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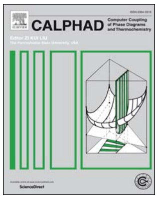

A CALPHAD assessment of the Al–Mn–C system supported by *ab initio* calculations

Florian Tang[a,*], Dimitri Bogdanovski[b], Irina Bajenova[c], Alexandra Khvan[c], Richard Dronskowski[b,d], Bengt Hallstedt[a]

[a] *Institute for Materials Applications in Mechanical Engineering, RWTH Aachen University, 52056 Aachen, Germany*
[b] *Institute of Inorganic Chemistry, RWTH Aachen University, 52056 Aachen, Germany*
[c] *Thermochemistry of Materials Scientific Research Centre, NUST MISIS, Leninsky prosp. 4, 119049 Moscow, Russia*
[d] *Jülich-Aachen Research Alliance (JARA-HPC), RWTH Aachen University, 52056 Aachen, Germany*

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ABSTRACT

frequently toggled from 1The Al–Mn–C ternary system has been thermodynamically evaluated using the CALPHAD method. Published data on phase equilibria have been critically examined and used to optimize the model parameters. The phase model for the κ $AlMn_3C$ phase ($E2_1$) has been changed to $(Al,Mn)_1(Al,Mn)_3(C,Va)_1$ for improved reproduction of stability ranges and phase equilibria at 1100 °C and 1200 °C. The solid solution phase parameters of γ-Mn, ε-AlMn, ε-Mn_4C have been adjusted to reproduce experimental ternary phase equilibria. Density functional theory-based *ab initio* calculations of enthalpies of formation at 0 K were performed to guide the modeling of the κ phase and elucidate general energetic trends. Reasonable liquidus temperatures were achieved by adjustments to the stability of the liquid phase. The Mn_5C_2 phase model was extended to $Mn_5(C,Al)_2$ which allows aluminium on the carbon sublattice. The CALPHAD calculations were performed with the optimized set of parameters and compared with the available experimental data and changes to previous work were elucidated.

1. Introduction

The quaternary Al–Fe–Mn–C system is the fundamental system for high manganese steels (HMnS). The current generation of advanced high strength steels (AHSS) employs complex microstructural and processing features such as twinning induced plasticity (TWIP), transformation induced plasticity (TRIP) and additionally precipitation of the κ phase $(Fe,Mn)_3AlC$ [1,2]. Typically, these microstructural features and mechanisms are activated by different processing routes and variation of alloying content [3]. Both the selection of the alloying content as well as crucial processing parameters such as heat treatment temperatures can be found with the help of thermodynamic calculations employing the CALPHAD method. The Al–Mn–C system is a crucial subsystem of the main quaternary system and therefore demands attention if the quaternary system is to be modeled realistically.

Schuster and Nowotny [4] suggested isothermal sections at 700 °C and 1000 °C after experimental investigations *via* X-ray diffraction (XRD) and light optical microscopy (LOM) on annealed and quenched samples. They reported the existence of the ternary $AlMn_3C$ compound with anti-perovskite $CaTiO_3$ structure. After that, no further experimental determination of phase constitution was performed until the recent works by Bajenova et al. [5,6] provided isothermal sections at 1100 °C and 1200 °C as well as experimental information about the liquidus surface in the Mn-rich region of the ternary systems by differential thermo-analysis (DTA), XRD, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Some additional interest of research has been directed towards a metastable ferromagnetic tetragonal phase (referred to as τ) with less than 2 wt% C and about 70 wt% Mn for its magnetic properties [7–12]. It can be formed after isothermal annealing of ε-AlMn by martensitic transition to its $L1_0$ tetragonal structure and is formed by subsequent quenching [13,14]. Due to the low alloying range and metastable phase constitution these works can not be considered useful for the assessment of the Al–Mn–C ternary system.

Even though the chemical and thermodynamic similarities of iron and manganese rightfully suggest a general similarity of the Al–Fe–C and Al–Mn–C systems, considerable differences can nonetheless be found, *e.g.* concerning the κ phase. For this phase a considerably different range of solubility and constitution can be found in the Al–Mn–C system in addition to a congruent melting point which can not be observed in Al–Fe–C.

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[*] Corresponding author.
E-mail address: f.tang@iwm.rwth-aachen.de (F. Tang).

