On the activation energy of the $\sigma$-phase formation in a pure and Ti-doped Fe–Cr alloy

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Abstract

The $\sigma$-phase formation in Fe$_{53.8}$Cr$_{46.2}$ and Fe$_{53.8}$Cr$_{46.2}$-0.3at%Ti by isothermal annealing in the temperature interval of 923–1003 K was investigated in situ by $^{57}$Fe Mössbauer spectroscopy. The process of transformation was successfully analyzed using the Johnson–Avrami–Mehl equation, and it was quantitatively described in terms of the activation energy, $E$ which was determined by several methods. The best-value of $E$ as average of all data was found to be equal to 196±2 kJ/mol for the Fe–Cr sample and to 153±2 kJ/mol for that doped with Ti. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The $\alpha$–$\sigma$ phase transformation is a solid-state transformation with nucleation and subsequent growth of second phase particles. Such transformations are usually analyzed according to the theory of nucleation and growth process developed independently by Johnson and Mehl [1] and by Avrami [2]. The equation of transformation, known as the Johnson–Avrami–Mehl (JAM) equation, reads as follows:

$$A = 1 - \exp[-(k \cdot t)^n]$$

(1)

where $A$ is the transformed volume fraction, $k$ is the rate constant, $n$ is a shape factor and $t$ is the time. The kinetics parameters $k$ and $n$ give useful information on the transformation. The former is related to the activation energy, $E$, through the Arrhenius equation of the form:

$$k = k_0 \cdot \exp(-E/R \cdot T)$$

(2)

where $k_0$ is the pre-exponential factor, $R$ is the gas constant and $T$ stands for the temperature. The exponent $n$ contains an information about mechanisms responsible for the transformation. The use of Eq. (2) for rate constants, hence for $E$, is universally accepted, though its exact theoretical justification is missing. As outlined in Ref. [3], the value of $E$ for heterogenous processes, such as the one discussed in this paper, should be considered as an effective activation energy i.e. as a weighted linear combination of activation energies of separate contributing processes.

Determination of an absolute value of $E$ from Eq. (2) in an isothermal process requires a knowledge of $k$ and $k_0$. The former quantity can be obtained by fitting Eq. (1) to the transformation kinetics, while determination of the latter necessitates measurement of several kinetics at various $T$. The method based on this approach is known as the rate constant method. In practice, there are several, more or less, simplified methods for evaluating $E$ without knowing $k_0$ [4,5]. The most frequent ones have been used and tested in this study on the transformation kinetics as measured in situ for pure and Ti-doped quasi-equiatomic Fe–Cr alloys. The experimental method used was $^{57}$Fe Mössbauer spectroscopy, and the purpose of the study was to see whether differences in the value of $E$ for the formation of the $\sigma$-phase, which can be found in literature [6–10], are due to the method of measurement or rather they originate from the method of data analysis in a particular study.
2. Experimental

2.1. Sample preparation

The samples used in this study, in the form of ~30 μm thick foils, were fine-grained alloys of Fe53.8Cr46.2 and Fe53.8Cr46.2-0.3 at.%Ti, whose detailed description and characterisation can be found elsewhere [10].

2.2. Measurement of the Mössbauer spectra

A study of the α-σ phase transformation was carried out in situ at various temperatures ranging from 923 to 1003 K, i.e. during an isothermal annealing in a vacuum furnace. 57Fe Mössbauer spectra were recorded automatically every 30 min in transmission geometry using a standard Mössbauer spectrometer. The γ-rays of 14.4 keV energy were supplied by a 57Co/Rh source whose initial activity was ~50 mCi. Typical spectra recorded can be seen in Ref. [9].

3. Results and discussion

3.1. Determination of the amount of the σ-phase

The amount of the σ-phase precipitated, $A_{\sigma}$, was determined in two ways. First, from the spectral area based on the following formula:

$$A_{\sigma}[^\%] = 100/(1 + f_{\alpha} \cdot S_\alpha/f_{\sigma} \cdot S_\sigma) \quad (3)$$

where $S_\alpha$ and $S_\sigma$ stand for the spectral area of the α- and σ-phase, respectively, and $f_{\alpha}$ and $f_{\sigma}$ are the recoil-less fractions for 57Fe atoms in the two phases. According to our previous studies $f_{\alpha}/f_{\sigma} = 1.15$ at 973 K, but the difference in the $f$-values can be neglected as far as the kinetics of the σ-phase formation is concerned [9]. Hence, in the present study formula (3) was used assuming that the $f$-factors were the same. The $S$-values were yielded by fitting the spectra with the least-squares iteration procedure.

