



Structural stability of intermetallic phases in the Si–Ti system. Point defects and chemical potentials in D8₈–Si₃Ti₅ phase

Catherine Colinet^{a,*}, Jean-Claude Tedenac^b

^aScience et Ingénierie des Matériaux et Procédés, UMR 5266, CNRS – INP Grenoble – UJF, BP 75, 38402 Saint Martin d'Hères Cedex, France

^bInstitut de Chimie Moléculaire et des Matériaux I.C.G., UMR-CNRS 5253, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

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ABSTRACT

The total energies of intermetallic compounds in the Si–Ti system are calculated employing electronic density functional theory (DFT). The calculations are performed for the experimentally observed compounds and selected structures at their ideal stoichiometry. The calculated formation enthalpies are in good agreement with the available experimental data. For the stable intermetallic compounds, the calculated zero-temperature lattice parameters agree well with those obtained experimentally at ambient temperature. The point defect formation energies in D8₈–Si₃Ti₅ (hP16, P6₃/mcm, prototype Mn₅Si₃) are obtained from first principles calculations. Four sublattices are introduced to account for the D8₈ structure and for the possibility of inserting atoms (2b Wyckoff positions of P6₃/mcm space group). The total energies of supercells containing one defect are calculated. A statistical model based on a mean-field approximation is used to obtain the defect concentrations, the chemical potentials and the Gibbs energy of formation as functions of temperature and deviation from stoichiometry. Analytical expressions of the defect concentrations, chemical potentials and Gibbs energy as functions of composition for various temperatures are provided. The off-stoichiometric domain of D8₈–Si₃Ti₅ is discussed.

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1. Introduction

The experimental Si–Ti phase diagram presents five intermetallic compounds SiTi₃ (tP32, P4₂/n, No 86, PTi₃-prototype), Si₃Ti₅ (D8₈, hP16, P6₃/mcm, No 193, Mn₅Si₃-prototype), Si₄Ti₅ (tP36, P4₁2₁2, No 92, Si₄Zr₅-prototype), SiTi (B27, oP8, Pnma, No 62, FeB-prototype), and Si₂Ti for which two crystal structures are reported C54 (oF24, Fddd, No 70) and C49 (oC12, Cmcm, No 63, ZrSi₂-prototype) [1,2]. Some years ago, Colinet et al. [3] performed *ab initio* calculations in order to clarify the allotropic structural properties of Si₂Ti. They found that at $T = 0$ K the C49 structure of Si₂Ti is the most stable phase whereas the C54 structure, which experimentally is considered to be the ground state, is less favourable. By including the free energy contributions of lattice vibrations and electronic excitations, they predicted a structural transition from C49 to C54 at about 1100 K.

In the Si–Ti phase diagram, the D8₈–Si₃Ti₅ compound is the only one displaying a domain of off-stoichiometry [2]. The unit cell of the prototype structure, D8₈–Mn₅Si₃, contains four Mn at 4d sites at

(1/3,2/3,0), six Mn at 6g sites at ($x_{\text{Mn}}, 0, 1/4$), and six Si at 6g sites at ($x_{\text{Si}}, 0, 1/4$). In the case of the D8₈–Sn₃Ti₅ phase [4], *ab initio* calculations have shown that, in the Sn-rich side, the Sn atoms occupy the 2b Wyckoff positions at (0,0,0) of the P6₃/mcm space group. Recently Williams et al. [5] have shown that interstitial additions of B, C, N or O in the 2b sites increase the stability of the D8₈ structure in the case of the Si₃Ti₅ compound.

The goal of the present study is to obtain the enthalpies of formation of the Si–Ti intermetallic compounds and the formation energies and volumes of point defects in D8₈–Si₃Ti₅ compound from *ab initio* electronic structure calculations based on density functional theory. To account for the D8₈ structure and for the possibility of inserting atoms in the 2b positions, four sublattices must be defined: the α sublattice (6g positions) occupied by Si atoms, the β_1 sublattice (6g positions) occupied by Ti atoms, the β_2 sublattice (4d positions) occupied by Ti atoms, and the γ sublattice (2b positions) not occupied in the stoichiometric compound at low temperature. With four sublattices, eight kinds of defects must be considered: vacancies on sublattices α , β_1 , β_2 : V^α , V^{β_1} , V^{β_2} , Si atoms in antisite position on β_1 or β_2 sites: Si^{β_1} , Si^{β_2} , Ti atoms in antisite position on α sites: Ti^α , and Si and Ti atoms in interstitial positions Si^γ and Ti^γ . In order to estimate the energy and volume of formation of vacancies, antisite defects, and interstitial atoms, we performed total energy calculations of two supercells, a hexagonal one with 32 atoms and an orthorhombic one with 64 atoms.

* Corresponding author. Science et Ingénierie des Matériaux et Procédés, Laboratoire de Thermodynamique et Physico-Chimie Metallurgiques, UMR 5266, CNRS – INP Grenoble – UJF, BP 75, 38402 Saint Martin d'Hères Cedex, France. Tel.: +33 4 76 82 67 47; fax: +33 4 76 82 67 45.

