Monatshefte für Chemie 136, 1899–1907 (2005)
DOI 10.1007/s00706-005-0385-9

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

CALPHAD-type Assessment of the Al–Mg–Si System

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Received September 12, 2004; accepted November 30, 2004

Summary. The parameters describing ternary interactions in the liquid phase of the Al–Mg–Si system have been improved slightly with respect to the COST 507 data base by accounting for a larger set of liquidus data than previously considered. As no other parameter was modified, the description thus obtained presents the same high efficiency for solid–solid equilibria as previously achieved, in particular, for the solubility limits in the Al-rich solid solution.

Keywords. Phase diagrams; Analytical description; CALPHAD; Aluminum; Magnesium; Silicon.

Introduction

Precise knowledge of the Al–Mg–Si system is of interest for applications of both aluminum and magnesium alloys. Accordingly, it has been the subject of many investigations and assessments since long [1], although most of them focused on the aluminium-rich corner. A few CALPHAD-type assessments using the lattice stabilities compiled by *Dinsdale* [2] are available [3–6] but the system may be reconsidered because it appears that none of these assessments discussed all the information available. Recently, reviews of the available information have been made by *Chakraborti* and *Lukas* [7] and *Kumar et al.* [8]. After a section devoted to the limiting binary systems, a more detailed presentation of the available information on the ternary system is given. Then, a new assessment of the ternary interaction parameters for the liquid phase is presented and predictions made with this new data are compared with available experimental information.

Binary Systems

Table 1 lists the binary solid phases, which are the only solid phases under consideration as there is no ternary stable solid phase appearing in the Al–Mg–Si

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Table 1. Characteristics of the stable solid phases of the Al–Mg–Si system [7]

Phase	Prototype	*Pearson* symbol	Space group	Lattice parameters (Å)	Formula (COST 507)
(Al)	Cu	c*F*4	$Fm\bar{3}m$	$a = 4.0494$	solid solution
(Mg)	Mg	h*P*2	$P63/mmc$	$a = 3.2094$ $c = 5.2107$	solid solution
Si	C (diamond)	c*F*8	$Fd3m$	$a = 5.4306$	solid solution
Mg_2Si	CaF_2	c*F*12	$Fm3m$	$a = 6.338$	Mg_2Si
β	Al_3Mg_2	c*F*1832	$Fd\bar{3}$	$a = 28.239$	$Al_{140}Mg_{89}$
ε	$Co_5Cr_2Mo_3$	h*R*53	$R\bar{3}$	$a = 12.8254$ $c = 21.7478$	$Al_{30}Mg_{23}$
γ	αMn	c*I*58	$I\bar{4}3m$	$a = 10.4811$ to 10.5791	$Mg_5(Mg,Al)_{12}(Al,Mg)_{12}$

system. The Al–Si system is quite well known and various assessments following the CALPHAD method are available, in particular as part of higher order system descriptions [6, 9–12]. As all of these assessments lead to very close results, the one selected for the COST 507 data bank [13], which is now public, was chosen for this work. The Mg–Si system has also been assessed several times in relation with the study of ternary systems, in particular Al–Mg–Si [3–6]. While the Mg–Si phase diagram appears to be well established, the authors of these assessments emphasized the very large discrepancies in the thermodynamic data reported for this system. As pointed out by *Feufel et al.* [4], this is unfortunate as the solubility limits of Mg and Si in the aluminum-rich phase are given by the boundary between the phase fields of this phase and of Mg_2Si, and thus by the *Gibbs* energy and enthalpy of formation of the compound. Although the description by *Yan* [6, 14] of the Mg–Si system may appear to be more effective than the others, it fails to reproduce this boundary. Moreover, this author did not represent the *Gibbs* energy function of the Mg_2Si phase in a way appropriate for extrapolation to higher order systems. *Kevorkov* [5, 15] carried out a new optimization in order to avoid a liquid miscibility gap appearing far above 2000°C as in the previous assessments. Because the assessment by *Kevorkov* [5, 15] was based on the previous work by *Xinyan Yan* [14], and will therefore suffer from the same drawbacks as detailed above, the description of the Mg–Si system given in the COST 507 data base was preferred considering that the miscibility gap in the liquid phase appears at temperatures much above any domain of interest.

