

Ordered Phases in Fe-Si Alloys: A First-Principles Study

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It is known that the formation of ordered phases causes the brittleness of electrical steels. We employed first-principles method in order to examine the possibility of the ordered-phases formation in Fe-Si alloys. It is found that the **D0₃-like ordered configuration is most stable among other atomic configurations in the ferromagnetic state**. In the paramagnetic state, for low Si concentration, the stability of the ordered configurations is comparable to that of disordered ones. However, **as Si content increases, the B2 ordered phase as well as the D0₃ phase becomes more stable than the disordered ones**.

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I. INTRODUCTION

Electrical steel is a soft magnetic material used for the cores in motors, transformers and power generators. The main alloying elements in electrical steels are iron and silicon. As silicon content increases, the energy dissipation during the magnetization process, so-called core loss, is reduced [1,2]. **Generally, 1 to 3 weight percent (wt.%) Si composition is widely accepted in commercial grades**. Especially, high silicon steel with **6.5 wt.% Si has attracted considerable attentions because it has zero magnetostriction [2]**. However, **when the silicon content is higher than about 3.5 wt.%, the material becomes too brittle to be manufactured into thin sheets by a conventional rolling process**. In order to avoid the rolling process in fabrication of high silicon steels, alternative methods such as physical vapor deposition [3] and chemical vapor deposition [4] have been suggested, but they are generally inadequate to commercialize because they are very expensive, harmful to the environment and complicated compared to the conventional rolling process.

It is widely recognized that the brittleness of electrical steels is induced by the formation of B2-FeSi and D0₃-Fe₃Si ordered phases [5–9]. We show the structures in

Fig. 1. In the B2 phase, all of the body-center sites of the body-centered cubic (bcc) structure are occupied by silicon atoms, and in the D0₃ phase, only half of the center sites are occupied in the form of crossed diagonal. As the cooling rate increases in experiment, the formation of the ordered phases is suppressed and at the same time the ductility of materials increases, and vice versa [6]. It is expected that when a dislocation crosses an ordered phase, an antiphase boundary (APB) is formed and the system energy increases. In order to relax the APB energy, a multiple of dislocation pairs should pass through together. For example, for the B2 and D0₃ phases, a pair and two pairs of dislocations will move together, respectively. Therefore, the movement of dislocations in ordered phases is restricted, which acts as one of the mechanisms for making materials brittle [6,7,10].

The ordered phases are usually observed by X-ray diffraction and transmission electron microscopy (TEM) [11]. However, since the fraction of the ordered phases is low, it is hard to quantify the formation of the ordered phases.

In this study, we investigate the stability of the B2 and D0₃ ordered phases in Fe-Si alloys by using first-principles methods. We consider various atomic configurations of the same Si concentration in Fe and compare the total energy of each state.

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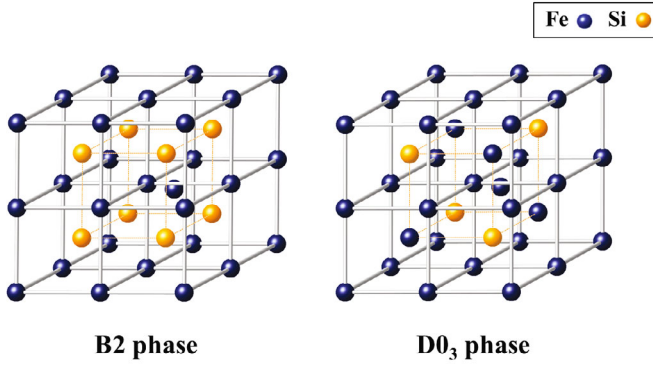


Fig. 1. (Color online) The B2 phase consists of two simple cubic sublattices of Fe atoms and Si atoms, respectively. In the D0₃ phase, only half of the sites of the Si sublattice of the B2 phase is filled with Si atoms.

II. CALCULATION DETAILS

We employed the first-principles total energy calculations based on density-functional theory (DFT) [12,13] as implemented in the exact muffin-tin orbitals (EMTO) method [14,15]. The Vienna Ab-initio Simulation Package (VASP) [16,17] was also used to test the reliability of the results from the EMTO method. The exchange-correlation interaction was treated within the generalized-gradient approximation [18].

