Mechanisms of Cr segregation to $C11_b/C40$ lamellar interface in $(Mo,Nb)Si_2$ duplex silicide: a phase-field study to bridge experimental and first-principles investigations

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Abstract

Cr segregation at lamellar interfaces in the $MoSi_2/NbSi_2$ duplex silicide was examined using a newly developed phase-field model to elucidate the mechanism of interfacial segregation, which is believed to improve the thermal stability of lamellar structures as well as creep resistance. This is because lamellar structures can improve the high-temperature strength, and the stabilization of the lamellar structures improves creep

resistance. The model takes into account the segregation energy determined using first-principles calculations to reflect the chemical interaction between the solute atoms and the interface, in addition to the elastic interaction. Cr segregation occurs at the interface when the segregation energy is considered, whereas no segregation occurs in the case where only the elastic interaction is considered. However, the extent of segregation was much smaller than that observed experimentally when the segregation energy was evaluated using first-principles calculations without considering lattice vibrations (i.e., the calculations were performed for 0 K). A simulation that took into consideration the segregation energy with the lattice vibrations at 1673 K resulted in segregation similar to that observed experimentally, where the Cr-added $\text{MoSi}_2/\text{NbSi}_2$ duplex silicide was equilibrated at 1673 K, namely, the temperature at which the segregation energy was calculated. Thus, it was revealed that the solute-interface chemical interaction and its temperature dependence are responsible for the interfacial segregation of Cr. These results suggest that the segregation energy needs to be taken into account in the search for more effective additive elements for improving the thermal stability of lamellar structures as well as the creep resistance.

Keywords: A. intermetallics; B. alloy design; D. interfaces; E. phase field modeling; G. energy systems

1. Introduction

Owing to its high melting temperature, low density, and good thermal conductivity [1], MoSi_2 with a $C11_b$ -structure (Fig. 1a) has attracted attention as a refractory material for gas power generation systems, which involve at ultrahigh temperatures, where Ni-based superalloys cannot withstand. Monolithic MoSi_2 exhibits good plastic deformability at low temperatures, owing to the operation of several slip systems. However, its fracture toughness at low temperatures and strength at high temperatures are

insufficient [2-5]. There have been many studies aiming to improve the mechanical properties of MoSi_2 by forming composites with other materials. For instance, MoSi_2 -based composites with ceramics such as Al_2O_3 and SiC exhibit improved high-temperature strengths. However, they exhibit poor thermal shock resistance and low-temperature toughness [6,7]. As another approach, reinforcing MoSi_2 by combining it with another silicide has been receiving attention [8-10]. Disilicides with (Fig.1b) are attractive for reinforcing the MoSi_2 matrix, as they exhibit anomalous strengthening and higher strength than does MoSi_2 [11-14]. Recently, Nakano et al. [9,10] developed $\text{MoSi}_2/\text{NbSi}_2$ duplex crystals with fine and well-oriented lamellar microstructures as a new promising candidate material to overcome the above-mentioned problems. The highly oriented lamellar composed of a $C11_b$ -type Mo-rich phase and a $C40$ -type Nb-rich phase, could be developed in the alloy, which had a nominal composition of $\text{Mo}_{0.85}\text{Nb}_{0.15}\text{Si}_2$, by unidirectional solidification using the floating-zone-melting method. This involved the growth of the $C40$ phase single crystals and subsequent annealing at the dual-phase temperatures. The obtained duplex crystals with oriented lamella exhibited superior high-temperature mechanical properties [15] and improved low-temperature fracture toughness [16,17]. The lamellar structure was relatively thermally stable and remained unchanged even after annealing at 1673 K for 168 h [10]. However, the lamellar structure coarsened and collapsed after prolonged annealing. Thus, the thermal stability of the lamellar structure needs to be improved further in order for the composite to be suitable for practical use. It was recently found that additive elements such as Cr and Zr drastically improve the thermal stability of lamellar structures in the $\text{MoSi}_2/\text{NbSi}_2$ duplex silicide [18,19]. For instance, the lamellae in the $(\text{Mo}_{0.85}\text{Nb}_{0.15})_{0.97}\text{Cr}_{0.03}\text{Si}_2$ alloy remain well defined for more than 336 h. It is believed that the improvement in the thermal stability of the lamellar structure is due to the decrease in the lattice misfit at the $C11_b/C40$ lamellar interface resulting from Cr segregation. That Cr segregation at the interface has already been

proved through scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) [18]. It has been suggested that Cr segregation changes the value of the lattice parameter in the vicinity of the lamellar interface, thus reducing the lattice misfit and improving the planarity and thermal stability of the lamellar structures [19]. However, the suggested mechanism of Cr segregation at the C11_b/C40 interface has not yet been proven. Further, the quantitative relationship between the extent of Cr segregation and the change in the lattice misfit remains unclear. In addition, it remains to be clarified whether Cr is the most suitable additive element for stabilizing the lamellar structure in MoSi₂/NbSi₂.

The phase-field method is a versatile technique for simulating the microstructural evolution and interfacial segregation in various materials on the basis of thermodynamics and the diffuse interface concept. Thus far, we have applied the phase-field method to study the microstructural evolution and segregation at interfaces such as stacking faults [20], twin boundaries [21], and antiphase boundaries [22]. In particular, this method has been used for quantitative investigations of interfacial segregation, which are difficult to be performed experimentally. The objective of this study was to elucidate the factors dominating the mechanism of interfacial segregation of additive elements in MoSi₂/NbSi₂ duplex silicide by using the phase-field method.

