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Non-equilibrium segregation of solute to grain boundary

Part II *Boron segregation on moving grain boundary during recrystallization in Fe–3%Si*

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Boron distribution on moving grain boundaries during recrystallization was investigated in Fe–3%Si by means of particle-tracking autoradiography. The experimental results indicated that at the beginning of recrystallization no boron segregation appears on moving boundaries, but as the holding time is increased and recrystallization continues, the boron segregation is intensified and persists with the new boundaries moving forward; as the holding time extends further, the recrystallization is nearly complete and the moving velocity of the boundary decreases, then the boron segregation begins to decrease and disappear. The maximum segregation on the moving boundaries is much higher than the equilibrium segregation estimated by the McLean equation at the same temperature. These results cannot be properly interpreted by the existing theories relating solute segregation to the boundaries.

1. Introduction

It has long been known that small additions of solute have significant effects on the recrystallization, grain growth and kinetics of phase transformation in metals. Theoretical and experimental investigations [1] have shown that foreign solute atoms influence the process of recrystallization due to a direct interaction between moving grain boundaries and foreign atoms. In 1983, Kasen [2] investigated the recrystallization and grain growth in dilute aluminium alloys by measuring residual resistance; his results indicated that the solute atoms could be absorbed constantly by migrating boundaries. During these processes, the solute enrichment ratio on migrating boundaries was much higher than the value estimated by the equilibrium segregation McLean equation, even up to boundary saturation. Recently, He *et al.* [3–5] have reported that in γ-Fe there is boron non-equilibrium segregation on static grain boundaries during continuous cooling and isothermal holding, and on moving boundaries during recrystallization after high-temperature deformation. The experimental results have also shown that there is no observable non-equilibrium segregation of boron to grain boundaries during cooling and isothermal holding in α-Fe [6]. For the non-equilibrium segregation during cooling and isothermal holding, some preliminary theoretical models have been proposed. However, up to now only limited theoretical and experimental studies have been undertaken on the non-equilibrium segregation of solute to grain boundary during recrystallization. In particular, no research work has been reported in bcc metals.

2. Experimental procedure

The composition of the material used in this study is shown in Table I. The alloy was prepared with a 25-kg induction furnace and contained Ti addition to protect boron. Before heat treatment, all specimens were heated to 1200 °C for 30 min under argon and cooled in the furnace to room temperature. The specimens were then machined to the size 6 × 20 mm. The procedures for heat treatment are given in Fig. 1. All heat treatments were done with heat simulator Gleeble-1500. In treatment D, the specimens were heated to temperature T_i and isothermally held (t_i), then the specimens were deformed 50%. Specimens were either cooled at a rate of 30 °C s^{-1} immediately after deformation, or isothermally held for 2 s after deformation and then quenched into ice-brine after holding for 2 s (experiments on undeformed specimens were also carried out under the same experimental conditions). Treatment D was to investigate the different boron distributions between deformed and undeformed specimens, and to study boron distribution during cooling and recrystallization after 50% deformation. In treatment E, the specimens were heated to 1000 °C and isothermally held for 5 min, and the specimens then deformed 20%; after deformation the

TABLE I Composition of the material tested (wt %)

