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Non-equilibrium segregation of solute to grain boundary

Part I *boron segregation in Fe–3%Si during cooling*

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The behaviour of boron segregation to grain boundaries in Fe–3%Si has been studied by means of particle tracking autoradiography. The results indicate that (i) the binding energy between boron atoms and grain boundaries is 55.7 ± 1.7 kJ mol^{-1}; (ii) in contrast to the nature of boron segregation in γ-Fe, no observable non-equilibrium segregation of boron to grain boundaries exists in Fe–3%Si alloy during cooling and isothermal holding.

1. Introduction

Impurity segregation and its influence on the properties of materials have been of interest for some time. Boron is among the elements which, as small additions, can change the properties of materials considerably. It is known that boron atoms are segregated to austenite grain boundaries [1] and improve the hardenability of steels [2]. The addition of boron also influences the recrystallization of high strength low alloy steel (HSLA) [3] and Fe–3%Si alloy [4].

The behaviour of boron segregation to grain boundaries has been studied extensively in austenite steels [5–8]. The results of these studies indicated that there are two kinds of boron segregation to austenite grain boundaries: equilibrium segregation and non-equilibrium segregation (the latter, i.e. quench-induced non-equilibrium segregation), and these two kinds of boron segregation can occur simultaneously or separately. However, as the time- and temperature-dependence of these two kinds of segregations are different, the shape of the resulting boron concentration profiles across grain boundaries and the width of those affected are quite different.

Although the phenomenon of non-equilibrium segregation was recognized 20 years ago, most studies have been carried out only in materials with f c c structure. This has prevented the development of a complete understanding of the underlying mechanism. In 1979, evidence for boron enrichment at grain boundaries in Fe–3%Si was reported [9] and it was thought to considerably influence the alloy recrystallization, but the segregation behaviour has not been investigated in detail. The present study is an investigation of the behaviour of boron segregation to grain boundaries during cooling and isothermally held in Fe–3%Si alloy. A comparison of the results with the behaviour of boron non-equilibrium segregation in austenite steels should lead to better understanding of the mechanism of non-equilibrium segregation.

2. Experimental procedure

2.1. Materials

The composition of the alloy used in this study is given in Table I. The alloy has a b c c structure in the experimental temperature range and thus is suitable for studies of the behaviour of boron segregation in α-Fe. The alloy was prepared with a 25-kg induction furnace and contained a Ti addition to protect the boron. The ingots were heated to 1150 °C and forged into 12-mm-diameter bars. Specimens were machined into the required sizes from the bar after the decarburized layers had been machined away (these layers were also assumed to have been depleted in boron).

2.2. Heat treatment of the specimens

2.2.1. Treatments A and B

Specimens were heated to 1200 °C for 30 min under argon and then cooled in the furnace to room temperature, then reheated to different temperatures, held for different times and quenched in ice-brine (Treatment A) or held for 30 min and cooled in air or quenched in water (Treatment B). The size of specimens in Treatment A was 8 × 4 mm, and in Treatment B, 10 × 12 mm. The heat-treatment schedules pertaining to those samples are shown schematically in Fig. 1a and b.

2.2.2. Treatment C

Disc specimens, 7 mm in diameter and 4 mm thick, were heated to 1200 °C for 600 s in argon atmosphere, then quenched and isothermally held in a Sn bath at

TABLE I Chemical compositions of iron alloys used (wt %)