2. Method

2.1. Phase-field model

As illustrated in Figs. 1a and b, both the C11_b tetragonal structure and the C40 hexagonal structure consist of two sublattices, that is, a transition metal (TM) sublattice (represented by the red spheres) and a Si sublattice (blue spheres). Although a small number of Si atoms can occupy the TM sites, this number is negligibly small [23]. Therefore, for the sake of simplicity, it is assumed that no antisite atoms are formed, that is, Si atoms cannot occupy the TM sites and *vice versa*. The C11_b and C40

structures may appear quite different from one another, but the atomic arrangement within an atomic layer on the (110) plane of the $C11_b$ phase and that on the (0001) plane of the $C40$ phase are nearly identical (Fig. 1c, d). The difference between the two crystal structures is in the sequence of the stacking layers. That is to say, the $C11_b$ structure exhibits ACAC-type stacking whereas the $C40$ structure shows ABDABD-type stacking. Coherent lamellar interfaces are formed parallel to the $(110)_{C11_b}$ and $(0001)_{C40}$ planes [10,24]. Six types of lamellar interfaces with different interconnecting layers can be formed. A previous study based on first-principles calculations had indicated that the interface with the stacking sequence of ...DABDAB|ACAC.... has the lowest interfacial energy.

Figure 2a illustrates the atomic arrangement of the lamellar interface with the lowest energy. Hereafter, the $C40$ phase is described as the matrix and is drawn on the left-hand side for explaining the phase-field model used, in contrast to the description in the Introduction. This is because the $C11_b$ phase precipitates from the $C40$ phase during the formation of the lamellar structure, and it is convenient to regard the $C40$ phase as the matrix in the model. The order parameter, φ , is defined so that $\varphi = 0$ represents the $C40$ phase and $\varphi = 1$ represents the $C11_b$ phase (Fig. 2b). In order to distinguish between the ACA-type stacking of the $C40$ structure and the ABD-type stacking of the $C11_b$ structure, the stacking of at least three layers need to be taken into account. For the D layer, which is indicated by the green arrow, the third layer (counted from itself) on the interface side is the B layer, which is within the ABD-type stacking of the $C40$ phase. However, for the A layer, which is indicated by the cyan arrow, the third layer (i.e., the A layer indicated by the purple arrow) is no more within the $C40$ structure but is in the $C11_b$ structure instead. Accordingly, we consider the A layer with the cyan arrow to be in an intermediate state between the $C40$ structure and the $C11_b$ structure. Similarly, the B layer with the blue arrow is also considered to be in an intermediate state. In the same manner, the A layer with the purple arrow and the C layer with the magenta arrow,

which are on the $C11_b$ side, are considered to be in an intermediate state as well. The layers in the intermediate states are considered to be within the diffuse-interface region. The D layer, which is indicated by the green arrow, and the A layer, which is indicated by the red arrow, are considered to be at the edges of the diffuse-interface region. Accordingly, the $C40/C11_b$ diffuse interface, which has a thickness of 6 atomic layers, is defined as the region where the order parameter changes continuously from 0 to 1.

2.2. Alloy composition and initial conditions

The composition of the duplex silicide used was $(\text{Mo}_{0.862}\text{Nb}_{0.138})_{0.97}\text{Cr}_{0.03}\text{Si}_2$. This composition was determined as follows. First, the equilibrium compositions of the $C40$ and $C11_b$ phases were calculated for a pseudobinary $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ alloy. Equal volumes of the $C40$ and $C11_b$ phases with equilibrium concentrations were connected. Then, Cr atoms in an amount of 1 at% were substituted uniformly at the TM sites in both the phases, while keeping the ratio of the Mo and Nb concentrations in each phase constant. This resulted in the composition being $(\text{Mo}_{0.862}\text{Nb}_{0.138})_{0.97}\text{Cr}_{0.03}\text{Si}_2$.

2.3. Free energy

In the phase-field simulations, the total free energy of the system needs to be described as a functional of the order parameter and the solute concentrations, which are functions of the position in the simulated space. The chemical free energy, the gradient energy, and the elastic strain energy are taken to be components of the total free energy. Each energy component is described in detail below.

2.3.1. Chemical free energy

The chemical free energy densities of the $C40$ and $C11_b$ phases were evaluated by the CALPHAD method [25] using thermodynamic data available in the literature [23, 26]. Because there were no thermodynamic data for the Mo-Si-Cr system, these were

estimated from the MoSi₂-CrSi₂ pseudobinary phase diagram [27] using the software Thermo-Calc. First, the energy densities of the C40 (f_{C40}) and C11_b phases (f_{C11b}) were calculated as functions of the temperature and composition using the CALPHAD method. Then, the chemical energy density, f_{chem} , of the intermediate state was defined as

$$f_{\text{chem}}(c_M, f) = f_{C40}(c_M)h(f) - f_{C11b}(c_M)(1 - h(f)) + W_{\text{interface}} \times g(f) \quad (1)$$

where $h(f)$ is the interpolation function and $g(f)$ is the double-well function. The interpolation function, $h(f)$, should increase monotonically with an increase in φ from 0 to 1, satisfying the conditions $h(0) = 0$, $h(1) = 1$, and $(dh/df)_{f=0} = (dh/df)_{f=1} = 0$. The double-well function, $g(f)$, should have two minima, namely, at $g(0) = 0$ and $g(1) = 0$. The first two terms of Eq. (1) are for interpolating the energies of the C40 and C11_b phases, respectively. The third term of Eq. (1) is for penalizing the intermediate state. $W_{\text{interface}}$ is a parameter that determines the magnitude of the energy penalty. Several types of functions have been suggested for $h(f)$ and $g(f)$. In this study, the following functions were employed:

$$h(f) = f - \frac{\sin(2\rho f)}{2\rho} \quad (2)$$

$$g(f) = \frac{1 - \cos(2\rho f)}{2\rho} \quad (3)$$

The value of $W_{\text{interface}}$ can be derived from the interfacial energy, γ , and the thickness of the diffuse interface, d , as $W_{\text{interface}} = \gamma/d$. In the present study, the value of $W_{\text{interface}}$ was determined to be 171 J/mol from $\gamma = 27.2$ mJ/m², which was determined from first-principles calculations [28], and $d=1.3$ nm, which is the thickness of the 6 atomic layers. The chemical free energy is plotted in Fig. 3 as a function of φ and the Nb concentration, with the concentrations of Si and Cr being fixed at $c_{\text{Si}} = 66.7$ at% and $c_{\text{Cr}} = 1.0$ at%, respectively. The free energy curves of the C40 ($\varphi = 0$) and C11_b phases ($\varphi = 1$) could be interpolated smoothly using the function $h(f)$, with the hump corresponding to the term $W_{\text{interface}} \times g(f)$ in Eq. (1).

2.3.2. Gradient energy

The gradient energy is the excess free energy associated with the inhomogeneities in the order parameter and the solute compositions. Here, Mo is considered the solvent while Nb and Cr are the solutes. The Nb and Cr concentrations (c_{Nb} and c_{Cr} , respectively) are defined as independent variables and the Mo concentration (c_{Mo}) is the dependent variable. The Si concentration is fixed at 2/3. Then, the gradient energy density is given by

$$f_{\text{grad}}(\nabla c_{\text{Nb}}, \nabla c_{\text{Cr}}, \nabla f) = k_{\text{Nb}}(\nabla c_{\text{Nb}})^2 + k_{\text{Cr}}(\nabla c_{\text{Cr}})^2 + k_{\text{NbCr}}\nabla c_{\text{Nb}}\nabla c_{\text{Cr}} + k_f(\nabla f)^2 \quad (4)$$

where k_f , k_M , and $k_{MM'}$ ($M \neq M'$, $M = \text{Nb, Cr}$) are the gradient energy coefficients for the order parameter, the concentration of the solute M , and the product of the concentration gradients of the different solutes, respectively. The value of k_f was determined to be 2.66×10^{-11} J/m from the interfacial energy (27.2 mJ/m²) and the interfacial thickness (1.3 nm) on the basis of the equilibrium-interface condition. It is usually difficult to determine the values of k_M and $k_{MM'}$. The values of the gradient energy coefficients can be derived *a priori* if the free energy density of the nonuniform system has been described as a function of the gradients. However, the description of the free energy used in the CALPHAD method, which was employed in the present study, is applicable only in the case of uniform systems. On the other hand, the gradient energy for the solute concentration can be neglected only in the case of an ideal solution and cannot be neglected for a model based on regular solutions, which was the one used in the present study on the basis of the CALPHAD method. It is quite difficult to determine the accurate value of the gradient energy coefficients. Therefore, in the present study, the largest possible gradient energy coefficients were estimated from the free energy curves of the C11_b and C40 phases in MoSi₂-NbSi₂, MoSi₂-CrSi₂, and NbSi₂-CrSi₂ pseudobinary systems by assuming that the energy penalty at the C40/C11_b interface can be attributed only to the compositional variation and the gradient energy

for the solute concentration. The method for deriving the solute gradient energy coefficient is described in the Appendix. As will be described in the Results section, the contribution of the gradient energy for the solute atoms was small even when the possible maximum values were used for the gradient energy coefficients.

2.3.3 Elastic strain energy

The elastic strain energy arising from the lattice mismatch between the $C40$ and $C11_b$ structures can be described on the basis of Hooke's law using the following equations.

$$f_{\text{str}}(c_{\text{Nb}}, c_{\text{Si}}, c_{\text{Cr}}, \phi) = \frac{1}{2} \int C_{ijkl} \varepsilon_{ij}^{\text{el}} \varepsilon_{kl}^{\text{el}} dV \quad (5)$$

$$\varepsilon_{ij}^{\text{el}} = \varepsilon_{ij}^{\text{total}} - \varepsilon_{ij}^{\text{eigen}}(c_{\text{Nb}}, c_{\text{Cr}}, \phi) \quad (6)$$

$$e_{ij}^{\text{eigen}}(c_{\text{Nb}}, c_{\text{Cr}}, f) = h_{ij, \text{Mo}} c_{\text{Mo}} f + h_{ij, \text{Nb}} c_{\text{Nb}} f + h_{ij, \text{Cr}} c_{\text{Cr}} f. \quad (7)$$

C_{ijkl} is the elastic constant, e_{ij}^{el} the elastic strain, e_{ij}^{total} the total strain, e_{ij}^{eigen} the eigenstrain, and η_{ij}^{el} the lattice mismatch. The lattice mismatch between the $C11_b$ phase and the $C40$ phase can be determined from the differences in the sizes of the equivalent supercells, which are given in Eq. (9). The lattice sizes of the $C40$ and $C11_b$ disilicides of each transition metal were calculated by defining equivalent supercells in the two crystal structures as follows:

$$\begin{aligned} l_1^{C40} &= 2\sqrt{3}a_{C40}, \quad l_1^{C11_b} = 2c_{C11_b} \\ l_2^{C40} &= a_{C40}, \quad l_2^{C11_b} = \sqrt{2}a_{C11_b} \\ l_3^{C40} &= 2c_{C40}, \quad l_3^{C11_b} = 3\sqrt{2}a_{C11_b} \end{aligned} \quad (8)$$

The lattice parameters and lattice sizes of the transition metal disilicides are listed in Table 1. The lattice sizes of CrSi_2 in all the three directions were smaller than those of MoSi_2 and NbSi_2 ; this was true for both the $C40$ and $C11_b$ structures.