C	Si	Mn	P	S	Al	Ti	B	Fe
0.016	2.86	0.065	0.009	0.002	0.11	0.042	0.0046	balance

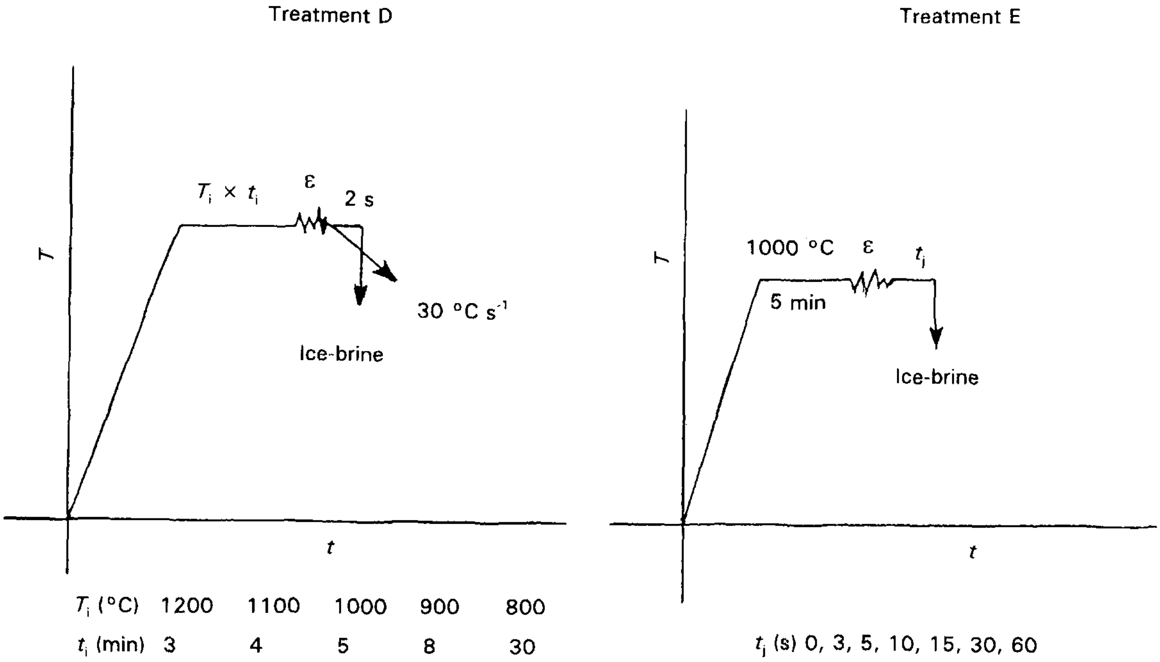


Figure 1 The procedures of heat treatment. Treatment D, $\varepsilon = 50\%$, $\dot{\varepsilon} = 5\ s^{-1}$; Treatment E, $\varepsilon = 20\%$, $\dot{\varepsilon} = 5\ s^{-1}$.

specimens were continuously held for time t_j, then quenched into ice-brine. Treatment E was to investigate the behaviour of boron segregation during isothermal recrystallization at 1000 °C. In all the above deformation experiments, the strain rate was $5\ s^{-1}$.

The boron distribution was revealed with the aid of particle-tracking autoradiography (PTA). A detailed procedure is given in Section 2.3 of [6].

3. Results

3.1. Boron distribution in deformed and undeformed specimens

Fig. 2 shows the boron distribution in deformed ($\varepsilon = 50\%$) and undeformed ($\varepsilon = 0$) specimens cooled from different temperatures with a cooling rate of $30\ °C\ s^{-1}$ (treatment D). It can be seen that boride is precipitated on grain boundaries in both cases. However the boron distribution in some deformed grains is not the same as the distribution in undeformed specimens above 1000 °C. In undeformed specimens, there are borides in the grain interior and there is no observable difference in boron distribution among grains. In the deformed samples, in some grains the boron distribution is similar to undeformed samples, although there is more boride, but in some other grains in the deformed sample, the boron distribution is nearly homogeneous and there is less and smaller boride (the picture at 1100 °C shows a typical case). From Fig. 2, below 1000 °C the boron distribution in deformed and undeformed specimens is similar, the only difference is that the grain boundaries in deformed samples are straight and parallel to each other, which presumably results in deformation.

In this experiment the cooling rate of $30\ °C\ s^{-1}$ is relatively low. The cooling process from 1200 to 1000 °C takes ~ 6 s, so it can be expected that specimens deformed above 1000 °C will produce partial recrystallization during cooling. Thus when the specimen deformed above 1000 °C was cooled at $30\ °C\ s^{-1}$ to ~ 900 °C, which is the start temperature of boride precipitation [6, 7], there are two kinds of grain in the sample: new or recrystallized grains, and old or deformed grains, which may be the reason for the difference in boron distribution among grains.

3.2. Boron distribution in deformed specimens quenched in ice-brine

In the above experiment, as the cooling rate is slow, boron segregation and boride precipitation are seen in the boundaries, which are formed during cooling. In order directly to observe boron distribution during recrystallization at high temperatures, the deformed specimen was quenched into ice-brine after holding ~ 2 s after 50% deformation. Although the 2 s is a short time, it is long enough to produce partial recrystallization in the specimens deformed (50%) at 1200 and 1100 °C (shown by metallographs of the specimens). Because the cooling rate is so fast ($> 600\ °C\ s^{-1}$), the boron distribution at high temperature (deformation temperature) can be kept to room temperature.

Fig. 3 shows the boron distribution in the specimens quenched from different temperatures. It can be seen that there are some curved bands of boron enrichment in the specimens deformed at 1200 and 1100 °C. However the experimental results in part 1 of this study [6] have shown that under the same experimental conditions and the same cooling rate, there is no observable boron segregation in the undeformed specimen quenched from 1200 and 1100 °C. Comparing the deformed with the undeformed specimen, we find recrystallization and boron segregation in the deformed specimen but not in the undeformed specimen. Moreover, the boron enrichment bands are curved, which is same as the form of the recrystallized boundary. Thus