Following a detailed experimental investigation, *Su et al.* [16] modified the central part of the Al–Mg phase diagram with respect to the version in the COST 507 data base. The resulting phase diagram is illustrated in Fig. 1. As a matter of fact, it is in agreement with the older assessment made by *Murray* [17] and accepted by *Chartrand* and *Pelton* [18]. In this diagram, the ζ phase reported by *Schürmann* and *Voss* [19] does not appear, while the ε phase is stable only up to about 410°C to decompose giving β and a commensurate variation of the γ phase. Metastable phases are readily formed on rapid cooling of alloys with compositions in the middle of the Al–Mg system, and this may account for the difficulty in establishing the phase diagram. *Liang et al.* [20] provided a CALPHAD-type

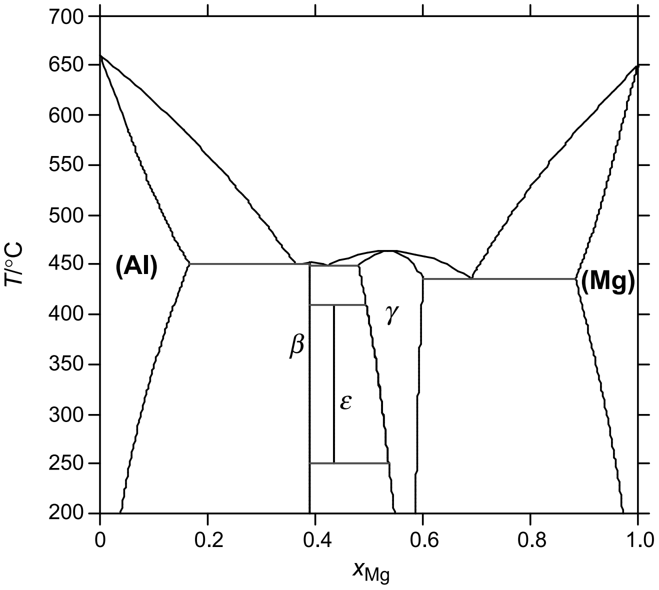

Fig. 1. Al–Mg phase diagram calculated with the COST 507 data base

assessment of the Al–Mg system which takes into account the work of *Su et al.* [16]. This description has been included in the COST 507 data base [13]. It will be used in the present study.

Ternary Al–Mg–Si System

There have been three experimental studies of the ternary liquidus [4, 21–22]. *Losana* [21] studied by thermal analysis the solidification and solid state transformations of 150 alloys with aluminum contents varying from 99 to 0.4 wt.%. The alloys were prepared from aluminum, magnesium, and silicon of respectively 99.8, 99.7, and 99.4 wt.% purity. The cooling rate varied between 100 and 400°C/h (1.67 and 6.67°C/min). The results of *Losana* have not been considered in the earlier CALPHAD-type assessments because of apparent discrepancies with other data, in particular for Mg-rich alloys [6]. Although the table provided by *Losana* undoubtedly contains typing errors that can be only partially corrected, it seemed of value to use this information for comparison purposes in the present work. Similarly, *Schürmann* and *Fisher* [22] studied the whole liquidus surface by thermal analysis (cooling rate not given), selecting alloys along 15 lines in the whole composition triangle. These authors used 99.0% purity silicon and observed, in some cases, the presence of intermetallic phases other than those expected. *Feufel et al.* [4] used high purity materials to prepare alloys with either 80, 85, 90, or 95 wt.% Al. These alloys were homogenized and then submitted to differential thermal analysis (scanning rate in the range 2 to 5°C/min) on heating and cooling. As it will be seen later, these three sets of data are in overall agreement. A few thermodynamic data are also available which are however limited to dilute Al-rich alloys. Table 2 lists the binary and ternary invariant equilibria involving the liquid phase with labels given by *Chakraborti* and *Lukas* [7].

