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Effect of crystal defects on solute atoms segregation during cooling

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Different quantity and configurations of crystal defects were obtained in an austenite of Fe-30%Ni alloy and an ultra low carbon bainitic steel by different deformations and annealing times at high temperature. The boron segregation at grain boundaries and subgrain boundaries during air cooling were revealed by means of particle tracking autoradiography technique. It was found that the non-equilibrium segregation was resisted in the deformed grains after recovery and polygonization, the boron depletion was more in the recrystallized grains than in the deformed original grains during the cooling. The subgrain boundaries and polygonized dislocation cells had a significant effect on the boron non-equilibrium segregation during the air cooling, but the quantity of dispersed dislocations had not. The result indicated that during segregation process the interaction of boron atoms with dislocations was sensitive to the dislocations configuration rather than the total number of defects in grain. © *2001 Kluwer Academic Publishers*

1. Introduction

It is well known that the solute atoms can segregate at grain boundaries and affect the properties of materials, numerous experimental and theoretical works have done on this topic [1–17]. The earlier works also indicated that the segregation of solute atom at grain boundaries has certain influence at grain boundary migration and phase transformation process [18]. He *et al.* (1991) [16] reported that the pre-deformation enhanced the degree of non-equilibrium segregation of solute atoms at grain boundaries in austenites. Recently, Cui *et al.* (1995) [19] investigated the recrystallization of hot deformed materials, it was found that the distributions of solute boron atoms had obvious difference between newly recrystallized grains and original deformed grains. Based on this phenomenon, a method distinguishing the new and old grains in the hot deformed materials was developed, but the mechanism of the phenomenon did not discuss. According to deformation and recrystallization theory, the quantity and configuration of crystal defects in deformed matrix would change during the recovery and recrystallization process in alloy after high temperature deformation, so that the diffusion of solute atoms from matrix to boundary during segregation is sure to be affected by the interactions between solute atoms and grain boundaries, subgrain boundaries, vacancies, dislocation nets, and results in a complicated segregation behavior in deformed materials which is never well defined by experiments.

The aims of this paper are to gain different density and configurations of defects by distinct heat treatments, and to investigate the effect of crystal defect state on boron non-equilibrium segregation during cooling by means of particle track autoradiography (PTA) technique.

2. Experimental procedure

2.1. Materials and test methods

The chemical compositions of two steels employed in the present work are given in Table I. The steels were melted in a vacuum induction furnace, and rolled into plates. Cylindrical specimens, 8 mm in diameter and 12 mm long, were machined out from the plates. In order to follow the static recrystallization of the autenites after high temperature deformation, an interrupted compression test method developed by Petkovic [20] was used in a Gleeble-1500 heat simulator, the procedure of heat treatment is illustrated in Fig. 1. The softening rate taking place during the first unloading period at high temperature can be calculated from the expression $X = (\sigma_m - \sigma_r)/(\sigma_m - \sigma_0)$, here σ_m is the maximum stress before the first unloading, σ_0 and σ_r are the yield stresses during first and second loading, respectively. An offset strain of 0.2% was used to define the yield stresses. Softening rates after isothermally holding for increasing times at 1000°C were estimated and given in Fig. 2. The softening consisted of two stages: recovery which corresponded to the early stage of softening (usually about 10%), and recrystallization (from 10%–100%). According to these softening rate vs. holding times curves, the degree of recrystallization was

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TABLE I Chemical compositions of the steels investigated (wt%)

Steel	C	Mn	Si	Al	Ti	Nb	B	P	S	N	Ni
N3	0.01	0.003	0.02	0.21	0.04	0.04	0.0023	0.0078	0.0044	–	29.57
B1	0.04	1.63	0.46	0.017	0.022	0.052	0.0020	0.019	0.002	0.0078	–

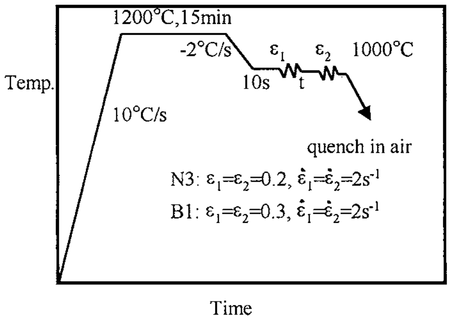

Figure 1 The procedure of the interrupted compression tests.