The equivalent supercells for both the $C11_b$ phase and the $C40$ phase could be

categorized as orthorhombic lattices, that is, all three axes were perpendicular to each other ($\alpha = \beta = \gamma = 90^\circ$) in both the equivalent supercells. In this case, the shear terms of the lattice mismatch were all zero, and we needed to consider only the orthogonal components of the eigenstrain attributable to the lattice mismatch.

For the sake of simplicity, homogeneous elasticity was assumed (i.e., the difference in the elastic moduli of the $C40$ and $C11_b$ phases was neglected), and the elastic constants of $C11_b$ - MoSi_2 [29] were used for the values of C_{ijkl} . e_{ij}^{eigen} was defined as a linear function of the order parameter, ϕ , and the solute concentrations on the basis of Vegard's law. The lattice mismatch for the transition metal, M , was defined using the lattice sizes of its disilicide, MSi_2 , as shown below.

$$\eta_{ij,M} = \begin{cases} (l_{i,\text{MSi}_2}^{C11_b} - l_{i,\text{MSi}_2}^{C40}) / l_{i,\text{MSi}_2}^{C40} & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad (9)$$

The lattice sizes l_1 , l_2 , and l_3 of the disilicides MoSi_2 , NbSi_2 , CrSi_2 , respectively, were derived from the lattice parameters of the $C40$ and $C11_b$ structures, which were determined using first-principles calculation. The lattice parameters included those of fictitious disilicides, which cannot thermodynamically have a $C40$ - or $C11_b$ -structure and thus do not exist. The ability to determine these values highlights the advantage of using first-principles calculations. The elasticity problem was solved by using Green's function in the formalism of Khachaturyan's microelasticity theory [30].

2.4. Time evolution

The total energy of the system, G_{sys} , can be calculated by integrating the summation of the chemical free energy, the gradient energy, and the elastic strain energy as follows:

$$G_{\text{sys}} = \int \left[f_{\text{chem}}(c_{\text{Nb}}, c_{\text{Si}}, c_{\text{Cr}}, \bar{f}) + f_{\text{grad}}(c_{\text{Nb}}, c_{\text{Si}}, c_{\text{Cr}}, \bar{f}) + f_{\text{str}}(c_{\text{Nb}}, c_{\text{Si}}, c_{\text{Cr}}, \bar{f}) \right] dV \quad (10)$$

G_{sys} is the functional of the solute concentrations and the order parameter, which are functions of the position in the simulated space. The solute concentrations c_{Nb} and c_{Cr} were independent variables because c_{Si} was fixed at $2/3$, as mentioned above. The

concentration of Mo could be treated as a dependent variable of c_{Nb} and c_{Cr} owing to the relation $c_{\text{Mo}} = 2/3 - c_{\text{Nb}} - c_{\text{Cr}}$. The spatial distributions of c_{Nb} , c_{Cr} , and φ evolved to decrease the total energy of the system (G_{sys}) such that the Cahn-Hilliard equation [31] for c_{Nb} and c_{Cr} and the Allen-Cahn equation [32] for φ could be solved simultaneously. The Cahn-Hilliard equation for a multielement system is

$$\frac{\partial c_M}{\partial t} = \left[\frac{D_M c_M}{kT} \left\{ (1 - c_M) \nabla \left(\frac{\delta G_{\text{sys}}}{\delta c_M} \right) - \sum_{M' \neq M} c_{M'} \nabla \left(\frac{\delta G_{\text{sys}}}{\delta c_{M'}} \right) \right\} \right] \quad (M, M' = \text{Nb, Cr}) \quad (11)$$

where D_M is the self-diffusion coefficient of the element M . The diffusion coefficients of transition metal atoms are assumed to be equal to that of the self-diffusion of Mo along the a -axis in $\text{C11}_b\text{-MoSi}_2$; this value is available in the literature [33]. The Allen-Cahn equation is

$$\frac{\partial \varphi}{\partial t} = -\alpha \left(\frac{\delta G_{\text{sys}}}{\delta \varphi} \right) \quad (12)$$

where α is the mobility for the transformation between the C40 phase and the C11_b phase. The evolutions of the distributions of the order parameter and the concentrations were determined by solving Eq. (11) and Eq. (12) simultaneously.

2.5. Simulation conditions

2.5.1 Equilibration of a static interface without segregation energy

In the initial condition, equal volumes of the C40 phase, which had a composition of $(\text{Mo}_{0.968}\text{Nb}_{0.032})_{0.97}\text{Cr}_{0.03}\text{Si}_2$, and the C11_b phase, whose composition was $(\text{Mo}_{0.756}\text{Nb}_{0.244})_{0.97}\text{Cr}_{0.03}\text{Si}_2$, were connected with a sharp interface at the center of the system. The overall alloy composition was $(\text{Mo}_{0.862}\text{Nb}_{0.138})_{0.97}\text{Cr}_{0.03}\text{Si}_2$, as mentioned above. The composition of each phase was determined as follows. First, the equilibrium compositions of the C40 and C11_b phases for the pseudobinary alloy with an overall composition of $(\text{Mo}_{0.862}\text{Nb}_{0.138})\text{Si}_2$ were calculated to be $(\text{Mo}_{0.756}\text{Nb}_{0.244})\text{Si}_2$ and $(\text{Mo}_{0.968}\text{Nb}_{0.032})\text{Si}_2$, respectively. Then, 1 at% transition metal atoms (i.e., Mo and Nb)