Table 2. Equilibria involving the liquid phase: experimental and calculated (this work) invariant reactions in the ternary Al–Mg–Si system (reactions are labelled according to *Kumar et al.* [8])

Reaction	Temperature (°C)	Mg (at. or wt.%)	Si (at. or wt.%)	Reference
Liquid = (Al) + Si + Mg_2Si	558	4.97	14.6	*
point E1	550	4.8	14.1	[22]
	560	5.1	12.6	[25]
	558			[4]
	557	5.5	13.6	this work
Liquid = Mg_2Si + (Al)	595	8.3	4.6	*
point e3	593			[22]
	595			[4]
	596	10.1	4.0	this work
Liquid = Mg_2Si + (Al) + β	448	33.9	0.07	*
point E2	444	34.5	<0.2	[22]
	448			[23]
	450	36.6	0.06	this work
Liquid = $Mg_2Si + \beta$ point e6	451	39.0	0.06	this work
Liquid = $Mg_2Si + \beta + \gamma$ point E3	449	42.5	0.05	this work
Liquid = $Mg_2Si + \beta + \gamma$ point e5	463	53.8	0.08	this work
Liquid = $Mg_2Si + \gamma$ + (Mg)	434	67.5	<0.2	[22]
point E4	436	69.9	<0.1	[23]
	436	69.0	0.06	this work

* *Hanemann E.* and *Schrader A.* ("Ternäre Legierungen des Aluminiums", Düsseldorf, 1952), cited by *Schürmann* and *Fischer* [22]

In the course of the optimization of the Al–Mg–Si system, *Chakraborti* and *Lukas* [3] first reassessed the Al–Si and Mg–Si systems using experimental information on both phase equilibria and thermodynamics. To describe the ternary system, these authors added ternary interaction parameters only for the liquid phase, arguing that the solubility of the third element is low for any of the solid phases in the system. They seem to have used data for solid-state equilibria corresponding only to the Al-rich corner. For equilibria involving the liquid phase, they mainly considered the work by *Schürmann* and *Fischer* [22]. In a later study, *Feufel et al.* [4] improved the available thermodynamic data, measuring the specific heat and formation enthalpy of Mg_2Si, and provided new vertical sections of the Al–Mg–Si system in the Al rich part, as mentioned above. These authors performed a new CALPHAD-type assessment of the system using both their new experimental information and the same data considered previously by *Chakraborti* and *Lukas* [3].

Owing to the large discrepancies in the thermodynamic data for the Mg–Si system and to the fact that ternary interactions in the Al rich fcc phase are too small to be considered, *Feufel et al.* [4] emphasized that the properties of the Mg–Si system could be optimized by also considering the solubility limits of Si and Mg in the aluminum rich phase. Both *Chakraborti* and *Lukas* [3] and *Feufel et al.* [4] considered that there was not enough information available to determine the temperature dependence of the coefficients describing the ternary interactions in the liquid phase and adopted a linear relationship between the constant and temperature dependant coefficients. This appears quite in contrast with the fact that the description of the interactions in the liquid phase of the Mg–Si system involves 5 temperature dependent parameters in both of these studies, corresponding to 8 independent coefficients. Finally, it is worth noting that *Xinyan Yan* [6] showed that the assessment of *Feufel et al.* [4] did not reproduce satisfactorily one of the sections determined by *Schürmann* and *Fischer* [22], numbered 15 in the original paper, and representing the isopleth at 2 wt.% Si.