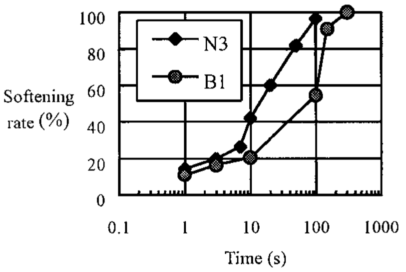

Figure 2 The softening rate vs. holding time curves at 1000°C.

estimated. Further details of this experimental method can be found in Ref. [20].

Technique of Particle Tracking Autoradiography (PTA) [21], based on the fission reaction $^{10}B(n,\alpha)^7Li$, was applied to reveal the location of boron atoms in the specimens. In the present work, a cellulose acetate film was used as solid detector and then the film-coated specimens were irradiated to an integrated flux of 5.6×10^{18} neutron/m^2, after that the films were etched and examined under an optical microscope.

2.2. Experimental design

In order to study the effects of quantity and distribution of crystal defects on non-equilibrium segregation of solute atoms, three procedures, similar to the interrupted compression test procedure in Fig. 1, were used to gain midway specimens in recrystallization process (Fig. 3).

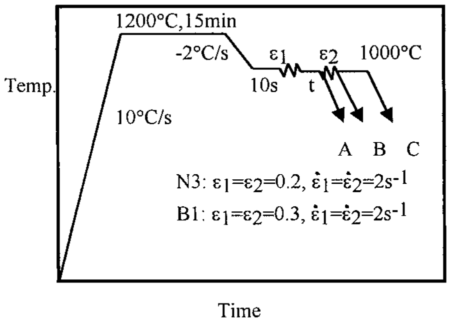

Figure 3 The procedures of treatment.

Treatment A: the specimen was isothermally held at 1200C for 15 min, then cooled to 1000C, after deformed, then unloaded and held for an increasing time. During holding, the recovery and recrystallization process took place, some new recrystallized grains formed and other old deformed matrix was recovery and polygonization. After holding, the specimens were quenched in water or cooled in air. The water-quenched specimens kept their boron distribution formed at isothermal holding and were regarded as the initial state of air-cooling. For the air-cooling specimens, during cooling the boron atoms had a relative time to diffusion and form the non-equilibrium segregation at grain boundaries, so that they could be used to show the difference of segregation process during cooling in new and old grains, in which had distinct dislocation density and configuration.

Treatment B: the specimens were subjected to the first time deformation and isothermally held, during the holding the recrystallization took place in some area. After that the specimens were undertaken second time compression and immediately cooled in air, the second deformation introduced a large number of deformation in both newly recrystallized grains and old original grains. Following that, the another time recovery and polygonization process did not have time to occur in whole specimens. This treatment was used to examine during air cooling the difference of non-equilibrium segregation process in new and old grains, which formed before second deformation, but both were added a strong distortion during second compression.

Treatment C: the specimens were undertaken two times compression, as treatment B, but after second deformation the specimens were annealed an selective time, during which the another time recovery and polygonization took place in both the new and old grains, but the new recrystallization had not started, following that, the specimens were cooled in air. This treatment was used to investigate the difference of segregation process during cooling between the new and old grains, but both had suffered second deformation and recovery.

3. Experimental results

3.1. The boron distribution in specimens after treatment A

Using the treatment A, the Fe-Ni alloy hold isothermally 7 seconds after deformation 20% at 1000C, then quenched in water. According to the softening curve in Fig. 2, the recrystallization just began at that time (about 10%), the boron distribution in this specimen revealed by the PTA technique is shown in Fig. 4 which basically kept the boron distribution before quenching. But due to the limited cooling rate of the 1500 Gleeble heat simulator, there was weak boron segregation at