C	Si	Mn	P	S	Al	Ti	B	Fe
0.017	2.87	0.063	0.008	0.002	0.12	0.043	0.0030	balance

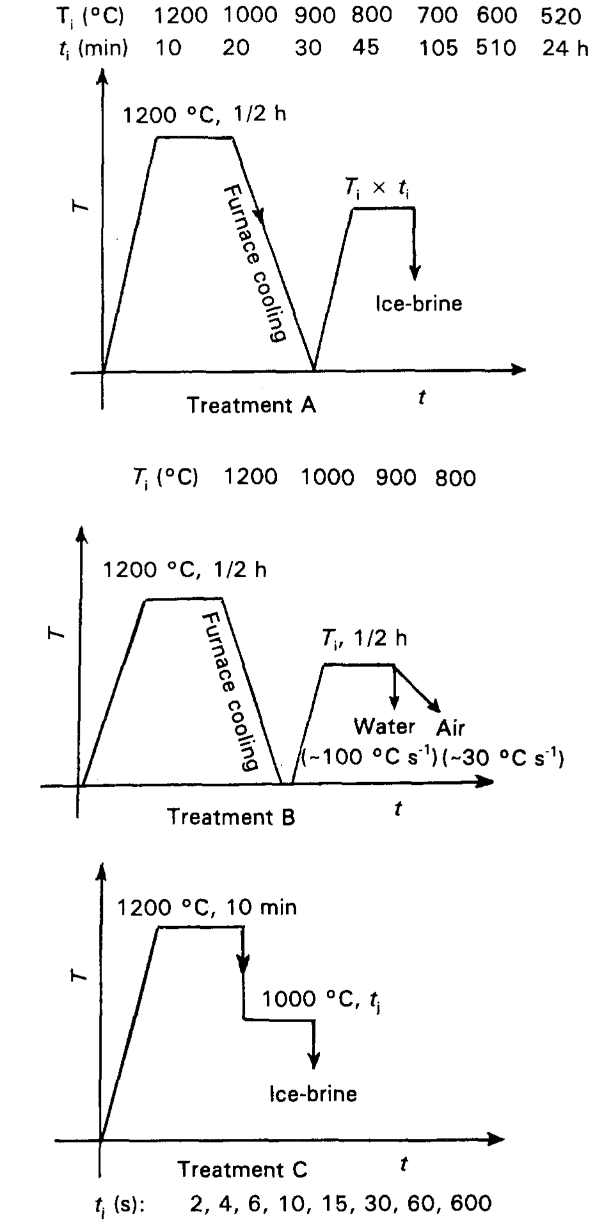


Figure 1 Schematic diagrams of the procedure of heat treatment.

1000 °C for increasing times, after which they were quenched in ice-brine. This treatment is described schematically in Fig. 1c.

2.3. Determination of the boron distribution

After heat treatment, the boron-depleted layers were removed from the surface of the samples and then samples were prepared for the metallograph. The boron distribution was revealed with the aid of the particle tracking autoradiography (PTA) technique, which was based on the $^{10}B(n,\alpha)^{7}$ Li fission reaction [10]. A cellulose acetate film was used as a solid detector, and the film-coated specimens were irradiated in a beam of thermal neutrons in a suitable reactor; the integrated flux was 1×10^{15} neutrons cm^{-2}. After etching in a strong alkaline solution and coating with chromium, the films were examined under an optical microscope. The detecting boron sensitivity of the PTA technique used in this study was ~ 1 p.p.m., and the spatial resolution was ~ 2 μm [10].

In order to enable the characteristics of the boron distribution revealed by PTA to be assessed semi-quantitatively, all the samples used for measurement purposes were irradiated with the same integrated flux, and all detective films were cut from a single, large piece of cellulose acetate film. The films were carefully etched and observed to obtain etch pits of similar size and homogeneous distribution.

3. Results

3.1. Equilibrium grain-boundary segregation of boron in Fe–3%Si

The samples, 8 × 4 mm, were heated to 1200 °C, and cooled in the furnace to room temperature, and then reheated to different temperatures and quenched in ice-brine (Treatment A). As the cooling rate was fast enough, the boron distribution at quenching temperature was basically kept to room temperature. The state of boron revealed by PTA is shown in Fig. 2. It can be seen that no observable boron segregation exists when the quenching temperatures are above 900 °C; below 900 °C their boron segregation and boride precipitation is seen in specimens. These have the characteristics of McLean equilibrium segregation.

Assuming that the area fraction S of etch pits is proportional to boron concentration C (i.e. $S = E\phi C$, where ϕ is the integrated flux of thermal neutrons and E is an experiment constant). The ratio of concentration in two regions is equal to the ratio of the area fractions of etch pits [5]. The average area fraction of etch pits was measured in the grain-boundary region of width 3.72 μm (w) (S_{gb}) and in the matrix (S_g) (Fig. 3). S_{gb}/S_g was defined to describe the degree of this segregation. The dependence of boundary segregation S_{gb}/S_g on quenching temperature is shown in Fig. 4. According to the theory of McLean equilibrium segregation [11],

$$\frac{C_{gb}}{C_g} = A\exp\left(\frac{Q}{RT}\right)$$

where C_{gb} and C_g are the solute concentrations at the grain boundary and matrix, respectively; Q is the binding energy of solute segregation to the grain boundary; A is a constant; T is the temperature.

If d is the width of the grain boundary, the average concentration C'_{gb} of boron in the grain-boundary region of width W ($W = 3.72$ μm) is $(d*C_{gb} + (W - d)*C_g)/W$. As $S_{gb}/S_g = C'_{gb}/C_g$, we have

$$\frac{S_{gb}}{S_g} = \frac{dC_{gb} + (W-d)C_g}{WC_g}$$

$$\because W \gg d$$

$$\therefore \frac{S_{gb}}{S_g} = \frac{d}{W}\frac{C_{gb}}{C_g} + 1$$

$$= \frac{d}{W}A\exp\left(\frac{Q}{RT}\right) + 1$$

$$\therefore \ln\left(\frac{S_{gb}}{S_g} - 1\right) = \frac{Q}{R}\frac{1}{T} + \ln\left(\frac{Ad}{W}\right)$$

