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The effect of pre-deformation on grain boundary non-equilibrium segregation during recrystallization in f.c.c alloy

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By means of the particle tracking autoradiography (PTA) technique, optical and electron microscopy, the non-equilibrium segregation of boron at moving boundary during recrystallization in Fe-30%Ni alloy was investigated. The influence of pre-deformation on the segregation was analysed. The results indicated that there was a abnormal boron segregation at the moving boundaries of the new grain during recrystallization. Its intensity was depended on the pre-deformation degree and the moving speed of the boundary. The TEM result showed that the dislocation density in front of moving boundary obviously increase. The phenomena are discussed in terms of the widening grain boundary mechanism.

1. Introduction

Solute atoms can efficiently retard recrystallization process of deformed metal at high temperature, due to the drag effect of solute atoms at moving boundaries. Mavropoulos [1, 2] pointed out that the simultaneous presence of boron and Nb is particularly effective in retarding austenite recrystallization of the ultra low carbon bainitic (ULCB) steels. Kasen [3, 4] investigated the recrystallization and grain growth processes in aluminium alloys by the measuring of electric resistance, his results indicated that the solute atoms could be absorbed constantly by moving boundaries, during the processes, the solute richness ratio at the moving boundaries was much bigger than the value estimated by equilibrium segregation. Recent years, it was found that there was an obvious non-equilibrium segregation of boron at moving boundaries during recrystallization [5], which effected the recrystallization process. In 1994, Sanhong Zhang *et al.* [6, 7] investigated the abnormal boron segregation phenomena in bcc Fe-3%Si alloy during recrystallization, and put forward the widening grain boundary mechanism of non-equilibrium segregation at moving boundaries. These works, above mentioned, all expected that this kind of segregation would be effected by the moving velocity boundaries during recrystallization, and by the dislocation density and the relaxation time of pre-deformed crystal. The aims of the present investigation were (i) to clear the characteristics of non-equilibrium segregation of boron at moving boundary during recrystallization. (ii) to study the influence of pre-deformation at the moving boundary segregation. A Fe-30% alloy was used in this work, which keeps fcc structure during present tests, this is advantageous for eliminating the influence of the phase transformation.

2. Experimental procedure

The alloy was prepared with a vacuum induction furnace, the ingots were heated to 1200 °C and forged into 13 mm-diameter bars, after homogenized at 1150 °C for 30 min then cooled in water. Specimens were machined into the size $\Phi 9 \times 15$ mm. The composition (wt%) of the alloy was: 30%Ni, 0.04%Nb, 0.0023%B, 0.083%Mn, 0.04%Ti, and the surplus was Fe. The heat treatments were conducted with heat simulator Gleeble-1500.

The recrystallization behavior of different pre-deformed alloys was measured with the interrupted compression method [8, 9]. Specimens were heated to 1200 °C for 15 min, in order to dissolve the precipitated phase, then cooled to 1000 °C and isothermal held for 10 s, the specimens were first time deformed 10%, 20%, and 40% respectively, and isothermally held for different time t_i, then were secondly deformed 20%, and cooled in air. In all the experiments, the strain rate was $2\ s^{-1}$. The softening curves determined in different pre-deformation steel are shown in Fig. 1,which is obtained by the mean stress ratio method [8]. If the softening of recovery is about 10% [9], the recrystallization–time (t_i) curves could be estimated (Fig. 2).

In order to understand the variation of microstructure and boron distribution during recrystallization, after first time deformation, the specimens were isothermally held for different times t_i (Table I), then quenched in water.

Specimens were observed with metallograph microscopy and transmission electron microscopy (TEM), the dislocation density of different pre-deformed specimens was determined and estimated by X-ray, the boron distribution was investigated with the aid of the particle tracking autoradiography (PTA) technique which is a method revealing the boron distribution on surface of

TABLE I Different deformation and isothermally holding time t_i

Pre-deformation	Holding time t_i
10%	1 s, 10 s, 50 s, 100 s, 200 s
20%	3 s, 7 s, 20 s, 50 s
40%	0.2 s, 0.5 s, 1s, 3 s, 5 s

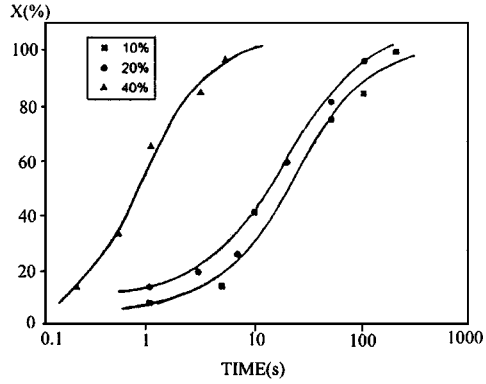

Figure 1 The softening curves after different pre-deformation.

