Study of a sigma-phase formation in an equiatomic Fe-V alloy

B F O Costa¹, ³, J Cieślak² and S M Dubiel²

¹CEMDRX, Department of Physics, University of Coimbra, P-3004-516, Coimbra, Portugal
²Faculty of Physics and Computer Science, AGH University of Science and Technology, 30-059 Kraków, Poland
E-mail: benilde@ci.uc.pt

Abstract. Kinetics of the α- to σ-phase transformation in an equiatomic Fe-V alloy has been studied by Mössbauer Spectroscopy and X-ray diffraction. The B2 superstructure seems to form prior to the precipitation of the σ-phase. The results obtained in this study give evidence that in the investigated interval, the transformation kinetics strongly depends on temperature. The kinetics of the α- to σ-phase transformation, as determined from the temperature dependence of the average hyperfine field derived from the Mössbauer spectra, has been quantitatively described in terms of the Johnson-Mehl-Avrami equation, from which the kinetics parameters $n$ and $k$ have been determined.

1. Introduction

According to the Fe-V phase diagram, a disordered bcc solid solution (α-phase) can be formed over an entire composition range. However, for certain compositions around 50%, the solution is not stable, and, upon annealing it transforms, depending on the temperature, either into the σ-phase with a complex tetragonal structure, or into the ordered metastable B2 phase. Precipitation of the σ-phase severely deteriorates Fe-based steel properties, and, in particular, decreases ductility and impact toughness, lowers the corrosion resistance and increases brittleness and cracking [1]. For as-melted alloys, the transformation into the σ-phase is rather slow and it requires a prolonged annealing time whose exact duration strongly depends on temperature [2].

In this study we were interested in the effect of temperature on the α- to σ-phase transformation in plastically deformed samples. It is known that a plastic deformation can significantly accelerate the formation of the σ-phase [3, 4].

2. Experimental

An equiatomic Fe-V alloy has been prepared in an induction furnace by melting together appropriate amounts of Fe (99.9 % purity) and V (99.7% purity) elements. The ingots were then cold-rolled down to form platelets of about 200 μm thickness, which were next isothermally annealed at various temperatures, $T_a$, namely 600°C, 700°C and 800°C for different periods.

X-ray diffraction (XRD) was performed at room temperature (RT) using Cu K$_\alpha$ radiation (λ = 0.154184 nm) to characterize the microstructural changes. $^{57}$Fe Mössbauer spectra were recorded at

³ Author to whom any correspondence should be addressed.
RT in a transmission geometry using a standard constant acceleration spectrometer. A $^{57}$Co source in Rh matrix with the activity of about 20 mCi was used. The spectra were analysed by a constrained Hesse-Rübartsch method [5] which yields a hyperfine magnetic field distribution, $P(B)$.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns taken on the Fe-V cold rolled sample annealed at 700ºC. It is observed that the full transformation from the $\alpha$- to $\sigma$-phase has taken place after 30 min. When analyzing the diffractogram obtained on the sample annealed at 700ºC for 2 min, it is evident that some structural change has taken place – see the shape of the peak at $2\theta \approx 135^\circ$. For the other temperatures of annealing the same transformation is observed, but it is slower at 600ºC and quicker at 800ºC. From the XRD patterns, it can be also concluded that while the structure had remained bcc, the lattice constant has decreased relative to the initial value which is indicative of the formation of $B2$ [2]. The Mössbauer spectroscopy also gives evidence that the transformation is fast, and that its rate grows with increasing isothermal annealing temperature. The Mössbauer spectra have dramatically changed their shape, as illustrated in Figure 2 for the annealing temperature of 700ºC, giving thereby an evidence that the hyperfine field has dramatically decreased. The quick decrease both of the lattice parameter of the bcc phase and that of the mean hyperfine field (Figure 2b) are characteristic features of the formation of the $B2$ superstructure [2]. This seems to be in agreement with a previous study according to which the $B2$ superstructure forms prior to the $\sigma$-phase in the equiatomic Fe-V system [6].

![Figure 1](image-url)

**Figure 1.** X-ray diffraction patterns of the Fe-V cold rolled sample annealed at 700ºC for the indicated periods.

Upon further annealing all the samples have eventually transformed into the $\sigma$-phase which was evident both from the XRD pattern as well as from the Mössbauer spectrum – see Fig. 2c.