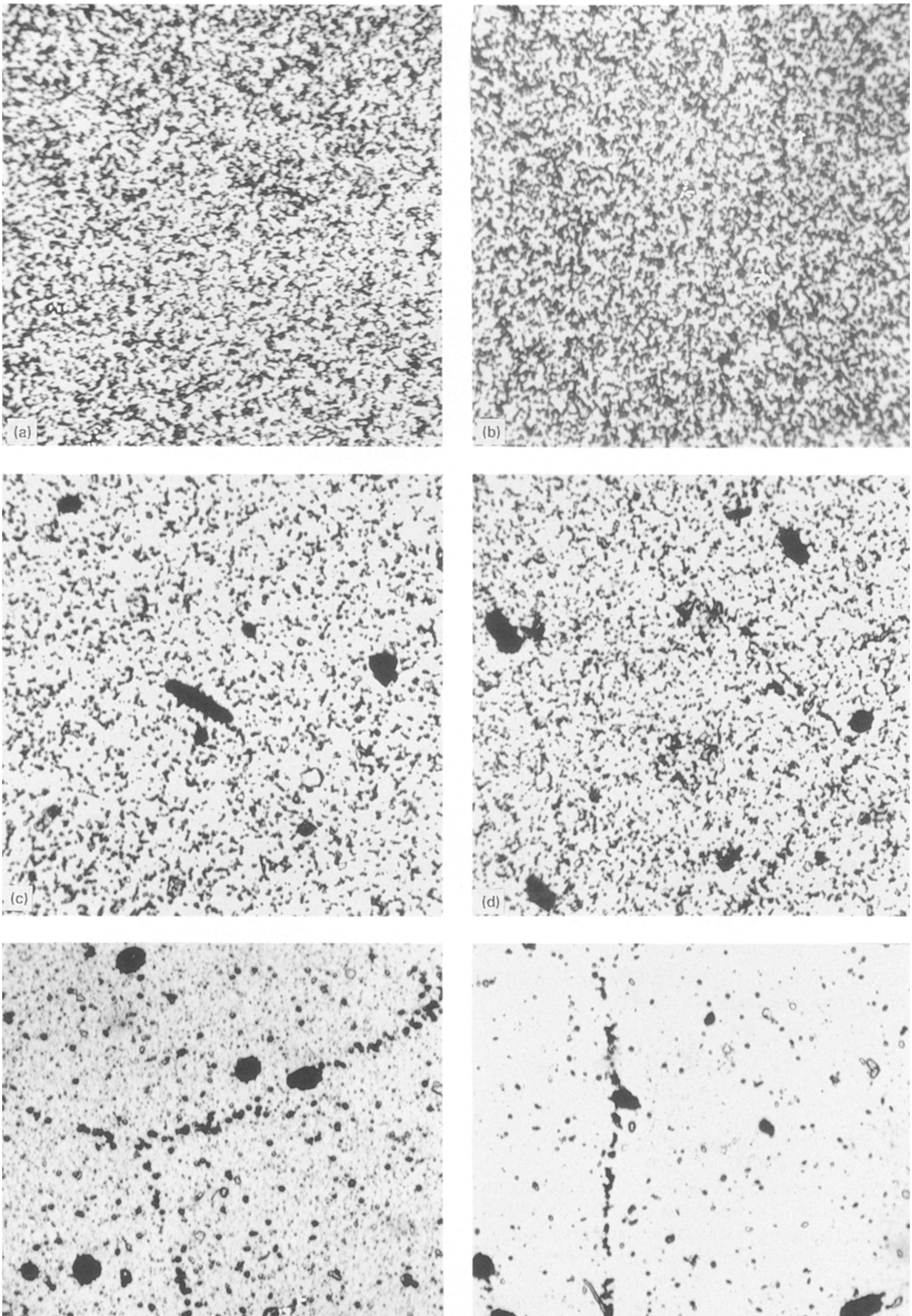


Figure 2 Boron distribution revealed by PTA in Fe–3%Si alloy ice-brine quenched from temperatures indicated. (a) 1200; (b) 1000; (c) 900; (d) 800; (e) 600; (f) 520 °C. Integrated irradiation flux: 1×10^{15} n cm^{-2}.

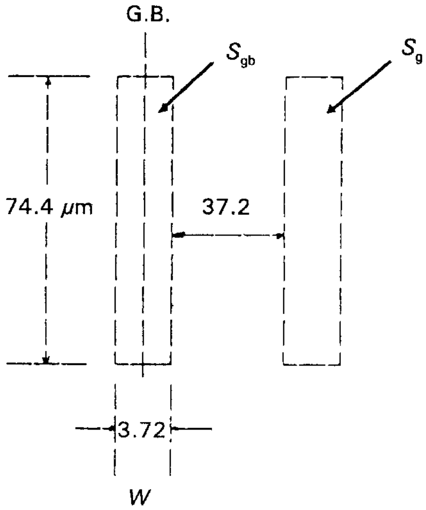


Figure 3 Schematic diagram to determine boron segregation at grain boundaries, S_{gb}/S_g. Gb, grain boundary.

