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Fe_3Si formation in Fe–Si diffusion couples

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Two different types of bulk diffusion couples for the Fe–Si system, i.e. Fe/Si and Fe/Fe_3Si, have been studied, with emphasis placed on the formation and growth of Fe_3Si. Results indicate that Fe_3Si forms initially in Fe/Si couples, followed by FeSi and then $FeSi_2$. Fe_3Si has a wide range of stoichiometry, from 10–25 at % Si; however, only stoichiometric Fe_3Si appeared in Fe_3Si diffusion layers of Fe/Si couples. Off-stoichiometric Fe_3Si formed in Fe_3Si/Fe couples. The free energy of Fe_3Si and Fe–Si affinity are used to explain Fe_3Si formation behaviour and the atomic diffusion mechanism in the Fe_3Si lattice.

1. Introduction

Recent work by one of the authors on bulk Fe–Si diffusion couples indicated that Fe_3Si, which forms between α-Fe and FeSi, is stoichiometric with a very narrow composition range [1]. This result appears to contradict the accepted version of the Fe–Si phase diagram (Fig. 1 [2]). Fe_3Si, according to the diagram, has a wide range of stoichiometry, i.e. 10–25 at % Si. In this paper, we examine this question more carefully and propose an explanation for this apparent discrepancy.

Stoichiometric Fe_3Si ($Fe_{75}Si_{25}$) has a DO_3 structure, i.e. a cubic superstructure consisting of four interpenetrating fcc sublattices, labelled A, B, C and D, with origins at the points (0, 0, 0) (1/4, 1/4, 1/4), (1/2, 1/2, 1/2) and (3/4, 3/4, 3/4) arranged regularly along the body diagonal (Fig. 2 [3]). Each A atom is at the centre of a cube with four B and four D atoms at the corners in tetrahedral arrangements. Similarly, each B atom is at the centre of a cube with four A and four C atoms at corners in cubic arrangements. In stoichiometric Fe_3Si, iron atoms occupy the A, C and B sites. Thus, the iron atoms on equivalent (both structurally and magnetically) A and C sites have tetrahedral point symmetry with four iron [B] and four silicon [D] atoms as nearest neighbours. The Fe[B] atoms have cubic point symmetry with eight Fe[A,C] atoms as nearest neighbours, as in elemental bcc iron. Table I illustrates the neighbour configurations of stoichiometric Fe_3Si [4].

For silicon compositions between 10 and 25 at %, off-stoichiometric Fe_3Si forms DO_3-related structures. Fe[A,C] sites can have either five iron and three silicon atoms as nearest neighbours or six iron and two silicon atoms as nearest neighbours [5]. The disordered, but DO_3-related, Fe–Si alloys of this type are labelled as $Fe_{3+y}Si_{1-y}$ and they exist in the composition range $0.4 \leqslant y \leqslant 1.0$ [3].

Paoletti and Passari [6] established that the magnetic moments of the two types of iron atoms were different; values of $2.4\mu_B$ and $1.2\mu_B$ (μ_B is the Bohr magneton) were reported for Fe[B] and Fe[A,C] atoms, respectively. More recent data [3] suggest values of $2.2–2.4\mu_B$ and $1.1–1.35\mu_B$ for Fe[B] and Fe[A,C]. Swintendick [5] was the first to show that energy-band calculations, based on a rigid-level spin-polarized model, were capable of explaining the different magnetic moments on A, C and B sites.

Preferential site occupancy by transition metal impurities substituted into Fe_3Si has been reported by several researchers [4, 7–9]. Impurities to the left of iron in the Periodic Table prefer Fe[B] sites and those beneath and to the right of iron enter Fe[A,C] sites.

Taking into account chemical and magnetic interaction, numerical values of energy parameters for the Fe–Si system have been determined using the Bragg–Williams–Gorsky (BWG) model and C_P (heat capacity) integration method [10–14]. The free energy of Fe_3Si was found to decrease with decreasing iron concentration at a fixed temperature. In addition, Fe–Si affinity was found to be higher than Fe–Fe affinity [15, 16].

In the present work, two types of Fe–Si diffusion couples, i.e. Fe–Si and Fe–Fe_3Si, are studied. The results obtained are discussed from the point of view of the free energy of Fe_3Si, Fe–Si affinity, Fe_3Si formation and atomic diffusion mechanisms in the Fe_3Si lattice.