Second, $A_{\sigma}$ was deduced from the average isomer shift, $<IS>$, as demonstrated in Ref. [9] where more details can be found. This approach is advantageous, especially in the early stages of transformation where decomposition of a spectrum into two subspectra is not an easy task due to similar spectral parameters.

3.2. Kinetics of transformation

As mentioned in the Introduction, the kinetics of the σ-phase formation can be analyzed by the Johnson–Avrami–Mehl (JAM) equation. For the $A_{\sigma}$-values it has the following form:

$$A_{\sigma}[^\%] = 100 - [1 - \exp(-(k \cdot t)^n)] \quad (4)$$

For the $<IS>$-values, the JAM equation can be expressed as follows:

$$< IS_{\alpha} > = (< IS_{\alpha} > - < IS_{\sigma} >) \cdot [1 - \exp(-(k \cdot t)^n)] + < IS_{\sigma} > \quad (5)$$

where $< IS_{\alpha} >$ and $< IS_{\sigma} >$ represent the average isomer shift of Fe atoms in the pure phases.

Examples of the kinetics data obtained in the two ways are plotted for the Fe53.8Cr46.2-0.3 at.%Ti in Fig. 1. Fig. 1a shows the $A_{\sigma}$-values as a function of annealing time, $t$, for the Ti-doped alloy, while Fig. 1b the corresponding dependence for the $<IS>$-values. A striking similarity between the two sets of data is obvious. They were analyzed in terms of Eqs. (4) and (5), respectively, and the best-fit kinetics parameters received are displayed in Tables 1 and 2. It can be seen they agree well with each other for a given sample which can be taken as evidence the two methods are equivalent. However, it should be here mentioned that the value of $k$, as determined at 973 K for the Ti-doped sample, is much smaller than the corresponding one given in Ref. [10] (~8 instead of ~29). A non strain-free state of the sample used in Ref. [10] could be the reason for the discrepancy.

3.3. Activation energy

Knowing $k$, the activation energy, $E$, can be determined from the Arrhenius equation. There are several methods of determining this quantity for isothermal transformations. The following were used in the present study:

3.3.1. (a) The rate constant [4]

Taking the logarithm of Eq. (2) results in the following expression:

$$\ln k = \ln k_o - E/R \cdot T \quad (6)$$

i.e. if a transformation conforms to the JAM equation a plot of $\ln k$ versus $1/T$ is linear. By fitting Eq. (6) to the experimental data a value of the activation energy, $E$, can be determined as well as that of $k_o$. Fig. 2 illustrates the appropriate graph for the studied samples together with the best-fit straight lines. The best-fit values of $k_o$ were found to be equal to $11.33 \times 10^6$ min$^{-1}$ for the Fe–Cr sample and $12.17 \times 10^6$ min$^{-1}$ for the Ti-doped one. Those of $E$ are displayed in Table 3. It can be noticed that the value of $k_o$ is for the Ti-doped alloy by a factor of 100 smaller than the one for the undoped alloy.

3.3.2. (b) The length of time between two different stages [4]

The activation energy can be also determined from the length of time, $dt = t_2 - t_1$, between two fixed stages
of transformation, $A_1$ and $A_2$ measured at various temperatures. In this case the following equation holds:

$$\ln \left( \frac{dA_\sigma}{dt} \right) = \text{const} - \ln k_0 - \frac{E}{R T}$$  \hspace{1cm} (7)

where $dA_\sigma = A_{\sigma}(t_2) - A_{\sigma}(t_1)$. Plotting $\ln \left( \frac{dA_\sigma}{dt} \right)$ versus $1/T$ gives again a straight line from the slope of which the activation energy can be determined. In the present study the determination of $E$ was performed with $A_{\sigma}(t_1) = 20\%$ and $A_{\sigma}(t_2) = 80\%$ i.e. very early and very late stages of the transformation have been excluded. The best-fit values of $E$ obtained in that way are presented in Table 3.

![Figure 1](image)

