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# Two types of boron segregation at austenite grain boundaries and their mutual relation

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The distribution of boron in 10 p.p.m. B-doped Fe–30 wt % Ni austenitic alloy was investigated by means of particle tracking autoradiography (PTA). It was shown that when quenched from a certain temperature between 750° C and 1220° C with medium cooling rates, both equilibrium and non-equilibrium grain boundary segregation of boron appeared in the alloy. The degree of segregation represented the sum of the two kinds of segregation of boron. A transition temperature, of approximately 950° C, was found below which the equilibrium grain-boundary segregation was dominant and above which the non-equilibrium grain-boundary segregation was dominant. For the degree of segregation achieved by these two types of segregation of boron there exists a temperature from 1000° C to 1050° C at which a minimum amount of segregation is obtained. It was also shown that non-equilibrium segregation of boron can considerably promote the precipitation of boride at grain boundaries.

## 1. Introduction

It is well known that when trace boron is added to steel and some high-temperature alloys, their properties can be considerably improved. It has been shown that the beneficial effect of boron is caused by the segregation of boron at austenite grain boundaries. It was believed for many years that the segregation of boron to grain boundaries was a kind of equilibrium segregation. During, the 1970s, it was shown experimentally that non-equilibrium segregation of boron at grain boundaries appears under many conditions [1–3], and that this segregation is developed during cooling. But until now there has been little investigation of the mutual relation between these two types of boron segregation. In the present work, two types of boron segregation at austenite grain boundaries and their mutual relation are investigated in detail.

## 2. Experimental methods

### 2.1. Experimental alloy

B-doped Fe–30 wt % Ni austenitic alloy was chosen as the experimental alloy to investigate the behaviour of boron segregation at austenite grain boundaries in a large range of solution treatment temperatures. The alloy was prepared by vacuum induction melting and then forged into a cylindrical bar, 12 mm in diameter. After the region of B-depletion of the bar was removed by lathing, it was cut into cylindrical discs, 8 mm in diameter and 2 mm in thickness. The alloy compositions are given in Table I.

TABLE I Alloy compositions (wt %)

| C | B | Ni | P | S | Ti | Fe |
|---|---|---|---|---|---|---|
| 0.008 | 0.001 | 29.1 | 0.009 | 0.006 | 0.033 | balance |

### 2.2. Heat treatment

All the sample discs were pre-heat-treated in argon at 1220° C for 0.5 h to gain the same grain size of approximately 290 $\mu$m in diameter in order to eliminate the effect on the level of boron segregation caused by the differences in grain size in the samples. The samples were then cooled at the rate of 600° C sec$^{-1}$ to room temperature.

The samples which were pre-heat-treated were respectively heated to 750, 850, 950, 1050, 1150 and 1220° C, again for a duration of 0.5 h, and then cooled to room-temperature at the rate of 1200° C sec$^{-1}$ and 50° C sec$^{-1}$ respectively.

### 2.3. Detecting boron

In the present work, the distribution of boron in the samples was detected by particle tracking autoradiography (PTA). AC foils were used as detecting foils; their detecting sensitivity to boron atoms is 1 p.p.m. and the spatial resolution is 2 $\mu$m [4]. The integral flux of hot neutron radiation of $1.3 \times 10^{15}$ cm$^{-2}$ was chosen for this work. The detecting foils were etched for 20 min by a water solution of 7.5 N NaOH. Then the surface of each detecting foil was sprayed with chromium and was observed with the optical microscope and measured with the image analyser.

## 3. Experimental results

### 3.1. PTA results

The distribution of boron in pre-heat-treated samples is shown in Fig. 1. It was shown that the continuous etching pit belts appear along the grain boundaries and no considerable precipitation of boride exists either in the grain centres or at the grain boundaries.

