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# Combined equilibrium and non-equilibrium segregation mechanism of temper embrittlement

SONG SHENHUA*, XU TINGDONG
*Department of Materials, Wuhan Iron and Steel University, Wuhan, Hubei 430081, China*

Grain boundary segregation of impurities like P, S, Sb, and others is the origin of temper embrittlement of low-alloy steels. Till now it has been assumed that the segregation is determined by an equilibrium segregation mechanism, but some open questions cannot be satisfactorily explained by the equilibrium segregation mechanism. In the present work, a combined equilibrium and non-equilibrium segregation mechanism of temper embrittlement was established and some open questions on temper embrittlement were addressed by means of the model. The model was applied to phosphorus segregation in an Fe–0.3% C–3.5% Ni–1.7% Cr–0.06% P steel.

## 1. Introduction

Temper embrittlement refers to the loss in toughness which occurs when a low-alloy steel is heated in the temperature range of approximately 350 to 600 °C or slowly cooled through this temperature range, and is now known to be caused by the segregation of certain impurities to grain boundaries, producing a tendency for intergranular brittle fracture and thus a shift in the ductile–brittle transition to higher temperatures [1–3].

Two treatments resulting in temper embrittlement can be distinguished. The first type occurs in steels with very high yield strengths after austenitizing and quenching and tempering for a short time ( ~ 1 h) at low temperatures ( < 400 °C). Behind the prior segregation in the austenite phase the precipitation of carbides plays an important part in this type of temper embrittlement [4]. The second kind of embrittlement is frequently observed if a low-alloy steel is tempered in the temperature range of 350–600 °C or slowly cooled there after tempering. Since the loss in toughness vanishes during a tempering above 600 °C but below the α-γ region and occurs again at a tempering in the same temperature range of 350–600 °C, it is often called reversible temper embrittlement.

The results of studies concerning the second kind of temper embrittlement can be summarized as follows:

1. The ductile–brittle transition temperature is directly dependent on the concentration of impurities (P, Sn, Sb, etc.) at grain boundaries.
2. With decreasing tempering temperature the grain boundary concentration of impurities increases. However, the tempering time becomes increasingly a determining factor at low temperatures.

Many authors [1–4] assume grain boundary impurity segregation to be caused by an equilibrium segregation mechanism. However, some questions cannot be satisfactorily explained by the equilibrium segregation mechanism. Some open questions that are not yet clear are [4]

1. Why does impurity segregation, and thus intergranular fracture, occur predominantly at prior austenite grain boundaries?
2. An intercritical heat treatment in the α-γ region, after austenitization but before tempering, may be used to reduce temper embrittlement, but the mechanism of reducing the embrittlement in this case is not yet clear.

For the above reasons, we consider that temper embrittlement caused by directly tempering after quenching is likely to be caused by a combined equilibrium and non-equilibrium grain boundary segregation of impurities. This is because, after steel is quenched, the excess saturation degree of vacancies in the steel is very large so that, with the help of vacancies, the impurity atoms diffuse to grain boundaries from the grain centres during tempering. This segregation behaviour is non-equilibrium.

Non-equilibrium segregation theory was established by Aust *et al.* [5] and Anthony [6]. The mechanism of non-equilibrium segregation relies on the formation of sufficient quantities of vacancy–impurity complexes. Impurity, vacancy and their recombined complex are in equilibrium with each other at a certain temperature. When material is properly maintained at a solution-treatment temperature it will, when quickly cooled to a certain lower temperature, exhibit a loss of vacancies along grain boundaries, i.e. at vacancy sinks, whereby it attains the equilibrium vacancy concentration at the low temperature. The decrease in the vacancy concentration causes the dissociation of the complexes into vacancies and impurity atoms. This in turn results in a decrease in the complex concentration near the grain boundary.

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*Present address: Institute of Polymer Technology and Materials Engineering, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK.