2. Experimental procedure

Diffusion couples were constructed from three different components: iron (99.95%), high-purity ⟨1 1 1⟩ oriented single-crystal silicon and an Fe–Si alloy. The Fe–Si alloy, containing 25 at % Si, was produced in an induction furnace under an inert atmosphere (10% Ar

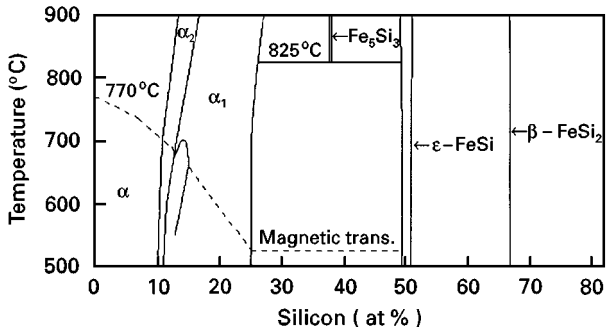


Figure 1 Fe–Si binary phase diagram.

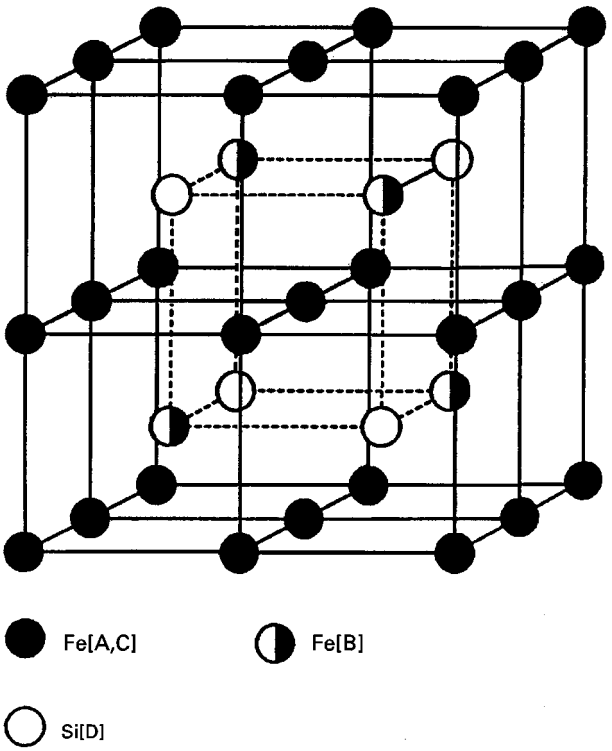


Figure 2 Schematic drawing of the Fe_3Si structure, showing the four different sites [3].

TABLE I Neighbour configuration in stoichiometric Fe_3Si [4]

Neighbour	1	2	3	4	5	6
R[a]	0.43	0.5	0.705	0.83	0.86	1.00
A, C	4B 4D	6A, C	12A, C	12B 12D	8 A, C	6 A, C
B	8 A, C	6D	12B	24A, C	8D	6B
D	8 A, C	6B	12D	24A, C	8B	6D

[a] R is the distance expressed as a fraction of the lattice parameter a.

and 90% He). After the alloy was made, a homogenization anneal was done at 1000 °C for 24 h. The diffusion couple assembly procedure has been given in detail elsewhere [1]; only a brief description will be given here. The surfaces of the iron, silicon and Fe–Si alloy were cut, ground and polished to thicknesses of 4.5, 3.0 and 4.5 mm, respectively; The faces of the pieces, that were to be in contact, were polished to a mirror finish on a 6 μm diamond wheel followed by polishing on a 0.05 μm Al_2O_3 wheel. Polishing was done shortly before fabrication of the couples, in order to minimize oxidation of the polished surfaces. The couples were clamped together, sealed individually in quartz tubes with ~1 g zirconium powder and annealed at 700 °C for times ranging from 7–1000 h. After heat treatment, the couples were sectioned perpendicular to the contact plane and examined by optical and scanning electron microscopy (SEM). Energy dispersive X-ray (EDX) spectroscopy was used to determine the composition and composition profiles. FeSi was used as a standard for quantitative EDX.