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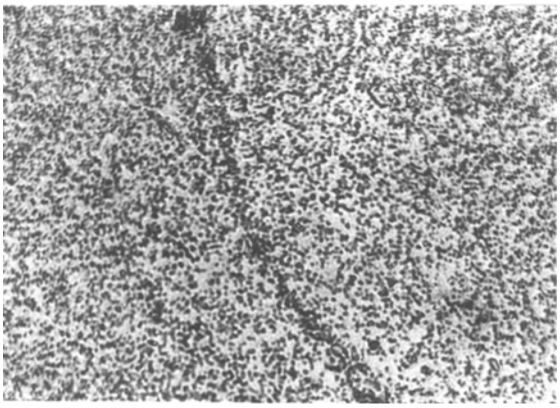

*Figure 1* The distribution of boron in the pre-heat-treated samples at 1220° C cooled at the rate of $600° \text{C sec}^{-1}$ (magnification × 450).

The distribution of boron in those samples cooled respectively from different quenching temperatures, that is, 750, 850, 950, 1050 and 1150° C and with a cooling rate of $1200° \text{C sec}^{-1}$, are shown in Fig. 2. It was clear that when quenched respectively from 1150 and 1050° C, the distributions of etching pits are homogeneous and no segregation of boron appears along the grain boundaries. The segregation of boron at the grain boundaries exists when quenched from the temperatures below 950° C and the level of segregation increases with decreasing quenching temperature.

The distributions of boron for the samples cooled respectively from different temperatures, 750, 850, 950, 1050, 1150 and 1220° C, and with a cooling rate of $50° \text{C sec}^{-1}$, are shown in Fig. 3. It can be seen that there exists a minimum level of segregation at the grain boundary when the quenching temperature is approximately between 1000 and 1050° C. The level of segregation increases with increasing quenching temperature when the quenching temperatures are higher than 1050° C. The level of segregation also increases with decreasing quenching temperature when it is lower than 1000° C. It should be noted that the level of boron segregation in the samples cooled at the rate of $50° \text{C sec}^{-1}$ were larger than those in the samples cooled at $1200° \text{C sec}^{-1}$ for the same quenching temperature.

## 3.2. Quantitative analyses

In order to determine further the behaviour of boron segregation at austenite grain boundaries, the distribution of etching pits of all the detecting foils were semi-quantitatively analysed by the M-2 image analyser.

