Short communication

Effect of titanium on the kinetics of the $\sigma$-phase formation in a coarse-grained Fe–Cr alloy

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Abstract

The influence of titanium on the kinetics of the $\sigma$-phase formation promoted by an isothermal annealing at $T = 973$ K was studied in coarse-grained quasi-equiatomic Fe–Cr alloys by using the $^{57}$Fe Mössbauer Spectroscopy. It was found that the kinetics could be well-described in terms of the Johnson–Avrami–Mehl equation. The addition of titanium (up to 3 at%) was revealed to affect the transformation kinetics in the following way: for $x_{Ti} \leq 1.5$ at%, its presence accelerates the process with the highest transformation rate for $x_{Ti} = 0.3$ at%, for $x_{Ti} \geq 1.5$ at%, titanium retards the formation of the $\sigma$-phase. Quantitatively, the effect of titanium on the kinetics was described in terms of a change of the effective activation energy.

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High-chromium ferritic steels are known for their excellent corrosion- and creep-resistant properties. Because of this they have found a wide application in various branches of industry, and are often used in service under elevated temperatures. This eventually results in an unwanted embrittlement which has two major microscopic reasons: (i) phase decomposition into Fe-rich, $\alpha$, and Cr-rich, $\alpha'$, phases, and (ii) precipitation of the $\sigma$-phase. It is, therefore, of technological importance to understand the underlying mechanisms responsible for (i) and (ii) processes. The basis of the whole stainless steel family is the Fe–Cr system, hence it is reasonable to assume its investigation may contribute to a better understanding of the two mechanisms responsible for the brittleness of the steels themselves. Consequently, Fe–Cr alloys have been regarded as a model system in such studies.

Annealing of Fe–Cr alloys in the temperature range of 575–775 K results in a formation of a miscibility gap accompanied by an enhanced embrittlement (the so-called “475°C brittleness”) [1]. The equilibrium structure consists of two phases, namely $\alpha$ and $\alpha'$. In the upper part of the miscibility gap the $\sigma$-phase is known to precipitate. Its stability domain extends from 1100 K down to a temperature of 700–775 K, so that it may coexist with $\alpha$ and $\alpha'$. A recent review on the phase decomposition in the Fe–Cr and stainless steels is given in Ref. [2].

In this report the results concerning the effect of titanium on the kinetics of the $\sigma$-phase formation in quasi-equiatomic Fe–Cr alloys are presented. As follows from the phase diagram of Fe–Cr–Ti, a quasi-equiatomic Fe–Cr alloy doped with a few per cent of Ti can be 100% transformed into the $\sigma$-phase [3].

Samples to be investigated in this study were prepared by melting appropriate amounts of Fe (99.95 % purity), Cr (99.5 % purity) and Ti (99.9 % purity) in a vacuum induction furnace. The ingots obtained were next cut into cubes of $5 \times 5 \times 5$ mm size which were subsequently solution-treated at 1473 K for 24 h followed by a water quenching. The samples obtained in that way were chemically analyzed by electron probe microanalysis (EPMA) and by a classical chemical method (CM). The chemical composition obtained by the two methods is displayed in Table 1. It can be seen that there is a systematic difference in the content of Ti as found by the two methods. An application of SEM revealed that some amount of Ti was not in the solution, but in the form of Ti-rich spots.
The samples were also characterized with respect to their microstructure i.e. a distribution of grain size was determined giving an average value of \( <D> = 386 \pm 8 \) \( \mu \text{m} \).

The transformation of the original \( \alpha \)-phase into the \( \sigma \)-phase was carried out by an isothermal annealing of the cubes at 973 K in a vacuum furnace. According to a previous study, the transformation rate at that temperature is the fastest [4].

The kinetics of the \( \sigma \)-phase formation was investigated by means of the \( ^{57}\text{Fe} \) Mössbauer Spectroscopy (MS). The method has proved to be a suitable tool for that purpose [5–8]. Room temperature spectra were recorded in a transmission geometry using a standard spectrometer and a \( ^{57}\text{Co}/\text{Rh} \) source of \( \approx 20 \) mCi activity. The samples for the Mössbauer measurements were in form of powder obtained by filing the cubes with a diamond file. Examples of typical spectra can be seen in Fig. 1. The distinction between the \( \alpha \) and the \( \sigma \) phases can be based on their Curie temperatures, \( T_c \). \( T_c \) for the \( \alpha \) is much larger than 295 K, hence the spectrum recorded at 295 K for the phase shows features characteristic of a magnetic sample (six-line pattern). \( T_c \) for the \( \sigma \) phase is much lower than 295 K, and consequently its recorded spectrum has a feature characteristic of a non-magnetic sample — in this case a pseudo-single line. The fraction of the \( \sigma \) phase, \( A_\sigma \), was determined from the spectral area of the subspectrum ascribed to the \( \sigma \)-phase, using the following formula:

\[
A_\sigma = 100/(1 + f_\sigma \cdot S_\sigma / f_\alpha \cdot S_\alpha)
\]  

(1)

where \( S_\alpha \) and \( S_\sigma \) stands for a spectral area due to the \( \alpha \)- and the \( \sigma \)-phase, respectively, while \( f_\sigma \) and \( f_\alpha \) are the recoiless fractions for \( ^{57}\text{Fe} \) atoms in the two phases. It was assumed that \( f_\alpha / f_\sigma = 1 \) (in fact, as shown in the Appendix, the ratio of the two \( f \)-factors is equal to 1.1, but the difference can be neglected as far as the kinetics of the \( \sigma \)-phase formation is concerned). The \( S \)-values were yielded by a least-squares analysis of the spectra. The \( A_\sigma \)-values obtained from formula (1) are displayed in Fig. 2 versus annealing time, \( t \), both for Ti-doped and undoped samples. It is evident that the presence of Ti in the studied sample significantly influences the formation of the \( \sigma \)-phase.

