degterov, G. Eriksson, C. Robelin and Y. Dessureault, The Modified Quasichemical Model I-Binary Solutions, Metallurgical and Materials Transactions B, Vol. 31B, 2000, p 651-659