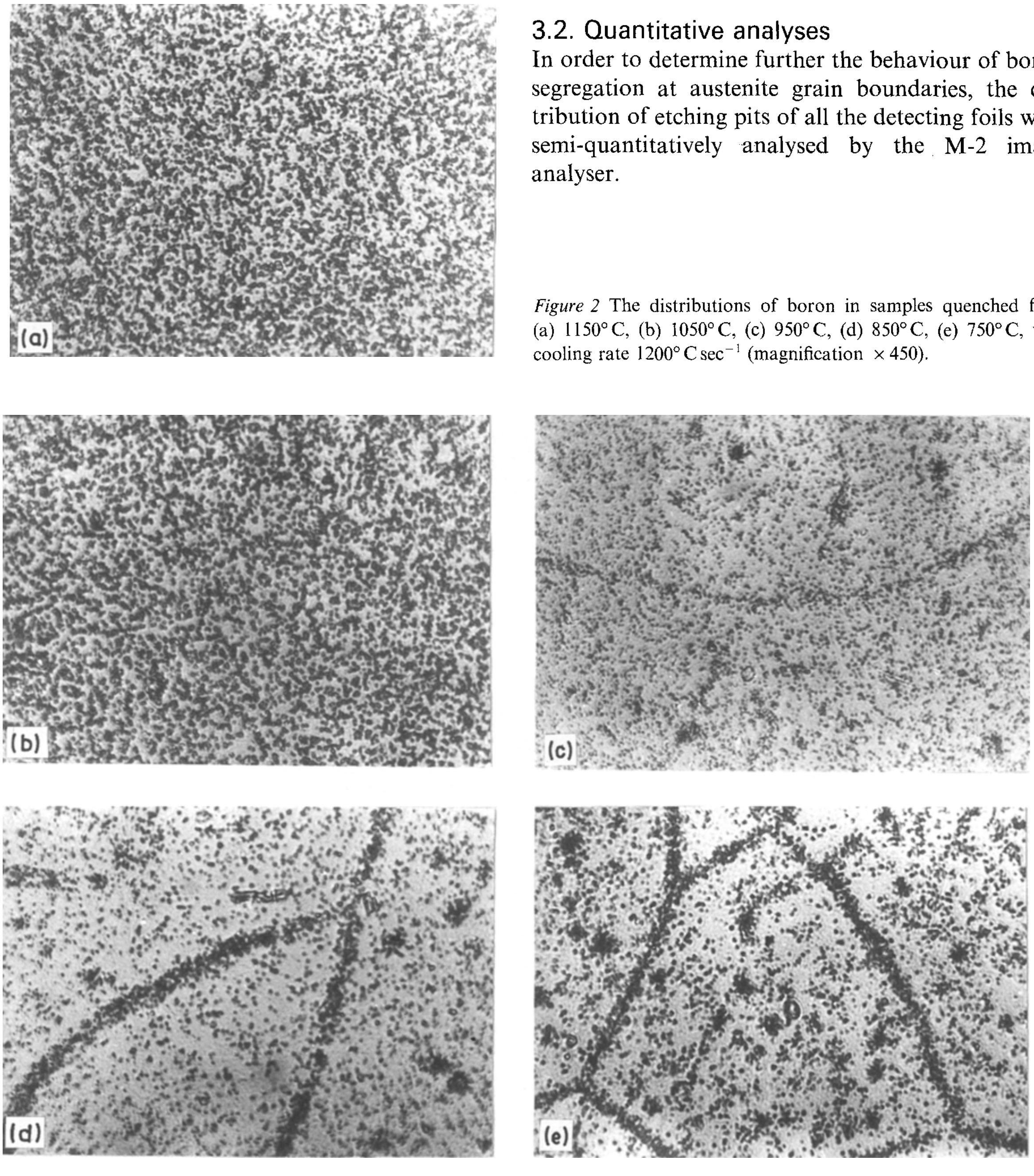

*Figure 2* The distributions of boron in samples quenched from (a) 1150° C, (b) 1050° C, (c) 950° C, (d) 850° C, (e) 750° C, with cooling rate $1200° \text{C sec}^{-1}$ (magnification × 450).