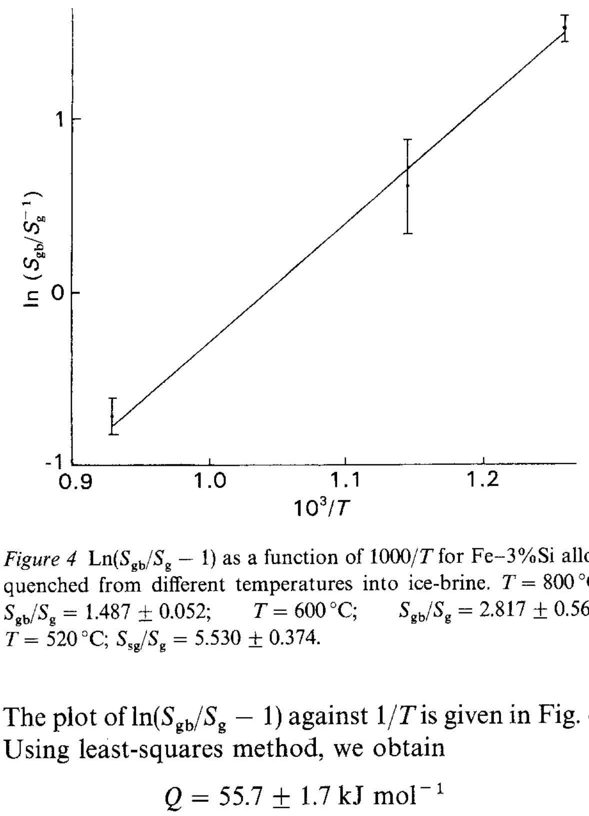


Figure 4 $\ln(S_{gb}/S_g - 1)$ as a function of $1000/T$ for Fe–3%Si alloy quenched from different temperatures into ice-brine. $T = 800\,°C$, $S_{gb}/S_g = 1.487 \pm 0.052$; $T = 600\,°C$; $S_{gb}/S_g = 2.817 \pm 0.568$; $T = 520\,°C$; $S_{sg}/S_g = 5.530 \pm 0.374$.

The plot of $\ln(S_{gb}/S_g - 1)$ against $1/T$ is given in Fig. 4. Using least-squares method, we obtain

$$Q = 55.7 \pm 1.7\ \text{kJ mol}^{-1}$$

$$Ad = 3.38 \pm 0.75\ \text{nm}$$

3.2. Boron distribution during cooling ($\sim 400\,°C\,s^{-1}$)

The heat-treatment procedure is shown in Fig. 1b (Treatment B). The specimen size is 10 × 12 mm, and the specimen is quenched in water after holding for 30 min at high temperature (the cooling rate is $\sim 400\,°C\,s^{-1}$).

The boron distributions are given in Fig. 5. As in the results given in Section 3.1, below 900 °C boron segregation and boride precipitation are seen. However boron segregation is seen along grain boundaries in the specimens quenched from high temperatures above 900 °C. This means that the cooling rate is not fast enough to inhibit segregation developing during cooling. The dependence of boundary segregation during cooling on quenching temperature was measured as it is a very important parameter for distinguishing the classification of segregation, i.e. equilibrium and/or non-equilibrium segregation [5, 6]. As in the above section, S_{gb}/S_g describes the degree of segregation. The values of S_{gb}/S_g at different quenching temperatures (1200, 1100 and 1000 °C) are given in Fig. 6. It can be seen that the segregation S_{gb}/S_g is not sensitive to quenching temperature in Fe–3%Si alloy.