The stability of the ordered and disordered phases in Fe-Si alloys was examined as follows. We constructed $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells with a conventional bcc unitcell, which contain 54 and 128 atoms in total, respectively. Using the supercell, we calculated and compared the total energies of the B2-like ordered, D0₃-like ordered, and disordered configurations of Fe and Si atoms. The disordered configurations were produced by randomly distributing Fe and Si atoms in the supercell. The number of possible configurations is very large. However, after considering a few of group symmetry, one can reduce the number of atomic configurations for Si substitution. In fact, we took a subset of the possible atomic configurations with a random number generator. We chose the compositions of 3 and 8 Si atoms among 54 atoms corresponding to 5.6 and 14.8 atomic percent (at.%) Si, respectively. Also, in order to investigate the behavior of Si-Si interaction in bcc Fe, we put two Si atoms in the same supercell and calculated total energies according to the distance between two Si atoms. We did not perform structural relaxation with the supercells because we are interested in the energy difference between structures and the relaxation effect will be mostly cancelled with each other. Both of the ferromagnetic (spin-polarized) and paramagnetic (non-spin-polarized) calculations were performed to understand the effects of magnetism on the stability of the ordered phases.

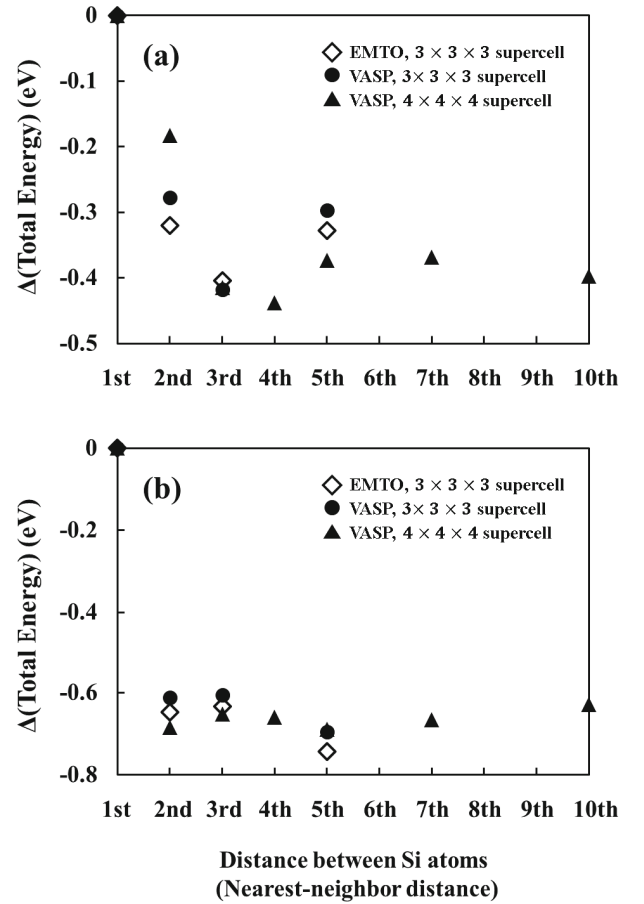


Fig. 2. The total energy versus the interatomic distance between 2 Si atoms in supercells. (a) and (b) represent the ferromagnetic and the paramagnetic state calculation, respectively. We set the total energy of the 1st nearest-neighbor configuration to zero.

III. RESULTS AND DISCUSSION

Figure 2 shows the variations of the total energy on the interatomic distance between 2 Si atoms in the supercells. The ferromagnetic case in Fig. 2(a) shows that Si atoms prefer to be positioned in around the 3rd nearest-neighbor distance of the bcc structure from each other. When Si atoms are too close, for example, in the 1st nearest-neighbor distance, the system becomes unstable. Therefore, Si atoms in Fe will not be positioned too close with each other. These results are consistent in both the EMTO method and the VASP. From the $4 \times 4 \times 4$ supercell calculations by the VASP, we find that the total energy hardly varies when Si atoms are separated more than the 5th nearest-neighbor distance. In the paramagnetic calculations in Fig. 2(b), the total energy of the 1st nearest-neighbor configuration is higher about 0.65 eV than other configurations, and it does not change much when Si atoms are separated farther. Therefore, all the