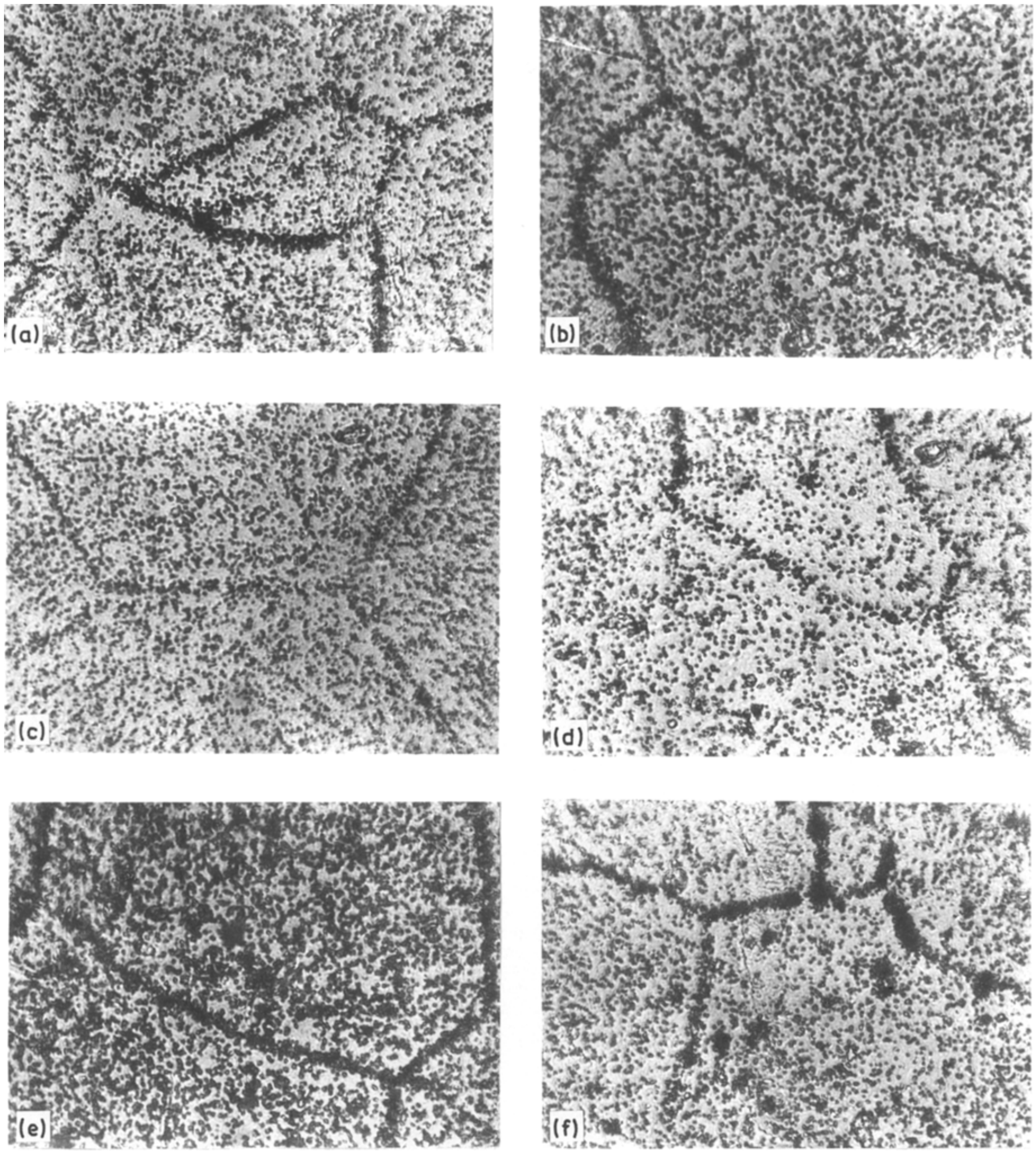

*Figure 3* The distributions of boron in the samples quenched from (a) 1220° C, (b) 1150° C, (c) 1050° C, (d) 950° C, (e) 850° C, (f) 750° C, at a cooling rate of 50° C sec$^{-1}$ (magnification × 450).

### 3.2.1. Quantitative analysing principle

According to the PTA method, the relationship between the etching pit density $\varrho$ (the number of the etching pits per unit area of detecting foil), the concentration $B$ of boron in the samples and the integral flux $\Phi$ of hot neutron radiation, is given by [4]

$$\varrho = CB\Phi \qquad (1)$$

where $C$ is a constant related to experimental conditions. Because the accurate determination of $C$ and $\Phi$ is very difficult, in this work we determined the relative variation of boron concentration between grain boundary region and grain centre region in the same sample to avoid measuring $C$ and $\Phi$. When the density and the size of the etching pits are large enough, because of the overlapping between etching pits of the detecting foils, the etching pit density which appeared on the detecting foils, which is called the apparent density of etching pits $\varrho'$, will be different from the etching pit density of Equation 1, which is called the true density $\varrho$. The relationship between the two kinds of etching pit densities is given by [5]

$$\varrho = -\ln(1 - \varrho' a)/a \qquad (2)$$

where $a$ is the area of single pit. It is clear that the true density $\varrho$ can be obtained by correcting the apparent density according to Equation 2. From Equation 2 we can get

$$A = -\ln(1 - A') \qquad (3)$$

where $A = \varrho a$ and $A' = \varrho' a$. $A'$ is the apparent area fraction, which is equal in number to the area occupied by etching pits in unit area of detecting foils.

