Solid State Communications 152 (2012) 989–993

Contents lists available at SciVerse ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

A first principles study of constitutional and thermal defects in $D8_m$-Si_3Nb_5

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ARTICLE INFO

Article history:
Received 3 October 2011
Received in revised form
12 March 2012
Accepted 20 March 2012
by J.R. Chelikowsky
Available online 29 March 2012

Keywords:
A. $D8_m$-Si_3Nb_5
D. Point-defects
D. Site occupancy
E. ab-initio Calculations

ABSTRACT

First principles calculations of point-defect enthalpies of formation are performed in the $D8_m$-Si_3Nb_5 compound. Four sublattices are introduced to account for the $D8_m$ structure. Based on a statistical–thermodynamic model, the defect concentrations are calculated as function of temperature and deviation from stoichiometry. For the stoichiometric composition, all the point-defect atomic concentrations remain very low even at the compound melting temperature. In the Si-rich $D8_m$-Si_3Nb_5, the constitutional defects are Si antisites on the Nb 4b sites of the $D8_m$ structure. The thermal defects are Si antisites on the 16k sites of the $D8_m$ structure, but their concentration remains very small even at high temperature. In the Nb-rich $D8_m$-Si_3Nb_5, the constitutional defects are Nb antisites on the 8h Si positions. The formation Gibbs energy of the $D8_m$-Si_3Nb_5 phase as well as the Si and Nb chemical potentials are obtained as function of the deviation from stoichiometry for various temperatures. The extension of the one-phase domain of $D8_m$-Si_3Nb_5 in the Si–Nb phase diagram is discussed.

1. Introduction

In the development of alloys with high temperature applications, intensive research is now performed in ternary or multicomponent alloys containing transition metals of Ti, V, or Cr columns, silicon and boron [1–4]. The knowledge of the corresponding phase diagrams is important in the search of multiphase structures. Experimental phase diagram determinations are part of the road map for materials and processing development. However, recent advances in phase diagram calculations (CALPHAD) [5,6] enable to obtain multicomponent phase diagrams with a reduced level of experimental effort. The basis is to obtain a thermodynamic description of a multicomponent system via extrapolation of the limiting binaries or ternaries and a limited number of experimental determinations. The Nb–Si system is the basis of interesting multicomponent alloys. The phase diagram displays two compounds C40-$NbSi_2$ and Nb_5Si_3 which presents two forms: the low temperature form α-Nb_5Si_3 which possesses the $D8_1$ structure (often called T_2) and the high temperature form β-Nb_5Si_3 which possesses the $D8_m$ structure (often called T_1) [6]. This high temperature phase presents a domain of off-stoichiometry in the Si-rich side. The Nb–Si phase diagram was calculated with the CALPHAD method by Fernandes et al. [7], however what are the defects in the Si-rich side of $D8_m$-Si_3Nb_5, antisites or vacancies, remains unsolved. The purpose of the present communication is to obtain the point-defect energies of formation in the compound $D8_m$-Si_3Nb_5 from ab-initio calculations and to calculate the point-defect concentrations by applying a thermodynamical–statistical model. The results of these calculations should allow to conclude if the Si solubility in $D8_m$-Si_3Nb_5 is due to Si substituting for Nb or to the presence of vacancies in the Nb positions. The $D8_m$ structure is centered tetragonal (*tI32*, space group: *I4/mcm*, No. 140, W_5Si_3 prototype) with a *c*/*a* ratio near 0.5. The Nb atoms occupy the 4b and 16k Wyckoff positions, as the Si atoms occupy the 4a and 8h positions of the *I4/mcm* space group (Fig. 1). An important point is also to know on which sites are the defects.