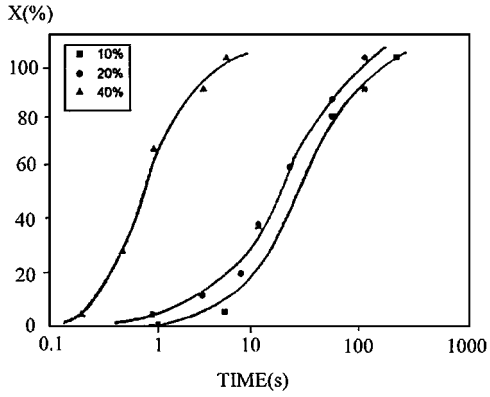

Figure 2 The recrystallization-time (t_i) curves.

samples [10]. A cellulose acetate film was used as a solid detector, the integrated flux of thermal neutrons was 5×10^{14} neutrons cm^{-2}.

3. Experimental results

3.1. Boron distribution during recrystallization

Fig. 3 is a PTA photograph which shows the situation of recrystllization and boron distribution in the sample that was deformed 40% at 1000 °C and then isothermal held for 0.2 s, it can be seen that because the size of sample used in Gleeble simulator is a little bigger, the boron non-equilibrium segregation could not be restrained completely during quenching in water, so that a slight segregation presents at all of the boundaries (original and new boundary), and draws the shape of grain. (the literature [11, 12] indicated that the non-equilibrium segregation could be restrained completely if the same alloy was quenching in ice brine, the boron distribution was homogeneous). On the other hand, it can be seen from Fig. 3 that some new grains formed by recrystallization are revealed, which mostly formed at triple points on the original boundaries and some at straight boundaries, the volume fraction of new grains

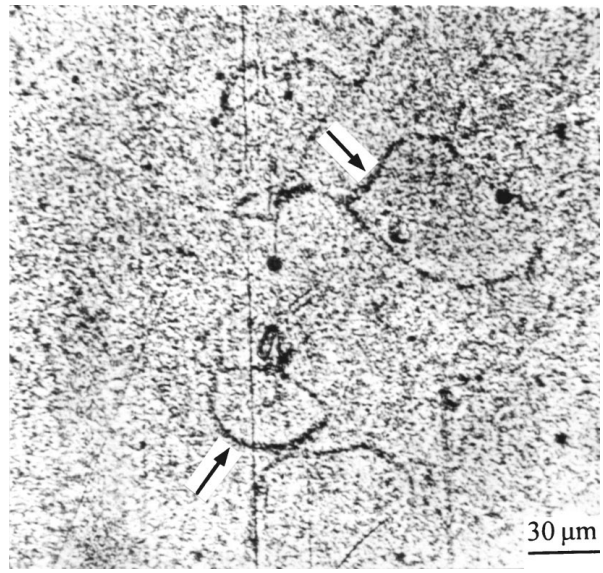

Figure 3 Boron distribution revealed by PTA in Fe-30%Ni alloy deformed 40% and then held for 0.2 s followed by quenched into water.

is about 5%. Fig. 3 also shows that the new grains are smaller, (i.e, their boundaries are more curved), and the boron segregation at boundaries between new and old grains (identified by arrows) is more intense than at the static original boundaries.

Fig. 4 shows the boron distribution and an optical micrograph in the same area (they have a mirror relation) of the sample which deformed 20% at 1000 °C and held 3 s and then quenched in water. It is clearly shown that the new recrystallization grains grew up on the original boundaries, and there is more strong segregation at the moving grains boundaries (MGB), but the boron segregation is very weak at the original boundaries (SGB).

Figs 5 and 6 shows the variation of boron distribution during recrystallization at 1000 °C after deformed 40% and 10% respectively.

