

Article

Effect of Nb Content on the Stability and Electronic Properties at bcc-Fe/NbN Interface

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Abstract

First-principles calculations based on density functional theory were employed to systematically investigate the atomic structure, stability, and Nb segregation behavior of the bcc-Fe(100)/NbN(100) interface. Convergence tests of surface energy determined that an interface model consisting of 7 bcc-Fe layers and 5 NbN layers is appropriate. The work of adhesion and interfacial energy were calculated for four interface configurations with different terminations. Interface 2 was identified as the most thermodynamically stable configuration, exhibiting a work of adhesion of 0.569 J/m² and an interfacial energy of 3.221 J/m². Nb atoms displayed pronounced site-selective segregation at the interface; the segregation tendency decreases in the order site 1 (−0.74 eV) > site 2 (−0.59 eV) > site 4 (−0.38 eV) > site 3 (−0.24 eV). Electronic structure analysis indicated that strong hybridization between Nb-4d and Fe-3d orbitals near the Fermi level leads to localized charge accumulation, which is the electronic origin of interfacial strengthening. As the Nb concentration increases from 1.6 at.% to 6.3 at.%, the segregation energy continuously drops from −0.74 eV to −1.55 eV, the work of adhesion monotonically increases from 0.569 J/m² to 0.786 J/m², and the interfacial energy decreases from 3.221 J/m² to 2.374 J/m², demonstrating that Nb segregation significantly enhances the interfacial stability. The calculation results provide a theoretical framework for understanding the experimentally observed evolution of Nb(C,N) precipitates and offer insights for the optimization of Nb microalloying in 442D ferritic stainless steel.

Keywords: first principles; bcc-Fe/NbN interface; segregation energy; interfacial stability

1. Introduction

Ferritic stainless steels are widely used in automotive exhaust systems, chemical equipment, and architectural decoration owing to their excellent resistance to stress corrosion cracking and relatively low cost [1–3]. To meet the stringent requirements for the combined strength and toughness demanded by increasingly harsh service environments, microalloying has become an important technical approach for improving the performance of these steels. Among the microalloying elements, niobium plays an irreplaceable role in ferritic stainless steels. Niobium not only forms thermodynamically stable Nb(C,N) nano-precipitates with carbon and nitrogen atoms during high-temperature processing, producing a strong precipitation strengthening effect but also suppresses recrystallization

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and grain growth by solute drag, thereby refining the grain structure [4–6]. The synergistic action of precipitation strengthening and grain refinement imparts excellent comprehensive mechanical properties, including strength, toughness, and corrosion resistance, to Nb-bearing ferritic stainless steels.

Previous systematic experimental investigations on cold-rolled 442D ferritic stainless steel have revealed the temperature-dependent precipitation behavior of Nb [7,8]. Recent kinetic studies further elucidate the nucleation and growth mechanisms of Nb(C,N) precipitates in ferritic matrices, establishing a quantitative link between heat treatment parameters and precipitate evolution [9]. Transmission electron microscopy (TEM) observations confirmed that after annealing at 800 °C, a high density of Nb(C,N) precipitate particles with sizes of 20–50 nm were uniformly distributed in the matrix. Energy-dispersive spectroscopy analysis demonstrated the co-localization of Nb, C, and N within the precipitates, confirming their chemical composition [10]. These nano-precipitates form a large number of coherent or semi-coherent heterogeneous interfaces with the bcc-Fe matrix, which exert a strong pinning effect on dislocation motion and constitute the microstructural foundation for the high strength of the material. When the heat treatment temperature exceeds 900 °C, Ostwald ripening begins to coarsen the precipitates, and the interface density and interface character change significantly; above 1100 °C, a substantial fraction of the precipitates dissolves back into the matrix, with a corresponding increase in the concentration of solute Nb [11,12]. The changes in precipitate morphology, size, and volume fraction inevitably affect the bonding state of the interfaces with the matrix and, consequently, influence the macroscopic mechanical properties. Therefore, a thorough understanding of the atomic-scale structure and bonding strength of the bcc-Fe/NbN interface is of great scientific significance for revealing the precipitation strengthening mechanism and for guiding the optimization of heat treatment processes.

However, heterogeneous interfaces are buried inside the material, and key parameters such as atomic arrangement, electronic density of states, and interfacial bonding energy are difficult to obtain directly and quantitatively by experimental means [13,14]. Although high-resolution transmission electron microscopy can provide atomic-scale imaging of interfaces, its ability to resolve the chemical bonding states and energetic characteristics at the interface is limited. This experimental bottleneck has confined the understanding of the intrinsic nature of the Nb(C,N)/ferrite interface to a phenomenological level, and there is an urgent need to reveal the fundamental mechanism of interfacial bonding from the electronic structure perspective through theoretical simulation. In recent years, first-principles calculations based on density functional theory have demonstrated remarkable capability in studying metal/ceramic heterogeneous interfaces. By calculating the work of adhesion, interfacial energy, and the segregation energy of alloying elements, the strength of interfacial bonding and the microscopic mechanism by which it is regulated by alloying elements can be quantitatively elucidated at the atomic-electronic level [15–19]. Particularly, systematic DFT investigations of interfacial bonding and electronic structure have provided atomic-scale insights into the adhesion mechanisms and segregation energetics at metal/ceramic boundaries [20]. Yao et al. [21] employed first-principles methods to calculate the electronic properties of the NbN/ α -Fe interface in shipbuilding steel, revealing the charge density distribution and bonding characteristics at the interface. Dong et al. [22] investigated the atomic structure and electronic properties of the NbC/TiC heterogeneous nucleation interface. Nevertheless, for the bcc-Fe/NbN interface, a systematic theoretical comparison of the stability of different termination configurations, the most probable segregation sites of Nb atoms at the interface and their electronic origins, as well as the quantitative influence of Nb concentration on the interfacial properties, is still lacking.