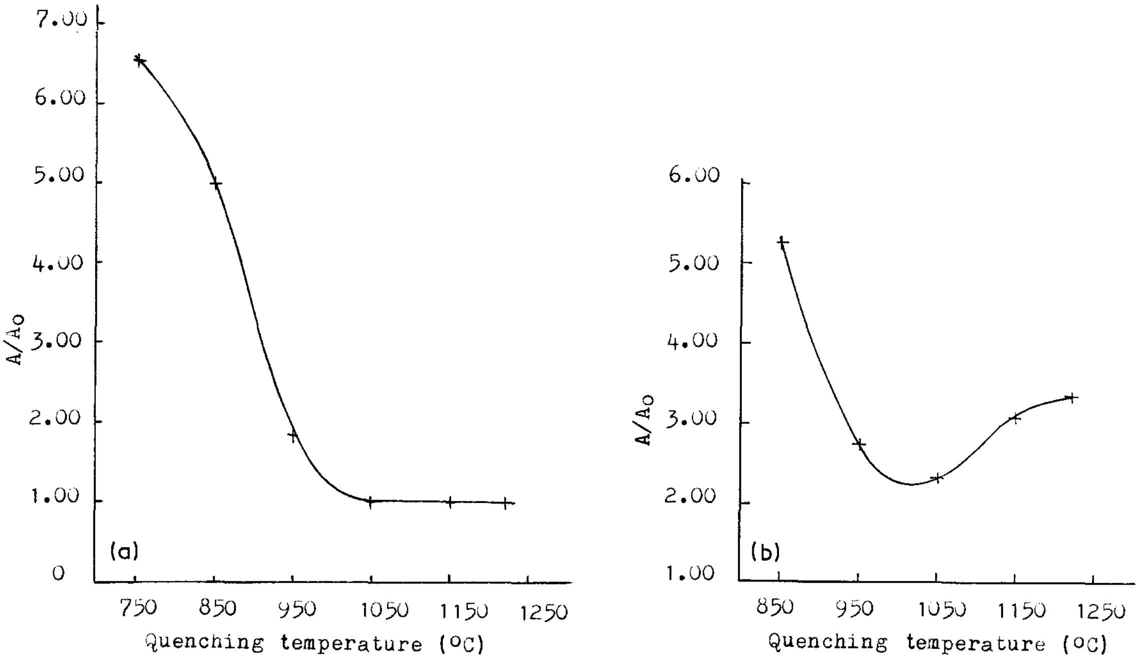

*Figure 4* $A/A_0$ as a function of quenching temperature for cooling rates (a) 1200° C sec$^{-1}$ and (b) 50° C sec$^{-1}$.

### *3.2.2. The sizes of etching pits for different samples*

In this work, the etching pit density will be replaced by the area fraction $A$, in measuring the distribution of boron. Therefore the measured results will be affected by the variation in etching pit size between different samples. In order to eliminate this effect of etching pit size on the measured results, more or less the same size of the etching pits was assumed for all the detecting foils of samples in this work. The average size of single etching pit for different samples was measured by means of M-2 image analyser and the results are shown in Table II, where it can be seen that the average areas of etching pits for different samples are between 0.87 and 1.13 $\mu$m$^2$, and the average diameters are between 1.04 and 1.19 $\mu$m. It therefore is reasonable to assume that the sizes of all the etching pits for different samples are almost identical.

### *3.2.3. The measured results of boron segregation level at grain boundaries*

Owing to the spatial resolution of PTA and the size of etching pits, a rectangular band of area $3 \times 40\,\mu\text{m}^2$ is chosen to determine the apparent area fraction inside the rectangular band. When the rectangular band was placed on the grain boundary the apparent area fraction measured was denoted by $A'$, and when placed on the grain centres it was denoted by $A'_0$. According to Equation 3, then the apparent area fractions $A'$ and $A'_0$ were corrected to give the true area fractions $A$ and $A_0$ respectively. The level of boron segregation at the grain boundaries is expressed by the ratio of $A/A_0$, which is called the relative level of grain-boundary segregation in this paper. The measured results of $A/A_0$ by image analyser, as a function of quenching temperatures, are shown in Fig. 4a for the samples cooled at the rate of 1200° C sec$^{-1}$, and are shown in Fig. 4b for the samples cooled at 50° C sec$^{-1}$. Fig. 4b shows that when the samples were cooled from a quenching temperature between about 1000° C and 1050° C, a minimum level of boron segregation was achieved.

From Fig. 4, it can be seen that the reults of boron segregation measured by image analyser are consistent with that shown by the photographs in Figs 2 and 3.