To get more quantitative insight into the issue, the \( A_\sigma \)-data were fitted in terms of the Johnson–Avrami–Mehl (JAM) equation:

\[
A_\sigma = 100 \cdot [1 - \exp(-kt^n)]
\]  

(2)

where \( k \) is a time constant and \( n \) is a form factor. Their best-fit values are presented in Table 2. They give a clear evidence that titanium affects both kinetics parameters, i.e. not only the rate of the transformation which is controlled by \( k \), but also the conditions of the transformation process through the values of \( n \) [9].
The influence of Ti on the α-σ phase transformation can also be expressed quantitatively in terms of a difference in the activation energy, $E$. For this purpose, the following equation can be used:

$$k = k_0 \exp \left( -\frac{E}{RT} \right)$$

(3)

where $E$ is the activation energy and $R$ the gas constant.

It should be here mentioned that $k$ is a function of the rates of nucleation and growth which, in turn, depend on solubilities and supersaturation besides the diffusion coefficient. Consequently, the value of $E$ as determined from the above equation should be regarded as an effective activation energy [10].

An absolute value of $E$ can be determined if two $A_{\alpha} = f(t)$-curves measured at various temperatures are known. As we measured the kinetics only at 973 K, we were in a position to determine a change of $E$, $\Delta E$, due to titanium with respect to the undoped sample. Assuming further the $k_0$ does not depend on the alloy composition, the following formula was used:

$$\Delta E = E_1 - E_2 = RT \ln \left( \frac{k_2}{k_1} \right)$$

(4)

where $E_2$ is the activation energy in the undoped sample, and $E_1$ that in the Ti-doped sample. The $\Delta E$-values obtained in that way are plotted in Fig. 3 versus titanium content. It is obvious that titanium effects the kinetics of transformation in a way depending on its content: for $x_{Ti} \leq 1.5$ at% its presence accelerates the transformation, with the highest rate for $x_{Ti} = 0.3$ at%. Here, the difference in the effective activation energy reaches about 14 kJ/mol. On the other hand, addition of more than 1.5 at% Ti retards the formation of the σ-phase.

<table>
<thead>
<tr>
<th>Ti [at%]</th>
<th>$n$</th>
<th>$k$ (min$^{-1}) \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>1.95</td>
</tr>
<tr>
<td>0.3</td>
<td>2.0</td>
<td>10.75</td>
</tr>
<tr>
<td>1.1</td>
<td>2.0</td>
<td>2.42</td>
</tr>
<tr>
<td>1.7</td>
<td>1.8</td>
<td>1.07</td>
</tr>
<tr>
<td>2.4</td>
<td>1.4</td>
<td>0.62</td>
</tr>
<tr>
<td>3.0</td>
<td>1.2</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 2
The best-fit kinetics parameters $n$ and $k$ as obtained by fitting the data shown in Fig. 2 in terms of the JAM-equation.

Fig. 3. The difference in the effective activation energy, $\Delta E$ (with respect to the one in the undoped sample) versus titanium content. The line is drawn to guide the eye.

Fig. 4. The relative amount of the σ-phase, $A_{\sigma}$, as derived from formula (1) with the ratio $f_{\alpha}/f_{\sigma} = 1$, versus the real amount of the σ-phase, $A_{\sigma}^W$. The solid line represents the best-fit to the data, and the dashed one the behaviour expected for the case the ratio is equal to 1.0.

Fig. 5. The amount of the σ-phase, $A_{\sigma}$, as obtained from formula (1) assuming the ratio of the $f$-factors is equal to 1.0 (circles), and to 1.1 (triangles). The curves represent the best-fits to the two sets of data in terms of the JAM-equation.
and the effect seems to have a saturation-like behaviour. The finding may be of a practical importance. The investigation of the influence of temperature and grain size on the formation of the $\sigma$-phase is in progress.

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Appendix

In order to determine the value of the $f_{\sigma}/f_a$ ratio, five two-phase samples of the Fe$_{53.8}$Cr$_{46.2}$0.3 at% Ti alloy with a well-defined amount of the $\sigma$-phase, $A_{\sigma}^W$, were prepared by mixing appropriate amounts of the pure phases. From the Mössbauer spectra recorded at RT on those samples, the $A_{\sigma}$-values were obtained using formula (1) and assuming the ratio be equal 1. Then a plot of $A_{\sigma}$ versus $A_{\sigma}^W$ was made (Fig. 4). The fit to the data yielded $f_{\sigma}/f_a = 1.10$ i.e. the amount of the $\sigma$-phase as determined from the spectral area is overestimated by 10%. To see whether or not a correction for the difference in the $f$-factors for the two phases is necessary in the study of the kinetics of the $\sigma$-phase formation, the $A_{\sigma}$-values were calculated from formula (1) once with the correction and again without it. The comparison of the two sets of the data is presented in Fig. 5. The lines represent there the best-fits in terms of the JAM equation. The best-fit kinetics parameters are also displayed in Table 3. It is clear that the correction in this case is not necessary.

References