3.3. Boron distribution during cooling ($\sim 30\,°C\,s^{-1}$)

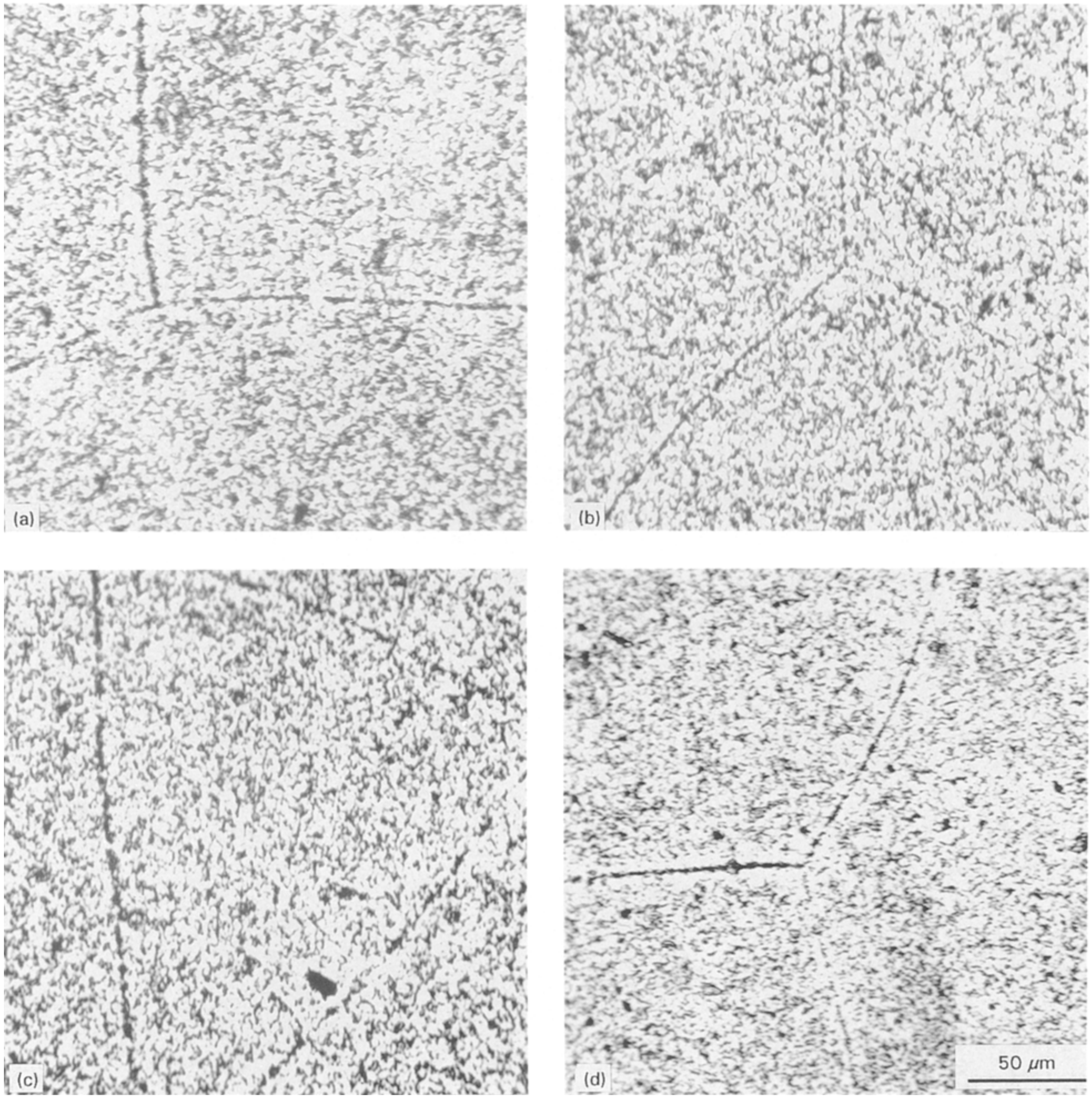
The boron distribution was revealed by PTA in air-cooled samples (Treatment B). The results are shown in Fig. 7. It can be seen that below 900 °C the results are similar with those presented in Section 3.2, but above 900 °C boron segregation and boride precipitation are seen, and a boron-depleted zone arises near the boundaries. The width of this boron-depleted zone can be used to describe the degree of enrichment and characterize the nature of segregation [5, 10]. For this purpose, employing the same method as used in the literature [5], we measured the width of the boron-depleted zones at different quenching temperatures: 1200, 1100 and 1000 °C. The results are shown in Fig. 8. It can be seen that the effect of quenching temperature on the width of the boron-depleted zone is very small.

3.4. Boron distribution during isothermal holding

It is known that the one of the main characteristics of non-equilibrium segregation is the appearance of a peak on the segregation-holding time curve [6, 12]. To characterize the nature of boron segregation in Fe–3%Si, boron segregation during isothermal holding (Treatment C) was investigated. The specimens were heated to 1200 °C and held for 600 s in argon atmosphere, then quenched and isothermally held in a Sn bath at 1000 °C. After holding for different times at 1000 °C, the specimens were quenched in ice-brine water. As the specimen size was very small (8 × 4 mm), the cooling rate of the specimens quenched in ice-brine water from 1000 °C was fast enough to inhibit segregation developing during the quenching process. The boron distributions at different times during isothermal holding at 1000 °C are given in Fig. 9. It is shown that the boron distribution is nearly homogeneous and no observable boron segregation occurs during the whole isothermal holding process.

4. Discussion

The results obtained in Section 3.1 indicate that the tendency of equilibrium segregation of boron to grain boundaries in Fe–3%Si (α-Fe) ($Q = 55.7\ \text{kJ mol}^{-1}$) is stronger than that in γ-Fe ($Q = 40.2\ \text{kJ mol}^{-1}$ [13]). The binding energy of boron segregation in Fe–3%Si ($55.7\ \text{kJ mol}^{-1}$) is also larger than the binding energy of carbon segregation in α-Fe ($50\ \text{kJ mol}^{-1}$) [14]. This