In the present work, the bcc-Fe(100)/NbN(100) coherent interface, which represents the typical interface between the experimentally observed Nb(C,N) precipitates and the ferrite matrix, is constructed using first-principles methods. It should be noted that NbN is employed as a simplified structural analogue for the experimentally observed Nb(C,N) precipitates. Both phases crystallize in the NaCl-type structure, and previous first-principles studies have demonstrated that the interfacial bonding in such metal/ceramic systems is dominated by Nb–Fe metallic interactions, with the anion species (C versus N) exerting a minor influence on the adhesion strength (<5%) [21]. Thus, the NbN model captures the essential physics of Nb segregation behavior at the precipitate/matrix interface as a reasonable first-order approximation. The potential effect of carbon incorporation on the quantitative values of interfacial energy and segregation energy will be addressed in future work. By systematically calculating the work of adhesion and interfacial energy of four interface configurations with different terminations, the thermodynamically most stable interface structure is determined. On this basis, the segregation tendency of Nb atoms at different crystallographic sites near the interface is examined, and the electronic structure origin of the site selectivity is revealed from the perspectives of density of states and charge density difference. Furthermore, the evolution of the interfacial segregation energy, work of adhesion, and interfacial energy is investigated as the Nb concentration is varied from 1.6 at.% to 6.3 at.%. The calculated results are compared with the precipitate evolution characteristics obtained in previous experiments, aiming to establish a multi-scale correlation linking precipitates, interface structure, and electronic properties, and to provide a theoretical basis for the optimal design of Nb microalloying processes in ferritic stainless steels.

2. Materials and Methods

2.1. Calculation Methods

All calculations in this work were performed using the CASTEP code implemented in Materials Studio 2020 (BIOVIA, San Diego, CA, USA) with the plane-wave pseudopotential method within the framework of density functional theory. The exchange-correlation functional was treated with the generalized gradient approximation in the Perdew–Burke–Ernzerhof (GGA-PBE) form. All calculations in this paper account for spin polarization and fully incorporate the ferromagnetism of bcc-Fe. The magnetic moment of Fe atoms at the interface due to bonding effects is 2.2 μB , which closely matches the experimental value of 2.22 μB . Prior to the production calculations, systematic convergence tests were performed to determine the appropriate plane-wave cutoff energy and k-point mesh. Figure 1 presents the convergence behavior of the total energy with respect to cutoff energy and k-point sampling for both bcc-Fe and NbN bulk phases. For bcc-Fe, the total energy decreases with increasing cutoff energy and converges when the cutoff exceeds 380 eV. A similar convergence behavior is observed for NbN, with the total energy stabilizing above 380 eV. Regarding k-point convergence, the total energies of both bcc-Fe and NbN converge when the Monkhorst–Pack mesh is denser than $4 \times 4 \times 4$. Based on these tests, a plane-wave cutoff energy of 380 eV and a $4 \times 4 \times 4$ k-point mesh were adopted for all bulk calculations. For surface and interface models, a $4 \times 4 \times 1$ k-point mesh was used, consistent with the reduced periodicity along the surface normal direction [16–18]. Geometry optimization was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The iterative self-consistent convergence criteria were as follows: total energy less than 1.0×10^{-5} eV/atom, average atomic force lower than 0.03 eV/Å, maximum stress deviation of 0.05 GPa, and displacement tolerance less than 0.01 Å. The valence electron configurations employed were N 2s²2p³, Fe 3d⁶4s², and Nb 4s²4p⁶4d⁴5s¹, where the Nb 4d states are fully treated as valence electrons to ensure accurate description of interfacial orbital hybridization.

Using the GGA-PBE functional, the properties of bulk NbN and bcc-Fe were calculated and compared with experimental values, as shown in Table 1. The small difference between the calculated and experimental data confirms the rationality of the chosen parameters.

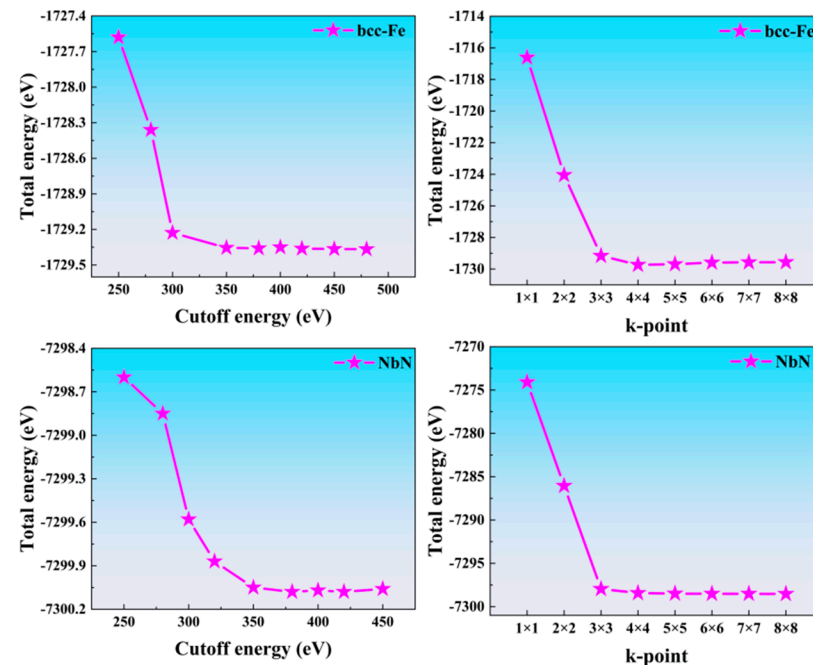


Figure 1. Convergence Test of Cutoff Energy and k-Points for bcc-Fe and NbN.

Table 1. Experimental (Expt) and calculated (GGA-PBE) lattice constants of bcc-Fe and NbN.