## 4. Discussion

### 4.1. Equilibrium segregation of boron

Figs 2 and 4a shows that when the samples were cooled from temperatures above 1050° C at a cooling rate of 1200° C sec$^{-1}$, the distribution of pits on the detecting foils was homogeneous and no segregation of boron to grain boundaries occurred. This means that when samples are held above 1050° C there is no considerable equilibrium segregation along the grain boundaries, and the cooling rate of 1200° C sec$^{-1}$ is quick enough to restrain the diffusion of boron completely during cooling. It can also be seen from

TABLE II The sizes of etching pit for different samples

| Quenching temperature (° C) | 750 | 850 | 850 | 950 | 950 | 1050 | 1150 | 1220 |
|---|---|---|---|---|---|---|---|---|
| Cooling rate (° C sec$^{-1}$) | 1200 | 1200 | 50 | 1200 | 50 | 50 | 50 | 50 |
| Total number of measured etching pits | 693 | 678 | 505 | 597 | 486 | 611 | 675 | 568 |
| Average area of etching pits ($\mu$m$^2$) | 0.87 | 0.96 | 0.88 | 1.05 | 0.95 | 0.96 | 1.13 | 0.97 |
| Average diameter of etching pits ($\mu$m) | 1.04 | 1.10 | 1.05 | 1.15 | 1.09 | 1.10 | 1.19 | 1.10 |

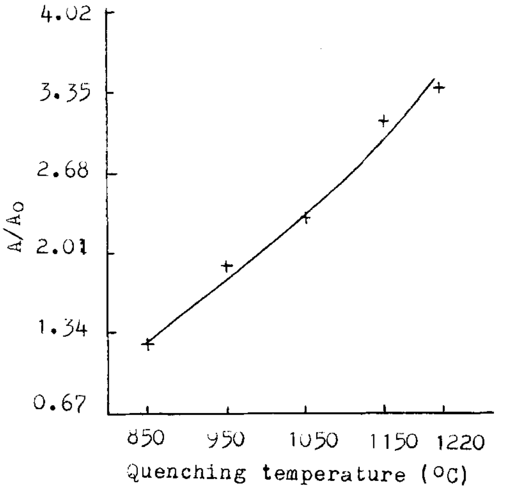

*Figure 5* $A/A_0$ during cooling as a function of quenching temperature for a cooling rate of 50° C sec$^{-1}$.

Figs 2 and 4a that when the quenching temperatures were below 1050° C, segregation along grain boundaries occurred in samples cooled at the rate of 1200° C sec$^{-1}$, and segregation increases when the quenching temperature is decreased. Obviously these segregations at grain boundaries occurred when samples were held at quenching temperatures and did not occur during the cooling. Therefore the segregation of boron to the grain boundary shown in Figs 2 and 4a is caused by the mechanism of equilibrium segregation. It should be noticed that the increase of segregation levels with the decrease in quenching temperatures is consistent with the law of equilibrium segregation of grain boundaries which is well known [6].

## 4.2. Non-equilibrium segregation of boron

Comparing the level of segregation of the samples cooled at the rate of 50° C sec$^{-1}$ with that of the samples cooled at 1200°C sec$^{-1}$ for the same quenching temperatures we find the following.

1. When the quenching temperatures are above 1050° C, there is considerable segregation along the grain boundaries for the samples cooled at rate of 50° C sec$^{-1}$ and no segregation for the samples cooled at 1200° C sec$^{-1}$. Therefore we can conclude that the segregation of the samples cooled at 50° C sec$^{-1}$ from the temperatures above 1050° C occurred during the cooling and it was caused mainly by the mechanism of non-equilibrium grain boundary segregation. It should be noticed that the levels of the segregation increase with increasing the quenching temperature, which is consistent with the well known law of non-equilibrium segregation to the grain boundaries.

2. When the quenching temperatures are below 1050° C, the level of segregation of the samples cooled at 50° C sec$^{-1}$ is considerably higher than that of the samples cooled at 1200° C sec$^{-1}$ for the same quenching temperatures. This means that the levels of segregation for the samples cooled at 50° C sec$^{-1}$ include both the amount of segregation occurring when holding at the quenching temperatures and the amount of segregation occurring during the cooling from the quenching temperatures, i.e. the levels of segregation shown in Figs 3 and 4b for the quenching temperatures below 1050° C are the sum of both the equilibrium segregation and non-equilibrium segregation of boron.