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Meanwhile, in regions remote from the grain boundary, where no other vacancy sinks are present, the concentrations of the vacancy and the complex are generally invariant. Consequently, a complex concentration gradient appears between the grain boundary and the regions beyond it. The gradient of complex concentration drives the complexes to diffuse to the grain boundary from regions remote from it. This diffusion leads excess impurity atoms to concentrate in the vicinity of grain boundary and results in non-equilibrium grain boundary segregation. It is evident that the larger the excess saturation level of vacancies in the grain centres, the larger the segregation level of impurities. In the present work, a combined equilibrium and non-equilibrium segregation mechanism of temper embrittlement was established and some open questions were addressed by means of the model.

## 2. Model

### 2.1. Kinetics of temper embrittlement

### *2.1.1. Equilibrium segregation*

McLean's model [7] is now used. This states that, for an impurity with binding energy to the lattice $Q$ at any temperature $T$, there will be an increased concentration of that impurity in a monolayer on boundaries and interfaces, $C_\infty(T)$. The driving force for this is the reduction of the energy $Q$ of the impurity on placing it in a strain-free region on the grain boundary. $C_\infty(T)$ is given by

$$C_\infty(T) = \frac{AC_g \exp(Q/kT)}{1 + AC_g \exp(Q/kT)} \tag{1}$$

where $C_g$ is the concentration of impurity in the matrix, $A$ is a constant representing the vibrational entropy of the grain boundary region and $k$ is the Boltzmann constant. McLean refined these ideas to account for time, correctly realizing that a finite time is required to accumulate the monolayer and that this is controlled by the diffusivity of the impurity in the matrix, $D_i$.

When the sample is so quickly cooled from a quenching temperature (or solution treatment temperature) $T_i$ to $T_j$ ($T_i > T_j$) that no mass transfer occurs in the sample during cooling and then held at temperature $T_j$, the equilibrium segregation kinetics, $C_b(t)$, derived by means of Equation 1, is

$$\frac{C_b(t) - C_\infty(T_i)}{C_\infty(T_j) - C_\infty(T_i)} = 1 - \exp\left(\frac{4D_i t}{\alpha_i^2 d_e^2}\right) \operatorname{erfc}\left(\frac{2(D_i t)^{1/2}}{\alpha_i d_e}\right) \tag{2}$$

where $C_b(t)$ is the concentration of impurity on the boundary after time $t$, $d_e$ is the thickness of the boundary ( ~ 1 nm), and $\alpha_i$ is given by

$$\alpha_i = \frac{C_\infty(T_j)}{C_g} \tag{3}$$

### *2.1.2. Non-equilibrium segregation*

The results of experiments [8, 9] on non-equilibrium grain boundary segregation have shown that non-equilibrium grain boundary segregation can be classified into segregation and desegregation. When a sample is quickly cooled from a higher quenching temperature to a certain lower one and then held at this lower temperature, there is a critical hold time for which the non-equilibrium segregation level will be maximum. If the holding time of the sample is shorter than the critical time, the segregation of the complexes from the grain centres to the grain boundary will be dominant and the process is called a segregation process; if the holding time is longer than the critical time, the process in which the diffusion of the impurity atoms from the boundary to the centres is dominant will also occur, called a desegregation process.

When a sample is quickly cooled to a lower-temperature, from a higher quenching one $T_o$ and then maintained at the lower temperature, the maximum concentration of non-equilibrium grain boundary segregation induced during holding at this lower temperature, $C_b^m(T)$, is given by [10]

$$C_b^m(T) = C_g\left(\frac{E_b}{E_f^v}\right)\exp\left(\frac{E_b - E_f^v}{kT_o} - \frac{E_b - E_f^v}{kT}\right) \tag{4}$$

where $C_g$ is the concentration of the impurity within the grain, $E_f^v$ the energy of vacancy formation, $k$ the Boltzmann constant and $E_b$ the vacancy–impurity atom binding energy, which is about 0.36 eV for P in an $\gamma$-Fe matrix [11].