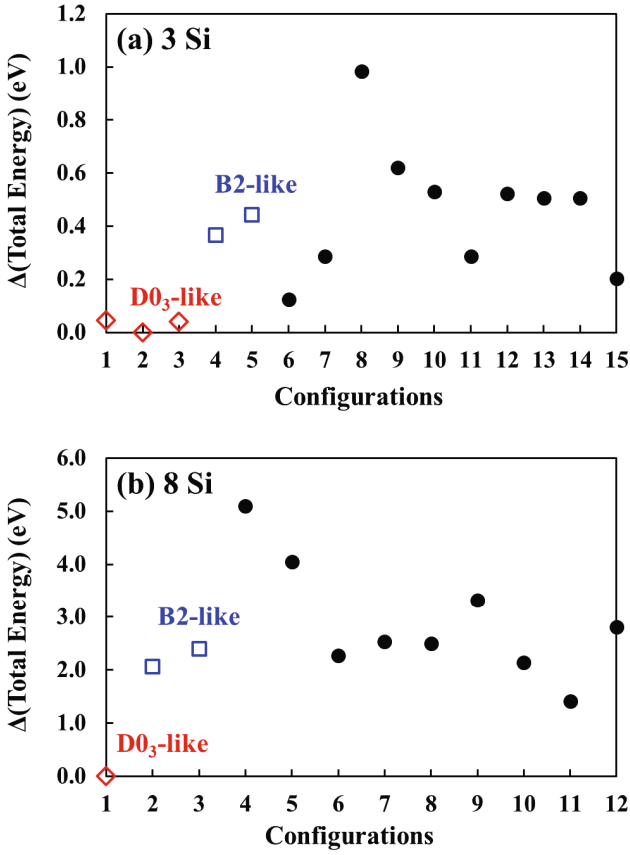


Fig. 3. (Color online) The total energies of various atomic configurations of Si atoms in the **ferromagnetic** Fe-Si alloys for (a) 3 (5.6 at.% Si) and (b) 8 Si atoms (14.8 at.% Si) in the 54 atoms supercell. The data corresponding to random, B2-like and D0₃-like ordered configurations are denoted by dots, squares and diamonds, respectively. We set the total energy of the D0₃-like ordered configuration to zero.

configurations of 2 Si atoms in the paramagnetic state are energetically almost equivalent except the 1st nearest-neighbor distance.

In Fig. 3, we show the total energy of various atomic configurations of multi-Si atoms in the ferromagnetic bcc-Fe. Figures 3(a) and (b) represent those for the compositions of 3 (5.6 at.% Si) and 8 Si atoms (14.8 at.% Si) among 54 atoms in total, respectively. For both cases, it is observed that the **D0₃-like ordered configuration is more stable than the B2-like and disordered ones**. In the D0₃ ordered phase, all Si-Si bonds are in relation of the 3rd nearest-neighbor distance which is the most preferential configuration as found with the results in Fig. 2(a). Therefore, the **D0₃ phase is naturally most stabilized**. On the other hands, the total energy of the B2-like ordered configuration is not lower than those of disordered ones. In the B2 phases, Si atoms are located in the 2nd nearest-neighbor distance and the higher energy of the 2nd nearest-neighbor configuration compared to the 3rd nearest-neighbor configuration shown in Fig. 2(a) gives