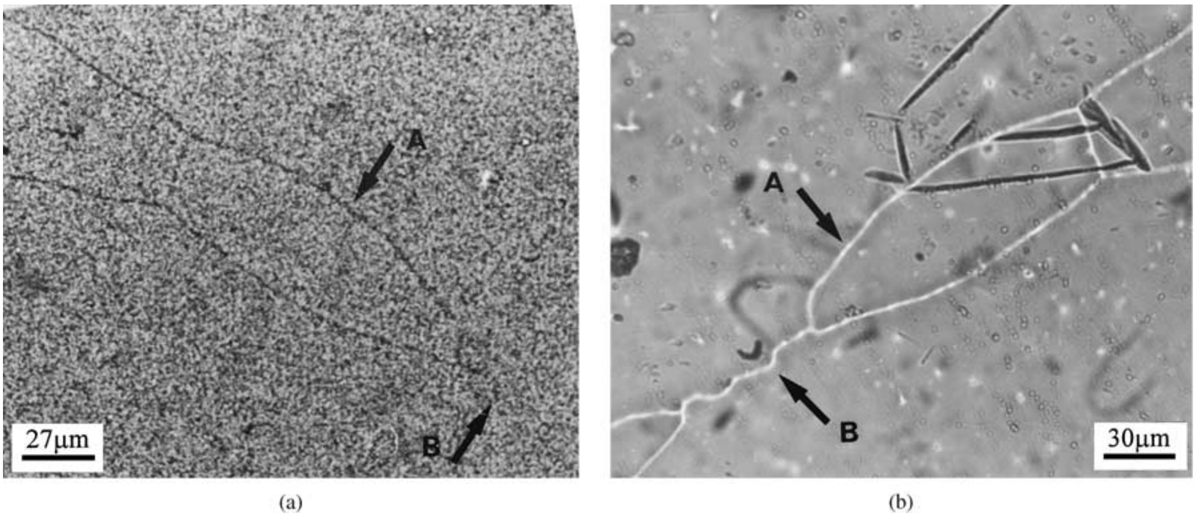

Figure 4 Fe-30%Ni alloy N3, hold for 7 s after 20% deformation at 1000°C, then quenched in water. (a) the boron distribution (PTA picture), (b) an optical micrograph in the same area which has a mirror relation to (a).

all grain boundaries, which was of quenching induced boron segregation [9] and bring out the boundary position of whole original deformed and new grains. It was also observed from Fig. 4 that the degree of boron segregation at the new grain boundaries (Marked A) was stronger than that on the old grain boundaries (Marked B), which was an abnormal segregation as a result of the grain boundary migration [14, 16, 22, 23] and was retained by quenching. In this case the boron distribution was uniform inside all grains. Instead of water quenching, air quenching has a lower cooling rate, there was an enough time to allow the boron atoms to diffuse to the grain boundaries during cooling and form the non-equilibrium segregation. The boron distribution in the specimens air-cooled after a holding time was revealed by the PTA technique in Fig. 5a and b for the ultra low carbon bainitic steel B1 and Fe-Ni alloy N3, respectively. It was found from Fig. 5 that the stronger boron segregation occurred at the new grain boundaries (A) and weaker segregation on the old grain boundaries (B).

Fig. 6 showed a low magnification PTA picture of specimen B1 quenched in air after treatment A (corresponding to Fig. 5b). From Figs 5 and 6, another important feature for air cooling samples could be observed that the boron concentration in the matrix of the new recrystallized grains and old deformed grains was obvious different (on PTA picture, the density of etching pits was different in the new and old grains). The new grains were white (the etching pits density lower), the boron atoms were badly depleted. Fig. 7 was another PTA image that got from air cooling sample but showed a large original deformed grain. It could be seen that in matrix of this deformed grain the etching pits density was higher and there was boron segregation on the deformation zone (Marked A) and some polygonized subgrain boundaries (Marked B). TEM examination (Fig. 8) showed that the deformed original grain consisted of many dislocation cells (also called fine subgrains) with size of about 1 micron in the Fe-30%Ni alloy after the recovery and recrystallization. It is noted that the fine dislocation cells (Fig. 8) and coarse subgrains (Fig. 7) both consist of dislocation walls (the dislocation density has some difference), PTA technique can only reveal bigger subgrain boundaries but fails to reveal fine subgrain (dislocation cell) boundaries duo to the limitation of PTA space resolution (about 1–2 micron).