Fig. 5a shows that after 40% deformation and holding 0.5 s the volume fraction of recrystallization grain rate is about 25–30%, the new grains had formed at the some original deformed boundaries (N place), the obvious boron segregation at the boundaries between the new and old grains can be seen, but at other boundaries only a little non-equilibrium segregation formed during cooling and drew their position (arrow place), the boron segregation at the new moving boundaries is more strong than at the original boundaries

When the holding time increased, the boron distribution of sample which isothermal held for 1 s (the recrystallization was about 60%) is shown in Fig. 5b. There are a few original boundaries (arrow place) in some regions, at which the boron segregation is still very weak, but at new boundaries the boron segregation are evident. Fig. 5c shows the sample held for 3 s, (the recrystallization was about 90%), the remainder of deformed grains (O place) was very few, the most new grains had grown up and joined each other, the movement of grain boundaries was stopped. It can be seen that when the impingement occurred, the boron segregation at this kind of grain boundaries was decreased or disappeared. When the holding time increased further, the recrystallization had finished, the boron

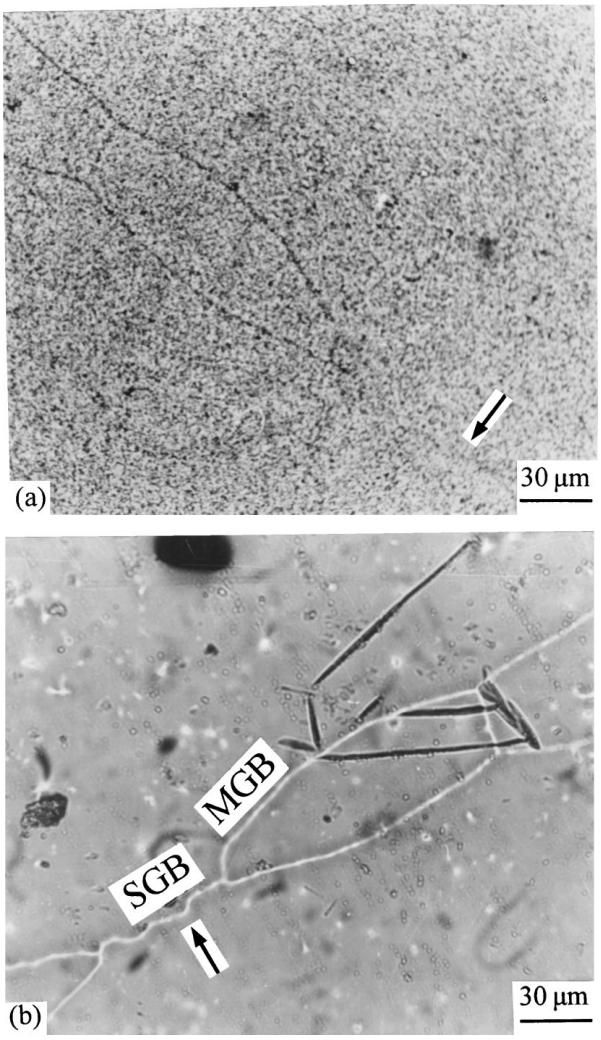

Figure 4 Boron distribution revealed by PTA (a) and optical micrograph (b) in Fe-30%Ni alloy deformed 20% and then held for 3 s followed by quenched into water.

distribution returned to the segregation state of the static grain boundaries shown in Fig. 3.

Fig. 6 showed the boron distribution of the sample deformed 10% at 1000 °C and isothermal held for 1 s, at this time the recrystallization didn't begin, there had a little non-equilibrium segregation at the original austenite deformed boundaries, induced by cooling process, it drew up the shape of grains. Isothermal held for 10 s, a few new grains nucleated mainly at the triple point (N place), there had obvious boron segregation at the new grains boundaries. Comparing Fig. 6b with Fig. 5a, it could be seen that the difference of boron segregation at the new and old grain boundaries was more evident with increasing the pre-deformation. When the holding time was increased again, the variations of segregation state during recrystallization was similar to that of samples with deformation 40%. Isothermal held for 200 s, the recrystallization had finished, the growing of new grains stopped, boron distribution (Fig. 6c) recovered basically to the state of Fig. 6a.

