The critical assessment of data for Al-Fe based intermetallic phases formed during solidification of aluminium alloys

A T Dinsdale[1], Changming Fang[1], Zhongyun Fan[1] and A V Khvan[2]
[1] BCAST, Brunel University London, Uxbridge, UB8 3PH, UK
[2] Thermochemistry of Materials SRC, MISiS, Moscow, Russia

Abstract

An understanding of the thermodynamic properties and phase diagram is fundamental to the control of the microstructure and the phases formed during solidification. This is particularly important as regards the control of harmful impurities such as iron during the solidification of commercial aluminium alloys where it is desirable to select conditions and compositions to avoid the precipitation of phases which cause deleterious mechanical properties. Calculations using critically assessed thermodynamic data to predict changes in phase constitution as an alloy solidifies offer a way to achieve the required control. This relies on the availability of high quality critically assessed thermodynamic datasets for the component binary and ternary systems, reliable models to extrapolate these data into systems with more components, and software which can then use these data to calculate the necessary phase equilibria.

This paper will be concerned with the critical assessment of data for systems containing multicomponent intermetallic phases containing iron which are important for the required control of impurities during solidification of aluminium alloys.

Keywords: Phase Equilibria, Thermodynamic data, Critical assessment

1. Introduction

The control of harmful impurities such as Fe in cast Al-Si alloys is becoming ever more important as the demand for the use of scrap materials increases. Traditionally manganese is added to prevent the formation of the harmful β-AlFeSi phase which leads to poor mechanical properties. Therefore an understanding of phase equilibria in the Al-Fe-Mn-Si system, the solubilities of elements in various intermetallic phases and the temperatures at which they form is a prerequisite for any successful process control. Phase diagrams and phase equilibria can be calculated reliably as long as the critically assessed thermodynamic data for the appropriate system are available. Twenty years ago a European collaborative project, COST507 [1], enabled the development of a thermodynamic database for light metal alloys, and in particular aluminium alloys. This database has become a standard reference point for the development of more extensive commercial databases. Since then data for a number of the key binary and ternary systems have been re-evaluated as new experimental or *ab initio* data have become available. However there has been no attempt hitherto to revise the key multicomponent datasets. In this paper decisions taken towards a reassessment of data for the key Al-Fe-Mn-Si system are described using the most reliable data for the binary systems and taking into account new experimental data where available. In particular, attention has been paid to the modelling of ternary and quaternary intermetallic phases to predict ultimately the undercooling necessary to precipitate specific phases. It is also hoped that it may be possible to predict the interfacial tension and segregation at the interface between the liquid alloy and any heterogeneous substrate such as TiB_2.

2. Binary systems

Al-Si

There have been many critical assessments of data for this system reflecting the importance of the system and the wealth of experimental data available. The phase diagram is a simple eutectic type with limited solubility of Si in fcc Al (up to 1.5 at.% at 850 K) and very low solubility of Al in crystalline Si. The critically assessed data of Feufel *et al.* [2] are considered to be the most reliable and have been used in the development of the new thermodynamic database.

Al-Fe

The most comprehensive assessment of the phase diagram information for the Al-Fe system was carried out by Kattner and Burton [3]. The system features a number of binary intermetallic phases mainly in the aluminium rich part of the system. The iron rich side of the system is characterised by a narrow γ-loop and an extensive solid solution of aluminium in bcc iron which undergoes chemical ordering towards the centre of the phase diagram and again at lower temperatures. Recently the phase diagram has been further studied by Ikeda *et al.* [4] and Stein and Palm [5].

The data for the system used in the COST507 database are from the unpublished assessment of Seiersten [6]. More recently Jacobs and Schmid-Fetzer [7] revised this assessment. For this present work the data from Sundman *et al.* [8] have been adopted.

Al-Mn

The accepted phase diagram for the Al-Mn system is based on that assessed by McAlister and Murray [9] supplemented by the more recent experimental results of Liu *et al.* [10]. The phase diagram shows a series of intermetallic phases on the aluminium rich side of the system, formed from the liquid by peritectic reaction, and a series of solid solution phases.