It is obvious that the maximum concentration $C_b^m(T)$ is only dependent on the difference between the quenching temperature $T_o$ and the lower temperature $T$, and is independent of the cooling rate from $T_o$ to $T$ and the holding time at $T$. Therefore Equation 4 is an important thermodynamic equation describing the non-equilibrium grain boundary segregation.

When the sample is so quickly cooled from a quenching (or solution-treatment) temperature $T_i$ to temperature $T_j$ ($T_i > T_j$) that no mass transfer occurs in the sample during cooling and held at temperature $T_j$, the non-equilibrium segregation kinetics, $C_b(t)$, derived by means of Equation 4, is given by [10]

$$\frac{C_b(t) - C_b^m(T_i)}{C_b^m(T_j) - C_b^m(T_i)} = 1 - \exp\left(\frac{4D_c t}{\alpha_j^2 d_n^2}\right) \times \operatorname{erfc}\left(\frac{2(D_c t)^{1/2}}{\alpha_j d_n}\right) \tag{5}$$

where $D_c$ is the coefficient of diffusion of complexes in the matrix, $t$ the holding time at temperature $T_j$, $d_n$ the width of the concentrated layer of impurities, $C_b^m(T_i)$ the maximum segregation level at $T_i$, i.e. the grain boundary concentration of segregant at the holding time $t = 0$ at temperature $T_j$, $\alpha_j = C_b^m(T_j)/C_g$, and

$$\operatorname{erfc}\left(\frac{2(D_c t)^{1/2}}{\alpha_j d_n}\right) = 1 - \frac{2}{\pi^{1/2}} \int_0^{2(D_c t)^{1/2}/\alpha_j d_n} \exp(-Y^2)\,dY$$

Data for $D_c$ are sparse and it is assumed here that $D_c$ is given by the product of the frequency factor for vacancy diffusion and the exponential term containing the average value of vacancy movement energy and impurity diffusion activation energy in the matrix.

Equation 5 is an isothermal kinetic relationship of non-equilibrium segregation for the segregation process. It describes the non-equilibrium segregation concentration $C_b(t)$ of impurity atoms at grain boundaries as a function of the holding time $t$ at temperature $T_j$ when the segregation process of the complexes to grain boundary from the grain centres is dominant. Using Equation 5, we may predict the non-equilibrium segregation level of impurities in the sample quenched from a higher temperature and then tempered at the tempering temperature.

As mentioned above, a critical time $t_c$ exists at some temperature. At some temperature when the critical time is longer than the effective time of impurity diffusion corresponding to the cooling process, $t_e$, the process in which the segregation is dominant occurs alone; whereas when $t_c$ is shorter than $t_e$, the process in which desegregation is dominant also appears. The critical time $t_c$ is given by [9, 13]

$$t_c = \frac{B^2 \ln(D_c/D_i)}{4\delta(D_c - D_i)} \tag{6}$$

where $\delta$ is a numerical factor and $B$ is the grain size.

When the effective time is longer than the critical time at temperature $T_j$, the process in which desegregation is dominant will take place. The segregation level of impurities at grain boundaries in this case, $C_b(t)$, is given by [10]

$$C_b(t) = C_g + \tfrac{1}{2}[C_b(t_c) - C_g]\left[\operatorname{erf}\left(\frac{dn/2}{[4D_i(t - t_c)]^{1/2}}\right) - \operatorname{erf}\left(\frac{-dn/2}{[4D_i(t - t_c)]^{1/2}}\right)\right] \tag{7}$$

where $t$ is the isothermal holding time at temperature $T_j$, $t_c = t_c(T_j)$ and $D_i$ is the diffusion coefficient of impurity atoms in the matrix. Evidently, Equation 7 is only concerned with desegregation. Thus the condition $t > t_c$ is necessary for Equation 7.