3.2. Change of the boron segregation at the moving grain boundaries

During recrystallization the boron segregation at the moving boundaries was more stronger than that at the

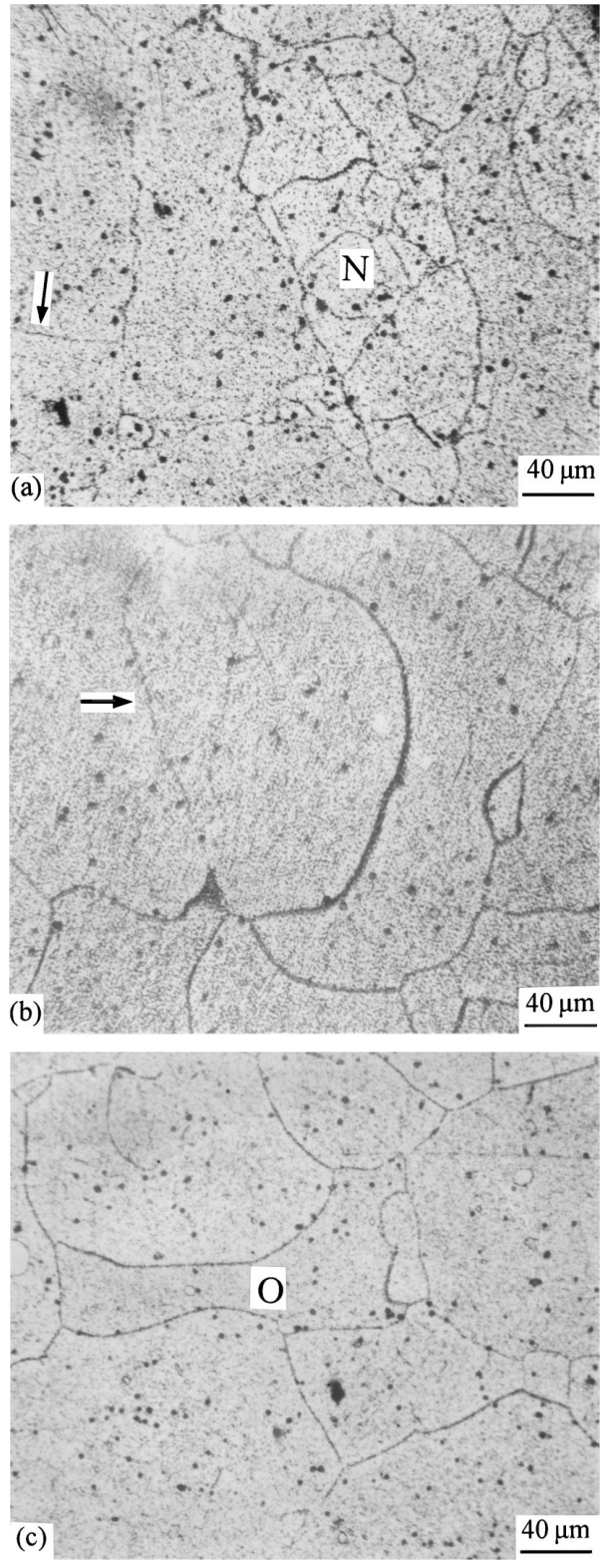

Figure 5 Boron distribution revealed by PTA in Fe-30%Ni alloy which deformed 40% and held for 0.5 s (a), 1 s (b), 3 s (c) then water quenched.

original boundaries, and the difference was varied with the pre-deformation. For understanding the evolution of boron segregation at boundaries semi-quantitatively, a measurement was carried out.

The measurement were conducted directly on the PTA micrographs , for ensuring the statistics accuracy, the PTA films of all samples were carefully etched, the etch pits size was similar. Because the width of grain boundaries segregation band was about 2 μ, on micrograph (at 1000×) the width of bands was 2 mm, a

