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Thermodynamic description of the Cr-Mn-Si system

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ABSTRACT

First-principles (Density Functional Theory and SQS) calculations and the Calphad method are combined to obtain a thermodynamic description of the Cr-Mn-Si system. Especially the mixing enthalpies and the magnetic moments in solid solutions with substitutions of Cr by Mn are calculated at 0 K using the DFT for different structures. Such data are then used together with the available literature data to obtain a general description of the ternary system.

1. Introduction

Chromium and manganese silicides are added in some steal compositions. They also take part in composite materials. From the thermoelectric point of view $CrSi_2$ and $MnSi_x$ are known to be used at high temperature, as sensors and T.E.G. elements. These preliminary remarks show the interest of the phase stability study in this ternary system.

Generating electricity from waste heat by means of “green” thermoelectric generators could reduce the global CO_2 footprint of industrial activities. Among the potential materials for thermoelectric applications, Higher Manganese Silicides (HMS) $MnSi_x$ (with x around 1.75) exhibit interesting figures-of-merit at the intermediate temperatures, where quantities of waste heat are lost (573 K to 873 K), [1,2] which explains why the transformation of this energy in electric power is attractive. Recent studies [3,4] have shown that it is possible to increase these figures-of-merit of HMS materials by doping with chromium.

In general the optimization of the synthesis of alloys needs the precise knowledge of the thermodynamic properties and an accurate description of the systems including binaries and ternaries. It is the case in these materials also. To be as accurate as possible, such descriptions have to be based on consistent thermodynamic values. Building the ternary database Cr-Mn-Si is, as a consequence, necessary to obtain a good description of the phase equilibria. Since only a few experimental data are available in this system, the thermodynamic assessment will be greatly supported by DFT calculations.

The paper is organized as follows: in Section 2, the literature data is discussed for the binary and ternary systems. In Section 3, the results concerning DFT calculations are presented, especially the calculation process is detailed and the influence of the size of the cell on the results is discussed. In Section 4, the ternary system is modeled using the Calphad method. Finally conclusions are given in Section 5.

2. Literature data

2.1. Binary systems

The Cr-Mn system is taken from Lee [5] and his database is used. The system is characterized by the existence of two non-stoichiometric sigma phases at low and high temperature (Fig. 1a).

A first version of the Cr-Si system was first assessed by Coughanowr et al. [6]. Based on new measurements of the invariant temperatures, Du et al. [7] reported a new database for the system. Finally, the melting behavior of Cr_5Si_3 was solved by Chen et al. [8] who assessed one more time the Cr-Si system (Fig. 1b). This last version is selected for this work (Fig. 1b).

Concerning Mn-Si, 7 different versions of the system have been published [7,9–14]. The versions of Shukla et al. [12] and Paek et al. [13] have been assessed using a quasichemical liquid model but they are not compatible with the bases of Lee [5] and Chen et al. [8] which are chosen in this work for the other binary systems. On the basis of new DTA experiments [14] and calculated data [15], the present authors have provided a new version of the Mn-Si system [14]. Especially, the variations to the stoichiometry in the R-Mn_6Si, ν-Mn_9Si_2 and $MnSi_x$ (HMS phase with x around 1.75) phases have been taken into consideration. This database will be used for this work (Fig. 1c).