3. Results

3.1. Fe–Si couples

An SEM backscattered electron image for an Fe–Si couple annealed at 700 °C for the shortest time studied (7 h) is shown in Fig. 3a. A corresponding composition profile is shown in Fig. 3b. This condition clearly represents the early stages of silicide formation and demonstrates that Fe_3Si forms initially in bulk couples. No FeSi or $FeSi_2$, the other two phases that would be expected to form at this temperature, were detected, at least within the resolution of the SEM. Fe_3Si was found to be stoichiometric, which is in agreement with previous work [1], with a composition corresponding to 27 ± 0.5 at % Si, which is

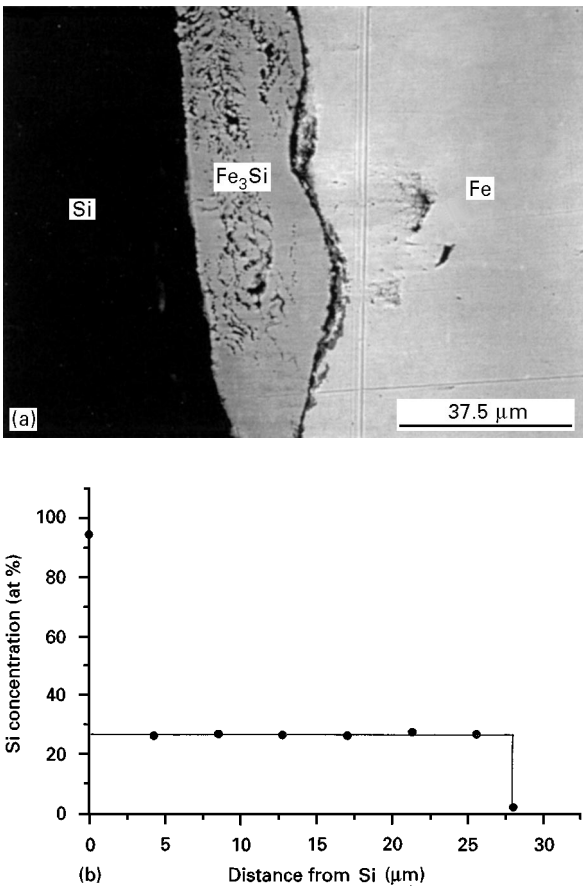


Figure 3 (a) SEM backscattered electron image of the diffusion zone of an Fe–Si couple annealed at 700 °C for 7 h. (b) Concentration profile for the couple in (a).

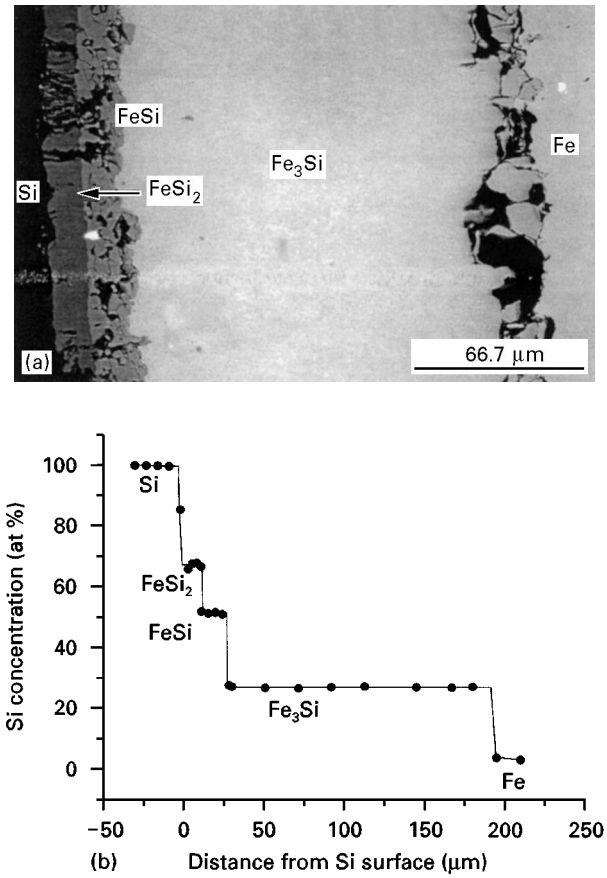


Figure 4 (a) SEM backscattered electron image of the diffusion zone of an Fe–Si couple annealed at 700 °C for 1007 h. (b) Concentration profile for the couple in (a).

slightly above the ideal value of 25 at % Si. The slightly higher silicon concentration, relative to the stoichiometric value, can be attributed to the fact that FeSi, and not Fe_3Si, was used as the standard for EDX analysis. In any case, it is clear that the composition of Fe_3Si is constant throughout the layer.