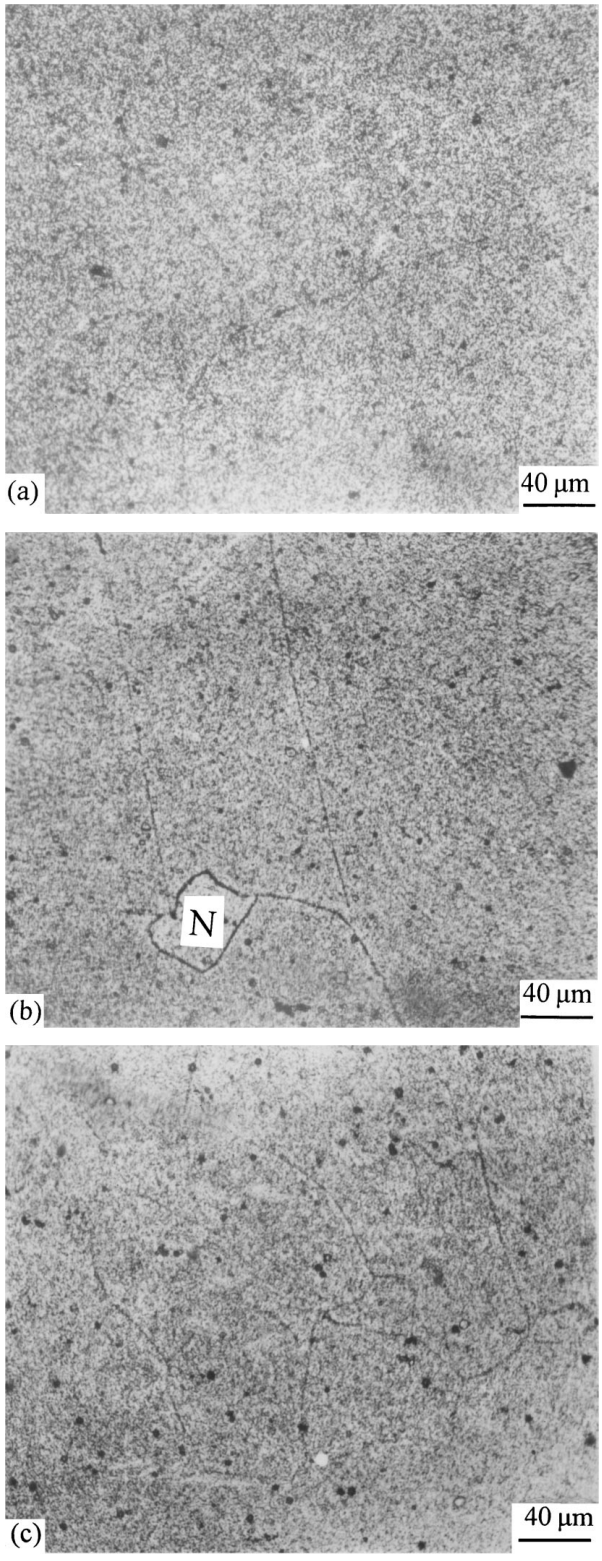

Figure 6 Boron distribution revealed by PTA in Fe-30%Ni alloy which deformed 10% and held for 1 s (a), 10 s (b), 200 s (c) then water quenched.

rectangular frame, 50 mm in length and 2 mm in width, was used to measure the etch pits density at the moving boundaries and in the matrix. According the relations between boron concentration and etch pits density [12], the ratios of boron concentration at moving boundaries (C) to average density within grains (C_0) was obtained. The 50 view fields of samples quenched in water during recrystallization were counted to get the average value of C/C_0. For eliminating the influence non-equilibrium segregation induced by relatively low cooling speed, the

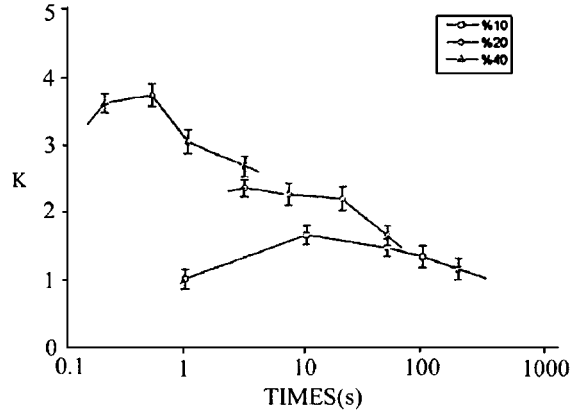

Figure 7 The relations between parameter K and holding times t_i after different pre-deformation.

ratio of boron density at original boundaries (C') to matrix boron density (C_0) was also measured with same method mentioned above. Owing to the sample sizes and cooling way was same used in this text, this ratio (C/C_0) was identical to every boundaries for all samples. A parameter $K = (C/C_0\text{-}C'/C_0 + 1)$ was defined to describe this abnormal segregation during recrystallization process. $K = 1$ indicated no other type of boron segregation except a little non-equilibrium segregation caused by cooling processes. The relations between K and holding times for different times for different pre-deformation sample are shown in Fig. 7.

It can be seen from Fig. 7 that the curves shapes after different pre-deformation were similar. Before recrystallization beginning, there was not any new grain boundaries, $K = 1$, as increasing of holding time, the recrystallization began, K values increased quickly, then the values keep the constant for several times. After different pre-deformation, the average values of K during recrystallization are: $\varepsilon = 10\%$, $K = 1.51$; $\varepsilon = 20\%$, $K = 2.28$; $\varepsilon = 40\%$, $K = 3.46$ respectively. The curves (in Fig. 7) begin to decrease at a point, compared with metallograph and softening curves, it was indicated that at this time the volume fraction of recrystallization is high, the new grains have grown to impingement occurred, the moving velocity of boundaries decreased quickly or stopped moving, the segregation degree begin to lower and disappeared at the last.