Phases	Method	a (Å)	V ₀ (Å ³)
bcc-Fe	Expt [23]	2.866	23.541
	GGA-PBE	2.860	23.394
NbN	Expt [24]	4.432	87.056
	GGA-PBE	4.418	86.234

2.2. Crystal Structure Model

The crystal structures of bcc-Fe and NbN are shown in Figure 2. NbN possesses an NaCl-type structure (B1, Pearson symbol cF8) with space group Fm-3m (No. 225); the ICSD Collection Code is 246144. Each unit cell contains four Nb atoms and four N atoms, with lattice constants $a = b = c = 4.45 \text{ Å}$, with $\alpha = \beta = \gamma = 90^\circ$. Ferrite exhibits a body-centered cubic atomic arrangement (A2, Pearson symbol cI2) with space group Im-3m (No. 229); the ICSD Collection Code is 43493. Each unit cell contains two Fe atoms, with lattice constants $a = b = c = 2.866 \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$.

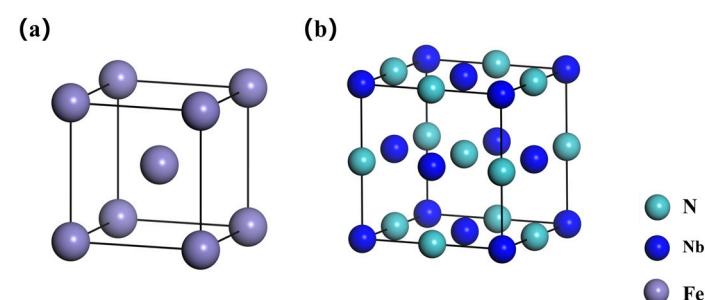


Figure 2. Crystal structures of bcc-Fe and NbN. (a) Fe(100); (b) NbN(100).

2.3. Surface Energy Characterization

The surface energy is a key parameter for characterizing the thermodynamic stability of a crystal surface; its physical essence is the energy required to cleave a crystal along a specific crystallographic plane to create new surfaces, and its magnitude directly reflects the relative stability of the surface structure. The surface energy of bcc-Fe(100) can be calculated using Equation (1) [22]:

$$E_{\text{Fe}}[E_{\text{slab}}(n) - n\Delta E]/2A \quad (1)$$

where $E_{\text{slab}}(n)$ is the total energy of the Fe(100) surface model (eV), n is the number of Fe atoms in the model, $\Delta E = E_{\text{slab}}^n - E_{\text{slab}}^{n-2}$ is the energy increment (eV/atom), and A is the area of the surface model (m²).

A is the area of the surface model (m²). Owing to the NaCl-type crystal structure of NbN, cleaving along the (100) plane yields two different surface terminations: one terminated by Nb atoms (Nb-termination) and the other terminated by N atoms (N-termination). To effectively suppress the dipole moment effect, all NbN(100) surface models were constructed with an odd number of atomic layers [15]. The surface energy of NbN(100) is given by:

$$E_{\text{NbN}} = [E_{\text{slab}}^{\text{NbN}} - N_{\text{n}}\mu_{\text{NbN}}^{\text{bulk}} - (N_{\text{Nb}} - N_{\text{N}})]/2A \quad (2)$$

where N_{Nb} and N_{N} are the numbers of Nb and N atoms in the NbN(100) surface model, $E_{\text{slab}}^{\text{NbN}}$ is the total energy of the surface model (eV), A is the surface area (m²), and $\mu_{\text{NbN}}^{\text{bulk}}$ is the chemical potential of bulk NbN (eV/atom).

Table 2 lists the surface energies of bcc-Fe(100) and NbN(100) with different numbers of atomic layers. For NbN(100), the surface energy converges rapidly with increasing layer number; when $n = 5$, the surface energy approaches 0.91 J/m². For bcc-Fe(100), the surface energy converges to 2.85 J/m² when $n \geq 7$. Based on these results and considering computational accuracy, an interface structure composed of 7 bcc-Fe layers and 5 NbN layers was selected, and a vacuum layer of 15 Å was added to eliminate interactions between the periodic images of the slabs.

Table 2. Surface energies of bcc-Fe(100) and NbN(100) as a function of layer number (J/m²).

n	bcc-Fe(100)	NbN(100)
3	3.47	1.24
5	2.86	0.91
7	2.85	0.93
9	2.86	0.91
11	2.85	0.92

When constructing the bcc-Fe(100)/NbN(100) heterogeneous interface, appropriate supercell expansions of the bcc-Fe(100) and NbN(100) unit cells are required to achieve lattice matching in the x - and y -directions. To calculate the lattice mismatch at the bcc-Fe(100)/NbN(100) interface, it is essential to adhere to the definition of interface matching, which requires a one-to-one correspondence between lattice basis vectors. The lattice mismatch formula is as follows:

$$\delta = \left| \frac{a_x - b_x}{b_x} + \frac{a_y - b_y}{b_y} \right| \quad (3)$$

where a_i and b_i ($i = x, y$) represent the distances along the x -axis and y -axis on either side of the interface, respectively. The calculation yields a minimum mismatch of 2.1%, indicating a co-lattice interface type (mismatch $\delta < 5\%$). The detailed interface formation process is illustrated in Figure 3.

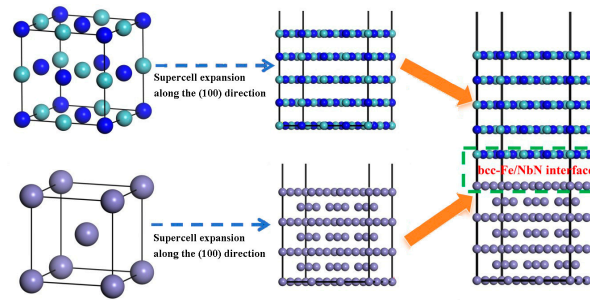


Figure 3. Construction process of the bcc-Fe(100)/NbN(100) interface.

There are two different stacking sequences for the bcc-Fe(100) surface and two different terminations for the NbN(100) surface, as shown in Figure 4. By combining these, four different bcc-Fe(100)/NbN(100) interface models were constructed, which are presented in Figure 5.