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Table 1
Crystallographic and structural data for the solid phases in the Al–Mn–C system.

Phase	Alias	Prototype	Space group	Pearson	Strukturbericht
γ	(Al), ($\gamma-$ Mn), fcc	Cu	Fm $\bar{3}$ m	cF4	A1
α-Mn		α-Mn	I $\bar{4}$ 3m	cI58	A12
β-Mn		β-Mn	$P4_132$	cP20	A13
δ-Mn	γ-AlMn	W	Im $\bar{3}$ m	cI2	A2
$Al_{12}Mn$		$Al_{12}W$	Im3	cI26	
Al_6Mn		Al_6Mn	Cmcm	oC28	$D2_h$
λ- Al_4Mn		–	$P6_3/m$	hP586	
μ- Al_4Mn		Al_4Mn	$P6_3/mmc$	hP574	
Al_4C_3		Al_4C_3	R $\bar{3}$ m	hR7	$D7_1$
$Al_{11}Mn_4$	(HT)	Al_3Mn	Pnma	oP156	
	(LT)	$Al_{11}Mn_4$	P $\bar{1}$	aP15	
Al_8Mn_5		Al_8Cr_5	R3m	hR26	$D8_{10}$
MnC		NaCl	Fm $\bar{3}$ m	cF4	B1
Mn_3C	cementite	Fe_3C	Pnma	oP16	$D0_{11}$
Mn_5C_2		Mn_5C_2	$C2/c$	mC28	
Mn_7C_3		Cr_7C_3	Pnma	oP40	$D10_1$
$Mn_{23}C_6$		$Cr_{23}C_6$	Fm $\bar{3}$ m	cF116	$D8_4$
ε	ε-AlMn, ε-Mn_4C	Mg	$P6_3/mmc$	hP2	A3
κ	$AlMn_3C$	$CaTiO_3$	Pm $\bar{3}$ m	cP5	$E2_1$
graphite	C	C	Fd $\bar{3}$ m	cF8	A9

2. Literature review

2.1. Al–C

The assessment of Al–C used in this work was done by Gröbner et al. [15], with modifications by Connetable et al. [16]. The stoichiometric Al_4C_3 carbide is the only stable intermediate phase which forms in a peritectic reaction ($L + (C) \leftrightarrow Al_4C_3$) at 2156 °C. Crystallographic information of all phases in the binary and ternary systems can be found in Table 1.

2.2. Al–Mn

The system is quite complex with four stoichiometric intermetallic phases, $Al_{12}Mn$, Al_6Mn, Al_4Mn (λ) and Al_4Mn (μ) on the aluminium-rich side. The $Al_{11}Mn_4$ phase is split into a stoichiometric low temperature version ($Al_{11}Mn_4$-LT) and a high temperature solution phase ($Al_{11}Mn_4$-HT) at temperatures from 900 °C to 1000 °C. For Al_8Mn_5 (γ-brass Al_8Cr_5 type) the stable phase region ranges from 32 to 54 wt% Mn, with the composition shifting to higher aluminium contents at higher temperatures and a peritectic dissolution at 1046 °C. On the Mn-rich side, the solid solution phases of manganese dominate the phase diagram. Whereas the fcc γ-Mn phase has only about 9 at% Al solubility for aluminium, β-Mn is stabilized by the addition of aluminium, up to as much as 40 at% Al bcc δ-Mn (Strukturbericht A2) is also stabilized up to 30 at% Al with the highest liquidus temperature of any Al-Mn mixture at about 1305 °C. Another stable phase region of bcc (A2) can be found in the 32–56 at% Mn range, called γ-AlMn. In between these bcc phases, hcp ε-AlMn can be found in a temperature range from 823 °C to 1281 °C. The cbcc α-Mn phase is stable below 707 °C and has very little solubility for aluminium.

Du et al. [17] evaluated all experimental data available at the time, performed experiments for the low-Al regime and introduced a corrected model of Al_8Mn_5 culminating in a thorough reassessment of the Al–Mn system. Recent assessments by Shukla and Pelton [18] and Asgar-Khan and Medraj [19] use the modified quasichemical model (MQM) for the liquid phase which can not be used in this work. Therefore, the assessment of Du et al. [17] is used for the Al–Mn system with some modifications of the $Al_{11}Mn_4$-HT model by Djurovic et al. (published in Hallstedt et al. [20]). The calculated phase diagram is shown in Fig. 1.