The preliminary results of TEM indicated that, in front of moving boundaries of new recrystallization grains, the dislocation density is much stronger than the original matrix of deformed grains. Fig. 8 shows a segment of new boundary, the difference of [110] direction between new grain (left) and the original deformed grain (light) is about 52°, there is a district (in deformed grain side nearby moving boundary), in which the dislocation density is much higher than in matrix of original deformed grains.

4. Discussion

4.1. Moving velocity of grain boundaries during recrystallization

Form results above, the difference of boron segregation at moving boundaries is the depended on the predeformation degree and the growing speed of new

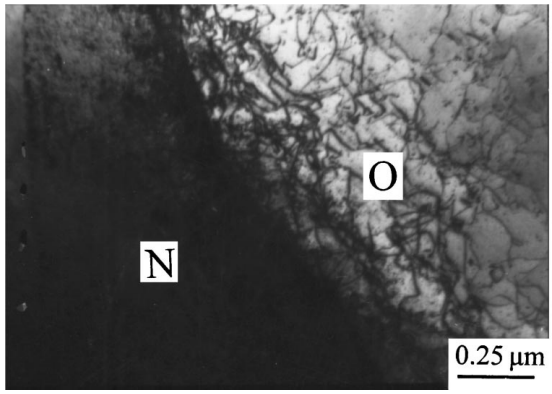

Figure 8 The dislocations in front of the moving boundaries, "O": deformed grain, "N": new grain.

grains (i.e. moving velocity of new grain boundaries) during recrystallization. The average moving velocity of new boundaries during recrystallization after different pre-deformation was estimated semi-quantitatively.

The metallograph and PTA results showed that the new grains nucleated and grew up mostly on the triple points of original boundaries after deformation 10% and 20% respectively. By geometrical method [5], if new grains grow to $r_c \approx d/4$ (r_c and d is the radius of new grain and the diameter of original grains respectively), their will nucleate only on the triple points, the new grains have same growing speed, when the new grains impinge each other and cover the whole original boundaries, and the volume fraction of new grain is about 50%–60%. So that, if the time $t_{0.5}$ of when the recrystallization is about 50% and the original grains diameter d is measured, the average velocity of new grains growing (i.e the new boundaries moving velocity) could be estimated by $V = r_c/t_{0.5}$. After deformation 40% it could be seen by PTA that there was some advantageous positions for nucleation along the old boundaries, in this case the average growing speed of new grains could be estimated by $V = r'_c/t_{0.3}$ [5].

The average grain diameters d of samples after different per-deformation were measured by metallograph, the samples were cut up vertical to the compression axis, after polishing and etching, the diameter of grains were measured (the grain diameter were big over 500 μm). Table II shows the measured d, $t_{0.5}$, $t_{0.3}$ and the estimated new boundaries moving speed V. It should point out that, the values are only a rough estimation, after different pre-deformation the grains were not equiaxed, it and all new grains could not nucleate and grow at same time, their will affect the estimation. According to the results, the relation between segregation and average speed can be plotted (showed in Fig. 9), the abnormal segregation K is a average value during recrystallization from new grains growing to impinging each other, it was evident from Fig. 9, that the average segregation obviously increase with the increasing of the grain boundaries moving velocity.

4.2. Boron segregation at moving grain boundaries

The solute drag theory of Cahn [13] was usually used to explain the interaction of solute atoms and grain boundaries, this theory predicted that solute atoms segregation at moving grain boundaries is always weaker than the segregation at static grain boundaries. The earlier works indicated that there was no thermodynamical equilibrium segregation at grain boundaries in ULCB steel and Fe-30%Ni alloys at 1000 °C [14]. According to the theory of Cahn, when the grain boundaries were moving at this temperature, no segregation can be observed by PTA method. But the present experiment indicated that the boron segregation at moving boundaries was stronger than that at static boundaries, this phenomenon perhaps relates to the structure of moving boundaries. In 1994, Sanhong Zhong put foreword the widening boundary mechanism [6, 7].

