Austenite to Ferrite Transformation in Fe–9 %Cr Alloys. II. Determination of Growth Rates

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Abstract. The paper continues theoretical analysis of austenite to ferrite transformation in an Fe–9 %Cr alloy demonstrating a typical site-saturation behaviour under the condition of diffusionless growth of α phase. In the previous paper the $K$ coefficient in the Avrami equations being the asymptotes of Cahn’s solution of the site-saturation transformation kinetics was used that contained a constant activation energy indicating the small value of the work of critical nucleus formation. This approach permitted to determine activation energy of transformation that was found to be equal to about 300 kJ/mole. In the present paper a new method of finding Cahn’s equation coefficients from bending point at isothermal curves plotted on double logarithmic scale is proposed. Actually this bending point is the intercept of the two above-mentioned asymptotes of the Cahn’s curve, and equating the formulae describing theses asymptotes allows to find the coefficients in question. Given the average austenite grain size, it permits to find numerical values of growth rates. The activation energy thus acquires the exact physical meaning of the energy barrier at the interphase interface; its value was found to be 286 kJ/mole, which is close to previous results. The growth rates were thus determined as a function of temperature and the TTT diagram for the alloy is calculated that shows close correspondence with experiment.

1. Introduction

In the first part of this paper [1] we presented an analysis of the experimental data for the austenite→ferrite transformation in a Fe–9.24 %Cr with 0.04 %C using the conventional approach based on Avrami equation

$$f(t)=1-\exp\left(-Kt^n\right)$$

(1)

where $f$ is the transformed volume fraction, $t$ is time, and $K$ and $n$ are coefficients. It is to be reminded that this alloy exhibits diffusionless mode of transformation due to boundary lines of the $\alpha + \gamma$ region having a common horizontal tangent near this concentration [2], and was repeatedly used as a model material to study the diffusionless transformation kinetics [3–9].

Coefficient $n$ was taken both as independent on time (and temperature) of transformation and as a variable parameter according to Cahn’s theory of nucleation site saturation on grain boundaries [10, 11], that replaces (1) with a more complex equation with two coefficients, $K_4$ and $K_1$:

$$f(t)=1-\exp\left[-K_1t\int_0^t\left[1-\exp\left(-\frac{2K_4}{K_1}\left(2x^3-3x^2+1\right)\right)\right]dx\right]$$

(2)
that asymptotically tends to

\[ f(t) = 1 - \exp(-K_it) \quad \text{and} \quad f(t) = 1 - \exp(-K_i t) \quad \text{(3)} \]

at early and late stages of transformation, respectively. Hence, not only \( K \) but also \( n \) does change in the course of transformation from 4 to 1. This change was clearly seen on experimental plots.

If all \( K \)'s are attached the form

\[ K_i^n = k \left( \frac{T_i - T}{T} \right)^n \exp \left( - \frac{U_i}{RT} \right) \quad \text{(4)} \]

substantiated in our previous works [12, 13], where \( T_i \) is the upper temperature limit of transformation, then all parameters can be found from relevant plots. The key feature of this equation is that the activation energies \( U_i \) are assumed independent on temperature due to small value of critical nucleus formation work [14–17].

For both considered models, the activation energy \( U \) was similar: 280–315 kJ/mole. Exponent \( m \) varied in the range 1.03–1.15 which is very close to the value \( m = 1 \) following from the theory of diffusionless growth [11, 18].

However, the finally calculated TTT diagrams of ferrite formation had a noticeable discrepancy with experimental ones, especially at temperatures remote from the “nose”.

In this paper the analysis will be continued.

2. Another Method of Finding Cahn’s Coefficients from Experimental Curves

In [1], the coefficients \( K_4 \) and \( K_i \) were taken from linear interpolation of initial and late parts of experimental plots on the scale \( \ln(-\ln(1-f)) \) — \( \ln t \). The values of \( U \) and \( m \) were then taken from the asymptotes of plots of \( \ln t \) versus \( 1/T \) at \( T \to 0 \), that are equal to \( U/R \). The shortcoming of this method is that the asymptote is determined not always precisely, which introduces some arbitrariness to the obtained values. So another method to find \( U \) and \( m \) can be proposed.