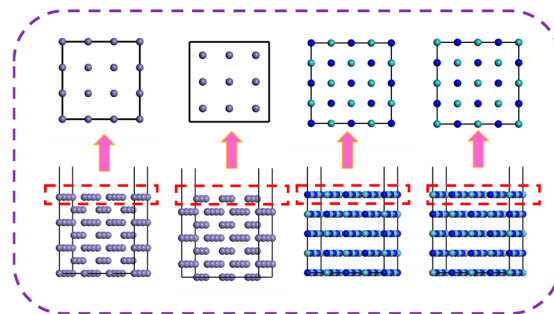


Figure 4. Termination models of bcc-Fe(100) and NbN(100).

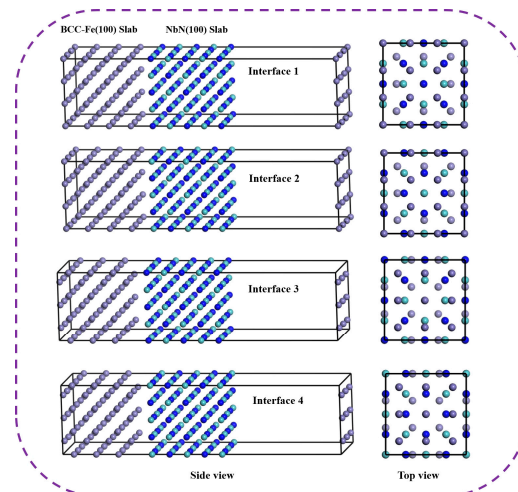


Figure 5. Four interface models of bcc-Fe(100)/NbN(100).

To ensure that spurious interactions between periodic slab images are fully eliminated, convergence tests with respect to vacuum layer thickness were performed. The surface energies of bcc-Fe(100) and NbN(100) were calculated with vacuum thicknesses of 10, 12, 15, and 18 Å, as summarized in Table 3. As the vacuum thickness increases from 10 Å to 15 Å, the surface energy of NbN(100) decreases from 0.947 J/m² to 0.910 J/m² ($\Delta = 0.037$ J/m²); further increasing to 18 Å changes the value by merely 0.002 J/m² (<0.3% relative variation). A similar trend is observed for bcc-Fe(100): the variation from 12 Å to 15 Å is 0.008 J/m², and from 15 Å to 18 Å is 0.002 J/m². The surface energies of both systems converge at 15 Å. Moreover, the odd-layer (5-layer) construction of the

NbN(100) slab effectively suppresses the surface dipole moment. Balancing computational accuracy and efficiency, a vacuum layer of 15 Å was adopted for all interface models.

Table 3. Surface energies of bcc-Fe(100) and NbN(100) as a function of vacuum layer thickness (J/m²).

Vacuum Thickness (Å)	bcc-Fe(100)	NbN(100)
10	2.872	0.947
12	2.858	0.921
15	2.850	0.910
18	2.848	0.908

2.4. Characterization of Interface Stability

After determining the configuration of the bcc-Fe(100)/NbN(100) coherent interface, the quantitative characterization of the interfacial bonding strength and adhesion properties becomes the core task in studying interfacial stability, with the work of separation, W_{sep} , being the key physical quantity. Its physical meaning is the energy required per unit area to reversibly separate a condensed heterogeneous interface into two independent free surfaces. The magnitude of the work of adhesion directly reflects the strength of the interfacial bonding [13]. The work of adhesion is calculated using the following formula:

$$W_{\text{sep}} = (E_{\alpha} + E_{\beta} - E_{\alpha/\beta})/A \quad (4)$$

where E_{α} and E_{β} are the total energies of the two relaxed free surfaces (eV), $E_{\alpha/\beta}$ is the total energy of the relaxed bcc-Fe(100)/NbN(100) interface (eV), and A is the area of the heterogeneous interface (m²).

In addition to the work of adhesion, the interfacial energy is another important quantity for quantitatively evaluating the thermodynamic stability of the bcc-Fe(100)/NbN(100) heterogeneous interface. Its core definition is the excess energy per unit area associated with the formation of the interface relative to the two independent free surfaces on either side [14]. The interfacial energy is expressed as:

$$\gamma_{\text{int}} = E_{\text{surf}}^{\text{Fe}} + E_{\text{surf}}^{\text{NbN}} - W_{\text{sep}} \quad (5)$$

where $E_{\text{surf}}^{\text{Fe}}$ and $E_{\text{surf}}^{\text{NbN}}$ are the surface energies of bcc-Fe(100) and NbN(100) (J/m²).

The calculated work of adhesion and interfacial energy are listed in Table 4. Interfaces 3 and 4 exhibit negative works of adhesion, indicating extremely weak interfacial bonding and thermodynamic instability; therefore, they were excluded from further investigation. Among the remaining two structures, Interfaces 1 and 2 have works of separation of 0.493 J/m² and 0.569 J/m² and interfacial energies of 3.297 J/m² and 3.221 J/m², respectively. Compared with Interface 1, Interface 2 possesses the highest work of adhesion and the lowest interfacial energy; thus, Interface 2 was selected as the object for all subsequent studies.

Table 4. Work of adhesion (W_{sep}) and interfacial energy (γ_{int}) of the different interface models.

Interface	W_{sep} (J/m ²)	γ_{int} (J/m ²)
1	0.493	3.297
2	0.569	3.221
3	−0.233	4.023
4	−0.163	3.953

3. Results

3.1. Characteristics of Nb(C,N) Precipitates and Matching with the Interface Model

As shown in Figure 6, after heat treatment at 800 °C for 2 min followed by water quenching, a high density of nano-sized precipitates with sizes of approximately 20–50 nm is uniformly dispersed in the 442D steel matrix. The samples were heated at a rate of 80 °C·min^{−1} to the target temperature, held for 2 min, and then rapidly cooled in water to preserve the high-temperature microstructure. Comparable TEM studies on Nb-microalloyed ferritic steels report similar precipitate dimensions and spatial distributions, confirming the reproducibility of the precipitation behavior under comparable thermal conditions [25]. The EDS elemental maps in Figure 6 reveal the co-localization of Nb, C, and N at the precipitate positions, confirming that these particles are Nb(C,N) compounds. The interfaces formed between these precipitates and the bcc-Fe matrix directly govern the precipitation, strengthening efficiency of the material.