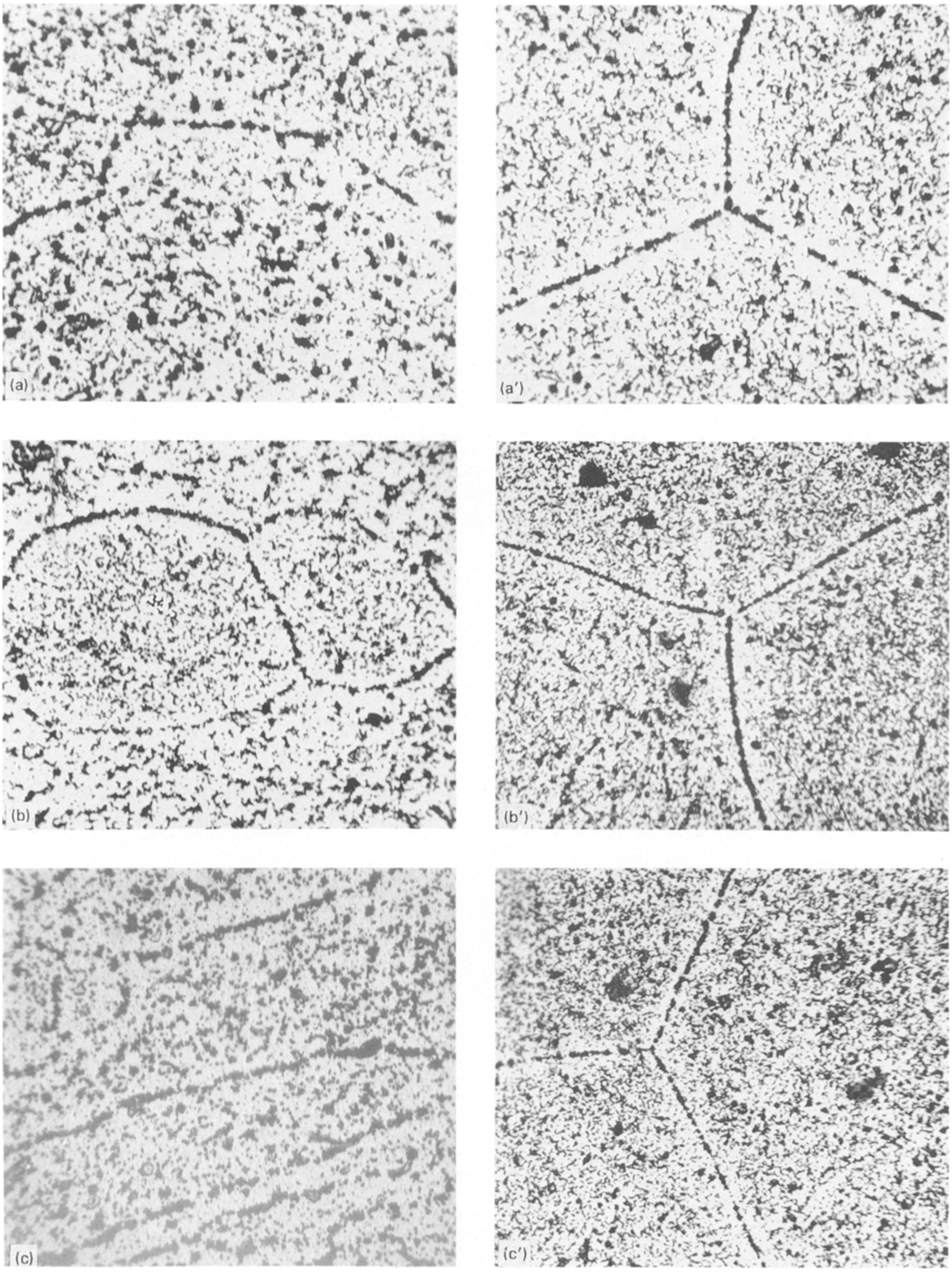
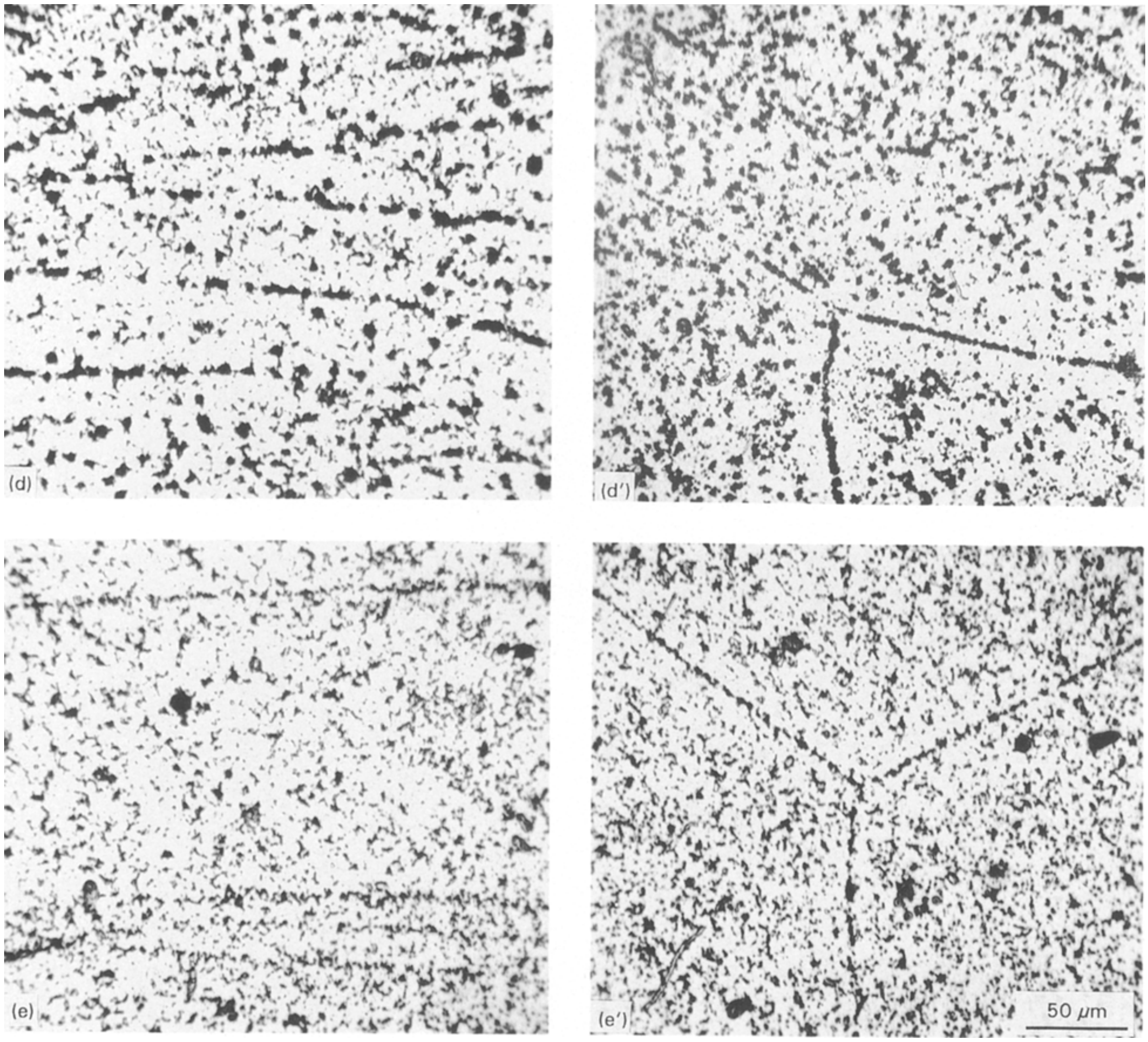


