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## Mössbauer-effect study of the phase separation in the Fe–Cr system

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**Abstract.** *In situ* and conventional room temperature <sup>57</sup>Fe-site Mössbauer spectroscopy (MS) were used to study the phase separation process in the Fe–Cr alloy system. It was shown that MS is well able to distinguish between (i) nucleation and growth and (ii) spinodal decomposition, the two mechanisms held responsible for the separation. The Fe-rich branch of the spinodal line was located at  $80.8 \leq x \leq 84$  at.% Fe at  $T = 415$  °C. It was also shown that the saturation of the average hyperfine field cannot be taken as an indicator of the termination of the separation process. The kinetics of the process dramatically depends on the aging temperature, being faster by a factor of 1.4 at  $T = 440$  °C than at  $T = 415$  °C.

### 1. Introduction

Among the numerous Fe-based binary alloy systems, the Fe–Cr one has been playing a particularly significant role. This stems from its interesting magnetic properties and also from its interesting crystallographic ones. As regards the former, the components of the system themselves represent classic examples of a ferromagnet and an antiferromagnet. The antiferromagnetism of chromium has become particularly attractive, as it has turned out to have a harmonically modulated electronic structure known as spin-density waves [1]. Alloying Fe with Cr drastically affects the magnetic properties of the alloy: addition of Cr into the Fe matrix gradually destroys the ferromagnetism, while doping Cr with Fe quenches the antiferromagnetic properties of the solvent, and eventually results in the formation of a state known as the spin glass [2]. One of the peculiar properties of that state in the system is that it can be re-entrant [3]. It should also be remembered that the phenomenon of giant magnetoresistance was discovered in Cr/Fe multilayers [4].

The Fe–Cr system also has interesting crystallographic properties. Although the two constituent elements alloyed together form primarily a bcc structure over the whole composition range, it is over a wide temperature and composition range metastable or unstable, and, on aging, either undergoes a transformation to the  $\sigma$ -phase or separates into the Fe-rich ( $\alpha$ ) and Cr-rich ( $\alpha'$ ) phases, depending on the aging temperature. The latter results in the formation of the so-called miscibility gap [5]. Although both phenomena occur on the microscale, they cause a dramatic change of macroscopic properties of the alloy—the most spectacular being an enhanced hardness and brittleness (the latter effect known as the ‘475 °C embrittlement’) with

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serious practical consequences in the light of the technological importance of high-chromium steels with Fe–Cr alloy as their main component.

The present study is concerned with the phase separation. Several aspects of the phenomenon have been of interest: the limits of the miscibility gap, the kinetics of the separation and the mechanisms involved. Both theoretical [6–10] and experimental [11–21] approaches to the issue were applied. The fact that the separation process takes place on the microscale ( $\sim 5$  nm) [19] and results in the formation of two interconnected phases having the same crystallographic structure, and differing only in composition, makes its experimental investigation quite difficult. Only microscopic composition-sensitive methods can be successfully used. Among them, Mössbauer spectroscopy (MS) [11–13, 15, 16], atom probe field-ion microscopy (APFIM) [14, 19–21] and small-angle x-ray or neutron scattering (SAS) [17, 18] have proved to be useful. With MS one can study and determine the limits of the miscibility gap [15, 16] as well as making a distinction between (i) the nucleation and growth and (ii) the spinodal decomposition [15, 22]. With APFIM and SAS techniques it is possible to get information on the kinetics of the phase separation as well as on the development of the microstructure.

In this study the results obtained with MS performed on a series of Fe–Cr samples both *in situ* at various temperatures and at room temperature will be presented and discussed.

## 2. Experimental procedure

### 2.1. Preparation and characterization of samples

Samples of  $\text{Fe}_x\text{Cr}_y$  alloys with  $1 \leq y \leq 68$  were prepared by melting appropriate amounts of 3N-purity iron and chromium in an induction vacuum furnace. Their chemical compositions were determined by electron microprobe analysis. For each sample five different point measurements were made and the values given in this paper represent averages. The maximum difference in the concentration of chromium for a given sample was between 0.2 and 0.5 at. %.