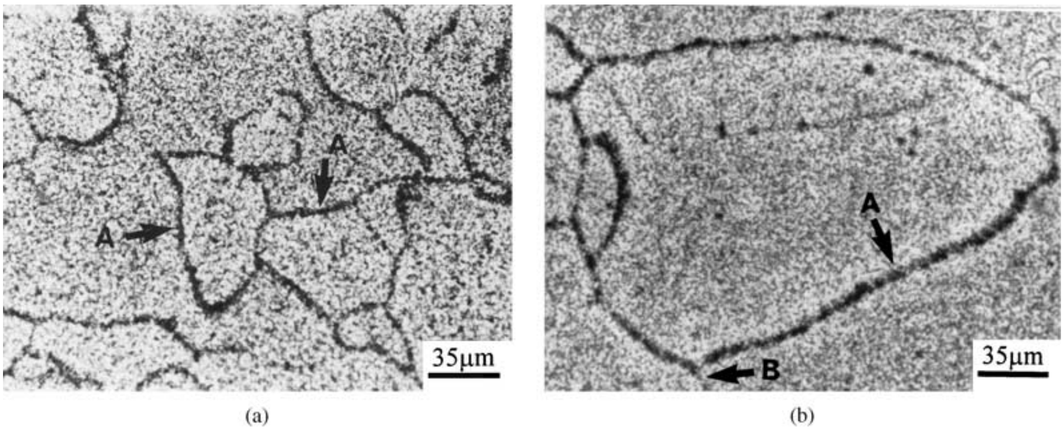

Figure 5 The boron distribution revealed by PTA Method, (a) ULCB steel B1, hold for 100 s after 30% deformation at 1000°C, then cooled in air. (b) alloy N3, hold for 7 s after 20% deformation at 1000°C, then cooled in air.

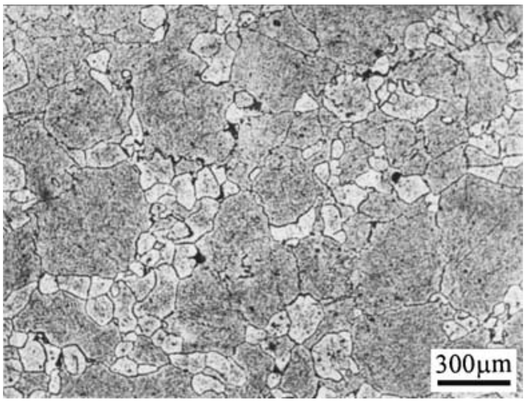

Figure 6 Low magnification morphology corresponding to the Fig. 5a.

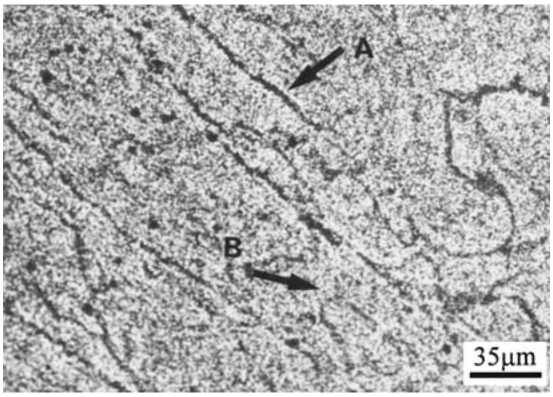

Figure 7 The boron distribution in a large original deformed grain in the Fe-30%Ni alloy revealed by PTA. The specimen was hold 3 s after deformation 20% at 1000°C, then cooled in air.

Figure 8 The electron microscopic contrast image of subgrains in the Fe-30%Ni alloy. The specimen was hold 3 s after deformation 20% at 1000°C, then quenched in water.

3.2. Boron segregation in specimens air-cooled after second compression

Using Treatment B, the specimens were hold 100 s (B1 alloy) and 7 s (N3 Alloy) after the first compression, the recovery and recrystallization took place, then compressed again and cooled immediately in air. The boron segregation was revealed by the PTA technique in Fig. 9a and b. It was found that the boron distribution in the new and old grains had a difference like that in the specimen without the second compression (Treatment A), the new grain boundaries had stronger boron segregation. It seems that the second compression did not affect the boron segregation process during cooling.