An SEM image and a concentration profile of an Fe–Si couple, annealed at 700 °C for 1007 h (longest annealing time), are shown in Fig. 4. Three silicide layers, corresponding to Fe_3Si, FeSi and $FeSi_2$, appear. FeSi was first observed to appear at ~23 h at 700 °C, while $FeSi_2$ was initially detected after 234 h. In both cases, the phases probably occurred sooner during annealing; however, the order of formation was Fe_3Si, FeSi and then $FeSi_2$. As observed for the lowest annealing time, the silicon concentration is constant within the Fe_3Si layer. At the Fe_3Si/α-Fe interface, there are some cracks and missing material. This is because Fe_3Si is brittle and is unable to deform during polishing like the α-Fe adjacent to it.

EDX results from all Fe–Si diffusion couples studied showed only stoichiometric Fe_3Si adjacent to α-Fe. More than 100 positions along the Fe_3Si/α-Fe interface of each couple were examined in order to confirm this result.

Fe_3Si growth was monitored to determine whether Fe_3Si grew continually throughout the annealing process. The thickness of the Fe_3Si layer is plotted as a function of the square root of annealing time in Fig. 5. It is clear that Fe_3Si continues to grow throughout

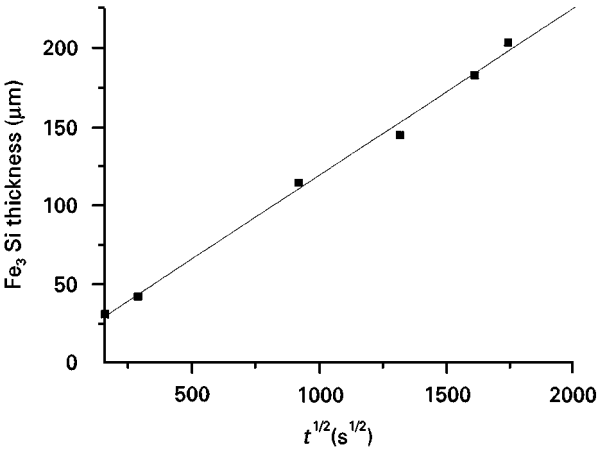


Figure 5 Plot of Fe_3Si layer thickness versus time for Fe–Si couples annealed at 700 °C.

annealing and the linear dependence indicates that growth is diffusion controlled.

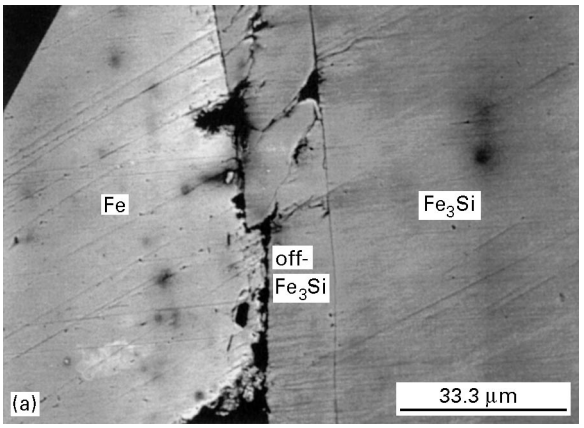
One possible explanation for the lack of off-stoichiometric Fe_3Si is that the Fe_3Si/α-Fe interface region had separated during annealing, cutting off the supply of iron. If this was indeed the case, Fe_3Si would convert to the most silicon-rich composition, i.e. stoichiometric Fe_3Si. We believe that this is not the reason for the observed phenomenon, as crack-free regions along the interface were observed and these contained only the stoichiometric form of Fe_3Si.