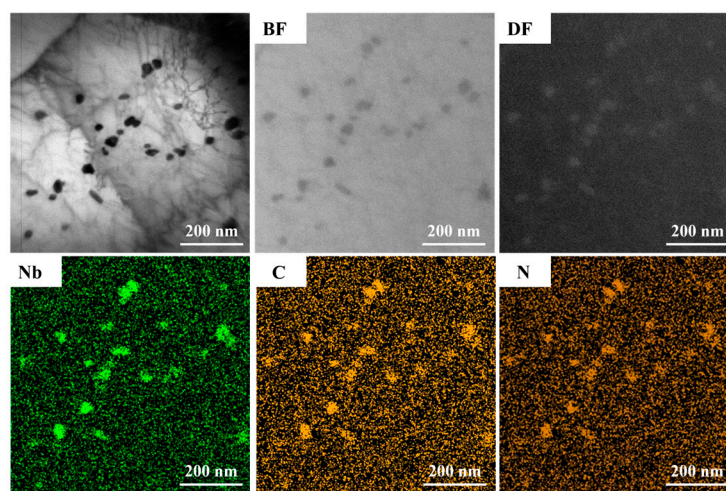


Figure 6. TEM morphology and elemental distribution of Nb(C,N) precipitates after heat treatment at 800 °C.

The bcc-Fe(100)/NbN(100) interface model constructed by first-principles calculations is an idealized atomic-scale representation of these actually existing phase boundaries. Here, NbN serves as a simplified model for the experimentally observed Nb(C,N) precipitates, given their identical NaCl-type crystal structure and the dominant role of Nb–Fe bonding at the interface [21]. While carbon substitution may induce minor quantitative variations in bond lengths and charge transfer, it is not expected to alter the qualitative conclusions regarding site-selective segregation and the trend of interfacial stabilization with increasing Nb content. The Nb concentration range adopted in the calculations (1.6–6.3 at.%) corresponds to the composition gradient that can exist at the precipitate/matrix interface. By calculating the work of adhesion and segregation energy as a function of Nb content, the bonding strength of these nano-precipitates with the matrix and its influence on material properties can be quantitatively understood. Jang and Kim [9] reported similar Nb(C,N) precipitate sizes (15–40 nm) after aging at 750 °C in ferritic steel, while Meng et al. [10] observed comparable precipitate distributions in Ti-Nb microalloyed 21%Cr ferritic stainless steel. These comparisons validate our experimental observations and place them in the context of established precipitation behavior in Nb-bearing ferritic stainless steels.

3.2. Site Preference of Nb at the bcc-Fe(100)/NbN(100) Interface

3.2.1. Segregation Energy of Nb at Different Interface Sites

The most favorable substitutional position for a Nb atom at the interface between the bcc-Fe and NbN matrices was identified by calculating the segregation energy. A more negative segregation energy indicates a stronger thermodynamic driving force for the Nb atom to occupy that site and remain there stably. The segregation energy was calculated using the following expression [15]:

$$E_{\text{seg}}(E_{\text{interface} + \text{Nb}} + \mu_{\text{Fe}}) - (E_{\text{interface}} + \mu_{\text{Nb}}) \quad (6)$$

where E_{seg} is the segregation energy after an Fe atom is replaced by Nb (eV), $E_{\text{interface}}$ and $E_{\text{interface} + \text{Nb}}$ are the total energies of the interface before and after segregation (eV), μ_{Nb} and μ_{Fe} represent the average energy per atom in the bcc-Nb and bcc-Fe crystal phases, respectively.

Based on the above calculations of interfacial energy and work of adhesion, Interface 2 was adopted as the basic model for the subsequent doping studies. Nb alloying element doping was performed by atomic substitution on the bcc-Fe side of the interface. Specifically, two Fe atomic layers adjacent to the interface were selected, and Nb atoms were substituted at different atomic positions, as illustrated in Figure 7.

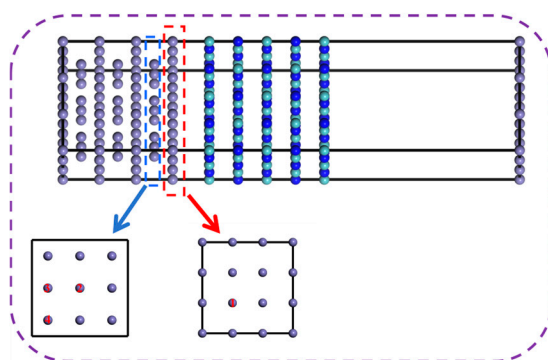


Figure 7. Substitution positions of Nb atoms at the interface.

Figure 8 presents the segregation energies of Nb at different sites in the bcc-Fe(100)/NbN(100) interface. The segregation tendency of Nb decreases in the order: site 1 > site 2 > site 4 > site 3. Site 1 exhibits the largest absolute value of segregation energy (−0.74 eV), providing the most pronounced thermodynamic driving force for Nb segregation, whereas site 3 shows the smallest absolute value, corresponding to the weakest driving force.

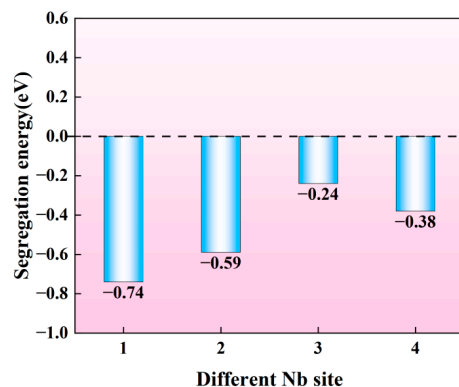


Figure 8. Segregation energy of Nb at different interfacial sites.