Reassessment of the Ternary Al–Mg–Si System

This reassessment was achieved using Thermocalc® with the same assumptions used previously, *i.e.*, that ternary interaction parameters are significant only for the liquid phase. By considering the largest possible set of experimental data for the liquidus temperatures, based on the works by *Schürmann* and *Fischer* [22] and *Feufel et al.* [4], the optimization procedure was repeated assuming 6 independent coefficients. It was found that the coefficients for the temperature dependent terms were not significant, so that only three constant coefficients were needed to describe the ternary interactions in the liquid. The values of these parameters are: $L_{Al} = +11882$, $L_{Mg} = -24207$, and $L_{Si} = -38223$.

A very good agreement was obtained with all the experimental information shown as isoplethal sections in the earlier works [4, 22]. Figure 2 shows the section

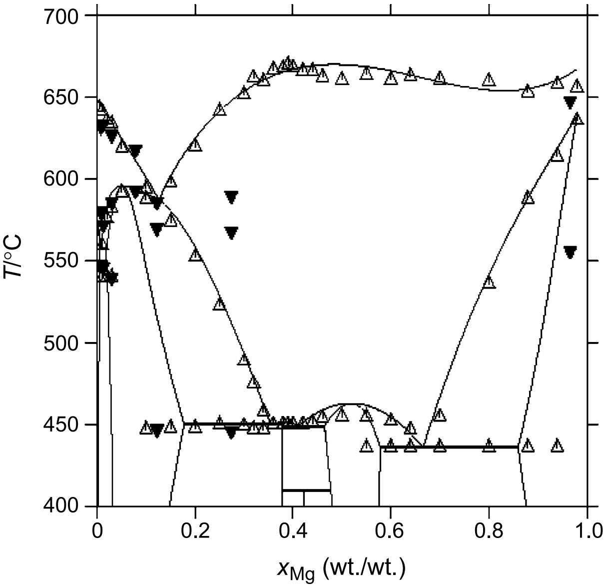

Fig. 2. Isoplethal section at 2 wt.% Si of the Al–Mg–Si system; open and solid triangles show experimental points from *Schürmann* and *Fischer* [22] and *Losana* [21], respectively

numbered 15 by *Schürmann* and *Fischer* [22] which was not well described by the previous assessment by *Feufel et al.* [4], as pointed out by *Xinyan Yan* [6]. In this figure, experimental points from *Schürmann* and *Fischer* [22] as well as from

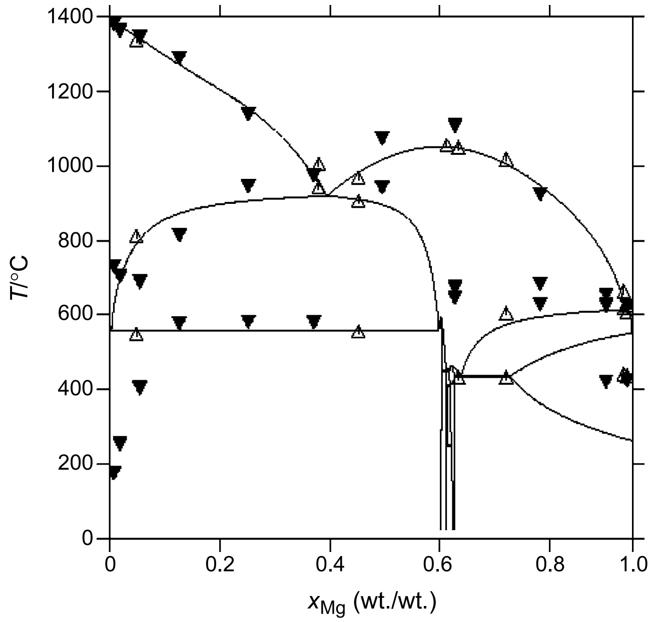

Fig. 3. Isoplethal section at 5 wt.% Al of the Al–Mg–Si system; open and solid triangles show experimental points from *Schürmann* and *Fischer* [22] and *Losana* [21], respectively