According to previous work [9, 13, 14], Equation 6 is only suitable for a high temperature range in which the maximum equilibrium segregation level is very small. At lower temperatures, since the maximum equilibrium segregation level, $C_\infty$ is larger and the process in which desegregation is dominant may be able to take place when the segregation concentration is larger than $C_\infty$. Consequently during tempering of steels, the process in which desegregation is dominant cannot occur before the segregation level to grain boundaries reaches the maximum equilibrium segregation one, $C_\infty$. In the present work, the grain boundary segregation level of P before reaching $C_\infty$ was only calculated, which is evidently consistent with the real case. Furthermore, since non-equilibrium segregation is a process of kinetics and occurs mainly during quenching and tempering of the sample, while equilibrium segregation is a process of thermodynamics and occurs mainly during tempering, the equilibrium segregation level during tempering and the non-equilibrium segregation one during quenching + tempering were calculated in this work. It should be noted that in the present work it is assumed that the diffusion of impurity atoms to the grain boundary does not affect that of impurity atom–vacancy complexes to the grain boundary and vice versa.

## 2.2. A method of calculating the segregation level of impurities in the tempered sample

Equilibrium grain boundary segregation occurs mainly during tempering of the sample and non-equilibrium segregation occurs mainly during quenching and tempering. Therefore, it is of considerable importance to calculate the segregation levels during quenching and tempering. This calculation has to be divided into two steps because the matrix during quenching is austenite and the matrix during tempering is ferrite. The first step of the calculation is calculation of the segregation level during quenching and the second step is of that during tempering.

### *2.2.1. Calculation of non-equilibrium segregation level during quenching*

As discussed elsewhere [9], any continuously cooling curve for a sample can be replaced by a corresponding stepped curve, each step of which is formed by horizontal and vertical segments so as to calculate an effective time $t_e$ at some temperature for this cooling process. The effective time formula of a stepped curve consisting of $n$ steps at temperature $T$ is given by [9]

$$t_e = \sum_{i=1}^{n} t_i \exp\left(-\frac{E_A(T - T_i)}{kTT_i}\right) \tag{8}$$

where $E_A$ is the activation energy for the diffusion of complexes in the matrix and it is assumed here that $E_A$ is given by the average value of the vacancy movement energy $E_m$ and the impurity atom diffusion activation energy; $t_i$ and $T_i$ are the isothermal holding time and temperature at the $i$th step of the stepped curve, respectively. When the chosen steps are small enough, the effective time corresponding to the stepped curve at some temperature will accurately enough be equal to that corresponding to the continuously cooling curve at the same temperature. It may be expected that the effect of diffusion of impurities (or complexes) during the continuous cooling is the same as that of impurities (or complexes) during isothermal holding for the effective time during cooling at the same temperature. This means that it is possible that calculation of the segregation levels of complexes during quenching may be changed into calculating that during isothermal holding at some temperature (chosen as 600 °C in this work) by means of the effective time concept. In this work $T$ in Equation 4 was chosen as 600 °C in calculation of the segregation level during quenching. This is because it is assumed here that very little diffusion will occur below 600 °C due to a larger quenching rate. For any sample quenched, we can gain the effective time corresponding to its quenching at 600 °C as above. The segregation levels in the quenched sample can be obtained by substituting the effective time into Equation 5. It is noted that $C_b^m(T_i)$ in Equation 5 is about equal to $C_g$ because the quenching temperature is higher.

### *2.2.2. Calculation of segregation level after tempering*

After the non-equilibrium segregation level during quenching is gained as above, the equilibrium and non-equilibrium segregation levels after tempering may be obtained by substituting the tempering time into Equations 2 and 5, respectively. In this calculation, $D_c$ and $D_i$ are the diffusion coefficients of complexes and impurities in the matrix (ferrite), respectively. The grain boundary concentrations of segregant at tempering time $t = 0$ at the tempering temperature, $C_\infty(T_i)$ in Equation 2 and $C_b^m(T_i)$ in Equation 5, should be equal to the non-equilibrium segregation level during quenching. Finally, the total level of impurity segregation after tempering is equal to the sum of levels of the two types of segregation minus $C_g$.