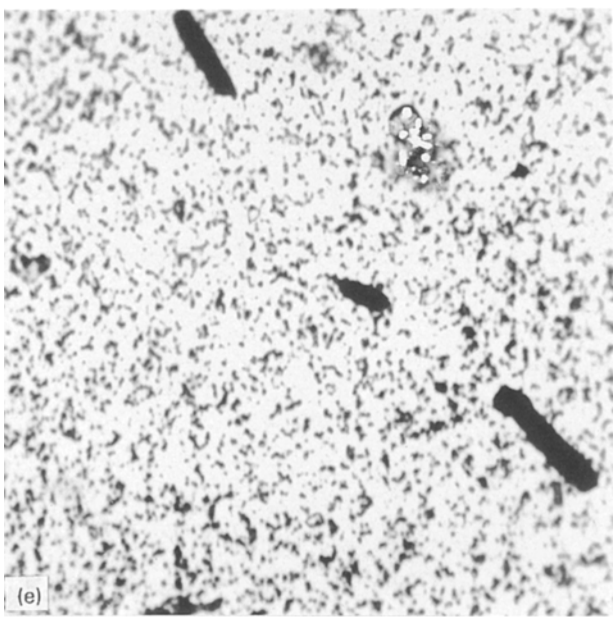


Figure 5 Boron distribution revealed by PTA in Fe–3%Si alloy quenched into water from the temperature indicated. (a) 1200; (b) 1100; (c) 1000; (d) 900; (e) 800 °C. Integrated irradiation flux: 1×10^{15} n cm^{-2}.

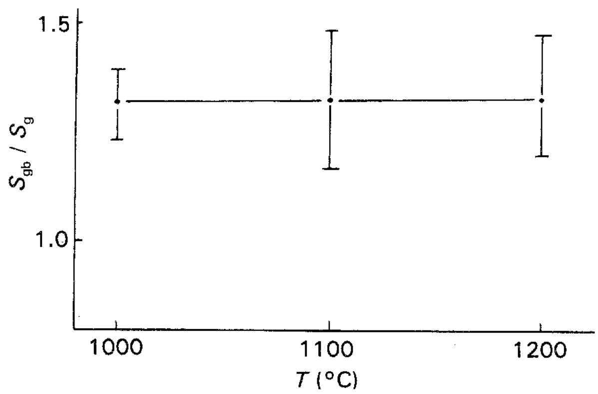
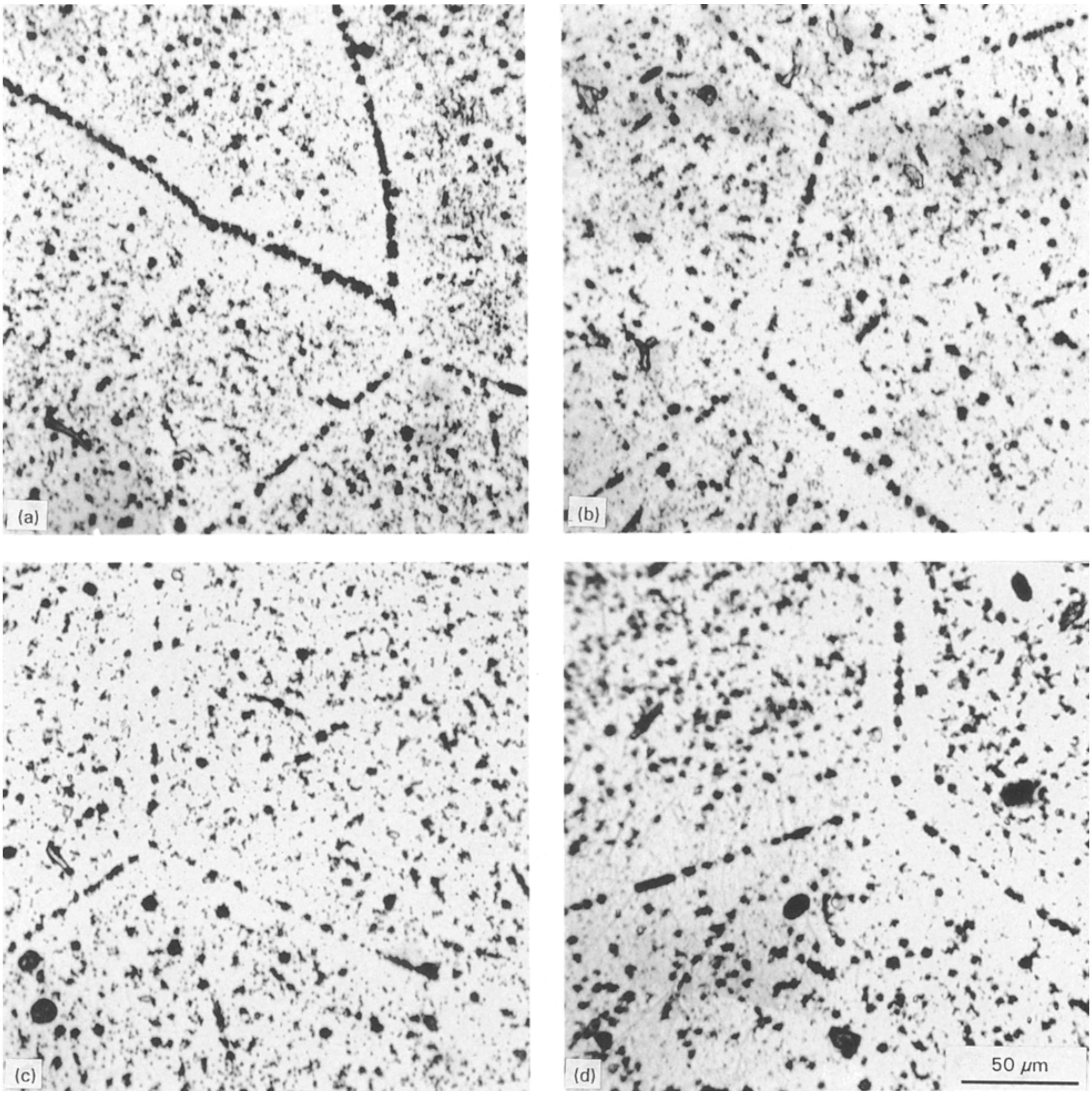