There have been a number of thermodynamic assessments for the Al-Mn system. The data in the COST507 database are from the work of Jansson [11]. Du *et al.* [12] revised this description incorporating the experimental data of Liu *et al.* [10]. For this work the assessment of Du *et al.* [12] has been adopted.

Fe-Si

The phase diagram for the Fe-Si system is rather well understood. There is complete miscibility in the liquid and considerable solubility of Si in bcc-Fe. This solid solution phase undergoes a second order transformation to the B2 phase for iron-rich compositions. The fcc phase is confined to a narrow γ-loop. A number of the intermetallic phases are stable over very limited ranges of temperature. The thermodynamic properties have been studied extensively.

The data in the COST507 database are from the assessment of Lacaze and Sundman [13]. Yuan *et al.* [14] noted that these predicted an inverted miscibility gap in the liquid phase for high temperatures and reassessed the data taking into account more recent experimental work. Their data have been adopted.

Fe-Mn

The phase diagram for the Fe-Mn system is based entirely on solutions emanating from the two elements. There is complete solubility in both the liquid and fcc phases and for both elements it is the bcc form that melts. The low temperature forms of manganese α-Mn and β-Mn dissolve substantial amounts of iron. However it is the fcc phase that dominates most of the phase diagram. The dataset in the COST507 database are from Huang [15]. The most recent assessment [16] uses a newer generation of data for the elements and cannot be used for this current work. While there have been other recent assessments, none have any advantages over the data of Huang [15] which has therefore been retained for use in this work.

Mn-Si

The phase diagram for the Mn-Si system is characterised by continuous mixing between the two components in the liquid phase, the formation of a large number of intermetallic compound phases, substantial solubility of silicon in the α-Mn and β-Mn phases with rather lower solubility in the higher temperature fcc and bcc phases. The solubility of Mn in crystalline silicon is very low. The dataset in the COST507 database is from the assessment of Tibbals [17]. These data were modified slightly by Du et al. [18] for their assessment of data for the Al-Mn-Si system. There have been two further assessments recently to correct the lack of agreement of the Tibbals' assessment with several invariant reactions and enthalpies of formation of intermetallic compounds. The assessment of Berche *et al.* [19] has been selected for use in this work.

3. Ternary systems

Al-Fe-Si

The phase diagram for this ternary system is extremely complicated featuring 11 ternary intermetallic phases many of which exist over appreciable ranges of homogeneity. Ghosh [20] carried out an extensive analysis of the phase diagram and crystallographic properties published prior to 1989. This was updated in the reviews of Du *et al.* [21] and Eleno *et al.* [22]. It is worth noting the extensive work carried out on the phase diagram by Krendelsberger et al. [23] and Marker *et al.* [24, 25] and on the thermodynamic properties of the intermetallic phases by Li *et al.* [26, 27].

The critical assessments of thermodynamic data [21, 22. 28] are all based on the assessed binary and ternary data developed in COST507 [1]. Of these the assessment of Du *et al.* [21] is the most thorough although the authors appear not to have considered the homogeneity ranges of the intermetallic phases closest to pure aluminium. This was covered by Eleno *et al.* [22]. According to Marker et al. [24] the experimental liquidus temperatures are rather higher than those predicted by the data of Du *et al.* [21].

In this work revised versions of the binary assessments have been used for a new critical assessment taking into account the most recent experimental information. An isothermal section calculated for 727°C is shown in Fig. 1.

Al-Fe-Mn

The phase diagram and crystal structure information for the system prior to 1990 was reviewed comprehensively by Ran [29]. This was updated by Raghavan [30, 31] and most recently by Lindahl and Selleby [32]. Further experimental work has been carried out [33-35]. The main features of the phase diagram are the extensive range of solid solutions for the bcc_a2, bcc_b2, fcc and β-Mn structures and the solubility of Mn in $Al_{13}Fe_4$ and Fe in the γ-brass Al_8Fe_5 phase.

Experimental thermodynamic data for the ternary system are limited to enthalpies of mixing in the liquid by Batalin et al. [36] and, more recently, enthalpies of formation of the Heusler phase Fe_2MnAl [37].