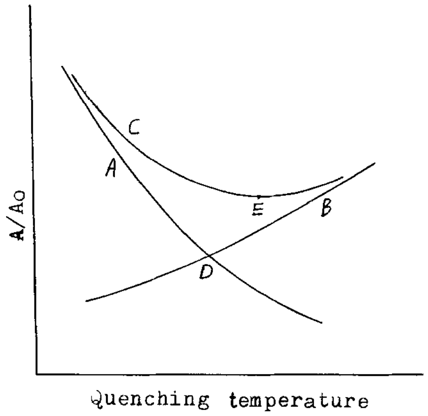

*Figure 6* Schematic diagram of segregation level as a function of quenching temperature C, found by adding the equilibrium segregation A to the non-equilibrium segregation B.

Deducting the amount of equilibrium segregation, shown in Fig. 4a, from the amout of segregation of samples, shown in Fig. 4b, for the corresponding quenching temperatures (adding one to the differences in order to include the background boron concentration of boron at grain boundaries) we can find the level of segregation, shown in Fig. 5, which increases as the quenching temperature increases. It is clear that the level of segregation shown in Fig. 5 will be determined mainly by the mechanisms of non-equilibirum grain boundary segregation [7, 8].

In Fig. 4b, there is a quenching temperature about between 1000° C and 1050° C, from which when a sample is cooled at 50° C sec$^{-1}$, a minimum of segregation at grain boundaries will be achieved. This temperature is called the minimum segregation temperature in the present work and obviously is affected by the cooling rate of samples.

## 4.3. Transition temperature between two kinds of segregation

Comparing Fig. 4a with Fig. 5, we find that when the quenching temperature is about 950° C the level of boron non-equilibrium segregation of the samples cooled at 50° C sec$^{-1}$ will be equal to the level of equilibrium segregation at 950° C: $A/A_0$ is between 1.85 and 1.89; when the quenching temperatures are higher than 950° C, the non-equilibirum segregation levels will be higher than the equilibrium segregation levels, and when they are lower than 950° C, the non-equilibrium segregation levels will be lower than the equilibrium segregation levels at this temperature. We call this temperature the transition temperature between equilibrium segregation and non-equilibrium segregation. It is obvious that the transition temperature will vary with the cooling rate of the sample, and is, in general, not equal to the minimum segregation temperature shown in Fig. 4b. This results from the fact that the rate of variation of equilibrium segregation with the quenching temperature is, in general, not equal to the rate of variation of non-equilibrium segregation with quenching temperature, as shown in Fig. 6. Therefore, it is not the case that the temperature of the minimum segregation level is the transition temperature between the two kinds of segregation, as claimed by Chu Youyi *et al.* [9].

### 4.4. Effect of boron segregation on boride precipitation

From Figs 2 and 3, it can be seen that no considerable amount of boride appears along the grain boundaries for the samples cooled at 1200° C $\sec^{-1}$, while a considerable amount of boride appears along the grain boundaries for the samples cooled at 50° C $\sec^{-1}$. This means that the amount of boride precipitation at grain boundaries increases with decreasing cooling rate at a certain quenching temperature for the experimental alloy. In equilibrium conditions, when the solubility of solute at the grain boundaries is equal to the concentration of solute, equilibrium segregation corresponds to the solute lattice solubility limit at the considered temperature and boride will precipitate [10]. Because of the existence of non-equilibrium segregation for the samples cooled at 50° C $\sec^{-1}$, an excess of solute concentration at the grain boundaries will promote the precipitation of boride. That is why the cooling rate will considerably affect the level of boride precipitation.

## 5. Conclusions

1. For 10 p.p.m. B-doped Fe–30 wt % Ni austenitic alloy when cooled at a medium rate both equilibrium and non-equilibrium segregation occurs at grain boundaries.
2. When held above 1050° C, no considerable equilibrium segregation will occur.
3. There is a transition temperature between equilibrium and non-equilibrium segregation. It is about 950° C for the experimental alloy cooled at 50° C $\sec^{-1}$.
4. The existence of non-equilibrium segregation will considerably promote the precipitation of boride.

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