Figure 6 Boron segregation S_{gb}/S_g as a function of quenching temperature in Fe–3%Si alloy cooled in water. $T = 1200\,°C$, $S_{gb}/S_g = 1.336 \pm 0.141$; $T = 1100\,°C$, $S_{gb}/S_g = 1.330 \pm 0.157$; $T = 1000\,°C$, $S_{gb}/S_g = 1.320 \pm 0.084$.



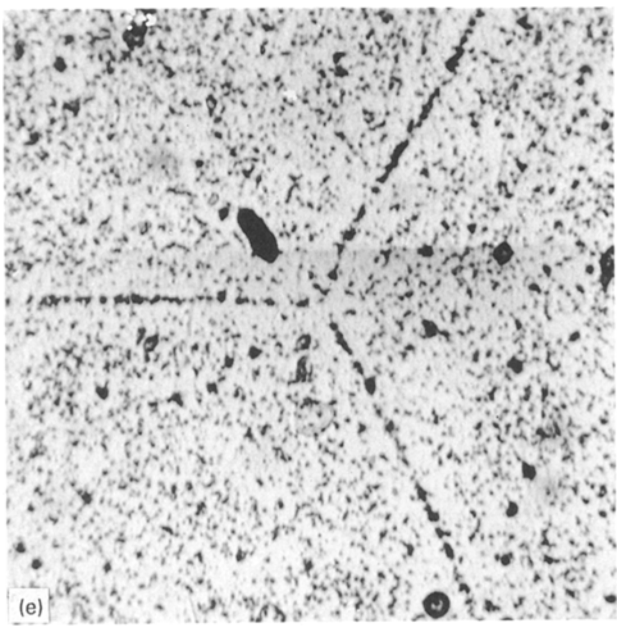


Figure 7 Boron distribution revealed by PTA in Fe–3%Si alloy cooled in air from the temperature indicated. (a) 1200; (b) 1100; (c) 1000; (d) 900; (e) 800 °C. Integrated irradiation flux: 1×10^{15} n cm^{-2}.

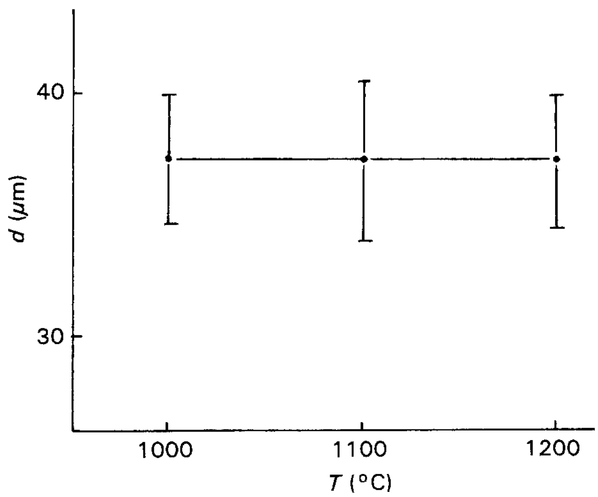


Figure 8 Width of boron-depleted zone d as a function of quenching temperature in Fe–3%Si alloy, air-cooled. $T = 1200$ °C, $d = 37.24 \pm 2.75$ μm; $T = 1100$ °C, $d = 37.27 \pm 3.27$ μm; $T = 1000$ °C, $d = 37.35 \pm 2.64$ μm.