3.3. Boron segregation in specimens air-cooled after holding times following second compression

Using Treatment C, the specimens were hold 10 s (B1) and 3 s (N3) following the second compression, then, air-cooled. The boron segregation was revealed by the PTA technique in Fig. 10a and b. The microscopic examination indicated that after second deformation the new recrystallization did not occur during the second annealing time, the new grain grown up during the first annealing time had become deformed grain and did not grow again now. It can be seen from Fig. 10 that the boron segregation took place on all grain boundaries within the same degree, the difference of boron distribution in the new and old grains disappeared.

4. Discussion

4.1. The cause of the difference of boron concentration in the new and old grains

Non equilibrium boron segregation at grain boundaries during continuous cooling involves the motion of excess vacancy-solute complexes towards the boundaries, many authors [4–16] have studied systematically this dynamical mechanism. The boron segregation at boundaries of newly recrystallized grain and old original deformed grain has reported in many places[14, 16, 22], but its mechanism was not confirmed. In Fig. 4, the specimen was isothermally hold 7 seconds after deformation at 1000C, then quenched in water. During holding the recrystallization began, but from Fig. 4 it could be found that uniform boron distributed in the matrix of all grains except weak boron segregation occurred on the migrating grain boundaries. This picture reflected the real distribution of boron during holding at high temperature and indicated that the recrystallization could not lead to the different of boron concentration in the matrix of new grains and old deformed grains. Thus, the difference of the boron densities in the new and old grains (Figs 5–7) was confirmed to take place in duration of air-cooling.

The Fe-30%Ni alloy N3 kept f.c.c. structure in the cooling process, it excluded the influence of phase transformation on microstructure and boron distribution. But after air cooling the boron distribution in the ultra low carbon bainitic steel B1 (Fig. 5) and the Fe-30%Ni alloy (Fig. 6) had the same characteristics, the similarity of phenomena indicated that the phase transformation did not change the boron distribution during air cooling.

The difference of boron concentration in matrix of new and old grain is caused by the distinct microstructure of newly recrystallized grain and original one, the former has a low dislocation density as a result of recrystallization when the cooling starts, the later consist of subgrains or polygonized dislocation cells. For example, in the specimen of Fe-30%Ni alloy which hold for 3 seconds and quenched in water, TEM showed its old grain consisted of many polygonized dislocation cells, the size of cell was inhomogeneous and the small one was about 1 micron, as shown in Fig. 8. Some deformation belts and bigger subgrains with size about several microns (or >10 micron) could also be observed

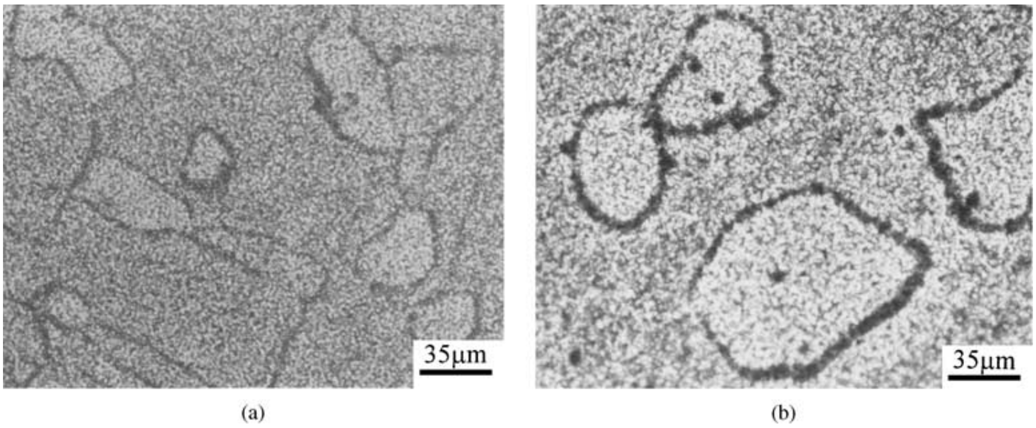

Figure 9 The boron distribution revealed by PTA Method, (a) ULCB steel B1, the specimen was hold 100 s after 30% deformation at 1000°C, deformed 30% again, then immediately cooled in air. (b) Fe-30Ni alloy N3, the specimen was hold 7 s after 20% deformation at 1000°C, deformed 20% again then immediately cooled in air.