## 2.3. Theoretical results

Mulford *et al.* [15] have shown bond weakening by phosphorus segregation at grain boundaries in a 3.5% Ni–1.7% Cr–0.06% P steel. Therefore let us apply now the above model to P in a 3.5% Ni–1.7% Cr steel. The composition of the steel, taken from Ogura *et al.* [16], is shown in Table I.

Nowadays, most of the researches with respect to temper embrittlement are done by the following heat-treatment. The heat-treatment steps of the sample are always quenching + toughening above 600 °C and then embrittlement between 350 and 600 °C, which, generally speaking, is not consistent with actual heat treatments and also not suitable for the above model. Consequently in the present work, theoretical results can only be obtained from the above model and they are not compared with observed data.

It is assumed that the heat-treatment steps of a sample 10 mm × 5 mm × 5 mm in size are

(i) austenitizing at 1300 and 1050 °C respectively and quenching at a rate of 250 °C s$^{-1}$; and

(ii) tempering at 500 and 450 °C, respectively, for up to 100 h.

The data used in calculating P segregation level during quenching and tempering are given in Table II. The vacancy–phosphorus binding energy $E_b$ was chosen as $E_b = 0.36$ eV. The concentration of P in the grain centres, $C_g$, was taken as the analysed concentration, taken from Table I and changed to the atomic percentage. The non-equilibrium grain boundary segregation width $d = 100$ nm was chosen. $D_c$ was given by the product of the frequency factor for vacancy diffusion and the exponential term containing the average value of vacancy movement energy and solute diffusion activation energy in the matrix.

TABLE I Composition of steel used in the theoretical calculation (wt %)

| C | Ni | Cr | P | S | Fe |
|---|---|---|---|---|---|
| 0.30 | 3.5 | 1.7 | 0.061 | 0.0034 | bal. |

The results of calculating P segregation during quenching + tempering are shown in Figs 1 and 2 which indicate the following:

1. The segregation level during quenching is about 4 at % for the sample quenched from 1300 °C (see Fig. 1), which is in agreement with the results of Ogura *et al.* [16].
2. At the same quenching temperature, the process of segregation kinetics in the sample tempered at 500 °C is much faster than that in the sample tempered at 450 °C, which is well known, but it should be noted that at the tempering temperatures of 500 and 450 °C, the kinetic processes of segregation for this model are all much quicker than those for McLean's model (see Fig. 1).
3. At the same tempering temperature and time, the segregation level in the sample quenched from 1300 °C is larger than that in the sample quenched from 1050 °C (see Fig. 2), which cannot be interpreted by the equilibrium segregation mechanism.

## 3. Discussion

A new interpretation of temper embrittlement results from the diffusion of impurities and impurity–vacancy complexes to grain boundaries from grain centres.

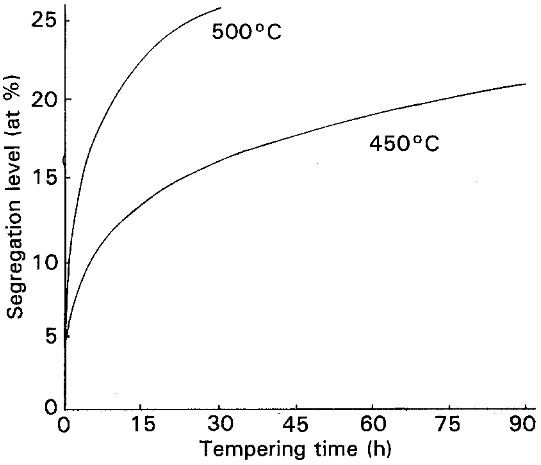

*Figure 1* Segregation levels of phosphorus as a function of tempering time in samples quenched at 250 °C s$^{-1}$ from 1300 °C and tempered at 500 °C ($C_\infty = 25$ at %) and 450 °C ($C_\infty = 33$ at %).