**Fig. 1.** Examples of the kinetics of the $\alpha$-$\sigma$ phase transformation at various temperatures shown for the Fe$_{53.8}$Cr$_{46.2}-0.3$ at.%Ti sample. The solid lines represent the best-fit to the data in terms of Eqs. (4) and (5), respectively.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$n$</th>
<th>$k$ (min$^{-1} \times 10^{-4}$)</th>
<th>$n$</th>
<th>$k$ (min$^{-1} \times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>943</td>
<td>1.8 ± 0.2</td>
<td>2.42 ± 0.07</td>
<td>1.6 ± 0.2</td>
<td>2.42 ± 0.07</td>
</tr>
<tr>
<td>953</td>
<td>1.8 ± 0.2</td>
<td>1.63 ± 0.05</td>
<td>1.3 ± 0.2</td>
<td>1.42 ± 0.05</td>
</tr>
<tr>
<td>963</td>
<td>3.7 ± 0.4</td>
<td>1.32 ± 0.03</td>
<td>2.8 ± 0.3</td>
<td>1.27 ± 0.03</td>
</tr>
<tr>
<td>968</td>
<td>1.8 ± 0.2</td>
<td>4.27 ± 0.10</td>
<td>1.6 ± 0.2</td>
<td>4.32 ± 0.12</td>
</tr>
<tr>
<td>973</td>
<td>3.0 ± 0.3</td>
<td>2.78 ± 0.07</td>
<td>2.7 ± 0.3</td>
<td>3.08 ± 0.10</td>
</tr>
<tr>
<td>978</td>
<td>1.9 ± 0.2</td>
<td>4.55 ± 0.12</td>
<td>1.6 ± 0.2</td>
<td>4.42 ± 0.12</td>
</tr>
</tbody>
</table>

**Table 1**
The best-fit values of the kinetics parameters, $k$ and $n$, as obtained by fitting the kinetics of transformation for the Fe$_{53.8}$Cr$_{46.2}$ sample at various $T$ using the JAM equation.
3.3.3. (c) The time to a given fraction \[4\]

The time required for a specified fraction of transformation, \(t_A\), fulfills the following equation:

\[
\ln t_A = \text{const} - \frac{E}{R} \cdot T
\]

(8)

It follows from Eq. (8) that the graph of \(\ln t_A\) versus \(1/T\) is linear and the slope of the line gives the value of \(E\). As in (b), the absolute value of \(k_o\) cannot be determined with this method. Table 3 contains the appropriate parameters of interest.

3.3.4. (d) The maximum transformation rate \[5\]

The activation energy in the isothermal processes can also be derived from the time for the maximum transformation rate, \(t_{\text{max}}\). The relationship between time and activation energy is as follows:

\[
\ln t_{\text{max}} = \text{const} - \frac{E}{R} \cdot T + \ln k_o
\]

(9)

i.e. the logarithm of the time for which \(dA/dt\) has maximum is a linear function of \(1/T\). Hence fitting the appropriate data with Eq. (9) yields the value of \(E\) while \(k_o\) is again unknown. Table 3 displays the best-fit parameters.

3.3.5. (e) Two-temperatures kinetics

The absolute value of \(E\) can be also evaluated by measuring two transformation kinetics at various temperatures, \(T_1\) and \(T_2\). Assuming that \(k_o(T_1) = k_o(T_2)\), the following equation can be written:

\[
E = \left(\frac{1}{R} \cdot T_1 - \frac{1}{R} \cdot T_2\right)^{-1} \ln \frac{k_1}{k_2}
\]

(10)

Using Eq. (10), the values of \(E\) could have been determined for all possible combinations of \(T_1\) and \(T_2\) at which the \(\alpha-\sigma\) transformation was measured in this study. The \(E\)-values determined in that way not only scatter over a wide range but are even negative.

From Table 3 where the values of \(E\) obtained with methods (a) through (d) are collected it can be seen they are rather consistent with each other, though the errors

---

### Table 3

<table>
<thead>
<tr>
<th>Method of analysis</th>
<th>(A_e) Eq. (4)</th>
<th>((IS)) Eq. (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k) ((\text{min}^{-1}) (\times 10^{-4}))</td>
<td>(n)</td>
<td>(k) ((\text{min}^{-1}) (\times 10^{-4}))</td>
</tr>
<tr>
<td>(T) (K)</td>
<td>(n)</td>
<td>(k) ((\text{min}^{-1}) (\times 10^{-4}))</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>923</td>
<td>1.2 ± 0.2</td>
<td>2.47 ± 0.12</td>
</tr>
<tr>
<td>933</td>
<td>1.7 ± 0.2</td>
<td>3.75 ± 0.10</td>
</tr>
<tr>
<td>943</td>
<td>3.7 ± 0.4</td>
<td>3.37 ± 0.08</td>
</tr>
<tr>
<td>953</td>
<td>3.1 ± 0.3</td>
<td>3.35 ± 0.08</td>
</tr>
<tr>
<td>963</td>
<td>2.2 ± 0.2</td>
<td>8.88 ± 0.22</td>
</tr>
<tr>
<td>968</td>
<td>3.5 ± 0.4</td>
<td>6.80 ± 0.17</td>
</tr>
<tr>
<td>973</td>
<td>3.0 ± 0.3</td>
<td>8.20 ± 0.20</td>
</tr>
<tr>
<td>978</td>
<td>4.4 ± 0.5</td>
<td>9.70 ± 0.25</td>
</tr>
<tr>
<td>983</td>
<td>2.5 ± 0.3</td>
<td>11.27 ± 0.28</td>
</tr>
<tr>
<td>993</td>
<td>2.7 ± 0.3</td>
<td>8.98 ± 0.22</td>
</tr>
<tr>
<td>1003</td>
<td>2.4 ± 0.4</td>
<td>14.67 ± 0.37</td>
</tr>
</tbody>
</table>