There have been a number of critical assessments of data for the Al-Fe-Mn system. The data in the COST507 database were assessed by Jansson and Chart [38]. The most recent assessment is from the work of Lindahl and Selleby [32]. An isothermal section for 800°C calculated using their data is shown in Figure 2.

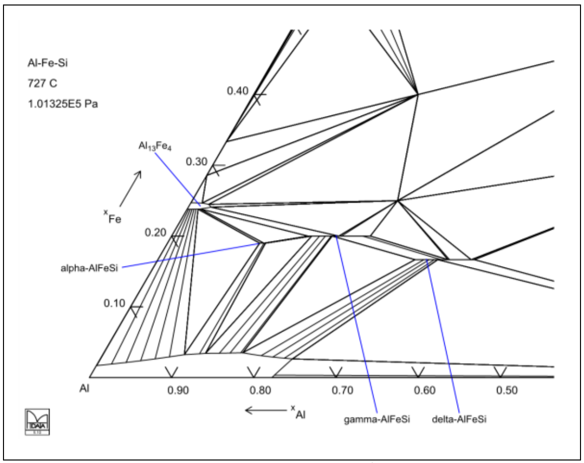

Figure 1: Calculated isothermal section of the Al-Fe-Si system at 727°C

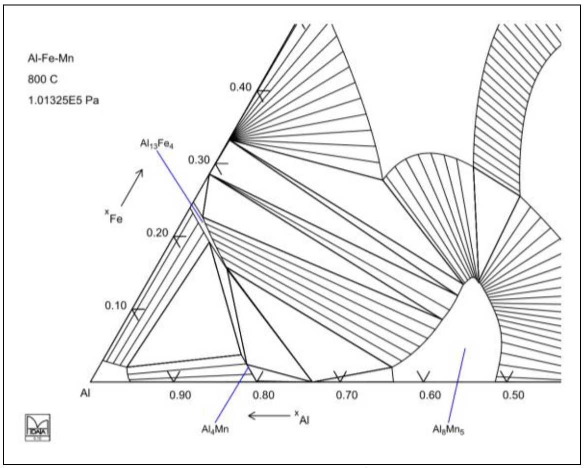

Figure 2: Calculated isothermal section of the Al-Fe-Mn system at 800°C

Al-Mn-Si

The experimental studies on the phase diagram and crystallographic structures of phases in the Al-Mn-Si system up to 1990 were reviewed by Prince [39]. Since then notable contributions have been made by Krendelsberger *et al.* [40] and Kalmykov *et al.* [41,42]. The main features of the phase diagram of the system are well established. Ten ternary intermetallic phases have been identified, many of which are stable over appreciable ranges of homogeneity. The enthalpy of formation of the important α-Al-Mn-Si phase has been determined by Legendre *et al.* [43].

The thermodynamic and phase diagram data for the Al rich part of the system were critically assessed by Rand as part of the COST507 project [1]. The agreement with experimental data is not satisfactory except for compositions close to pure Al. More recently Du *et al.* [18] have carried out an assessment covering the whole composition range. For this work the basic approach of Du *et al.* has been followed but using more recent assessed data for the Al-Si and Al-Mn systems. A calculated isothermal section for 550°C is shown in Figure 3.

Fe-Mn-Si

The COST507 database incorporated the critically assessed data for the Fe-Mn-Si system from Forsberg and Agren [44] and this has been retained in all the assessments of higher order systems involving Al with these elements. More recently the system has been reassessed by Zheng *et al.* [45]. This assessment appears to be in good agreement with experimental phase diagram data for the system although they did not apparently consider the experimental thermodynamic data for the ternary system of Zaitsev and Mogutnov [46].

For this work a new assessment has been carried out based on the adopted assessments of the binary systems.