As it can be seen from figure 1 of [1], experimental plots on double logarithmic scale usually have a break that corresponds to saturation of nucleation sites and transfer from the first to the second line obeying equation (3). So for the break point \( (t^*, f^*) \) the following equation should fulfill:

\[ 4 \ln f^* + \ln K_4 = \ln f^* + \ln K_i, \quad \text{or} \quad \ln f^* = \frac{1}{3} \ln K_i - \frac{1}{3} \ln K_4. \quad \text{(5)} \]

Substituting this to equation (3), one can find that

\[ \ln(-\ln(1-f^*)) = \frac{2}{3} \ln K_i - \frac{1}{3} \ln K_4, \quad \text{(6)} \]

\[ \ln K_4 = \ln(-\ln(1-f^*)) - 4 \ln f^* \quad \text{and} \quad \ln K_i = \ln(-\ln(1-f^*)) - \ln f^*. \quad \text{(7)} \]

In terms of coefficients \( \alpha_s = \left( \frac{\pi}{3} I_s \omega^2 \right)^{1/3}, \quad \beta_s = \frac{2}{V} \omega \cdot \frac{1}{\alpha_s}, \) where \( I_s \) is nucleation rate per unit grain face area, \( \omega \) is growth rate and \( S/V \) is grain face area per unit volume [19], that were used in [1],

\[ K_4 = \frac{1}{2} \alpha_s^4 \beta_s, \quad K_i = \alpha_s \beta_s, \quad \text{(8)} \]

and thus

\[ \ln \alpha_s = -\ln f^* + \frac{1}{3} \ln 2, \quad \ln \beta_s = \ln(-\ln(1-f^*)) - \frac{1}{3} \ln 2. \quad \text{(9)} \]
If we use again equation (4) for temperature dependence of $K_4$ and $K_1$ then the plots of
\[
\ln K_i^{\frac{s}{m}} - m \ln \frac{T_s - T}{T}
\]
against $(1/T)$ are expected to be linear with the slope of $(-U/R)$:
\[
\ln K_i^{\frac{s}{m}} - m \ln \frac{T_s - T}{T} = \ln k_i - \frac{U_i}{RT}.
\] (10)

These plots for the Fe–9 %Cr alloy in question are presented in figure 1. As in [1], $T_s$ was accepted
815 °C, exponent $m = 1$, and Avrami exponents $n$ were taken from figure 1 of the paper [1] for
the corresponding part of the isothermal curve. One can see that experimental points lie really on straight
lines. The slopes of these lines yield $U = 230$ and $286$ kJ/mole for $K_4$ and $K_1$, respectively. The latter
value is closer to those obtained by other methods [1].

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Plots of $y = \ln K_i^{\frac{s}{m}} - m \ln \frac{T_s - T}{T}$ vs. $\frac{1}{T}$.
1 — for $K_4$, 2 — for $K_1$ (calculated using equations (7)).

3. Finding Growth Rates

It is worth recalling that from the original Cahn’s theory [10] the product $K_i = \alpha_i \beta_i$ is equal to
\[
K_i = \alpha_i \beta_i = 2 \frac{S}{V} \omega.
\] (11)

It can easily be shown that the ratio $(2SD/V)$ for cubic octahedra filling the volume without gaps and
intersections equals $\eta = 6.696$ ($D$ is the “diameter” of a cubic octahedron taken as a distance between its
opposite square faces). If we assume $D$ as the average grain diameter on the microsection, then equation
(11) may be re-written in the form
\[
\omega = \frac{D}{\eta} K_i \text{ or } \omega = \frac{D}{\eta} \alpha_i \beta_i.
\] (12)

Analysis of micrographs of the alloy after partial transformation (some of them were presented in [8])
gives $D$ for the alloy considered to be approximately $75 \mu$m. This permits to calculate quantitative values
of the growth rate $\omega$ for each transformation temperature.