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3 were replaced with those of Cr, keeping the ratio $c_{\text{Nb}}/c_{\text{Mo}}$ constant. The system
4 simulated was 24 nm long. A one-dimensional (1D) simulation box with 256 grid points
5 was used. The periodic boundary condition was employed at the edges of the grid to
6 calculate the elastic strain energy. Because of the periodic boundary condition, it was
7 imagined that another interface was formed on the edges of the grid. The profiles of the
8 order parameter and the solute concentrations were symmetric about the center of the
9 two interfaces. Therefore, only the middle half of the system is displayed in the results.
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11 [Figure 4](#) shows the profiles of the order parameter and solute concentrations under the
12 initial condition. The distributions of the order parameter and solute concentrations are
13 relaxed until an equilibrium is reached at 1673 K. The simulations were performed for
14 two cases, namely, while taking the elastic strain energy into account and while not
15 doing so. The effects of the relaxation of the lattice misfit were examined by comparing
16 the results for the two cases.
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33 *2.5.2 Equilibration of a static interface with segregation energy*

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35 In the simulations described above, the diffuse interface was defined as a region
36 where the local state monotonically changes from the $C40$ phase to the $C11_b$ phase, with
37 the energy penalty determined by the double-well potential, as is often the case with
38 conventional phase-field simulations. In such cases, chemical interactions between the
39 interface and the solute atoms (i.e., the Cr on-site energy difference between the bulk
40 and the interface) are not taken into account, and segregation owing to chemical
41 solute-interface interactions cannot be simulated. Here, an improved model was
42 developed by taking into account the interactions between the additive atoms and the
43 atomic layers within the diffuse interface. In order to take into account the stability of
44 the additive elements at each atomic layer around the interface, the segregation energies
45 were determined through first-principles calculations. The procedure for determining
46 the segregation energy through first-principles calculations has been described in detail
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previously [28]. A summary of the procedure is as follows. First, a superlattice with the interface is formed, as depicted in Fig. 2a. Then, the energies of superlattices that have the additive Cr atoms at the TM sites on one of the 6 atomic layers within the diffuse interface are calculated through first-principles calculations. The energy of the superlattice in which a Cr atom is located on the layer on the C40 matrix side of the diffuse interface (i.e., the g layer in Fig. 2a) is used as the reference state energy. For conventional alloys, the chemical interactions between the interface and the solute atoms can be evaluated by taking into account only the electronic internal energy. Recently, theoretical studies have revealed that lattice vibrations could play a significant role in determining the phase stability in alloys [34-37]. The segregation energy was calculated by taking into account the vibrational free energy contributions. It was found that the segregation energies of Cr atoms at the atomic layers within the interface region changed differently with an increase in the temperature. This suggested that the temperature affected the segregation energy function of Cr atoms, owing to its vibrational contribution. Therefore, segregation energies with a vibrational contribution were used in the present study.

In order to use the discrete data on the segregation energy in the continuum model of the phase-field method, a continuous function of the order parameter, φ , which describes the energy change due to the change in the locations of the Cr atoms within the diffuse interface is needed. This function should be differentiable with respect to φ over the entire range of $0 < \varphi < 1$. As the simplest case of this function, the segregation energy function was defined by using Gaussian functions to connect the discrete points corresponding to the segregation energies for the discrete values of φ corresponding to the positions of the atomic layers within the interface region. Simply by adjusting the peak positions and broadnesses of the Gaussian functions, we could use them to generate the segregation function to fit the discrete points.

First, the energy of a Cr atom in the C40 phase ($\varphi = 0$) and that in the C11_b phase

($\phi=1$) are defined as 0 and $\Delta e_{\phi=1.0}$, respectively. Then, a function $E_{\text{Cr}}^{\text{base}}(f)$ is defined by interpolating these energies simply using the interpolation function $\{1 - \cos(p\phi)\}/2$ as $E_{\text{Cr}}^{\text{base}}(\phi) = \Delta e_{\phi=1.0} \{1 - \cos(\pi\phi)\}/2$ (13)

The function $E_{\text{Cr}}^{\text{base}}(\phi)$ is used as the baseline to describe the energy of a Cr atom within the diffuse interface, where $0 < \phi < 1$. The segregation energy function $E_{\text{Cr}}^{\text{seg}}(\phi)$ is described as

$$E_{\text{Cr}}^{\text{seg}}(\phi) = \Delta e_{\phi=0.2} \exp\left\{\frac{-(\phi-0.2)^2}{b}\right\} + \Delta e_{\phi=0.4} \exp\left\{\frac{-(\phi-0.4)^2}{b}\right\} + \Delta e_{\phi=0.6} \exp\left\{\frac{-(\phi-0.6)^2}{b}\right\} + \Delta e_{\phi=0.8} \exp\left\{\frac{-(\phi-0.8)^2}{b}\right\} + \Delta e_{\phi=1.0} \left\{\frac{1 - \cos(\pi\phi)}{2}\right\} \quad (14)$$

where $\Delta e_{\phi=p}$'s ($p = 0.2, 0.4, 0.6, 0.8$) are the deviations from $E_{\text{Cr}}^{\text{base}}(f)$ of the segregation energies of Cr atoms located at the 2nd, 3rd, 4th, and 5th layer from the C40 side edge ($\phi = 0$), and b is a constant that determines the spread of the Gaussian functions. The Gaussian functions are used as to connect the segregation energies smoothly.

Figure 5a shows the Cr segregation energies at the 6 atomic layers as determined using first-principles calculations as well as the segregation energy function used for interpolating the segregation energies. The black points represent the segregation energies at 1673 K, determined by taking in account the electronic internal energy as well as the vibrational free energy contributions [28]. The solid line represents the segregation energy function recalculated for 1673 K and fitted to the segregation energies at 1673 K. The double circles and the dotted line represent the previously used segregation energies and the segregation energy function determined using only the electronic internal energy, respectively; these are shown for comparison. It can be seen that the segregation energies at the layers corresponding to $\phi = 0.6$ and $\phi = 1.0$ were significantly lowered by the lattice vibrations and that the decreases were approximately 0.1 eV. It should be noted that the energy at $\phi = 0.6$ is lower than that at $\phi = 0$ (C40

matrix). The segregation energy is determined by both the electronic interactions and the harmonic interactions between the vibrating atoms. However, as of now, it is difficult to determine its physical origin.