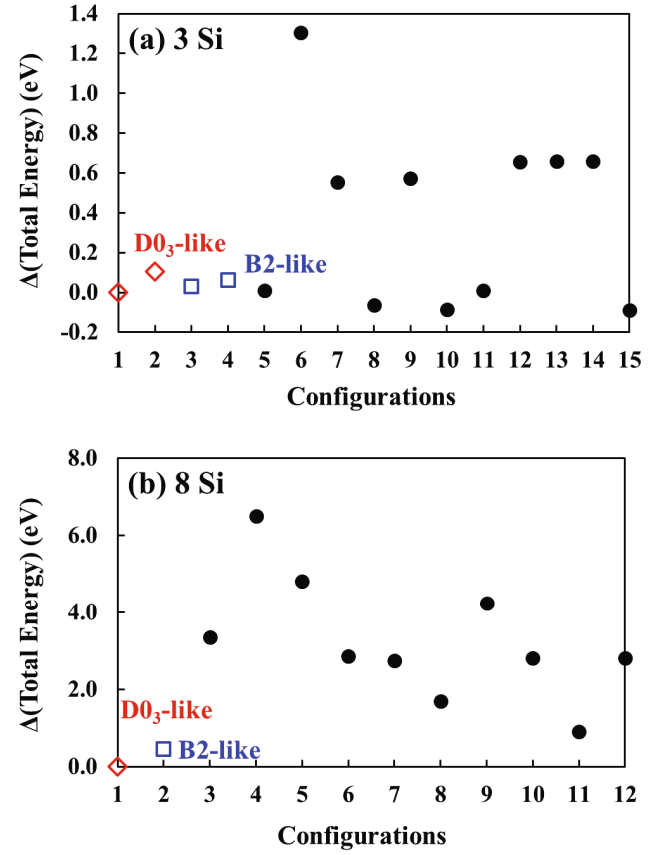


Fig. 4. (Color online) The total energies of various atomic configurations of Si atoms in the **paramagnetic** Fe-Si alloys for (a) 3 (5.6 at.% Si) and (b) 8 Si atoms (14.8 at.% Si) in the 54 atoms supercell. The data corresponding to random, B2-like and D0₃-like ordered configurations are denoted by dots, squares and diamonds, respectively. We set the total energy of the D0₃-like ordered configuration to zero.

rise to a relatively unstable state. Therefore, the behavior of the total energy of multi-Si configuration in Fe can be understood by taking into account of the pairwise interatomic interaction between Si atoms. Although we do not show the atomic structure explicitly, configuration 8 in Fig. 3(a) has mostly the 1st nearest-neighbor pairs resulting in the highest energy state.

Figure 4 shows the total energy of 3 Si and 8 Si cases in the paramagnetic state. In 3 Si shown in Fig. 4(a), the ordered configurations do not show higher stability than the disordered ones. This can also be well understood by considering the pairwise interactions of Si atoms in Fig. 2(b). **Since there is no preferential position between two Si atoms, it seems that the ordered configuration is not distinguished by other disordered configurations except those containing the 1st nearest-neighbor Si pair**. However, interestingly, as Si content increases, the B2-like ordered configuration as well as the D0₃-like configuration becomes more stable than disordered ones (see Fig. 4(b)). This result may come from the many-body

effect, which is beyond the simple pairwise interaction of Si atoms. It is evident that increasing Si concentration promotes the ordered phases formation. Also, it is remarkable that the B2-like ordered configuration is more stabilized than the disordered ones, which is not the case in the ferromagnetic state. This indicates that the transition from the ferromagnetic to paramagnetic state provides a driving force for the B2 phases formation. The previous report shows that the magnetic moment of the B2 phase is nearly zero in the paramagnetic state [19].

We would like to emphasize that the present results well explain the phase diagram of Fe-Si alloys [20,21]. In the ferromagnetic state, the stability of the B2 ordered phase is comparable to those of disordered states. On the other hands, in the paramagnetic state, the B2 phase is more stable than the disordered states. These results are consistent with the experimental observation that when the temperature decreases from above the Curie temperature (T_C) to below, the region of the B2 phase shrinks by the expansion of the disordered phases region [21, 22]. Also, our calculations show that in the ferromagnetic state, the D0₃ phase has a higher stability than the B2 phase. This also supports that the region of the D0₃ phase in the phase diagram expands reducing the region of the B2 phases below T_C . We showed that as Si concentration increases, the stability of the ordered configuration especially the D0₃ phase increases both in the ferromagnetic and paramagnetic states. This fact can be checked with that the permissible temperature range for the ordered phases formation becomes larger as Si concentration increases [20]. For example, the ordered phases region exists up to 800 °C at 12 at.% Si, but 1000 °C at 15 at.% Si.

IV. CONCLUSION

Using first-principles methods, we investigated the structural stability of the B2 and D0₃ ordered phases in Fe-Si alloys. It was shown that the D0₃ phase is the most stable in the ferromagnetic state. Magnetism enhances the stability of the ordered phases. In the paramagnetic state, for low silicon concentration, the stability of the ordered phase is similar to those of the disordered ones. However, as silicon content increases, the stability of the ordered phases becomes higher than the disordered phases. Also, it seems that the B2 ordered phases prefer forming in paramagnetic state to forming in ferromagnetic state. It is left as a future work to find an alloying element which prevents the formation of the ordered phases to solve the brittleness problem of electrical steels.

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