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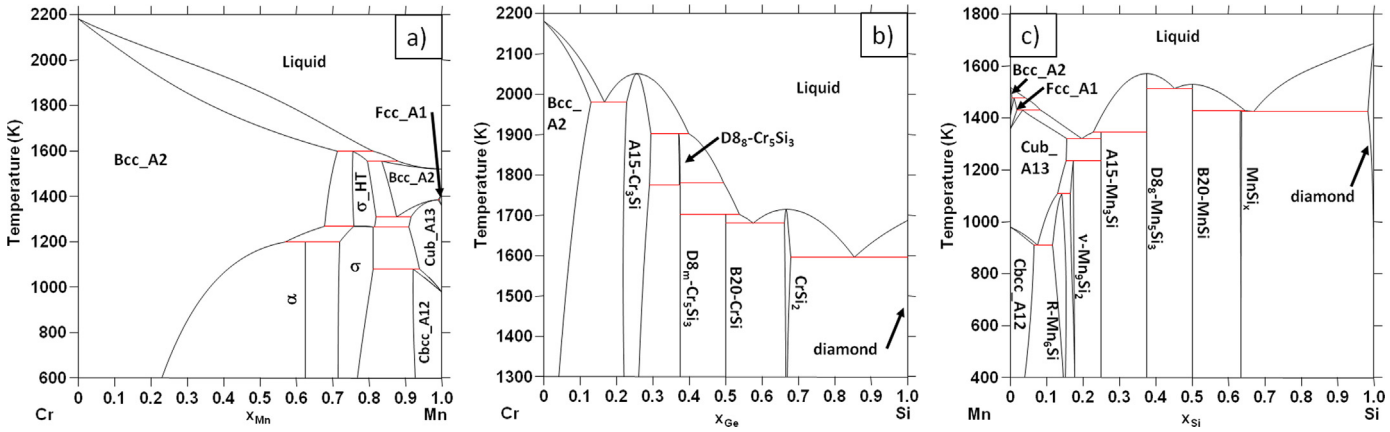

Fig. 1. The three assessed binary phase diagrams of the database: (a) Cr-Mn of Lee [5]; (b) Cr-Si of Chen et al. [8]; (c) Mn-Si of Berche et al. [14].

2.2. Cr-Mn-Si system

The crystallographic structures of the various binary phases are presented in Table 1. According to these data, only two possible continuous solid solutions can exist. The first one is based on the B20 structure between MnSi and CrSi, the second one is only present at high temperature in the $D8_8$ structure between Mn_5Si_3 and Cr_5Si_3.

On the silicon side, the solid solution was investigated by Burger et al. [17] claiming that after annealing 18 days at 1173 K, the samples in this solid solution exhibit only the B20 crystallographic structure. The evolution of the cell parameter is described by a Vegard's law.

The solubility of manganese in the C40 $CrSi_2$ phase was measured by Wittman et al. [18] and Sato et al. [19]. The limit is given at 8.3 at% Mn by Wittman et al. at an undetermined temperature and at 7.3 at% Mn between 1173 K and 1373 K by Sato. These values are in a relative good agreement and they have been considered.

Similarly, the solubility of chromium in the $MnSi_x$ phase is measured at 2 at% by Abrikosov et al. [20] and at 4 at% by Wittman et al. [18]. Cr-doped HMS phases have been synthesized at 2 and 6 at% by Ivanova [3] and 3 and 5 at% by Ponnambalam et al. [4], however, it was not possible to check the purity of the samples since no XRD or SEM analyses are published by the authors.

Moreover, Abrikosov et al. [20] synthesized several alloys between C40 $CrSi_2$ and the $MnSi_x$ phase. The alloys have been analyzed by thermal analyses. The thermal arrest (Fig. 2) cannot have been correctly interpreted since the HMS phase was supposed to have congruent melting. In this work, only temperatures of thermal arrests are taken into consideration.

Alloys with silicon contents up to 30 at% have been investigated at 1273 K by Gupta et al. [21]. The solubility domain of the sigma phase is presented. Especially, the existence of chromium solubility in the $D0_3$ Mn_3Si phase has been noticed (around 8 at% Cr). Similarly, 40 at% of Mn can be added in the A15 Cr_3Si structure. Bardos et al. [22] also investigates the solubility range of chromium and silicon in the β-Mn (Cub_A13 structure) at 1273 K.