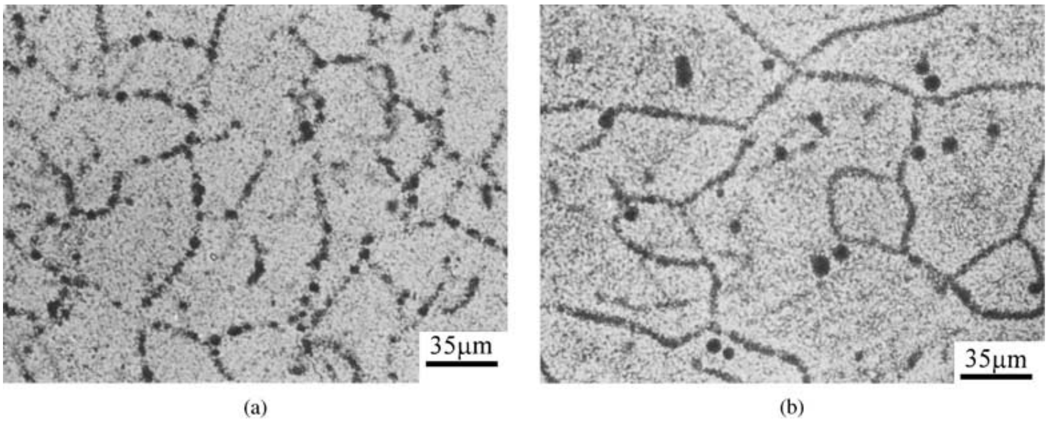

Figure 10 The boron distribution revealed by PTA Method, (a) B1 steel, the specimen was hold 50 s after 30% deformation at 1000°C, deformed 20% again, and hold 30 s, then cooled in air. (b) N3 alloy, the specimen was hold 7 s after 20% deformation at 1000°C, deformed 20% again, and hold 3 s, then cooled in air.

in deformed grains in metallurgical scale, as shown in Fig. 7. The PTA technique with resolution of 1 micron has a limited ability to reveal the subgrain with the size being about several microns, but failed to reveal the subgrains or dislocation cells with the size being estimated to be lower than 1 micron. For newly recrystallized grains, the dislocation density was lower and the subgrain and cell structure was not clear, Fig. 11 shows a corner of a new grain which has a tangled dislocations cell boundary and just enters into the old deformed grain.

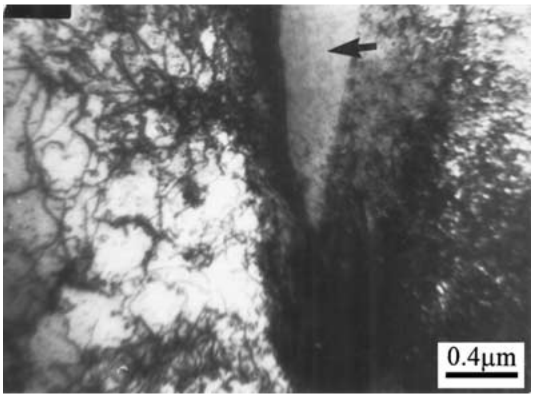

Figure 11 TEM contrast image of a new gain in the Fe-30%Ni alloy. The specimen was hold 7 s after deformation 20% at 1000°C, then quenched in water.

4.2. Boron depleted zone near new and old grain boundaries in specimen cooled in air

Figs 5, 6 and 9 all showed that the boron concentration (etching pit density) in the newly recrystallized grains was lower than in the old grains. But if scrutinize, the boron density was not uniform in the new grains, for the large new grains it was higher at the center of grain. The boron density in the old original grains had a higher level, but there was a narrow boron depleted zone along the grain boundaries. The earlier work [6, 11] pointed out that the boron atoms segregated at grain boundaries come from the narrow boron depleted zone at the two sides of the grain boundaries. It seems that the difference of boron density in the new and old grains is arisen from the wider boron depleted zone in the new gains and the narrow boron depleted zone in the old grains. For small new grains the boron depleted zone occupies the whole grains and they seem to have a bright contrast in the PTA picture. However, in old deformed grain, the boron depleted zone is less and a large number of boron atoms are retained in the matrix. This result concluded that the boron atoms diffuse “faster” in the new grains than in the old grains during the air-cooling, the segregation process was somehow resisted in the deformed grains. Comparing the results of the treatment B and C, this phenomenon could be explained.