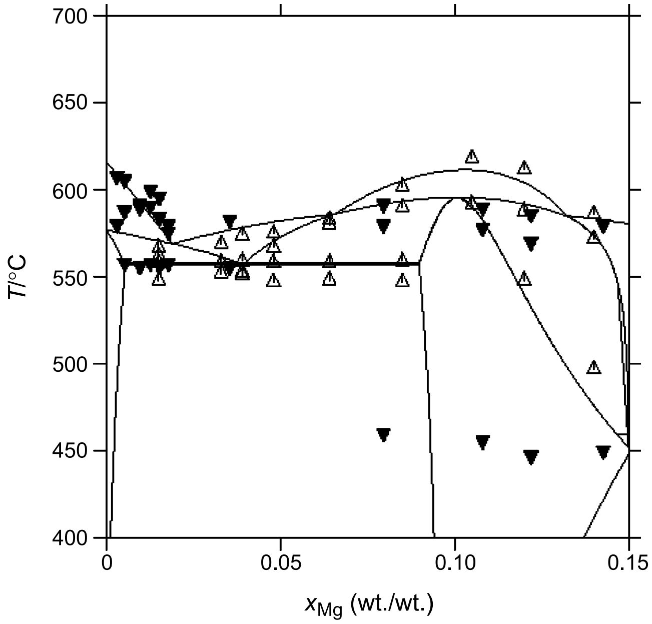

Fig. 4. Isoplethal section at 85 wt.% Al of the Al–Mg–Si system; open and solid triangles show experimental points from *Feufel et al.* [4] and *Losana* [21], respectively

Losana [21] are shown. As a matter of fact, these latter results show a degree of scatter for the liquidus temperatures while they show very good consistency with other data for the terminal (eutectic) reactions. Similarly, Fig. 3 compares the predicted isoplethal section for 5 wt.% Al with data from *Losana* [21] and a few results taken from *Schürmann* and *Fischer* [22]. The agreement appears again quite satisfactory for the liquidus but this figure shows that detailed examination of the effect of microsegregation on the solidification path during thermal analysis could be of interest. Figure 4 presents the isoplethal section at 85 at.% Al with experimental data from *Feufel et al.* [4] and *Losana* [21]. The overall agreement obtained appears to be much better than the one shown by *Kevorkov* [5]. For any other section, the agreement obtained was as good as the ones shown by *Xinyan Yan* [6] or *Kevorkov* [5].

In a parallel investigation [23], solidification and solid-state equilibria of Mg rich alloys were studied. Using as-cast and heat treated alloys with 30, 45, and 70 wt.% Mg, respectively, 3.5, 3, and 2 wt.% Si, it was verified that the Al–Mg compounds do not contain any significant amount of Si, in practical terms less than the resolution of EDS, *i.e.*, about 0.1 wt.%. DTA analysis gives 448°C and 436°C as the temperatures for points E2 and E4, respectively. These temperatures compare well with those reported in Table 2. Using a sample of alloy of composition Al-70Mg-2Si heat treated at 300°C for seven months in a quartz ampoule filled with argon, it was possible to characterize the equilibrium between (Mg), Mg_2Si, and γ. The composition of the (Mg) phase is reported on the calculated isothermal section in Fig. 5. As expected, the Al content in (Mg) in equilibrium with γ and Mg_2Si does not differ significantly from its value in the binary system. This result is however very different from the only other reported data, from *Rokhlin* and *Peplyan* [24] who studied the phase boundaries between the two phase domain