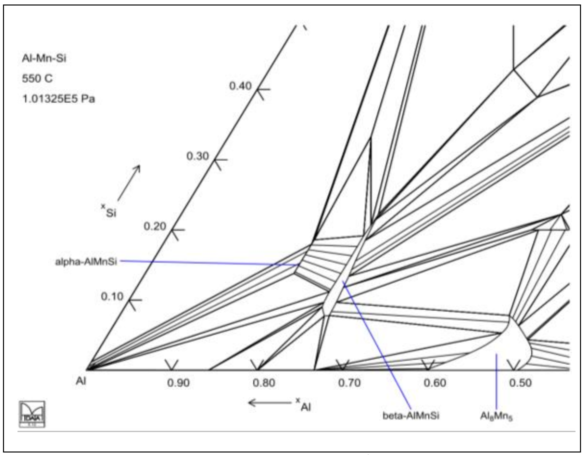

Figure 3: Calculated isothermal section of the Al-Mn-Si system at 550°C

4. Al-Fe-Mn-Si

Phase equilibria in this key quaternary system are extremely complex. In addition to the liquid and the terminal solid solution phases, there are at least 16 ternary intermetallic compounds and 18 binary intermetallic phases, many of which dissolve appreciable amounts of one or both of the other elements. The phase diagram for the quaternary system is based largely on the work of Phillips and Varley [47] and Phragmen [48] supplemented by the work of Zakharov *et al.* [49-51], Munson [52], Barlock and Mondolfo [53] and others. Of particular importance is the extent of the solubility of Fe in the α-AlMnSi (Al_9Mn_2Si) and β-AlMnSi ($Mn_3(Al,Si)_{10}$) phases and the possible existence of a quaternary phase $Al_{15}(Fe,Mn)_3Si_2$.

In addition to the original COST507 database there have been three published critical assessments of data for this key system. Balitchev *et al.* [54] accepted the experimental results of Zakharov *et al.* showing the formation of a quaternary intermetallic phase which they modelled as stoichiometric, but did not for allow any solution of Fe in the Al-Mn-Si intermetallic phases.

Du *et al.* [55] also used the COST507 database as a basis for their assessment of the Al-Fe-Mg-Mn-Si system. They used Liu and Chang's data [28] for the Al-Fe-Si system and revised the COST507 data for liquid phase in the Al-Fe-Mn system. For the quaternary system Du *et al.* also introduced data for the quaternary phase which was assigned the composition $Al_{16}Fe_2Mn_2Si_3$ but also took into account the solubility of Fe in α-AlMnSi. They considered a much wider range of experimental data than Balitchev *et al.* and obtained better overall agreement with all the data.

The most recent assessment of data for the aluminium rich corner of the systems is by Lacaze *et al.* [56] – see for example Figure 4. Again the dataset was based heavily on the COST507 database and the authors limited their changes to the data for the intermetallic phases and their ranges of solubility. In particular they incorporated a revised dataset for the Al-Fe-Si system [22] but modified the models for α-AlMnSi and β-AlMnSi to allow for the substitution of Mn by Fe. They chose not to incorporate data for any quaternary intermetallic phase preferring to choose the experimental results of Munson [52] and Barlock and Mondolfo [53] in preference to those of Zakharov *et al.* [49-51].

This work is also based on the same conclusions as those made by Lacaze *et al.* [56] but now based on more recent assessments of the component binary systems.

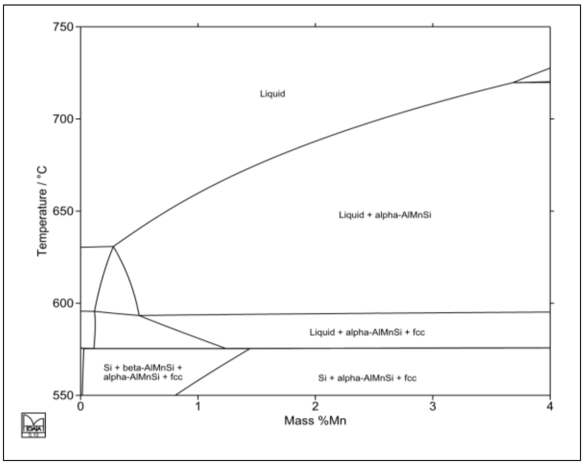

Figure 4: Calculated isopleth corresponding to 2wt%Fe and 10wt%Si in the Al-Fe-Mn-Si system.

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