According to Zhang's mechanism, the non-equilibrium segregation of solute atom at moving boundaries was concerned with moving boundary structures. During the recrystallization, the new grains with low dislocation density would replace the original deformed grains with high dislocation density, the grain boundaries would move forward, a large number of dislocations would be annihilated in the grain boundaries. Because of the long-distance stress fields of dislocations [13], the process of dislocation annihilation in grain boundaries need an appreciable time (relaxation time τ). Before the dislocation completely disappeared, this dislocation would give the boundaries an extra distortion area, and the local boundary thickness will increase [7]. During recrystallization, the new boundaries continuously moved forward, the dislocations would move into the grain boundaries and annihilated, when the moving speed of the grain boundaries was at certain value, a dynamic balance would reach between entering and annihilating, and induce the boundary width increasing during recrystallization process, this mechanism led to a strong segregation at the moving boundaries.

TABLE II The new boundaries speed during recrystallization after different pre-deformation

Deformation (%)	d (m)	r_c (m)	$t_{0.5}$ (s)	V (m/s)
10	5.488×10^{-4}	1.372×10^{-4}	20	6.86×10^{-6}
20	5.482×10^{-4}	1.371×10^{-4}	15	9.00×10^{-6}
40	5.474×10^{-4}	0.684×10^{-4}	0.6 ($t_{0.3}$)	1.14×10^{-4}

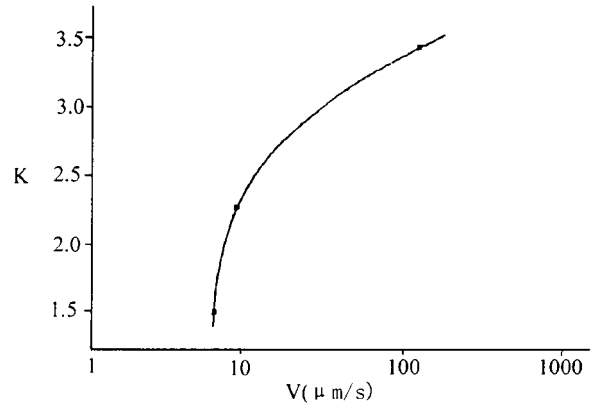

Figure 9 Relations between abnormal segregation parameter K and average moving velocity of new boundaries.

Using a similar method of Cahn, Zhang got a equation of the moving boundary maximal segregation [7]:

$$\frac{C_{gb}}{C_0} = 1 + \left(\frac{1}{W}\right)(e^{U_0/RT} - 1)\,(d_0 + d_\tau \rho \tau V) \quad (1)$$

Where W the width of boundary segregation area, U_0 binding energy of solute segregation to grain boundary, d_0 the static boundary width, T the experimental temperature, τ the dislocation relaxation time on the grain boundary, ρ average dislocation density of deformed crystal, V the boundary moving speed, d_τ the increment of average with of unity area boundary during τ, when a length of dislocation entering into boundary. Equation 1 was obtained under condition $D_{gb} \gg V\delta$, Where D_{gb} is the diffusion coefficient of solute in grain boundaries, $\delta = d_0 + d_\tau \rho \tau V$, is moving boundary width.

In order to apple the equation to the present work, the X-ray diffraction method was used to measured the dislocation density ρ after deformation 10%, 20% and 40% at 1000 °C respectively. The half-high width and integral width of (222) diffraction peaks were measured, the coherent scattering district size D_1 were calculated by Ergun's method, this coherent scattering district was divided by sub-boundaries, so the coherent scattering district size reflected the dislocation density in deformed matrix, the dislocation density could be estimated by the coherent scattering district size. Using the method of Ergun [15], the dislocation density ρ was estimated with the order of magnitude, the related data were given in Table III.

In $\gamma -$ Fe, lattice parameter $a_0 = 3.65$ Å, the thickness of static boundaries $d_0 = 2a_0$. According to the literature [7], the $d_\tau = \pi r_0^2 \times r_0$ was the radius of dislocation core, in fcc structure, the common dislocation Burgers vector was $b = \frac{\sqrt{2}}{2}a_0$, the core radius was $1.5b$.

About τ, the dislocation delocalization process is controlled by atom diffusion, Pumphery [16] pointed out that when the width of the dislocation core along boundary was delocalized to 100 nm (S_m), the lattice dislocation could be thought to disappear completely. Thus we obtain the relaxation time τ of dislocation disappearance, $\sqrt{D\tau} = S_m$, so $\tau = S_m^2/D$ ($S_m \sim$ 100 nm), where D was the self-diffusion coefficient, in γ-Fe, $D = 4.9 \times 10^{-5}\ \exp(-284100/RT)$ [17], when $T = 1000$ °C, $D = 1.067 \times 10^{-16}$ m^2/s. $U_0 = 3.95 \times 10^4$ J/mol [7]. The related data values of Equation 1 were shown in Table IV.