More recently, Petrova et al. [23] studied the interface between $MnSi_{1.75}$ ($MnSi_x$) and C40 $CrSi_2$ at 1120 K. The first phase which is formed in contact with $MnSi_x$ is a MnSi (B20) phase containing 2 at% Cr. The next phase is Mn_5Si_3 ($D8_8$ structure) with 18 at% Cr. Then two Cr_3Si phases (A15) are noticed with 30 at% Mn and 19 at% Mn. Finally a solid solution of Cr containing 1 at% Mn and 5 at% Si appears in contact with pure chromium.

Taking into account all these data, a hypothetical isotherm section of the Cr-Mn-Si system at around 1120–1273 K is drawn in Fig. 3a. According to this description, five solid solutions exist in the A15-Cr_3Si, $D0_3$-Mn_3Si, $D8_8$-Mn_5Si_3, B20-MnSi and C40-$CrSi_2$

Table 1
Crystallographic data (struktur-bericht, prototype and Pearson's symbol) of the phases [16].

Name	Struktur-bericht	Prototype	Pearson symbol	Space group	Phases
Bcc_A2	A2	W	cI2	*Im-3m*	Cr, δ-Mn
Fcc_A1	A1	Cu	cF4	*Fm-3m*	γ-Mn
Cub_A13	A13	β-Mn	cP20	$P4_132$	β-Mn
Cbcc_A12	A12	α-Mn	cI58	*I-43m*	α-Mn
Diamond	A4	C (diamond)	cF8	*Fd-3m*	Si
B20	B20	Fe-Si	cP8	$P2_13$	CrSi, MnSi
A15	A15	Ni_3Sn	cP8	*Pm-3n*	Cr_3Si
D03	$D0_3$	BiF_3	cF16	*Fm-3m*	Mn_3Si
$D8_m$	$D8_m$	W_5Si_3	tI32	*I4/mcm*	Cr_5Si_3, Mn_5Si_3
$D8_8$	$D8_8$	Mn_5Si_3	hP116	$P6_3/mcm$	Cr_5Si_3
Sigma	$D8_b$	σ-phase	tP30	$P4_2/mnm$	σ-CrMn
Sigma-HT	$D8_b$	σ-phase	tP30	$P4_2/mnm$	σHT-CrMn
Alpha	–	α-Mn	–	–	α-CrMn
$Mn_{11}Si_{19}$	–	$Mn_{11}Si_{19}$	tP120	*P-4n2*	$MnSi_x$
R_Mn_6Si	$D8_5$	R_Mn_6Si	hR53	*R-3*	R-Mn_6Si
NU_Mn_9Si_2	–	NU_Mn_9Si_2	oI186	*Immm*	ν-Mn_9Si_2
$CrSi_2$	C40	$CrSi_2$	hP9	$P6_222$	$CrSi_2$

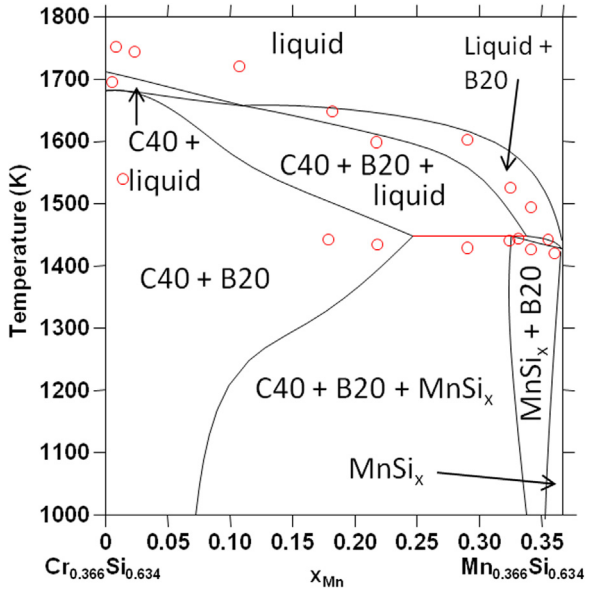

Fig. 2. Isopleth section at 63.4 at% Si and thermal arrests measured by Abrikosov et al. [20].