Figure 2 Boron distribution revealed by PTA in Fe–3%Si alloy deformed (ε = 50%, left) and undeformed (right), cooled at 30 °C s^{-1} from the temperature indicated. (a) 1200; (b) 1100; (c) 1000: (d) 900; (e) 800 °C.

the boundaries, which boron segregates to in the deformed specimen, are likely to be newly formed boundaries during recrystallization. (The experiment results in the next section will provide further evidence).

In the specimens deformed at 900 and 800 °C, there is no curved band of boron enrichment. This is because the deformation temperature is so low that no recrystallization occurs during deformation and cooling.



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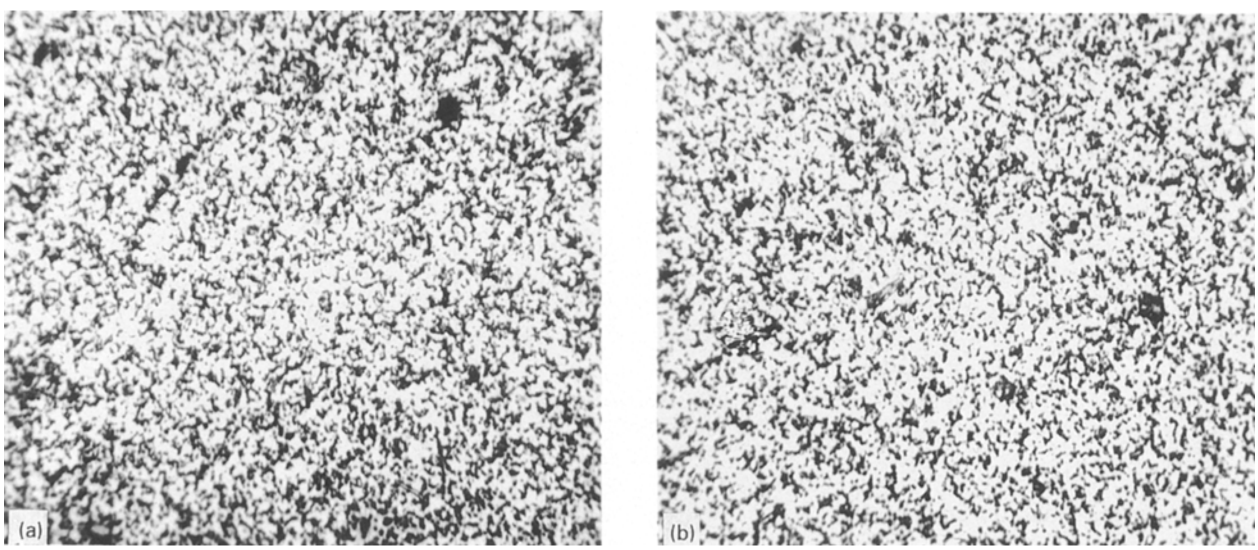
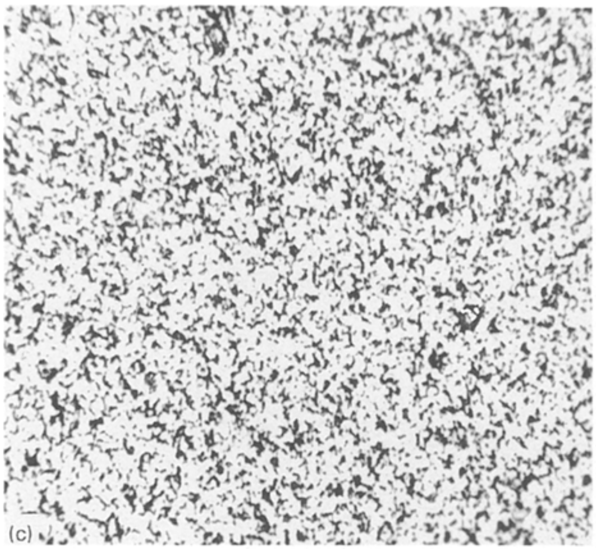