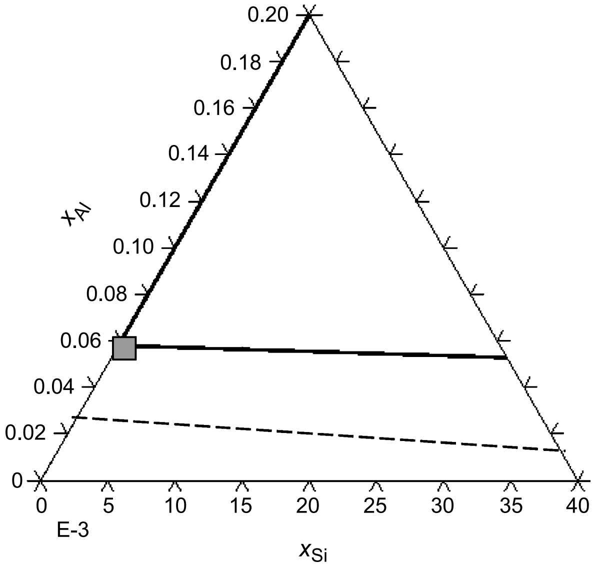

Fig. 5. Isothermal section at 300°C comparing the calculated (solid line) and experimental (dashed line) [24] limit between the (Mg) + Mg_2Si and (Mg) + Mg_2Si + γ phase fields

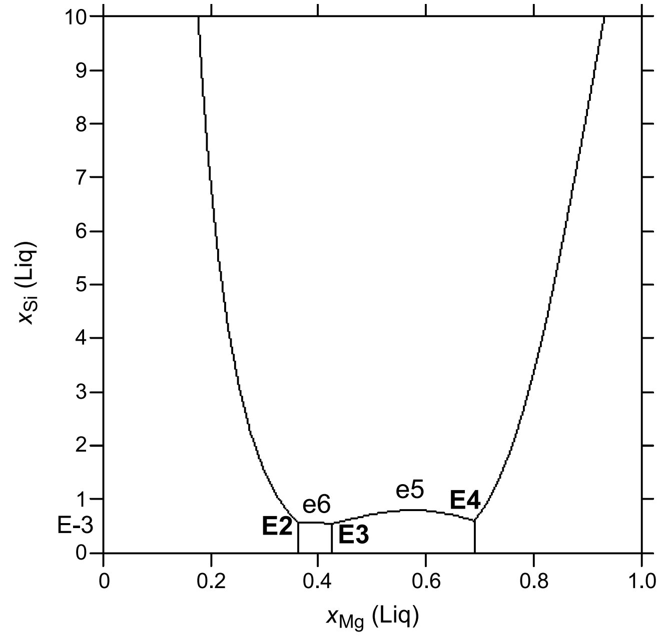

Fig. 6. Enlargement of the liquidus projection close to the Al–Mg binary edge

(Mg) + Mg_2Si and the three phase domain (Mg) + $Mg_2Si + \gamma$ at 300, 400, and 430°C. In Fig. 5, it is seen that there is a huge discrepancy between the limit proposed by these authors at 300°C and the present experimental and calculated limits. A similar difference appears between the calculated limit and the data from *Rokhlin* and *Peplyan* [24] for the other temperatures. It seems reasonable to disregard their results.

Finally, Fig. 6 shows the liquidus projection along the monovariant lines close to the Al–Mg side of the ternary system. There are three invariant eutectic points appearing with two saddle points in between. The calculated temperatures for points E2 (450°C) and E4 (436°C) are in good agreement with experimental data (Table 2). The temperature of point E3 could not be determined experimentally and is calculated to be at 449°C. Unfortunately, no experimental information is available to check if the compositions of these points are correct.

Conclusion

The description of the interaction parameters in the liquid phase of the Al–Mg–Si system as given in the COST 507 data base has been improved slightly by accounting for a larger set of liquidus data than considered previously. The best description was obtained by assuming temperature independent parameters. As no other parameter was modified, the data set thus obtained maintains its highly efficient description of the solid–solid equilibria which was due in particular to an appropriate description of the properties of the Mg_2Si phase [4]. This capability appears as an essential feature when comparing the present results to those recently proposed in similar CALPHAD-type assessments of the Al–Mg–Si system [5–6].

Acknowledgements

Partial support from ESA through the MICAST project under contract number 14347/00/NL/SH is greatly appreciated.

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