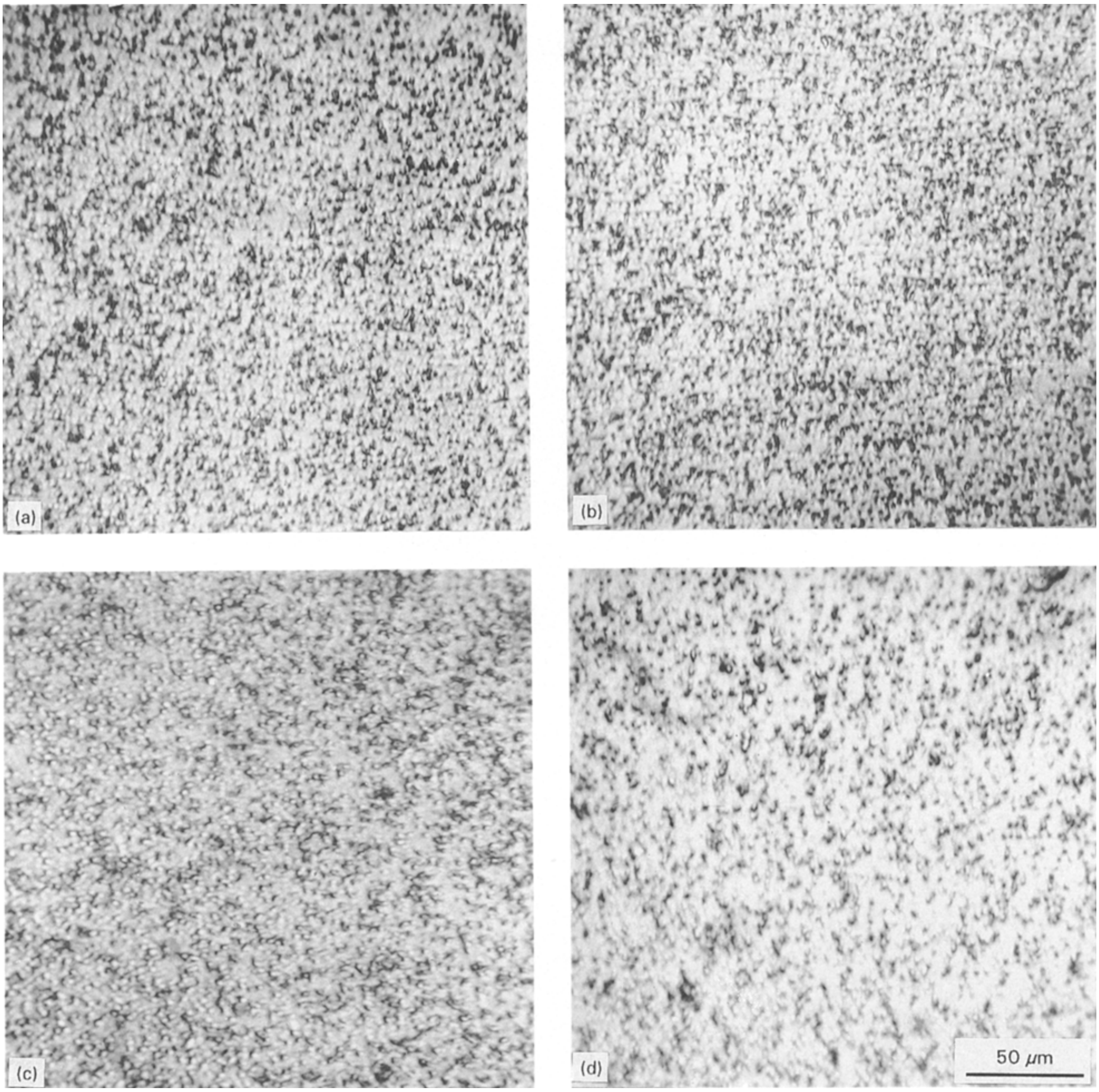


Figure 9 Boron distribution revealed by PTA in Fe–3%Si alloy held at 1000 °C and quenched into ice-brine after holding at times indicated. (a) 4; (b) 6; (c) 10; (d) 15 s. Integrated irradiation flux: 1×10^{15} n cm^{-2}.

means that boron is a very strong boundary adhesion element in α-Fe.

It is known that there is a non-equilibrium segregation of boron to grain boundaries in γ-Fe [5–7]. The main characters of non-equilibrium segregation of boron in γ-Fe are: (i) the non-equilibrium segregation is enhanced by increasing quenching temperature, and is sensitive to the cooling rate; (ii) the width of the boron-depleted zone increases as the quenching temperature increases; (iii) there is a peak on the segregation–holding-time curve during isothermal holding. Comparing these characteristics with the results in Sections 3.2–3.4, it is concluded that there was no observable non-equilibrium segregation of boron to grain boundaries in Fe–3%Si. The experimental results indicate that the behaviour of boron segregation in Fe–3%Si alloy during cooling and during the isothermal holding process belongs to the typical nature of equilibrium segregation dynamics [11, 15]. The non-equilibrium segregation of boron to grain boundaries in γ-Fe during cooling has been analysed by Williams [16], Faulkner [17], He *et al.* [5, 6] and Chu [18]. According to their views, the non-equilibrium segregation is controlled by the diffusivity of point defects and the interactions among point defects. So the difference between the segregation dynamics of boron in γ-Fe and in α-Fe may be explained by the mechanism of non-equilibrium segregation and point-defect properties in α-Fe and γ-Fe. On the other hand, based on the point-defect properties of boron in α-Fe and γ-Fe, the different behaviours of boron segregation in α-Fe and γ-Fe are helpful to a fuller understanding of the mechanism of non-equilibrium segregation [19].

5. Conclusions

1. The tendency of equilibrium segregation of boron to grain boundaries in Fe–3%Si is very strong.

The binding energy between boron and grain boundaries is 55.7 ± 1.7 kJ mol^{-1}.

2. In contrast to the nature of boron segregation in γ-Fe, no observable non-equilibrium segregation of boron to the grain boundary exists in Fe–3%Si during cooling and isothermal holding.

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