The segregation energy, $E_{\text{Cr}}^{\text{seg}}(\phi)$, given by Eq. (14), is for a unit concentration of solute atoms. Because the local excess energy due to segregation should be proportional to the solute local concentration when one neglects interactions among the solute atoms, the product of the segregation energy function and the Cr concentration (i.e., $E_{\text{Cr}}^{\text{seg}}(\phi) \cdot c_{\text{Cr}}$) is added to the local free energy density. This excess energy is shown in Fig. 5b as a function of the order parameter and the Cr concentration only for the case in which the vibrational contribution is considered. There are peaks along the lines corresponding to $\phi = 0.4$ and $\phi = 0.8$, while there is a valley along the line $\phi = 0.6$. The height of peak and the depth of the valley decrease with a decrease in the Cr concentration. The relaxation of the static interface was simulated under the same initial condition as that used in the simulation in which the segregation energy was considered (see Section 2.5.1).

It might appear that there is no need to perform a 1D phase-field simulation of interface equilibration as first-principles calculations of the segregation energy have already been performed. However, the first-principles calculations did not take into account the interface lattice misfit, as it is computationally very expensive and nearly impossible to perform first-principles calculations related to the relaxation of the misfit. Thus, a combination of first-principles calculations and phase-field simulations is required. Further, the first-principles calculations were performed for an interface between the $C11_b$ and $C40$ phases with the identical composition of MoSi_2 , i.e. Nb-free system. Therefore the 1D phase- field simulation using the first principles calculation result was needed to take into account the effect of Nb on the interfacial segregation.

3. Results

3.1. Equilibrated static interface without segregation energy

Figures 6a-d show the equilibrated profiles of the order parameter, ϕ , and the concentrations of Mo, Nb, and Cr near the C40/C11_b interface for the case where Cr is included as an additive element under the condition described in Section 2.5.1. Here, the segregation energy is not taken into account in order to examine only the effect of elastic-strain relaxation on the segregation. The results of the cases with and without the elastic strain energy are presented by the solid and dotted lines, respectively. There is no significant difference between the results for the cases with and without the elastic strain energy. Mo and Nb atoms are distributed in both phases; however, Cr atoms are distributed mostly in the C40 phase. As a result, the volume fraction of the C40 phase has increased. Although the distribution of Cr atoms has changed significantly from that corresponding to the initial conditions, no segregation is observed at the interface, contrary to what was seen in the experimental results [18]. The concentration of Nb in the C11_b phase in the case where the elastic strain energy was considered (solid line) was slightly lower than that in the counter case (dotted line). However, the difference was as small as 0.1 at%. The difference due to the presence and absence of elasticity on the profiles of Cr-concentration was smaller; the value of c_{Cr} was 1.6 at% in the C40 phase and 0 at% in the C11_b phase in both cases. Thus, the effect of the elasticity on the solute distribution was very small, and it was difficult to attribute the experimentally observed Cr segregation to the relaxation of the lattice misfit. Figures 6e-g show the distribution of the elastic strain (e_{11}^{el} , e_{22}^{el} , and e_{33}^{el}). The result obtained without considering the elastic strain energy (dotted lines) is also superimposed for comparison. There is little difference between the two results. The elastic strain, which is calculated using Eq. (6), changes continuously in the interface region. The absolute values of the elastic strain components, e_{11}^{el} , e_{22}^{el} , and e_{33}^{el} , are as large as approximately 0.5, 1, and 1 %, respectively. Further, they vary significantly in the interface region even after the

relaxation. Thus, the relaxation of the lattice misfit owing to solute redistribution is not very significant. This implies that the experimentally observed strong Cr segregation cannot be attributed to the relaxation of the lattice misfit but is caused by another mechanism.

3.2. Equilibrated static interface with segregation energy

Figures 7 show the equilibrated profiles of the order parameter (Fig.7a) and the solute concentrations (Figs.7b-d) simulated using the segregation energy while considering the lattice vibrational contribution. Unlike the results obtained without taking into account the segregation energy (Figs. 6a-d), the extent of Cr segregation at the interface was quite significant. Figures 7e-g are the solute concentration profiles measured experimentally using transmission electron microscopy (TEM)/EDS [18] across the equilibrated interface in the Cr-added duplex silicide $\text{MoSi}_2/\text{NbSi}_2$ at 1673 K, that is, at the same temperature at which the segregation energy was calculated while taking the lattice vibrations into account. Even though the ranges of the horizontal axis corresponding to the simulation and experimental results were different, probably because of the resolution of the EDS system used, the profiles were similar in the sense that the Cr concentration was higher than that in the C40 matrix, as was the case with the X-ray intensity corresponding to Cr. The ratios of the concentrations of the other elements (i.e., of Mo and Nb) in the C40 phase and C11_b phases were also similar to those of the X-ray intensities determined using EDS. Thus, the simulated segregation profile was qualitatively in good agreement with that obtained experimentally. This suggests that Cr segregation at the C40-NbSi₂/C11_b-MoSi₂ interface was mostly due to the segregation energy. However, the Cr concentration at the interface appeared to be relatively lower than the experimentally measured peak concentration, which was nearly two times higher than the average concentration.