Figure 3 Boron distribution revealed by PTA in Fe–3%Si alloy annealed at the temperature indicated and quenched into ice-brine after deformation (ε = 50%). (a) 1200; (b) 1100; (c) 1000; (d) 900; (e) 800 °C.



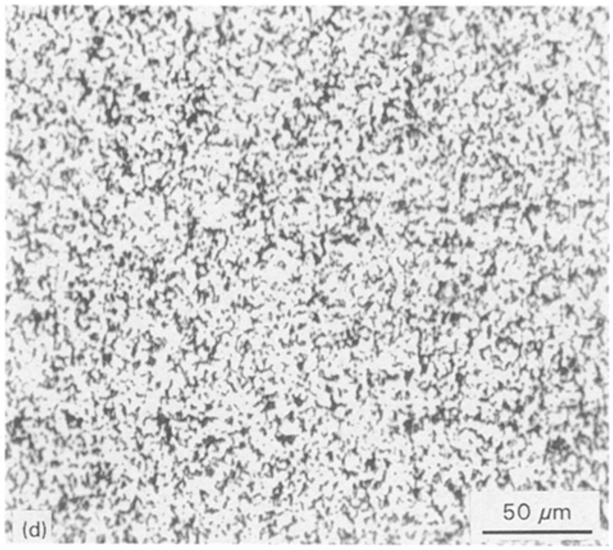
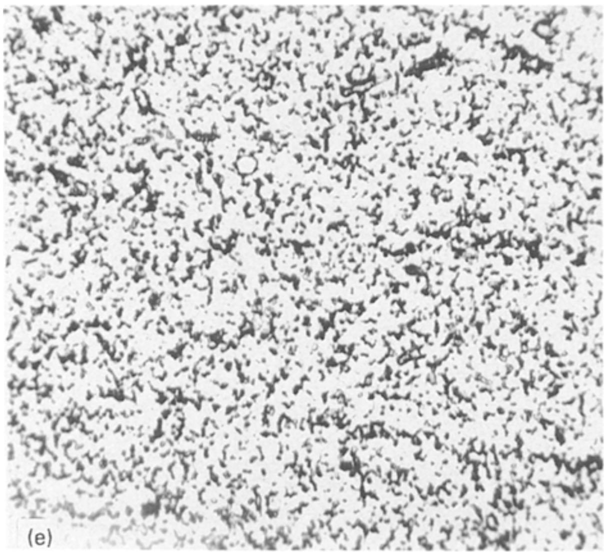


Figure 3 Continued.



3.3. Boron distribution during isothermal recrystallization at 1000 °C

In the present work, the samples were quenched into ice-brine after deformation and held for increasing holding times at 1000 °C. The procedure of heat treatment is given in Fig. 1 (Treatment E). The experimental results indicate that the boron distribution in the samples annealed for 0 and 3 s after deformation at 1000 °C is almost homogeneous, and no boron segregation is observed. The segregation arises at certain curved boundaries after holding for 5, 10, 15 and 30 s. When the holding time is increased to 60 s, the boron segregation begins to decrease and disappear. Fig. 4 shows the boron distribution of samples annealed for 0, 10, 30 and 60 s at 1000 °C after 20% deformation. From the observations on the specimen metallograph and the soft curve of recrystallization [7], it is found that the process of segregation corresponds to the process of recrystallization in the specimens. Fig. 5 shows a metallograph of the specimen held for 15 s after deformation.