E-mail address: ccolinet@simap.grenoble-inp.fr (C. Colinet).

The formation energies and volumes of the defects may be used to evaluate the equilibrium concentrations of point defects as a function of temperature, pressure and composition within the framework of a statistical mechanical approach. In the previous work concerning the $D8_8\text{-Sn}_3\text{Ti}_5$ phase [4], we have developed a simple statistical model in the canonical ensemble. The basic assumptions are that the energy and volume of formation of the compound depend linearly of the defect concentrations and that the entropy is calculated assuming a random distribution of the species on the lattice sites. This model is applied to the $D8_8\text{-Si}_3\text{Ti}_5$ phase. It allows us to calculate the defect concentrations as well as the thermodynamic function of the alloy composition at various temperatures. A simplified analytical treatment is proposed for the defect concentrations at low temperatures. In the case of $D8_8\text{-Si}_3\text{Ti}_5$ compound, this treatment is applicable until its congruent melting temperature at 2122 °C. Analytical expressions of the Gibbs energy of formation as well as the Si and Ti chemical potentials are derived. The equilibrium with the $tP36\text{-Si}_4\text{Ti}_5$ compound is discussed. To the best of our knowledge, neither experimental nor theoretical investigations of the point defects energies have been performed in the $D8_8\text{-Si}_3\text{Ti}_5$ compound.

2. Computational details

The density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP) [6], making use of the projector augmented waves (PAW) technique [7,8]. The calculations include four valence electrons for Si ($3s^2 3p^2$ electronic configuration) and ten valence electrons for Ti ($3p^6 3d^3 4s^1$ electronic configuration), the semi-core 3p orbitals of Ti are considered as valence electrons. A plane-wave cutoff energy of 300 eV for both elements has been taken. For the generalized gradient approximation (GGA) exchange correlation functional, the Perdew–Wang parameterization (PW91) was applied [9]. For the Brillouin-zone integration, the Methfessel–Paxton [10] technique with a modest smearing of the one-electron levels (0.1 eV) was used. Care was taken so that a sufficient number of k points for the Brillouin-zone integration was chosen for each structure. A Gamma centred k -point grid was used for the hexagonal structures. For the other structures, a Monkhorst–Pack [11] grid was used. In each case, the number of k points has been chosen in such a way that the number of k points in the irreducible Brillouin-zone multiplied by the number of atoms in the cell is of the order of 500. In this way, convergent results are achieved for lattice parameters and total energies. All calculations have been performed using the “accurate” setting within VASP to avoid wrap-around errors.

To determine the defect formation energies and volumes in the $D8_8\text{-Si}_3\text{Ti}_5$ phase, we performed calculations on a $1 \times 1 \times 2$ hexagonal supercell containing 32 atoms (called in the following hexa2) with a Gamma centred $4 \times 4 \times 4$ k -point grid. The lattice parameters of this cell are a_{hcp} , and $2c_{\text{hcp}}$ where a_{hcp} and c_{hcp} are the lattice parameters of the $D8_8$ unit cell. The reliability of the results was checked by calculations for an orthorhombic supercell that contains 64 atoms with the following parameters a_{hcp} , $a_{\text{hcp}}\sqrt{3}$, and $2c_{\text{hcp}}$ (called in the following ortho2). A Monkhorst–Pack [11] $3 \times 3 \times 3$ k -point grid was used in the calculations. Successive relaxations of the volume, c/a ratio, and internal coordinates were performed provided that the structure remains hexagonal or orthorhombic with $b = a\sqrt{3}$ in order to save the original hexagonal symmetry of the structure.

3. Enthalpies of formation of Si–Ti compounds

The enthalpy of formation, $\Delta_f H(\text{Si}_x\text{Ti}_{1-x})$, is obtained from the minimum total energy of the compound (expressed per atom) by

subtracting the composition-weighted minimum total energies of pure Si in the diamond structure (A4) and pure hexagonal close-packed (A3) Ti:

$$\Delta_f H(\text{Si}_x\text{Ti}_{1-x}) = E_{\text{Si}_x\text{Ti}_{1-x}}^{\text{min}} - xE_{\text{A4-Si}}^{\text{min}} - (1-x)E_{\text{A3-Ti}}^{\text{min}} \quad (1)$$