3.2. Fe_3Si–Fe couples

A scanning electron micrograph and a corresponding concentration profile of the diffusion zone between Fe_3Si and α-Fe, for a couple annealed at 700 °C for 120 h, are shown in Fig. 6. A variable composition layer, identified as off-stoichiometric Fe_3Si (Fig. 6a), is present at the Fe_3Si/α-Fe interface. The layer thickness (~15–20 μm) was of the same order as the Fe_3Si thickness in the Fe/Si couples annealed at 700 °C for only 7 h. Other couples produced similar results, i.e. off-stoichiometric Fe_3Si formed between Fe_3Si and Fe, and the Fe_3Si growth rate was considerably lower compared with stoichiometric Fe_3Si growth in Fe–Si couples.

4. Discussion

According to the accepted version of the Fe–Si phase diagram (Fig. 1), Fe_3Si exists over a wide composition range (11–25 at % Si) at 600–700 °C. A concentration profile, then, from an Fe–Si diffusion couple annealed in this temperature range, should show a smooth transition from α-Fe to Fe_3Si. Composition profiles obtained here, and from a previous study [1], from Fe–Si couples indicate that only stoichiometric Fe_3Si, and not $Fe_{3+y}Si_{1-y}$, forms. The concentration profiles (Figs 3b and 4b) have a vertical segment between stoichiometric Fe_3Si and α-Fe. On the other hand, off-stoichiometric Fe_3Si does form in Fe–Fe_3Si diffusion couples. The reason for this behaviour will be discussed below.



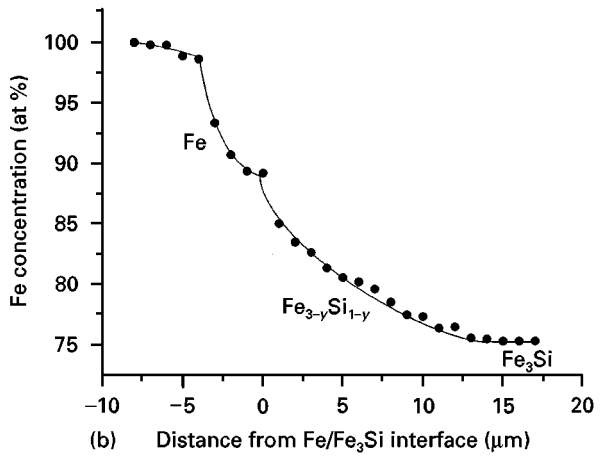


Figure 6 (a) SEM backscattered electron image of the diffusion zone of an Fe_3Si–Fe couple annealed at 700 °C for 120 h. (b) Concentration profile for the couple in (a).

In a phase transformation, in general, there are two main factors controlling phase formation, i.e. thermodynamics (free energy change) and kinetics. Free energy calculations can be done, taking into account chemical and magnetic interactions, using a BWG model [10–14]. Calculations are briefly outlined below.

The most stable configuration corresponds to the minimum value in the configurational free energy, F_k

$$F_k = U_k - TS_k \tag{1}$$

U_k is the internal energy and can be expressed as

$$\begin{aligned} U_k = U_k^o &- N\{4[W + J(2q-1)^2]x^2 \\ &- 3wx^2 + 3/2w(y^2+z^2)\} \\ &- NC_{Fe}C_{Si}\{4[W + J(2q-1)^2] + 3w\} \\ &+ 4NC_{Fe}J(2q-1)^2 \end{aligned} \tag{2}$$

where

$$\begin{aligned} U_k^o = N\{&4(C_{Fe}V_{FeFe} + C_{Si}V_{SiSi}) \\ &+ 3(C_{Fe}v_{FeFe} + C_{Si}v_{SiSi})\} \end{aligned} \tag{3}$$

S_k is the entropy term and has two components.

$$S_k = S_k^c + S_k^q \tag{4}$$

The chemical term is given as

$$S_k^c = -kN/4\sum(p_{Fe}^L \ln p_{Fe}^L + p_{Si}^L \ln p_{Si}^L) \tag{5}$$

and the magnetic term is

$$S_k^q = -kNC_{Fe}[q\ln q + (1-q)\ln(1-q)] \tag{6}$$

k is the Boltzman constant, while W and w are the chemical interchange energies for the process for nearest neighbours and next nearest neighbours, respectively.