Form the Equation 1, the results of C_{gb}/C_0 were $\varepsilon = 10\%$, $C_{gb}/C_0 = 1.762$; $\varepsilon = 20\%$, $C_{gb}/C_0 = 2.882$; and $\varepsilon = 40\%$, $C_{gb}/C_0 = 212.4$. Where C_{gb}/C_0 was the segregation ratio at the steady state, i.e. the maximum segregation on moving boundaries.

The experimental results 3.2 showed that: when $\varepsilon = 10\%$, $K = 1.51$; $\varepsilon = 20\%$, $K = 2.28$; and $\varepsilon = 40\%$, $K = 3.46$. Where K was the measured average segregation scale during the recrystallization process.

After deformation of 10% and 20% the experimental values was in agreement with the theoretical estimated values, the error arised from the different of the average value and the maximum. But there was a significant disparity when $\varepsilon = 40\%$. From [7],the $D_{gb} \gg V\delta$ is the precondition of Equation 1, because the D_{gb} (boron diffusion coefficient along grain boundary in Fe-30%Ni) is short of data, perhaps the $D_g = 1.9 \times 10^{-6} \exp(-1.15 \times 105/RT)$ m^2/s (boron diffusion coefficient in Fe-30%Ni) can be used to analyse the result above mentioned [18]. When $\varepsilon =$ 10% and $\varepsilon = 20\%$, according to the Table III $D_g \gg V\delta$ is valid, in general $D_{gb} > D_g$, so the $D_{gb} \gg V\delta$ is available. But in case of $\varepsilon = 40\%$, the V increase more than one order of magnitude, and by the widening grain boundary mechanism [7] the δ increase more than two order of magnitude, so the pre-condition of Equation 1 is difficult to satisfy.

The results estimated by the widening mechanism are agreed with the results measured if the predeformation is the middle grade. When the deformation is higher, the moving speed of the boundaries during the recrystallization is very fast, the mechanism has to study further. In present work, the TEM results showed that, in front of moving boundaries there is a district in which the dislocation density is much higher than the deformed matrix. The solute atoms may be aggregated in this region, the relationship between the width of this region and the value estimated by widening mechanism will be investigate in future.

TABLE III The dislocation density estimated from x-ray diffract data

Pre-deformation	Half-high width (angular)	Integral width (angular)	D_1 (angstrom)	ρ (cm)$^{-2}$
Guide sample (0%)	0.260	0.320		
10%	0.320	0.403	1976.68	7.7×10^9
20%	0.348	0.439	1521.45	1.3×10^{10}
40%	0.363	0.493	623.14	7.7×10^{10}

5. Conclusions

(1) The softening curves were measured with the interrupted compression method in Fe-Ni alloy, which was deformed 10%, 20% and 40% respectively at 1000 °C and then isothermal held. From curves the recrystallization dynamics processes were estimated. The moving speed of the boundaries when the new grains were growing up during the high temperature recrystallization process was measured by semiquantitatively method.

TABLE IV The parameters used in Equation 1

deformation (%)	W (m)	U_0 (J/mol)	T(k)	d_0 (m)	τ(s)	ρ (1/m^2)	V (m/s)	$d\tau$(m^2)
10	2×10^{-6}	3.95×10^4	1273	7.3×10^{-10}	93.72	7.7×10^{13}	6.08×10^{-6}	8.34×10^{-19}
20	2×10^{-6}	3.95×10^4	1273	7.3×10^{-10}	93.72	1.3×10^{14}	9.00×10^{-6}	8.34×10^{-19}
40	2×10^{-6}	3.95×10^4	1273	7.3×10^{-10}	93.72	7.7×10^{14}	1.71×10^{-4}	8.34×10^{-19}

(2) There is a obvious non-equilibrium boron segregation at the moving new grain boundaries during recrystallization. It is more intense than the segregation at the original boundaries and continuous increase with the pre-deformation increasing. When the new grains are impingement and the boundaries met each other, the movement of boundaries is stopped, the segregation at the boundaries decrease gradually, or disappear.

(3) After the different pre-deformation the maximum segregation at moving new boundaries increase with increasing of pre-strain ε, and it is related with the moving velocity of the recrystallization grain boundaries. The results are basically agreed with the estimation of the widening grain boundary mechanism.

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