The difference between the two results, namely, the one where the elastic strain energy

was considered and the one where it was not, was very small; this was also the case when the segregation energy was not considered (Figs. 6a-d). The changes in the Nb and Cr concentrations owing to the elastic strain energy were all less than 0.1 at% in both phases. The Cr concentration at the peak segregation was also nearly equal at approximately 0.9 at%. That is to say, there was no significant effect of the elastic strain on the segregation profiles. Therefore, the segregation energy (i.e., the chemical interaction between the solute atoms and the interface) appeared to be primarily responsible for the segregation. However, the simulated extent of solute segregation appeared to be smaller than the experimentally detected one [18].

4. Discussion

4.1. Contributions of the various energy components to segregation

The extent of Cr segregation at the $C40/C11_b$ interface noticed in the simulation (Fig. 7d) was comparable to that measured experimentally using STEM-EDS (Fig. 7g) in the sense that the Cr concentration at the $C40/C11_b$ interface was higher than those in the $C40$ and $C11_b$ lamellae. Two possible reasons had been suggested for this phenomenon in previous studies [19, 33]. One is the relaxation of the lattice misfit by interfacial segregation [19], and the other is attributable to the segregation energy, that is, the chemical interaction between the solute Cr and the interface, including the electronic and lattice vibrational contributions, whose importance has recently been highlighted through first-principles calculations [28]. In the first-principles calculations to determine the segregation energy, the interatomic distance at the $C11_b/C40$ interface was fixed to the value used for $C11_b\text{-MoSi}_2$; this was true for both the $C11_b$ side and the $C40$ side. This restriction of the interatomic distance was necessary to perform the calculations, as one would need to use an unrealistically large supercell to take into account the elastic relaxation at the interface. This is nearly impossible even under highly parallelized state-of-the-art computational environments. Therefore, the effect of

the relaxation of the lattice misfit was examined using the phase-field method. Next, we discuss the primary factors responsible for the segregation.

Figure 8 shows the profiles of the components of the diffusion potentials for Cr as determined using the CALPHAD method. These are the chemical free energy, the gradient energy, the elastic energy, and the segregation energy, that is, the chemical potential, the gradient potential, the elastic potential, and the segregation potential, respectively. The variation in the elastic potential across the interface was smaller than those in the other components (i.e., the segregation potential, the gradient potential, and the chemical potential) by more than one order of magnitude. This can explain why the concentration profiles were not affected when one included the elastic energy. This seems to be a characteristic of the $\text{MoSi}_2\text{-NbSi}_2$ system, in which the chemical interactions between the solute atoms are strong. A study in which the same calculation method was employed to investigate solute segregation at stacking faults in cobalt alloys has shown that the elastic strain has additional significant effects [20].

4.2. Possible reasons for the differences in the experimental and simulation results

There were a few differences between the experimentally measured extent of segregation and the simulated one. The experimentally measured extent of Cr segregation (Fig. 7g) was higher than that simulated. In spite of the broadness of the segregation peak of the experimentally observed Cr concentration, the height of the peak was nearly double the background height. This suggests that the number of segregated Cr atoms was much higher than that simulated in the present study. There are three possible reasons for the differences between the simulated profile and the experimental one.

4.2.1. Gradient energy coefficient of Cr

The first is the gradient energy, which inhibits steep variations in the concentration and

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3 hence sharp segregation. The gradient energy for the Nb concentration was derived
4 from the maximum energy penalty for the intermediate state between the C40 phase and
5 the C11_b phase with respect to the common tangent of the free energy curves of the
6 two-phases in the MoSi₂-NbSi₂ pseudobinary system, as described in the Appendix.
7 However, the gradient energy for the Cr concentration could not be derived in the same
8 manner, because the free energy curves for the two phases in the MoSi₂-CrSi₂ system
9 did not intersect. This suggests that the energy penalty between the two phases in this
10 system and the gradient energy derived from it were very low or negative; however, no
11 definite values were derived. In the present study, a gradient energy one-tenth of that for
12 the Nb concentration was used for the Cr concentration by way of trial. The use of a
13 smaller gradient energy for the Cr concentration would result in more steep segregation.
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28 *4.2.2. Effect of Nb on the Cr segregation energy*

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30 The second possible reason for the difference between the experimental and simulation
31 results is related to the segregation energy determined through first-principles
32 calculations [28]. The segregation energy of Cr was calculated for the interface between
33 the (0001) plane of the C40 phase and the (1 1 0) plane of the C11_b phase, with the
34 composition being MoSi₂ for both phases. The segregation energy may depend on the
35 existence of Nb solute atoms and may change to make the segregation more prominent
36 after the addition of Nb although the segregation energy calculated without the lattice
37 vibration, was not affected significantly by the presence of Nb atom at an Mo-site.
38 However, it is computationally very expensive to examine the effect of Nb addition on
39 the Cr segregation energy because of the large number of configurations of the Cr and
40 Nb atoms. Using first-principles calculations to determine the Cr segregation energy in
41 Mo-Nb-Si-Cr quaternary systems remains a challenge for the future.
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58 *4.2.3. Effect of interface migration*

The third reason is the related to the solute redistribution associated with interfacial migration during the growth of the $C11_b$ phase. The lamellar structures of the $C40$ and $C11_b$ phases are formed by the nucleation and growth of Mo-rich $C11_b$ lamellae from the $C40$ matrix, which is supersaturated with Mo. Because Nb and Cr atoms are partitioned preferentially to the $C40$ phase, they are expelled from the growing $C11_b$ phase and pile up in front of the migrating $C11_b/C40$ interface. Thus, Cr segregation can take place during the solute redistribution associated with interface migration. It might be suggested that the interface segregation detected experimentally is affected by the redistribution during the growth of the $C11_b$ phase. That is to say, the solute piles up at the migrating interface. To address this issue, experiments to measure the solute diffusivities are underway.