TABLE II Data used in the theoretical calculation

| Parameter | In the ferrite range | | In the austenite range | |
|---|---|---|---|---|
| $D_i$ (m$^2$ s$^{-1}$) | $2.9 \times 10^{-4} \exp(-2.39/kT)$ | [17] | $2.83 \times 10^{-3} \exp(-3.03/kT)$ | [17] |
| $D_c$ (m$^2$ s$^{-1}$) | $5 \times 10^{-5} \exp(-1.80/kT)$ | [13] | $5 \times 10^{-5} \exp(-2.11/kT)$ | [13] |
| $E_f^v$ (eV) | 1.6 | [12, 18] | 1.6 | [12, 18] |
| $E_m$ (eV) | 1.2 | [12, 18] | 1.2 | [12, 18] |
| $C_g$ (at %) | 0.11 | | 0.11 | |
| $E_b$ (eV) | | | 0.36 | [11] |
| $A$ | 0.775 | [19] | | |
| $Q$ (eV) | 0.397 | [19] | | |

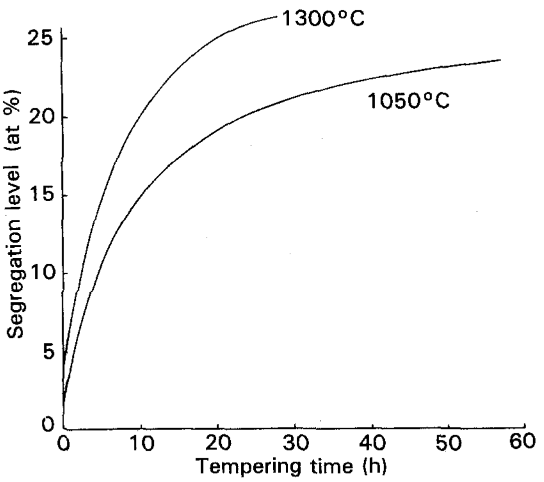

*Figure 2* Segregation levels of phosphorus as a function of tempering time in samples quenched at $250\,°\mathrm{C\,s^{-1}}$ from 1300 and 1050 °C and tempered at 500 °C ($C_\infty = 25$ at%).

Theoretically, this model is reasonable. This is because the excess saturation degree of vacancies in a steel quenched from a higher temperature is very large. In this case, a large number of impurity–vacancy complexes would appear because the vacancy and the impurity atom possess a certain binding energy. When the steel is tempered, a loss of vacancies along grain boundaries, i.e. at vacancy sinks, will be exhibited in order to reach the equilibrium vacancy concentration at the tempering temperature. Therefore a complex concentration gradient will appear between the grain boundary and the grain centres. The gradient of complex concentration drives the complexes to diffuse to the grain boundary from regions remote from it. This diffusion of complexes results in excess impurities concentrating near the grain boundary and leads to non-equilibrium grain boundary segregation. Of course, the above processes also occur during quenching. Consequently during quenching and tempering of the sample, impurity–vacancy complexes diffuse to grain boundaries to cause non-equilibrium segregation at the same time as impurities diffuse to grain boundaries to cause equilibrium segregation. However, since the equilibrium segregation is a process of thermodynamics, the segregation level of the impurity during quenching of the sample is very small and may be neglected.