Assuming that the shape of the Mössbauer spectrum corresponding to the $B2$ superstructure is not changing with annealing time, the kinetics of the $\sigma$-phase formation was followed by studying the temperature dependence of the average hyperfine field, $\langle B \rangle$, which, to our knowledge, is a procedure that has been for the first time used in the study of the kinetics of the $\sigma$-phase formation. Figure 2 shows also the hyperfine field distribution curves obtained as a function of the annealing time for the three different annealing temperatures.

The time dependence of the isothermal decrease of $\langle B \rangle$ has been fitted using Johnson-Mehl-Avrami (JMA) type equation, of the form:

$$ F = 1 - \exp[-(kt)^n] $$

(1)
where $F$ is the relative fraction of the $\sigma$-phase precipitated after the isothermal annealing time $t$, $k$ is the rate of formation and $n$ is the Avrami form factor.

The relative fraction $F$ has been determined by normalizing the $\langle B(t)\rangle$-values to the initial value of the average hyperfine field of the pure $\alpha$-phase, $\langle B\rangle_\alpha$ corresponding to 100% $\alpha$-phase. The plots based on $F$-quantity are shown in Figure 3b, while the fitted values of $n$ and $k$ are given in Table 1.

**Figure 2.** Room temperature $^{57}$Fe Mössbauer spectra, and the corresponding hyperfine field distribution curves (right-hand side), for Fe-V cold rolled sample annealed at 700ºC and for different periods shown (a) $\alpha$-phase; (b) $B_2$ phase and (c) $\sigma$-phase.

From Figure 3b, it can be deduced that at 800ºC the transformation from $\alpha$- to $\sigma$-phase is the quickest one, and it takes about 2 min to be completed. At 700ºC the full transformation takes about 25 min and there is one process prior to the formation of $\sigma$, while at 600ºC the full transformation takes about 1500 min and there are two processes preceding the formation of $\sigma$. The first one can be ascribed to the ordering of $\alpha$ into $B_2$ (it takes ca. 1000 min), and the second one is related to the transformation of $B_2$ into $\sigma$ (it takes ca. 6 min).

The transformation rate to the $\sigma$-phase (3$^{rd}$ step in Table 1) increases with increasing temperature, as already mentioned above.

In order to interpret the third regime, ascribed to the precipitation of the $\sigma$-phase, the $n$ values can be compared to theoretical ones [7]. The obtained values indicate a diffusion controlled growth mechanism with zero or decreasing nucleation rate, which agrees with the literature data on the transformation mechanism in other systems [6-8].

In summary, the kinetics of the $\alpha$- to $\sigma$-phase transformation in an equiatomic Fe-V alloy that was determined from the temperature dependence of the average hyperfine field measured by means of the Mössbauer Spectroscopy, has been quantitatively described in terms of the Johnson-Mehl-Avrami equation.
Figure 3. (a) Hyperfine field distribution as a function of annealing time for different annealing temperatures; (b) Johnson-Mehl-Avrami plots from the data in figure (a). Dotted lines in (b) are guides to the eye, indicating stabilization of final stage of transformation.

Table 1. Values of $n$ and $k$ obtained from the fits to the data in Figure 3b to the Johnson-Mehl-Avrami equation.

| Annealing Temperature | 1st step | 2nd step | 3rd step |
|-----------------------|----------|----------|----------|
| 600ºC                 | 0.72     | 0.075    | 1.70     | $n$    |
|                       | 9.04     | 1.57     | 0.07     | $k$ (h$^{-1}$) |
| 700ºC                 | 0.25     | 2.1      |          | $n$    |
|                       | 12.42    | 4.33     |          | $k$ (h$^{-1}$) |
| 800ºC                 | 1.45     |          |          | $n$    |
|                       | 59.5     |          |          | $k$ (h$^{-1}$) |

From the JMA-equation the kinetics parameters $n$ and $k$ have been calculated. The results obtained give evidence that there are different steps in the transformation depending on the annealing temperature. For $T_a = 600ºC$ and 700º the ordered B2 superstructure forms prior to the precipitation of the $\sigma$-phase.

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