Since $\omega$ for the diffusionless transformation is described by an equation similar to equation (4) [11]:
\[
\omega = k_\alpha \frac{T_s - T}{T} \exp \left( \frac{-U}{RT} \right),
\] (13)

then the plots of $\ln \omega - \ln ((T_s - T)/T)$ against $(1/T)$ are to be linear with the slope of $(-U/R)$, where $U$ is no
more some “effective” activation energy of transformation, but has an exact physical meaning of the
activation energy for an atom to cross the $\gamma/\alpha$ interphase interface.
Calculated values of $\omega$ (both by the first of equations (12) using the values obtained from the break on isothermal curves and by the second of equations (12) using the values of $\alpha_3\beta_3$ from the previous analysis done in [1]) and $\ln \omega - \ln ((T - T)/T)$ as a function of reverse temperature are shown in figures 2, a and b. One can see from figure 2, a that $\omega$ demonstrates a characteristic behaviour with a “nose” at approximately 780 °C, and calculated curves coincide well with the experimental ones. Figure 2, b shows that the plots are actually linear, and the activation energy of growth is equal to 286 and 272 kJ/mole for the values of $\omega$ obtained by the first and the second of equations (12) respectively. This is very close to the activation energy of self-diffusion in $\gamma$ iron of 284 kJ/mole [20].

![Figure 2](image1.png)

**Figure 2.** Growth rate $\omega$ (a) and the value of $\gamma = \ln \omega - \ln ((T - T)/T)$ (b) as a function of reverse temperature. 1 – values obtained in previous analysis [1] and calculated using the second of equations (12); 2 – values obtained in this work and calculated using the first of equations (12). Points are derived from experimental data, lines are calculated (see text).

4. **Calculation of TTT Diagram**

At last, let us try and use the new method of finding the coefficients of Cahn’s equation to construct a complete TTT diagram. For simplicity, we will not use the complete form of this equation (2), but limit ourselves to two asymptotes (3). The time at which the transfer from $n = 4$ to $n = 1$ is to be done can be calculated using equations (5) and (4):

$$
\ln r^* = \frac{1}{3} \ln K_i \left( \frac{T - T}{T} \right) \exp \left( \frac{U_i}{RT} \right) = \ln \left[ \frac{K_i}{k_i} \right] \left( \frac{T - T}{T} \right) \exp \left( \frac{U_i}{RT} \right) \exp \left( -\frac{1}{2} \frac{U_i - 4 U_2}{RT} \right),
$$

(14)

The equation to calculate a TTT diagram will then look as follows:

$$
f(t) = \begin{cases} 
1 - \exp(-K_i t^4) & \text{if } t \leq t^*; \\
1 - \exp(-K_i t) & \text{if } t > t^*. 
\end{cases}
$$

(15)

Figure 3 presents the results of calculation. Figure 3, a reproduces results of calculation from previous work (Figure 3, b in [1]), when $\alpha_3$ and $\beta_3$ coefficients were determined with their separate activation energies from the $\ln t$ vs. $T^{-1}$ plots. Figure 3, b is based on the results of the present work where activation energies for $K_4$ and $K_1$ coefficients were determined from the intersection of straight lines on double logarithmic scale ($\ln k_4 = 25.97$, $\ln k_1 = 32.33$; $U_4 = 230$, $U_1 = 286$ kJ/mole).
One can see that the TTT diagram calculated with the values obtained by the method described in this work is in much better correspondence with experimental one, even though the exact Cahn’s solution was replaced by simple equation (15).

Figure 3. TTT diagrams for the Fe–9.24 %Cr alloy. Points are experimental data [7], lines are calculated: a — by exact Cahn’s solution with the parameter values obtained in [1], b — by approximate equation (15) with the parameter values obtained in this work (see text). Dashed line on plot b indicates the time \( t^* \) at which the \( n \) exponent changes from 4 to 1.

5. Summary
1. A new method of finding Cahn’s equation coefficients by bending point at isothermal curves plotted on double logarithmic scale is proposed.
2. Numerical values of growth rates in the Fe–9.24 %Cr are determined.
3. The TTT diagram for the alloy is calculated that shows close correspondence with experiment.

6. References
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