Fig. 6 shows an optical micrograph and boron distribution in the same area of the specimen annealed for 10 s after 20% deformation. As the boron distribution is observed from the film coated on the specimen surface, the specimen micrograph picture and boron distribution picture have a mirror relation. It is clearly shown that no segregation appears on the original boundaries (static boundaries, straight) but there is a clear segregation along the recrystallization boundaries (moving boundaries, curved).

These results indicate that after deformation at the beginning of recrystallization at 1000 °C, no boron segregation appears on static and moving boundaries. As the holding time is increased and recrystallization continues, boron segregation on the moving boundaries is intensified and persists with the new boundaries moving forward, but there is still no segregation on static boundaries. As the holding time is extended further, the recrystallization is nearly ended and the moving boundary velocity decreases, the boron segregation begins to decrease and finally disappears.

The average area fraction of etch pits is measured in the grain-boundary region (width 6.42 μm) (S_{gb}) and in the matrix (S_g). The ratio of the etch-pit area fraction in the grain boundary region (S_{gb}) to the intragranular etch pit area fraction (S_g) is defined to describe this enrichment. Using a Q-900 quantitative metallograph instrument, we obtain an average enrichment rate S_{gb}/S_g on recrystallized boundaries in the specimens held for 10, 15 and 30 s of 1.6 ± 0.1.

4. Discussion

In Section 3.1, the differences in boron distribution (Fig. 2) among grains in specimens deformed above 1000 °C are described as resulting from the differences in the grains. As there is recrystallization in the specimens during cooling, there exist simultaneously deformed grains and recrystallized grains in the specimen. In the deformed grain, since the dislocation density is so high, a sub-grain boundary net is formed