2. Computational details and results

The density functional (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) [8], making use of the projector augmented waves (PAW) technique [9,10]. The calculations include four valence electrons for Si ($3s^2$ $3p^2$ electronic configuration) and thirteen valence electrons for Nb ($4s^2$ $4p^6$ $4d^4$ $5s^1$ electronic configuration), the semi-core 4p and 4s orbitals of Nb are considered as valence electrons. A plane-wave cutoff energy of 350 eV for both elements has been taken. For the generalized gradient approximation (GGA) exchange correlation functional, the Perdew–Burke–Ernzerhof parameterization (PBE) was applied [11]. For the Brillouin-zone integration, the Methfessel–Paxton [12] technique with a modest smearing of the one-electron levels (0.2 eV) was used. For the $D8_m$ structure,

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http://dx.doi.org/10.1016/j.ssc.2012.03.001

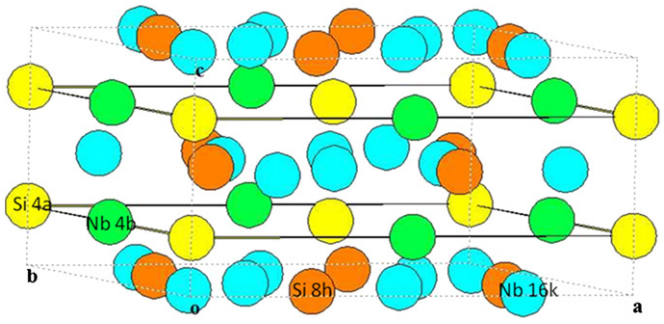

Fig. 1. (Color online) $D8_m$-Si_3Nb_5 structure. Yellow circles: Si atoms in the 4a Wyckoff positions. Orange circles: Si atomes in the 8h Wyckoff positions. Green circles: Nb atoms in the 4b Wyckoff positions. Blue circles: Nb atoms in the 16k Wyckoff positions.

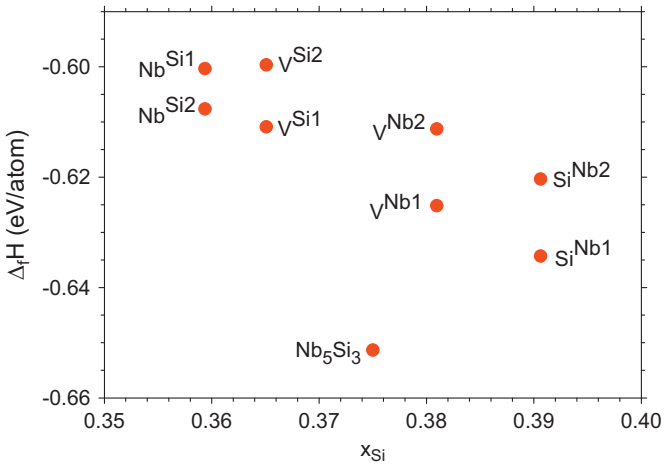

Fig. 2. (Color online) Enthalpies of formation of $D8_m$-Si_3Nb_5 and of the supercells containing one defect. Si_1 positions correspond to the 4a Wyckoff positions, Si_2 to the 8h Wyckoff positions, Nb_1 to the 4b Wyckoff positions, and Nb_2 to the 16k Wyckoff positions.

a Monkhorst–Pack [13] grid was used ($6\times6\times6$ k-point grid). The calculated lattice parameters are $a=10.088$ Å and $b=5.109$ Å in good agreement with the values reported in Pearson's Handbook [14].

To determine the defect formation energies and volumes in the $D8_m$-Si_3Nb_5 phase, we performed the ab-initio calculations on a $1\times1\times2$ supercell of 64 sites ($4\times4\times4$ k-point grid). This supercell has a near cubic shape. One defect, either an antisite or a vacancy, was introduced in the supercell. For each defect, there is two possible positions among the chosen Wyckoff position. Successive relaxations were performed: volume, shape, and positions. Care was taken that the cell remains tetragonal. The energies of formation of the supercell containing one defect are presented in Fig. 2; the reference states of the formation energies are A4-Si and A2-Nb. It is already clear from this figure that the Si atoms in antisite position have a preference for the 4b positions of Nb atoms and that the creation of vacancies on the Nb sites either in 4b or 8h positions is energetically less favorable. In the Nb-rich side the formation of defects is energetically not favorable, that explains why the $D8_m$-Si_3Nb_5 does not present any detected deviation from stoichiometry in this region. The point-defect volumes of formation have also been calculated and we have concluded that the influence of pressure on the defect enthalpies of reaction can be neglected at ordinary pressure.