$$W = -2V_{FeSi} + V_{FeFe} + V_{SiSi} \tag{7}$$

$$w = -2v_{FeSi} + v_{FeFe} + v_{SiSi} \tag{8}$$

J is the magnetic interchange energy and N is the number of lattice sites. The chemical order parameters (x, y and z) are defined by the occupation probabilities, p_{Fe}^L, of iron in the four sublattices (L = A, B, C or D).

$$x = 1/4(p_{Fe}^A + p_{Fe}^C - p_{Fe}^B - p_{Fe}^D) \tag{9}$$

$$y = 1/2(p_{Fe}^B - p_{Fe}^D) \tag{10}$$

$$z = 1/2(p_{Fe}^A - p_{Fe}^C) \tag{11}$$

$$p_{Fe}^A = C_{Fe} + x + z \tag{12}$$

$$p_{Fe}^C = C_{Fe} + x - z \tag{13}$$

$$p_{Fe}^B = C_{Fe} - x + y \tag{14}$$

$$p_{Fe}^D = C_{Fe} - x - y \tag{15}$$

$$p_{Si}^L = 1 - p_{Fe}^L (L = A, B, C, D) \tag{16}$$

$C_{Fe} = (1 - C_{Si})$ is the atomic concentration of iron. The magnetic order parameter is defined by spin state: $0.5 < q < 1$.

Free energy calculations for Fe_3Si as a function of silicon atom fraction are shown in Fig. 7 for a temperature of 700 °C. The free energy decreases with increasing silicon fraction from 0.12 to 0.25 (12–25 at % Si). Thermodynamically, then, stoichiometric Fe_3Si is the most stable form of Fe_3Si, and would be expected to form preferentially to off-stoichiometric Fe_3Si.

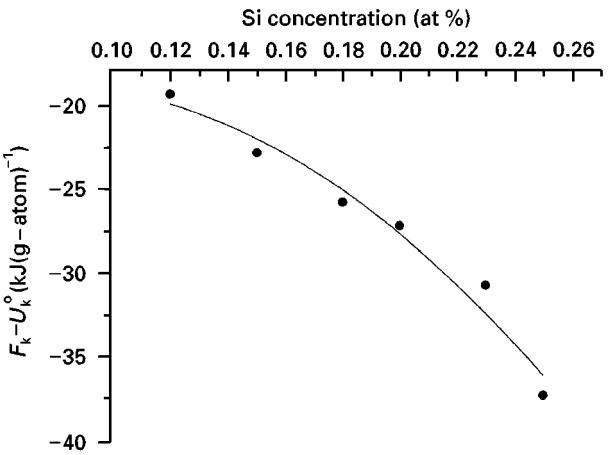


Figure 7 Plot of the difference between the configurational free energy term F_k and the internal energy term U_k^o, which is not a function of the order parameter, versus silicon atom fraction at 700 °C.

Reaction kinetics in diffusion couples are influenced by diffusional processes. Wever and Frohberg [16] and Bakker and Westerveld [17] have proposed that during diffusion in ordered DO_3 lattices, the dominant species (iron in this case) jumps between the three iron sublattices only, i.e. A, C and B sublattices. This model has been confirmed by Sepiol and Vogl [18] using quasielastic Mössbauer spectroscopy (QMS) and quasielastic incoherent neutron scattering (QNS). Strong affinity exists between neighbouring iron and silicon atoms in Fe_3Si, which has been confirmed by Mössbauer spectroscopy [14]. It was found that silicon atoms share their 3s and 3p electrons with neighbouring iron atoms, thus filling the 3d states of the iron atoms. Garba and Jacobs [15] also calculated the affinity of Fe_3Si, using a tight binding model, and showed that a stronger affinity exists between neighbouring iron and silicon atoms than between neighbouring iron and iron atoms. Therefore, it is easier for iron to occupy iron sites than silicon sites, when iron atoms are diffusing in Fe_3Si. If iron atoms only diffuse via A, C and B sites in stoichiometric Fe_3Si, the system structure and free energy will be unchanged.