3.2.2. Density of States of Nb at Different Interface Sites

Figure 9 shows the density of states (DOS) for the clean bcc-Fe(100)/NbN(100) interface and for the interfaces after Nb segregation at different sites. Complementary first-principles investigations of the NbN/ α -Fe interface report similar Nb-4d/Fe-3d hybridization patterns near the Fermi level, corroborating the electronic origin of interfacial strengthening identified in our analysis [26,27]. Combined with the segregation energy results in Figure 8, the DOS analysis can reveal the electronic-level mechanism by which Nb segregation regulates interfacial stability. Comparing the clean interface in Figure 9a with the doped interfaces in Figure 9b–e, it is evident that the introduction of Nb generates a significant electronic contribution near the Fermi level, which is dominated by Nb-4d states. In particular, the doping at site 1 (Figure 9b) produces the sharpest d-state peak at the Fermi level, indicating the strongest orbital hybridization between Nb and interfacial Fe atoms, which is consistent with the most negative segregation energy (−0.74 eV) obtained for this site. Further decomposition of the orbital contributions reveals that the electronic states near the Fermi level mainly arise from the hybridization of Nb-4d and Fe-3d orbitals. In the energy range from −4 eV to −1 eV, bonding-state overlaps between Nb-d and Fe-d orbitals are observed, while the corresponding antibonding states appear between 1 eV and 3 eV. At site 1, the occupation of bonding states is clearly dominant and the antibonding states remain unoccupied, indicating a strong covalent character of the Nb–Fe bond. This constitutes the electronic-structure origin of the most negative segregation energy at this site. In contrast, for site 3 (Figure 9d), the degree of d-d orbital overlap is significantly reduced and the bonding interaction is weakened, in line with its segregation energy being the closest to zero. The DOS analysis thus elucidates the electronic-structure origin of the site-dependent segregation energy. As the segregation energy increases from site 1 to site 3 (−0.74 eV to −0.24 eV), the intensity of the Nb-4d DOS peak at the Fermi level successively decreases, and the d-band center gradually shifts away from the Fermi level. This demonstrates that the strength of the Nb–interface interaction directly determines the thermodynamic driving force for segregation: stronger d-d orbital hybridization leads to a larger energy gain, thereby promoting Nb segregation toward the interface.

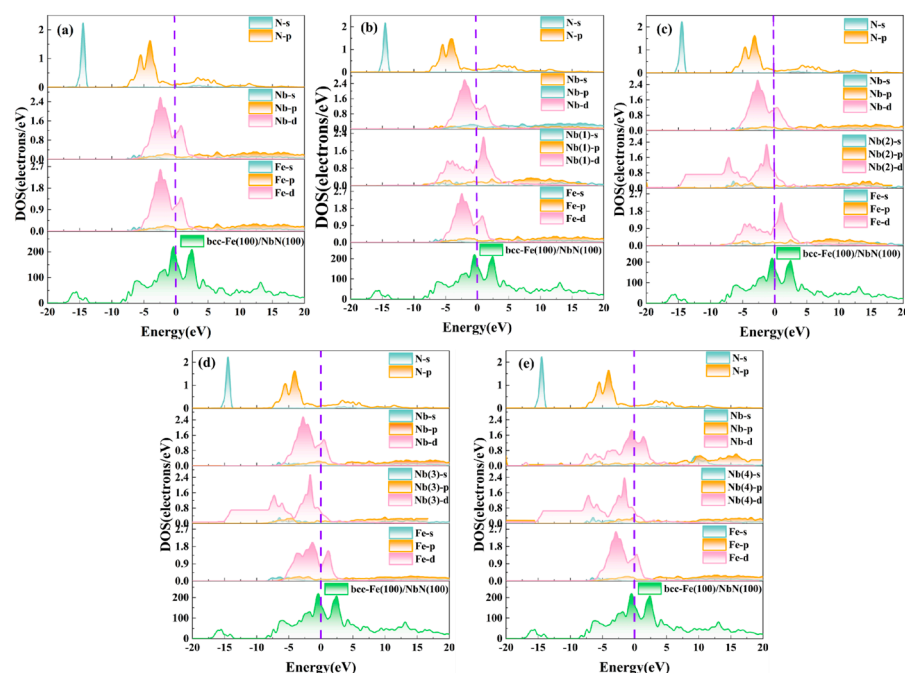


Figure 9. Density of states after Nb segregation at different interface sites: (a) clean interface, (b) site 1, (c) site 2, (d) site 3, and (e) site 4.

3.2.3. Charge Density Difference of Nb at Different Interface Sites

The charge density difference was calculated using Equation (7) to visualize the re-distribution of electrons upon Nb segregation.

$$\Delta\rho = \rho_{\text{Nb doped interface}} - \rho_{\text{clean interface}} - \rho_{\text{Nb}} + \rho_{\text{Fe}} \quad (7)$$

where $\rho_{\text{Nb doped interface}}$ and $\rho_{\text{clean interface}}$ are the total charge densities of the doped and clean interfaces, and ρ_{Nb} and ρ_{Fe} are the charge densities of the isolated Nb and Fe atoms at their respective positions in the supercell. Red regions denote charge accumulation and blue regions denote charge depletion. The dashed circles highlight the Nb atom positions for clarity. Figure 10 shows the charge density difference distribution of niobium (Nb) after site-specific segregation, with contour surfaces defined at $\pm 0.05 \text{ e} \text{ \AA}^{-3}$; the red region represents charge accumulation zones and the blue region represents charge depletion zones. As shown in Figure 10a, the Nb atom at site 1 is surrounded by the most extensive and continuous red charge-accumulation region, forming a clear charge bridge with the neighboring Fe atoms. This indicates strong hybridization between Nb-4d and Fe-3d orbitals and the strongest interfacial covalent bonding. The range of the red accumulation region at site 2 (Figure 10b) is slightly reduced, while the charge bridging remains relatively intact. For site 3 and site 4 (Figure 10c,d), the red accumulation regions become successively smaller, and the charge bridges are progressively broken, reflecting the weakening of the interfacial bonding interaction. This trend in charge distribution is fully consistent with the calculated interfacial segregation energies: site 1 exhibits the most negative segregation energy and the highest interfacial stability, whereas site 3 exhibits the least negative segregation energy and the weakest interfacial bonding. The charge density difference analysis confirms at the electronic level that Nb segregation forms localized charge-accumulation regions, strengthens the Nb–Fe bonds, and thereby serves as the core mechanism for enhancing interfacial stability.