5. Conclusions

The mechanism responsible for the segregation of Cr to the $C11_b/C40$ lamellar interface in a $\text{MoSi}_2\text{-NbSi}_2$ alloy was investigated using a new phase-field model that took into account various factors, including the elastic energy and segregation energy, on the basis of first-principles calculations, along with the effects of lattice vibrations. Simulations of interface relaxation were performed under various conditions both by taking these factors into consideration and without doing so. Cr segregation comparable to that measured experimentally could be reproduced when the segregation energy was taken into account along with the lattice vibrations, whereas no segregation was noticed in the case where only the elastic energy was taken into account. Further, it was found that Cr segregation does not induce significant relaxation of the lattice misfit. Thus, it could be surmised that the segregation energy, including the effects of the lattice vibrations, is responsible for Cr segregation and not the relaxation of the lattice misfit. These findings suggest that it is important to take into account the segregation energy in

addition to the elastic interactions when searching for more effective additive elements to improve the thermal stability of lamellar structures in disilicides as well as the creep resistance of these materials.

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Appendix

When deriving the gradient energy coefficient, K , using Equation (4), which is the one used in the simulations performed in this study, the calculations are based on an equilibrated profile of the free energy.

Figure A1 shows the free energy data used to derive the gradient energy coefficient for the solute concentration. Figure A1a shows the free energy curves of the C11_b and C40 phases in the MoSi₂-NbSi₂ pseudobinary system at 1673 K, and Fig. A1b shows the energy penalty for the compositions deviating from the equilibrium ones.

The gradient energy for the Nb concentration was derived from the maximum energy penalty $\Delta f = 380$ J/mol. The possible maximum gradient energy coefficient can be derived by assuming that the maximum energy penalty is equal to the gradient energy for the Nb concentration in equilibrium; this is analogous to the free energy

condition for an equilibrated flat interface (i.e., to “Eq (2.14)” in Cahn and Hilliard’s study [31]), which is expressed as

$$\Delta f(c) = \kappa (dc/dx)^2$$

where $\Delta f(c)$ is the energy penalty, κ is the gradient energy, c is the solute concentration, and x is the one-dimensional coordinate. When using this equation to derive the gradient energy coefficient, one needs to assume that the gradient energy for the phase-field order parameter is zero. This assumption may not be accurate and may result in an overestimation of the value of the gradient energy for solute concentration. Therefore, we used the derived value only for confirming that the contribution of the gradient energy was negligibly small, as the true value of the gradient energy coefficient should be smaller than the value estimated in this manner.

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Table 1. Lattice parameters (nm) of transition metal (Mo, Nb, Cr) disilicides evaluated by first principles calculation, and lattice sizes (nm) defined by Eq. (9).

$C11_b$			$C40$		
	a	c	a	c	
MoSi ₂	0.3217	0.8277	0.4613	0.6619	
NbSi ₂	0.3290	0.7865	0.4819	0.6627	
CrSi ₂	0.3082	0.7534	0.4404	0.6369	

$C11_b$				$C40$		
	l_1	l_2	l_3	l_1	l_2	l_3
MoSi ₂	1.5730	1.3649	1.3649	1.5980	1.3839	1.3238
NbSi ₂	1.6554	1.3958	1.3958	1.6694	1.4457	1.3254
CrSi ₂	1.5068	1.3076	1.3076	1.5256	1.3212	1.2738

Fig. 1. Unit cells of (a) $C11_b$ -structure and (b) $C40$ -structure. Large balls show transition metals (Mo or Nb atoms) and small ones show Si atoms. Atomic arrangements on (c) (110) -plane of $C11_b$ -phase and (d) (0001) -plane of $C40$ -phase, which are parallel to the $C11_b/C40$ lamellar interface.

Fig. 2. (a) Atomic layers around the lamellar interface with the lowest interfacial energy and (b) definition of the order parameter. The green dotted boxes represent corresponding volumes in C40- and C11_b-structures for comparing the lattice sizes the structures.

Fig. 3. Free energy of $(\text{Mo}, \text{Nb})\text{Si}_2$ as a function of the order parameter φ and Nb concentration c_{Nb} at 1673 K.

Fig. 4. Initial distributions of (a) the order parameter and solute concentrations of (b) Mo, (c) Nb and (d) Cr across the interface.

Fig. 5. (a) Segregation energy of Cr on atomic layers in the diffuse interface calculated by first principles calculation (black solid circles) and segregation energy function defined to interpolate the segregation energies as a function of the order parameter ϕ . (b) Landscape of segregation energy as a function of the order parameter ϕ and concentration of additive Cr (c_{Cr}).

Fig. 6. (a-d) Profiles of (a) the order parameter and solute concentrations of (b) Mo, (c) Nb, (d) Cr across the interface. (e-g) Profiles of elastic strain in (e) x-direction, (f) y-direction and (g) z-direction. Solid and dotted lines show the results for the cases with and without elastic strain energy, respectively.

Fig.7. (a-d) Profiles of (a) order parameter and solute concentrations of (b) Mo, (c) Nb, and (d) Cr simulated by taking into the elastic strain energy. (e-g) Experimental concentration profiles of solute atoms (e) Mo, (f) Nb, and Cr measured by TEM-EDS [18].

Fig. 8. Profiles of components of diffusion potentials for Cr from chemical free energy, gradient energy, elastic energy and segregation energy, i.e. chemical potential, gradient potential, elastic potential and segregation potential, respectively. The variation of elastic potential across the interface is much smaller than those of segregation potential, gradient potential and chemical potential by a factor of more than one order of magnitude.

Fig A1. (a) Gibbs free energies of $C11_b$ -phase and $C40$ -phase for $MoSi_2$ - $NbSi_2$ pseudo binary system at 1673 K as a function of Nb concentration. (b) Energy penalty for the $C11_b$ phase and $C40$ phase with compositions deviating from the equilibrium ones.