Table 1
Values of the point-defect enthalpies of formation.

Defect	x_{Si}	H_d (eV/defect)
Si^{Nb_1}	0.3906	1.090
Si^{Nb_2}	0.3906	1.983
V^{Nb_1}	0.381	1.648
V^{Nb_2}	0.381	2.525
Nb^{Si_1}	0.3594	3.264
Nb^{Si_2}	0.3594	2.795
V^{Si_1}	0.3651	2.548
V^{Si_2}	0.3651	3.255

The enthalpy of formation of the compound with defects is written as [15]

$$\Delta_f H = \Delta_f H^\circ(Si_{3/8}Nb_{5/8}) + \sum_d x_d H_d \quad (1)$$

x_d is the defect atomic concentration, H_d is the defect formation enthalpy. $\Delta_f H^\circ(Si_{3/8}Nb_{5/8})$ is the enthalpy of formation of the perfectly ordered stoichiometric compound defined among the relation $\Delta_f H^\circ = H(Si_{3/8}Nb_{5/8}) - \frac{3}{8}H^\circ_{Si} - \frac{5}{8}H^\circ_{Nb}$ with H°_{Si} and H°_{Nb} the reference enthalpies of pure A4-Si and A2-Nb, respectively. The values of the defect enthalpies of formation, H_d, are reported in Table 1. The values of the point-defect enthalpies of formation are strongly positive (more than 1 eV), therefore the formation of defects will occur only at high temperature. Let us quote that the point-defect enthalpies of formation have been calculated in the $D8_1$-Si_3Nb_5 by Chen et al. [16]. They obtained very large values (>2.02 eV/defect), this explains why no deviation from stoichiometry is observed in the $D8_1$-Si_3Nb_5 compound.

3. Statistical model

3.1. Assumptions and basic equations

The statistical model we have developed in the present work is an extension to four sublattices of the model proposed by Hagen and Finnis [17] in the case of two sublattices. In the following, we shall consider an $Si_{3/8}Nb_{5/8}$ ordered alloy with four Si atoms on the sites of sublattice Si_1 (4a Wyckoff positions), eight Si atoms on the sites of sublattice Si_2 (8h Wyckoff positions), four Nb atoms on the sites of sublattice Nb_1 (4b Wyckoff positions) and sixteen Nb atoms on the sites of sublattice Nb_2 (16b Wyckoff positions). Each site of each sublattice, Si_1, Si_2, Nb_1, Nb_2, is occupied either by its own atom or an atom of the other kind (antisite defect) or a vacancy (V). There are therefore twelve species for which the site concentrations on each sublattice are defined: the c_i^ξ concentration of i=Si, Nb, V on the sublattice $\xi=Si_1$, Si_2, Nb_1, Nb_2. The numbers of Si_1, Si_2, Nb_1, and Nb_2 sublattice sites are $N^{Si_1}=4N$, $N^{Si_2}=8N$, $N^{Nb_1}=4N$, $N^{Nb_2}=16N$, where the number N of formula units can vary owing the creation or annihilation of vacancies on all the sublattices when the temperature or the stoichiometry varies. The total number of Si and Nb atoms in the specimen is conserved (canonical ensemble). There are thirteen unknowns, twelve site concentrations c_i^ξ and the number of formula units. They satisfy the following six constrains. The four sum rules for concentrations on each sublattice ξ are given by: $c^\xi_{Si}+c^\xi_{Nb}+c^\xi_V=1$. The fixed total numbers n_{Si} and n_{Nb} of Si and Nb atoms are, respectively, given by

$$N(4c^{Si_1}_{Si}+8c^{Si_2}_{Si}+4c^{Nb_1}_{Si}+16c^{Nb_2}_{Si})=n_{Si}$$

and

$$N(4c^{Si_1}_{Nb}+8c^{Si_2}_{Nb}+4c^{Nb_1}_{Nb}+16c^{Nb_2}_{Nb})=n_{Nb}$$