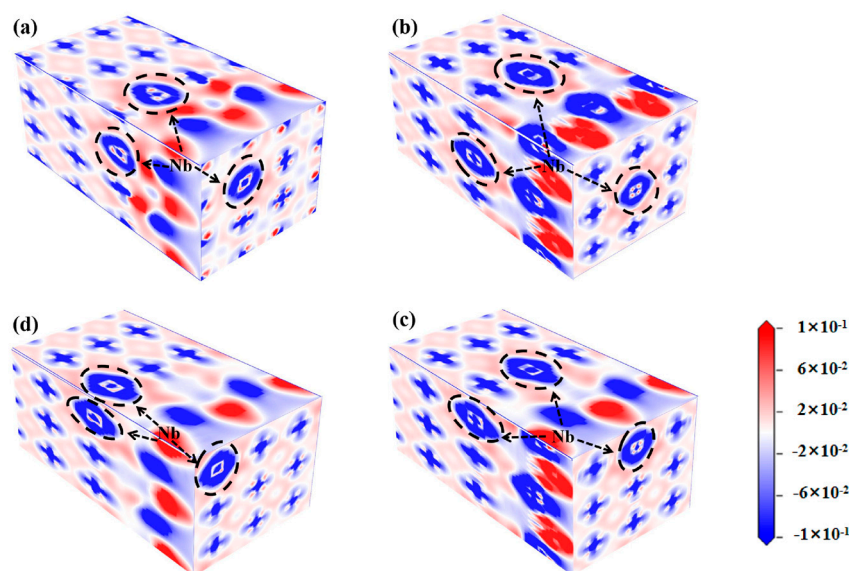


Figure 10. Charge density difference after Nb segregation at different interface sites: (a) site 1, (b) site 2, (c) site 3, and (d) site 4.

3.3. Effect of Nb Segregation on the Stability of the bcc-Fe(100)/NbN(100) Interface

3.3.1. Segregation Energy as a Function of Nb Content

Figure 11 presents the segregation energy at the bcc-Fe(100)/NbN(100) interface for different Nb contents. The interfacial segregation energy decreases continuously as the

Nb content increases from -0.74 eV at 1.6 at.% to -1.55 eV at 6.3 at.%. The rate of decrease slows down with increasing Nb content, suggesting that Nb–Nb interactions exert a significant influence on the interfacial segregation behavior. The persistently negative segregation energy indicates that the thermodynamic driving force for Nb segregation to the interface intensifies with increasing Nb content, implying enhanced interfacial stability.

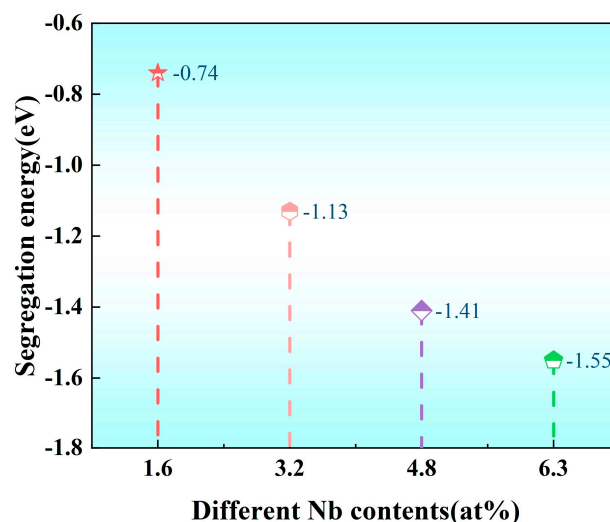


Figure 11. Segregation energy of the interface after doping with different Nb contents.

3.3.2. Effect of Nb Content on Interface Stability

Table 5 lists interfacial spacing, the work of adhesion and interfacial energy of the bcc-Fe(100)/NbN(100) interface at various Nb contents. The data show that Nb doping significantly improves the interfacial bonding properties. As the Nb content increases from 0 (clean interface) to 6.3 at.%, the work of adhesion increases monotonically from 0.569 J/m² to 0.786 J/m², corresponding to a 38.1% enhancement. Correspondingly, the interfacial energy decreases from 3.221 J/m² to 2.374 J/m², a reduction of 26.3%. This trend is highly consistent with the variation in segregation energy shown in Figure 11 more negative segregation energy correlates with a higher work of adhesion and a lower the interfacial energy, indicating an inherent correlation between the thermodynamic driving force for Nb segregation and the interfacial strengthening effect. To further characterize the structural response to Nb segregation, the relaxed interfacial spacing of Interface 2 was examined as a function of Nb content. As summarized in Table 5, the interfacial spacing exhibits a non-monotonic variation: it contracts slightly from 2.15 Å (clean) to 2.12 Å at 3.2 at.%, then expands to 2.20 Å at 6.3 at.%. This behavior reflects the competition between chemical bonding and atomic size effects. At low Nb contents, the strong Nb–Fe bonding at the most favorable sites (Site 1) pulls the interface atoms closer together. Beyond 3.2 at.%, subsequent Nb atoms occupy less favorable sites with shorter Nb–Nb distances, leading to repulsive interactions that expand the interfacial spacing. This structural trend correlates with the diminishing returns in adhesion energy increment observed in Table 5.

Table 5. Interfacial spacing (d), work of adhesion (W_{sep}) and interfacial energy (γ_{int}) of interface structures with different Nb contents.