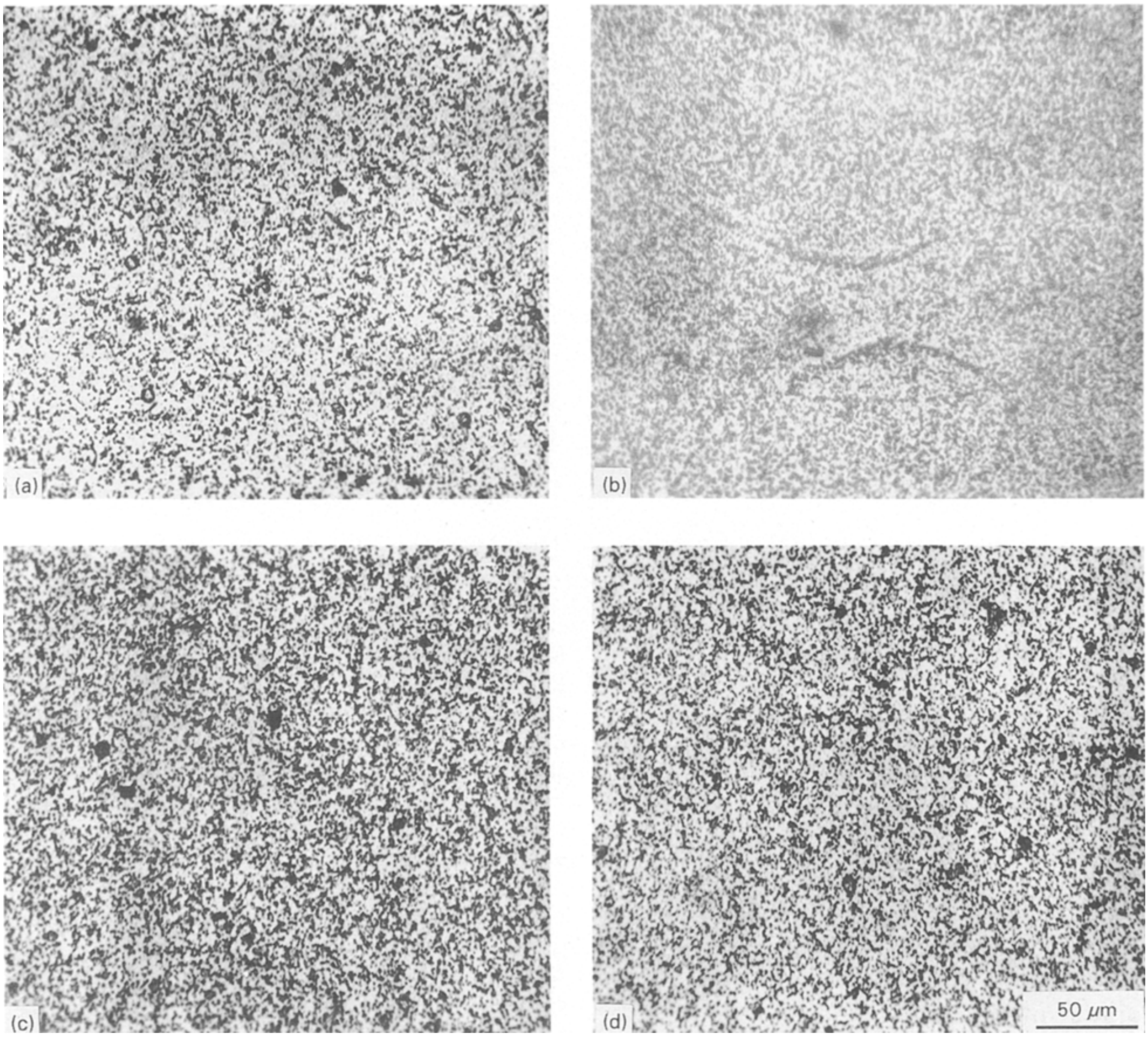


Figure 4 Boron distribution in Fe–3%Si alloy after 20% deformation at 1000 °C. The samples are quenched into ice-brine after holding the time indicated. (a) 0; (b) 10; (c) 30; (d) 60 s.

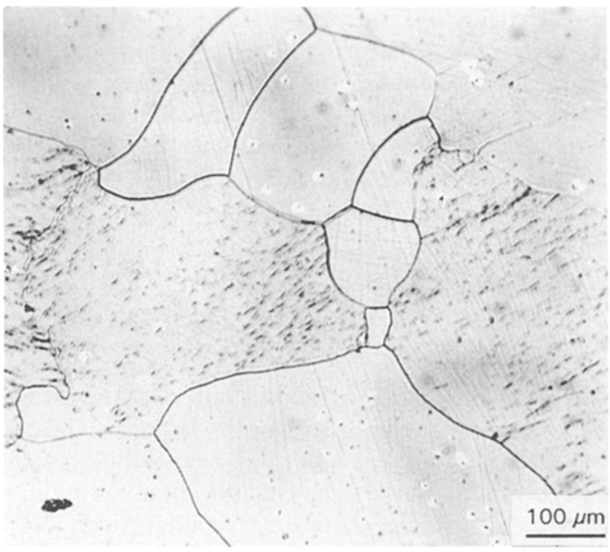


Figure 5 Optical micrograph of Fe–3%Si alloy held 15 s after 20% deformation at 1000 °C quenched into ice-brine.

within this grain. As the specimen was cooled from high temperature with a low cooling rate, the boride would precipitate both at the grain boundaries, and (although less) at the sub-grain boundaries. Thus in the deformed grains there is boride within the grains. However, in recrystallized grains the dislocation density is very low and there is no sub-grain boundary net— as the boride precipitates first at the boundaries and dislocations, there are almost no boride interior recrystallized grains (Fig. 7 shows a typical example). Thus the deformed and recrystallized grains result in a different boron distribution among grains in the deformed specimen cooled from high temperature after deformation.

From Sections 3.2 and 3.3 it can be seen that there is a considerable segregation of boron to recrystallized grain boundaries in Fe–3%Si, although there is no observable segregation at grain boundaries in any recrystallization specimens under the same experimental conditions [6, 7]. This type of solute