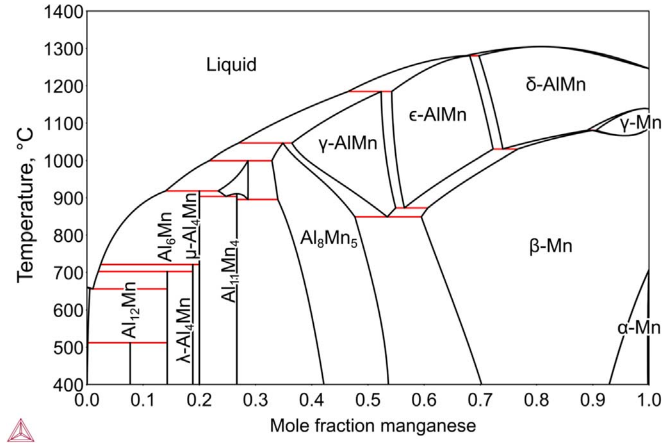

Fig. 1. Binary Al–Mn phase as used in this work. Mostly the description of Du et al. [17] is used with additional order modeling of Djurovic et al. (published in [20]).

2.3. Mn–C

Four stoichiometric carbides, $Mn_{23}C_6$, Mn_3C, Mn_5C_2 and Mn_7C_3, exist in the 20–30 at% C range [21–23]. The carbon-rich side of the diagram is dominated by graphite and Mn_7C_3. On the manganese-rich side solid solution phases of manganese (α-, β-, γ- and δ-Mn) as well as the ε-Mn_4C phase are present. The latter is a hexagonal close packed (Strukturbericht A3) phase with carbon occupying the interstitial lattice site with a solution range of about 15–25 at% C at temperatures above 950 °C similar to ε-AlMn of the Al–Mn binary. Due to the large solution range for carbon, it is sometimes referred to as Mn_4C_{1-x}. The low-temperature allotropic form of manganese, cbcc α-Mn (Strukturbericht A12), dissolves carbon up to 7 at% C. It is stabilized by carbon and forms peritectoidally at 818 °C, $\gamma - \mathrm{Mn} + \beta - \mathrm{Mn} \rightarrow \alpha - \mathrm{Mn}$. Another allotropic form of manganese, β-Mn, has less than 1 at% solubility for carbon and is constricted by the fcc γ-Mn phase field which extends into the binary system up to 13 at% C and to a temperature range from 752 °C to 1242 °C which is much wider than the 1087–1138 °C range of the allotropic pure manganese form. It is the primary phase of solidification in the 1.5–13 Cat% range. The fourth allotropic phase of manganese, bcc δ-Mn, is stable in a narrow composition range for 0–0.15 at% C

All available experimental data and computational formation enthalpies of the carbides were incorporated into a new assessment by Djurovic et al. [23] which is used in this work. A modification of the fcc (γ-Mn) phase was made in the present work, see Section 5.

2.4. Al–Mn–C

Experimental determination of phase constitution in the Al–Mn–C ternary system is challenging due to the high evaporation rate of manganese and complex solid state transformations in the Mn-rich part of the system. Schuster and Nowotny [4] suggest two isothermal sections at 700 °C and 1000 °C and the existence of a stoichiometric compound of κ ($AlMn_3C$), an anti-perovskite of $CaTiO_3$ type. Schuster and Nowotny [4] also report the primary crystallization of arc-melted $AlMn_3C$. Notably the suggested isothermal section at 1000 °C does not include the phases ε-Mn_4C, $Mn_{23}C_6$ or Mn_3C which are stable in the Mn–C binary subsystem.

Recently, Bajenova et al. [5,6] provided experimental results for the Mn-rich corner of the ternary system on the basis of about 30 specimens by means of DTA, XRD and SEM. Liquidus and solidus temperatures for alloys over 55 at% Mn were determined as well as isothermal sections at 1100 °C and 1200 °C.

For a thermodynamic description of the Al–Mn–C ternary system the constitution and homogeneity range of the κ $AlMn_3C$ phase is essential since it takes part in almost all invariant equilibria. Bajenova et al. [5]