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Fig. 2. The dependence of \(\ln k\) on \(1/T\) for the studied samples. The straight lines represent the best-fits to the experimental data in terms of Eq. (6).
The values of the activation energy, $E$, as found by means of various methods used. The difference in $E$ for the studied samples, $\Delta E$, is also displayed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$</td>
<td>(a) $k$</td>
<td>197 ± 118</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>(b) $dA/dt$</td>
<td>260 ± 37</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>(c) $t_{90%}$</td>
<td>218 ± 120</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>(d) $t_{\text{max}}$</td>
<td>244 ± 151</td>
</tr>
</tbody>
</table>

The advantage of using method (a) is that it, in addition to the activation energy, enables determination of $k_0$. The knowledge of the latter is very important as it allows determination of the absolute value of $E$ using method (a) for a kinetics measured at one temperature, only. For this case, the Arrhenius equation can be written as:

$$E = R \cdot T \cdot \ln \frac{k_0}{k} \quad (11)$$

The $k_0$ values yielded by method (a) were used to determine the $E$-values from Eq. (11) for all temperatures of isothermal transformations carried out in the present study. The results of this procedure which are displayed in Table 4 are very consistent with each other.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ (min$^{-1}$) $\times 10^{-4}$</th>
<th>$k_0$ (min$^{-1}$)</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$</td>
<td>943</td>
<td>2.42</td>
<td>193</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$</td>
<td>953</td>
<td>1.52</td>
<td>198</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>963</td>
<td>1.29</td>
<td>202</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>968</td>
<td>4.22</td>
<td>193</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>973</td>
<td>2.94</td>
<td>197</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>978</td>
<td>4.48</td>
<td>195</td>
</tr>
<tr>
<td>Fe$<em>{53.8}$Cr$</em>{46.2}$-0.3 at.%Ti</td>
<td>978</td>
<td>4.48</td>
<td>196 ± 2</td>
</tr>
</tbody>
</table>

The maximum difference in $E$ is 9 kJ/mol for the Fe$_{53.8}$Cr$_{46.2}$ sample and 5 kJ/mol for the Ti-doped one. Hence the value of $\langle E \rangle = 196 \pm 2$ kJ/mol should be treated as the best value of the effective activation energy for the $\alpha$–$\sigma$ phase transformation in the Fe$_{53.8}$Cr$_{46.2}$ alloy, and that of $\langle E \rangle = 153 \pm 2$ kJ/mol as the best one for the Fe$_{53.8}$Cr$_{46.2}$-0.3 at.%Ti alloy. In other words, the presence of 0.3 at.%Ti accelerates the transformation by decreasing the activation energy by $\sim 43$ kJ/mol. This is about twice as much as previously determined neglecting the difference in the $k_o$-value [10]. From Table 3 it then follows that the values of $E$ similar to $\langle E \rangle$ were obtained with methods (a) and (c) i.e. it seems they are the best to determine the activation energy, if $k_o$ is unknown. The result also means the $\sigma$-phase formation is symmetric in time i.e. the same information can be obtained by studying the kinetics between the stages $A_1 = 0$ and $A_2 = 0.5$ as between $A_1...0.5$ and $A_2 = 1.0$.

4. Conclusions

Based on the results presented in this study, the following conclusions can be drawn:

1. Isothermal $\alpha$–$\sigma$ phase transformation in the Fe–Cr system can be well described in terms of the Johnson–Avrami–Mehl equation.
2. Effective activation energy can be determined with various methods and it ranges between 197 and 260 kJ/mol for the Fe$_{53.8}$Cr$_{46.2}$ alloy and between 119 and 183 kJ/mol for the Fe$_{53.8}$Cr$_{46.2}$–0.5 at.%Ti alloy.
3. The best value of $E$ determined as the average over all performed kinetics based on the knowledge of $k_0$ is equal to $\langle E \rangle = 196 \pm 2$ kJ/mol for the pure, and to $\langle E \rangle = 153 \pm 2$ kJ/mol for the Ti-doped Fe–Cr alloy.
4. The value of $k_0$ is equal to $11.33 \times 10^6$ min$^{-1}$ for the undoped sample and to $12.17 \times 10^4$ min$^{-1}$ for the Ti-doped one.
5. The two-temperature method is very unreliable, so it should not be used for determination of the activation energy.

References