The values of these enthalpies of formation are reported in Table 1. Apart from the phases that appear stable in the experimental phase diagram, we calculated the enthalpies of formation of Si–Ti compounds in some structures which are stable in systems of p-elements with early transition metals or rare earths (RE). The results are displayed in Fig. 1, where the ground-state line has been drawn. The enthalpies of formation of the phases $D8_8\text{-Si}_3\text{Ti}_5$, Si_4Ti_5 (prototype Si_4Zr_5), B27–SiTi and C49– Si_2Ti , which are reported stable in the literature are on this convex hull. However, at $T = 0$ K, the enthalpy of formation of the SiTi_3 compound with the PTi_3 -prototype structure is slightly above the ground-state line. The question of the stability of this phase is controversial [12]. The PTi_3 -type structure is stable in Hf–Ge system and in (Si, Ge)–(Nb, Ta) systems. For the SiTi_3 composition, the prototype structure Ni_3P has an enthalpy of formation which is only 1.5 kJ/mol of atoms less negative than the one of the PTi_3 -prototype structure. The Ni_3P -type structure is stable in Bi–Zr, Sb–Hf, Zr–Sb, Ge–Ta systems for example. The DO_{19} structure which is found to be the ground state in numerous systems such as Sn–Ti, Ga–Ti, Al–Ti is less stable. The A15 structure which is found stable in systems of Si-based systems with transition metals of the V and Cr columns is also less stable.

The SiTi_2 compound in the C22 structure (F_2P -prototype) has an enthalpy of formation which is on the ground-state line (see Fig. 1). In the absence of experimental information, it might be possible that this compound is stable only at very low temperature and therefore is impossible to synthesize from high temperature. At the same composition, the C16 structure has an enthalpy of formation which is only one kJ less negative than the one of C22 structure. The C16 structure (Al_2Cu -type) is often stable at this composition in transition metal-p elements alloys (AlHf_2 , AlTh_2 , SiZr_2 , SiTa_2 , GaZr_2 , SiHf_2 , InZr_2 for example crystallize in the C16 structure). In the case of the SiTi_2 compound, the enthalpy of formation of B8_2 structure is well above the one of the C22 structure.

Table 1
Enthalpies of formation of selected Si–Ti compounds referred to A4-Si and A4-Ti.

	Pearson symbol	Prototype	Strukturbericht designation	Space group	Number	$\Delta_f H$ (kJ/mol of atoms)
SiTi_3	tP32	PTi_3		$\text{P4}_2/\text{n}$	$\text{N}^\circ 86$	–47.11
SiTi_3	hP8	NiSn_3	D019	$\text{P6}_3/\text{mmc}$	$\text{N}^\circ 194$	–43.88
SiTi_3	cP8	Cr_3Si	A15	$\text{Pm}(-3)\text{n}$	$\text{N}^\circ 223$	–42.36
SiTi_3	tI32	Ni_3P		$\text{I}(-4)$	$\text{N}^\circ 82$	–45.50
SiTi_2	hP9	Fe_2P	C22	$\text{P}(-6)2\text{m}$	$\text{N}^\circ 189$	–64.67
SiTi_2	hP6	InNi_2	B8_2	$\text{P6}_3/\text{mcm}$	$\text{N}^\circ 194$	–59.42
SiTi_2	tI12	Al_2Cu	C16	I4/mcm	$\text{N}^\circ 140$	–63.70
$\text{Si}_6\text{Ti}_{11}$	hP17		Half-filled D8_8	$\text{P6}_3/\text{mcm}$	$\text{N}^\circ 193$	–55.94 ^a –57.68 ^b
Si_3Ti_5	hP16	Mn_5Si_3	D8_8	$\text{P6}_3/\text{mcm}$	$\text{N}^\circ 193$	–72.53
Si_3Ti_5	tI32	W_5Si_3	D8_{m}	I4/mcm	$\text{N}^\circ 140$	–70.45
Si_3Ti_5	tI32	Br_5Si_3	D8_1	I4/mcm	$\text{N}^\circ 140$	–67.94
Si_2Ti_3	tP10	Si_2U_3	D5_a	$\text{P4}/\text{mbm}$	$\text{N}^\circ 127$	–71.98
$\text{Si}_7\text{Ti}_{10}$	hP17		Half-filled D8_8	$\text{P6}_3/\text{mcm}$	$\text{N}^\circ 193$	–70.51 ^a –71.00 ^b
Si_4Ti_5	hP18	Ga_4Ti_5	Filled D8_8	$\text{P6}_3/\text{mcm}$	$\text{N}^\circ 193$	–69.08
Si_4Ti_5	tP36	Si_4Zr_5		$\text{P4}_12,2$	$\text{N}^\circ 92$	–74.63
Si_4Ti_5	oP36	Ge_4Sm_5		Pnma	$\text{N}^\circ 62$	–74.30
SiTi	oP8	FeB	B27	Pnma	$\text{N}^\circ 62$	–72.23
SiTi	oC8	CrB	B33	Cmcm	$\text{N}^\circ 63$	–72.04
Si_2Ti	oC12	ZrSi_2	C49	Cmcm	$\text{N}^\circ 63$	–51.30
Si_2Ti	oF24	TiSi_2	C54	$\text{Fd}\ddot{d}$	$\text{N}^\circ 70$	–49.87
Si_2Ti	hP9	CrSi_2	C40	P6_22	$\text{N}^\circ 180$	–48.38

^a With the characteristics of the coordinates of the $\text{P6}_3/\text{mcm}$ space group.

^b Full relaxation of the coordinates.

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