In off-stoichiometric Fe_3Si, a fraction of the iron atoms must occupy antisite positions on the D sublattice [18,19]. The antistructure has a slightly lower density and a slightly higher vacancy concentration than the ordered structure [17, 20]. Therefore, one might intuitively expect the antistructure to exhibit faster diffusion rates due to the higher vacancy concentration. Kikuchi and Sato [21], however, have shown that in an antisite disordered structure, an atom that has jumped to the "wrong" sublattice does not return immediately to a "correct" position, thereby inhibiting migration over long distances. As the iron concentration increases in Fe_3Si, the number of antisite positions increases which leads to a reduction in the diffusion coefficient. Diffusivities have been measured for stoichiometric and off-stoichiometric Fe_3Si [18]. At 720 °C, the diffusivity for $Fe_{80}Si_{20}$ is a factor of five to ten times lower than that for stoichiometric Fe_3Si.

One can conclude from the above arguments that not only is stoichiometric Fe_3Si thermodynamically the most stable form of Fe_3Si, but its growth is also kinetically preferred over off-stoichiometric Fe_3Si. As such, only stoichiometric Fe_3Si would be expected in Fe/Si couples. In the Fe/Fe_3Si couples, off-stoichiometric Fe_3Si forms at the interface, but grows more slowly as a result of slower diffusion rates through the antistructure.

5. Conclusions

1. In the Fe_3Si diffusion layer of Fe–Si diffusion couples, only stoichiometric Fe_3Si forms. Off-stoichiometric Fe_3Si forms in Fe_3Si–Fe couples. These results are explained based on thermodynamic and kinetic arguments.

2. The thickness of the Fe_3Si layer in Fe–Si diffusion couples increases linearly as a function of the square root of the diffusion time.

3. At 700 °C stoichiometric Fe_3Si is the most stable form of Fe_3Si.

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References

1. N. R. BALDWIN and D. G. IVEY, *J. Phase Equilib.* **16** (1995) 1.
2. O. KUBASCHEWSKI, "Iron-Binary Phase Diagrams" (Springer, New York, 1982) p. 136.
3. J. KUDRNOVSKY, N. E. CHRISTENSEN and O. K. ANDERSEN, *Phys. Rev. B* (7) **43** (1993) 5924.
4. J. L. BUDNICK, T. ZHENGQUAN and D. M. PEASE, *Physica B* **158** (1989) 31.
5. A. C. SWINTENDICK, *Solid State Commun.* **19** (1976) 511.
6. A. PAOLETTI and L. PASSARI, *Nuovo Cim.* **XXXII** (1964) 1449.
7. T. J. BURCH, T. LITRENTA and J. I. BUDENICK, *Phys. Rev. Lett.* **33** (1974) 421.
8. C. BLAAUW, G. R. MACKAY and W. LEIPER, *Solid State Commun.* **18** (1975) 729.
9. S. PICKART, T. LITRENTA, T. J. BURCH and J. I. BUDINICK, *Phys. Lett. A* **53** (1975) 321.
10. G. INDEN and W. PITSCH, *Z.Metallkde* **62** (1971) 627.
11. G. SCHLATTE, G. INDEN and W. PITSCH, *ibid.* **65** (1974) 94.
12. G. INDEN and W. PITSCH, *ibid.* **63** (1972) 253.
13. G. INDEN, *ibid.* **68** (1977) 529.
14. M. B. STEARNS, *Phys. Rev.* **147** (1966) 439.
15. E. J. D. GARBA and R. L. JACOBS, *Phys. F Met. Phys.* **16** (1986) 1485.
16. H. WEVER and G. FROHBERG, *Z. Metallkde* **65** (1974) 747.
17. H. BAKKER and J. P. A. WESTERVELD, *Phys. Status Solidi b* **145** (1988) 409.
18. B. SEPIOL and G. VOGL, *Phys. Rev. Lett.* **71** (1993) 731.
19. K. SZYMAÑSKI, L. DOBRZYÑOKI and R. BURZYÑSKA, *Hyperf. Interact.* **59** (1990) 477.
20. K. SZYMAÑSKI, S. LEFEBVRE and M. BESSIERE, *Mater. Sci. Forum* **166–169** (1994) 433.
21. R. KIKUCHI and H. SATO, *Phys. Rev.B* **28** (1983) 648.

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