Content (at.%)	d (Å)	W_{sep} (J/m ²)	ΔW_{sep} (J/m ²)	γ_{int} (J/m ²)	$\Delta \gamma_{\text{int}}$ (J/m ²)
Clean	2.15	0.569	0	3.221	0
1.6	2.13	0.658	0.089	2.913	−0.308

3.2	2.12	0.722	0.153	2.651	−0.570
4.8	2.16	0.761	0.192	2.470	−0.751
6.3	2.20	0.786	0.217	2.374	−0.847

A closer examination of the influence mechanism reveals a distinct decreasing efficiency of Nb strengthening. Specifically, the first Nb atom (1.6 at.%) contributes 0.089 J/m² to the work of adhesion, whereas the unit contributions of the second, third, and fourth Nb atoms (corresponding to 3.2 at.%, 4.8 at.%, and 6.3 at.%) successively drop to 0.064 J/m², 0.039 J/m², and 0.025 J/m²; the strengthening efficiency of the fourth Nb atom is only 28% of that of the first atom. This phenomenon can be understood from two aspects. First, Nb atoms preferentially occupy the sites with the strongest interfacial bonding (e.g., site 1 with a segregation energy of −0.74 eV), and subsequent Nb atoms are forced to occupy sites with weaker bonding (sites 2, 3, and 4), leading to a diminishing individual contribution. Second, as the Nb–Nb distance decreases, the interaction between Nb atoms intensifies, partially offsetting the gain from the Nb–Fe/N interfacial bonding. This reflects the combined effect of site-competition in the interfacial chemical environment and atomic interactions.

The range of Nb concentrations simulated in this study (1.6–6.3 at.%) encompasses a reasonable interval of possible local Nb enrichment near the precipitate/matrix interface. In combination with TEM observations, most Nb atoms exist as Nb(C,N) precipitates at 800 °C. Although the total interfacial area is large, the local Nb enrichment near the interface can be high while the solute Nb content in the matrix is relatively low. At 1100 °C, extensive dissolution of precipitates increases the solute Nb content in the matrix. The simulation results show that with increasing Nb concentration, the segregation driving force is enhanced and the interfacial stability improves, providing a unified atomic-scale perspective for understanding the interfacial behavior under different heat treatment conditions. Moreover, the results help to explain why, even after precipitate coarsening or dissolution at high temperatures, solute Nb atoms may still contribute to the interfacial bonding strength by segregating to the residual interfaces, thereby affecting the macroscopic properties of the material. In real materials, however, the partitioning of Nb between solid solution and precipitates is governed by multiple factors including temperature and diffusion kinetics and is a dynamic equilibrium process. Future studies can combine phase diagram calculations and diffusion simulations to establish a more precise quantitative correlation. In practical heat treatment processes, the segregation rate of Nb atoms is governed by the diffusion coefficient and temperature. Under low-temperature or short-duration conditions, the system may not reach thermodynamic equilibrium. The calculated results in this work represent the limiting segregation behavior at equilibrium, serving as a thermodynamic benchmark for optimizing heat treatment protocols. Future studies will employ transition state searches or *ab initio* molecular dynamics to investigate the associated kinetic barriers.

4. Conclusions

Based on the morphology, size, and elemental distribution characteristics of Nb(C,N) precipitates obtained by TEM characterization, a bcc-Fe(100)/NbN(100) interface model was constructed, and first-principles calculations based on density functional theory were systematically performed to investigate the influence of Nb content on the interfacial stability and segregation behavior. The main conclusions are as follows:

1. Interface 2 exhibits the highest work of adhesion (0.569 J/m²) and the lowest interfacial energy (3.221 J/m²) and is therefore identified as the thermodynamically most stable configuration. Interfaces 3 and 4 show negative works of adhesion and are

thermodynamically unstable. Based on convergence tests, an interface model consisting of 7 bcc-Fe layers and 5 NbN layers was adopted. The present study employs NbN as a simplified model for Nb(C,N) precipitates based on their structural similarity and the dominant Nb–Fe interfacial bonding. Future work will construct explicit Nb(C,N) interface models to quantitatively assess the effect of carbon on interfacial properties.

2. The site-selective segregation mechanism of Nb atoms at the interface was revealed. The calculated segregation tendency follows the order: site 1 (−0.74 eV) > site 2 (−0.59 eV) > site 4 (−0.38 eV) > site 3 (−0.24 eV). Density-of-states analysis demonstrates that significant hybridization occurs between Nb-4d and Fe-3d orbitals near the Fermi level, forming strong covalent interactions. Charge density difference analysis confirms at the electronic level that Nb segregation generates localized charge-accumulation regions and strengthens Nb–Fe bonding.
3. The influence of Nb content on interfacial stability was elucidated. As the Nb concentration increases from 1.6 at.% to 6.3 at.%, the segregation energy continuously decreases from −0.74 eV to −1.55 eV, the work of adhesion increases monotonically, and the interfacial energy decreases monotonically, indicating that Nb segregation significantly enhances the interfacial stability. This trend is consistent with the experimental observations and provides an atomic-scale microscopic explanation for the interfacial behavior under different heat treatment conditions.

It should be noted that the coherent bcc-Fe(100)/NbN(100) interface model employed in this study involves two idealized simplifications. First, the stoichiometric NbN(100) termination is adopted as the thermodynamically stable baseline; non-stoichiometric terminations (e.g., Nb-rich or N-deficient surfaces) could alter the local atomic coordination and electronic structure, though the primary Nb–Fe interfacial bonding is expected to remain dominant. Second, the experimentally observed Nb(C,N) precipitates (20–50 nm) likely exhibit semi-coherent interfaces with misfit dislocations, rather than the ideal coherent (100)/(100) orientation assumed here. Nevertheless, the qualitative conclusion that Nb segregation enhances interfacial stability is expected to hold for both non-stoichiometric and semi-coherent interfaces, as solute segregation typically preferentially occurs at defect sites and high-energy regions, thereby further reducing the interfacial energy. Systematic investigations of these effects will be undertaken in future work to complement the current framework.

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