The theoretical results in Fig. 1 show that the segregation level of P at tempering time $t = 0$, i.e. during quenching, is about 4 at % which is generally consistent with the observed result of approximately 5 at % [16] and reaches the maximum equilibrium segregation level of about 24 at % at the tempering time of 25 h for a sample quenched from 1300 °C and tempered at 500 °C. However, the segregation level of P at a tempering time of 90 h for the sample quenched from 1300 °C and tempered at 450 °C only reaches approximately 21 at %, which is much less than the maximum equilibrium segregation level of about 33 at %; at the same quenching temperature and tempering time, the segregation level of P in the sample tempered at 500 °C is much larger than that in the sample tempered at 450 °C. However, it may be thought that with increasing tempering time, the segregation level of P in the sample tempered at 450 °C will gradually increase and be larger than that in the sample tempered at 500 °C. The above results have well been known, but it should be noted that at temperatures of 500 and 450 °C, the kinetic processes of segregation for the model are all far faster than those for McLean's model. This is because 9/10 of the time necessary for reaching the maximum equilibrium grain boundary segregation concentration, $t_{9/10}$, is given by [7]

$$t_{9/10} = 468\,\alpha^2 d^2/64 D_\mathrm{i} \qquad (9)$$

where $d$ is the width of the grain boundary which is about 1 nm, $D_\mathrm{i}$ is the diffusion coefficient of impurity atoms in the matrix and $\alpha$ is the enrichment ratio of impurities. For the $\alpha$-Fe matrix and P in it, $\alpha$ is about 224 at 500 °C and 301 at 450 °C, and $D_\mathrm{i}$ is given by Table II. Therefore, substituting for $d$, $\alpha$ and $D_\mathrm{i}$ in Equation 9 gives $t_{9/10} = 1311$ h at 500 °C and 28108 h at 450 °C.

From the above discussion, we may see that excess saturation vacancies in the quenched sample play an important role in the tempering process of the steel, whereas this was not considered in the equilibrium segregation mechanism of temper embrittlement.

The theoretical results in Fig. 2 show that for the same tempering temperature and time, the segregating level of P in the sample quenched from 1300 °C is larger than that in the sample quenched from 1050 °C, which cannot satisfactorily be explained by the equilibrium segregation model but can be explained by the model suggested in this work. This is because the higher the quenching temperature is, the larger is the excess saturation degree of vacancies in the quenched sample, and the larger is the non-equilibrium grain boundary segregation during quenching and tempering. The above results can be used to interpret why an intercritical heat treatment in the $\alpha$-$\gamma$ region after austenitization but before tempering may be used to reduce temper embrittlement [4].

Moreover, Fig. 2 also shows that the quenching temperature apparently affects the kinetic process of tempering. When the sample is tempered at 500 °C, the segregation level of P reaches approximately the maximum equilibrium segregation level at a tempering time of 25 h for a quenching temperature of 1300 °C, but at 60 h for a quenching temperature of 1050 °C. This is because the excess saturation degree of vacancies in the sample quenched from 1300 °C is much larger than that in the sample quenched from 1050 °C.

Since the segregation of P at prior austenite grain boundaries is the accumulation of equilibrium and non-equilibrium segregation in the two processes of quenching and tempering, whereas the segregation at ferrite grain boundaries occurs only during tempering, the segregation level of P at prior austenite grain boundaries is much larger than that at ferrite grain boundaries. Consequently the intergranular fracture caused by impurity segregation occurs predominantly at prior austenite grain boundaries, which was reported by Briant and Banerji [4].

The width of the concentrated layer along grain boundaries, $d_\mathrm{n}$, was chosen as 100 nm in the calculations of the present work. This is because the non-equilibrium segregation is a kinetic process. Therefore, the segregation extent is generally larger and may be up to tens of millimicrometres [13, 20–23].

The coefficient of diffusion of complexes in the matrix, $D_c$, is given by the product of the frequency factor for vacancy diffusion and the exponential term containing the average value of the vacancy movement energy and the impurity diffusion activation energy in the matrix. This is reasonable because the diffusion of complexes is related not only to the movement of vacancies but also to that of impurities.

## 4. Summary

A new mechanism of temper embrittlement, a combined equilibrium and non-equilibrium grain boundary segregation mechanism, has been developed. Theoretically, some open questions on temper embrittlement may satisfactorily be explained. The calculation results obtained by the new model agree satisfactorily with the existing observed data [16].

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