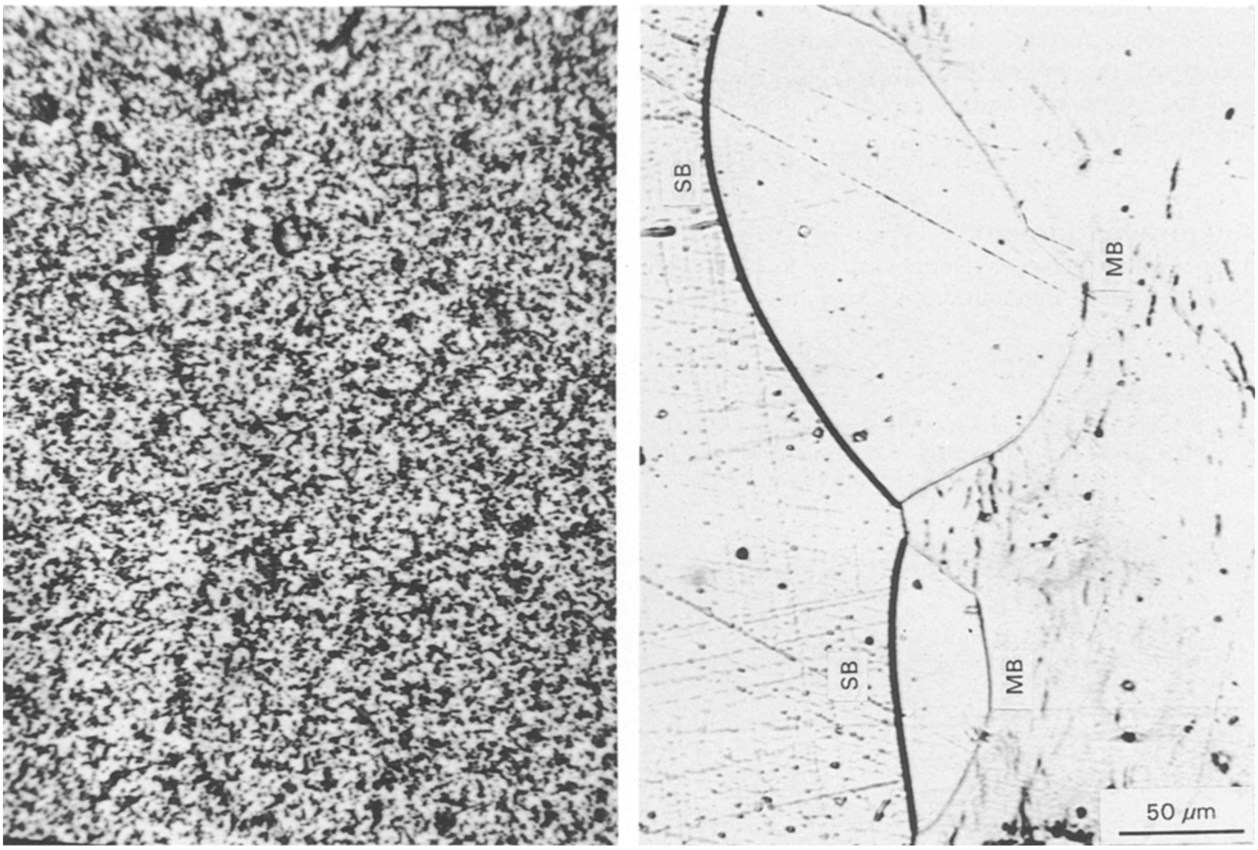


Figure 6 Boron distribution (left) and optical micrograph (right) in Fe–3%Si alloy after 20% deformation at 1000 °C. The sample is quenched into ice-brine after holding for 10 s. SB, static boundary; MB, moving boundary.

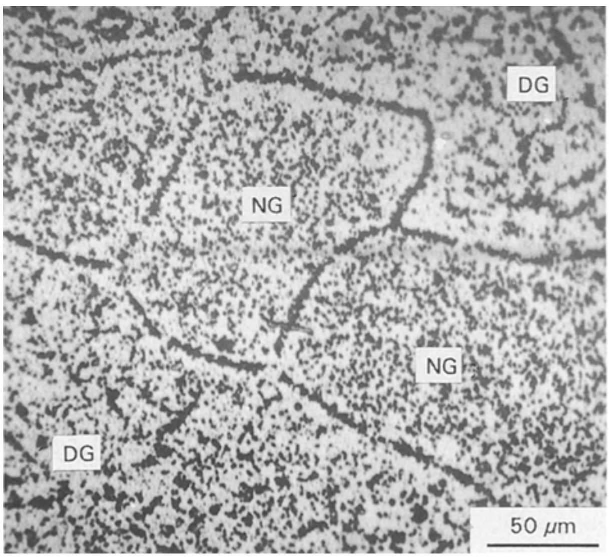


Figure 7 Boron distribution in Fe–3%Si alloy annealed at 1100 ° C, and cooled at 30 °C S^{-1} after deformation ($\varepsilon = 50\%$). NG, new grain; DG, deformed grain.

segregation cannot be properly interpreted by the existing theories relating solute segregation to moving boundaries. According to the solute drag theory of Cahn [8], for the solute atoms of $Q > 0$ (where Q is the binding energy between solute atoms and grain boundary) the solute segregation on moving boundaries is not higher than the equilibrium segregation estimated by McLean's equation [9] at the same temperature, in contrast to the present experimental results. A relaxation mechanism of dislocation disappearing in moving boundaries seems able to account for this perversive segregation. During the recrystallization process, a large number of dislocations annihilated in the moving boundary will cause the boundary to have an extra distortion area, and thus the boundary thickness is increased. The increase in the moving boundary width leads to a bigger area that solute atoms can segregate to. Under certain conditions there will be higher segregation on moving boundaries than on static boundaries. Further detail on the mechanism of this segregation is given in part 3 of this study [10].

5. Conclusion

A non-equilibrium segregation of boron on the moving grain boundaries during recrystallization is observed in Fe–3%Si alloy, although under the same conditions there is no observable segregation on the static boundaries. The non-equilibrium segregation process on recrystallized grain boundaries corresponds to the recrystallization process. During isothermal recrystallization at the beginning of recrystallization, no boron segregation appears on moving boundaries. As the holding time is increased and recrystallization is continued, the boron segregation on moving boundaries is intensified and persists with the new boundaries moving forward. As the holding time extends further, the recrystallization is nearly completed, the moving boundary velocity decreases, and the boron segregation begins to decrease and finally disappears.

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