4.3. The effect of dislocation quantity and configuration on the boron segregation

Figs 5 and 9 had the same characteristics, but the microstructure in the specimens was difference. In Fig. 5, the specimen annealed for a time after the first compression, the newly recrystallized grain had a low dislocation density as a result of recrystallization, while the old original grain consisted of many fine subgrain structures as a result of recovery. In Fig. 9, the second compression introduced large strains and dense dislocations in both the recrystallized grains and the original grains. Comparing to the Fig. 5, in spite of having high strain in all grains in Fig. 9, the addition of dispersed dislocations and excess vacancies did not obviously change the way of the formation of the boron non-equilibrium segregation and the excess vacancies will enhance the segregation [11].

In treatment C, during the holding time after the second compression, the recovery occurred but recrystallization did not happened in the most grains, in the matrix the strains reduced and most dislocations disappeared or reconfigured, i.e. polygonization. After air-cooling, the boron-depleted zone along all grain boundaries was narrow, the same boron segregation degree was found in the new and old grains as demonstrated in Fig. 10. The high dense dislocations introduced by the second compression had evolved into subgrain structures through the polygonization (Fig. 12). Thus, all grains had the same microstructure (subgrain inside the grains), the segregation process was resisted during air-cooling.

During the non-equilibrium segregation the boron atoms will diffuse to the boundaries (no matter what mechanism, vacancy-solute complexes motion or others), during the way they will interact with the grain boundary, subgrain boundary (dislocations wall), and the dispersed dislocations. The above experimental results indicated that the boron diffusion in recrystallized grains was “faster” than in the polygonized original grains. After second deformation, although the number of dispersed dislocations was increase, which much more than the number of dislocations in the recovered grains, but they did not affect the boron segregation behavior as Fig. 9. Only after polygonization or recovery again, the dislocations annihilated each other, and the dispersed dislocation formed up the subgrain boundaries or dislocation walls, this dislocation configuration resisted the segregation evidently. Therefore, these results implied that in non-equilibrium segregation process the interaction of boron atom with dislocations was sensitive to dislocations configuration rather than the total number of defects in grain.

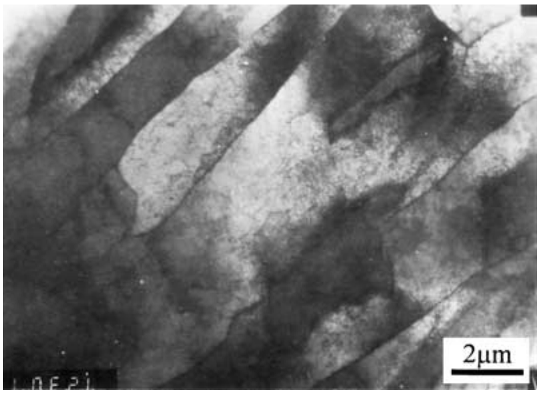

Figure 12 TEM contrast image of subgrains in the Fe-30%Ni alloy. The specimen was hold 7 s after deformation 20% at 1000°C, deformed 20% again, and annealed 7 s, then quenched in water.

5. Conclusion

Different quantity and configurations of crystal defects were obtained by experimental arrangements of deformations and annealing times at high temperature. Boron non-equilibrium segregation at grain boundaries and subgrain boundaries during air-cooling were revealed by the PTA technique. It was found that

(1) In austenite of Fe-30%Ni alloy and ultra low carbon bainitic steel, the boron non-equilibrium segregation during cooling was resisted in the deformed original grains after recovery, the boron-depleted zone was narrow, and segregation degree was decrease.

(2) The boron segregation was enhanced in the newly recrystallized grains, the boron depleted zone was wider, this led to lower boron concentration in the small grains.

(3) The second compression introduced dense dislocations in both recrystallized grains and original grains, but the dispersed dislocations did not change the way of the formation of the boron segregation.

(4) The holding time after the second compression gave a recovery time for the deformed grains, the dispersed dislocations evolved into subgrain microstructure, while the segregation was resisted in all grains. During cooling the interaction of boron atom with the dislocations was sensitive to dislocations configuration rather than the total number of the defects in grains.

Acknowledgements

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