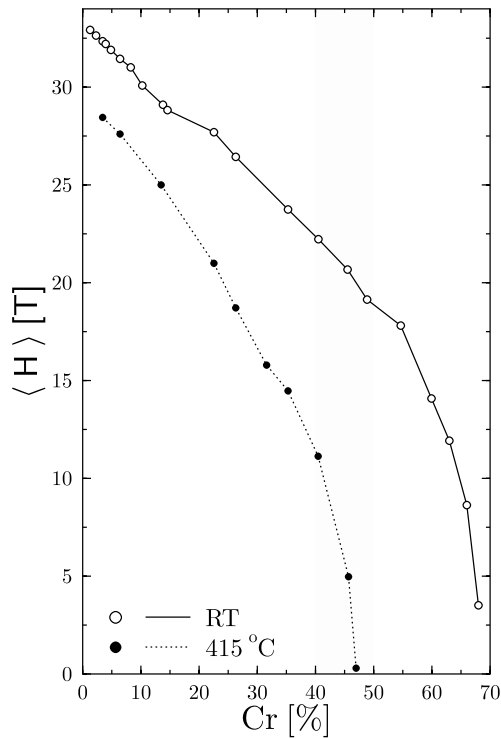
### 2.2. Mössbauer spectra measurements

For the Mössbauer-effect measurements the alloys were rolled down to a thickness of  $\approx 30$   $\mu\text{m}$  and then vacuum annealed for an hour at  $T = 900$   $^\circ\text{C}$  to remove strain. The  $^{57}\text{Fe}$ -site spectra were recorded in transmission geometry both at room temperature and at elevated temperatures (*in situ*) with a  $^{57}\text{Co}/\text{Rh}$  source and a standard spectrometer equipped with a vacuum Mössbauer furnace for the *in situ* measurements. The temperature in the latter case was kept constant to within 0.1 K.

## 3. Results and discussion

### 3.1. Room temperature or *in situ* measurements?

The phase separation can be studied by MS either by recording the spectra at room temperature for samples that were previously subjected to isothermal annealing for various periods, or, alternatively, *in situ* at the temperature at which the separation process occurs. One of the obvious advantages of the latter method is that it is faster and more economic. The whole process of separation at the given  $T$  can be studied for a single sample, while the alternative approach requires many samples of a given composition annealed for various times at the chosen  $T$ . Another advantage of the *in situ* measurements becomes clear from figure 1 which illustrates the dependence of the average hyperfine field,  $\langle H \rangle$ , on the Cr content,  $y$ , as measured at room temperature (open symbols) and *in situ* at 415  $^\circ\text{C}$  (full symbols). For the alloys with

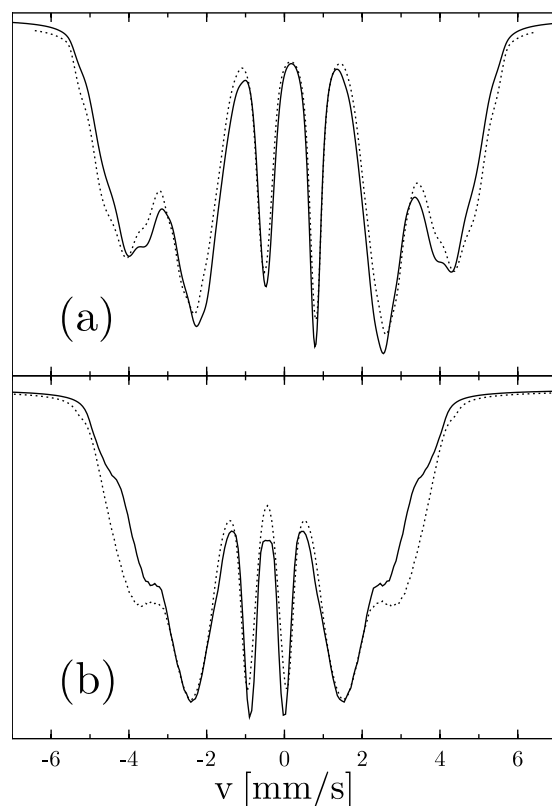


**Figure 1.** The average hyperfine field,  $\langle H \rangle$ , as obtained from Mössbauer spectra recorded at room temperature (open symbols) and at 415 °C (full symbols).

$y \leq 50$  the slope of the  $\langle H \rangle = f(y)$  plot is much steeper for the *in situ* curve, and, particularly, for the  $40 \leq y \leq 50$  range. This means that the spectra recorded *in situ* are much more sensitive to the separation-induced changes in the sample than those recorded at room temperature. In other words, the *in situ* method is more suitable for studying the process of the phase separation. The difference in sensitivity of the spectra recorded with the two approaches can be seen in figure 2 which shows them as measured (a) at room temperature and (b) *in situ* at 415 °C, for an Fe<sub>70</sub>Cr<sub>30</sub> alloy before aging (solid line) and after aging for an hour (dotted line).

### 3.2. *In situ* measurements

In view of the above-presented advantages of the *in situ* method, it was used to investigate the separation process in the samples studied. The spectra, of which examples can be seen in figure 3, were recorded at 415 °C for a series of Fe–Cr alloys. They were analysed in terms of the hyperfine-field distribution method, which yielded average hyperfine-field values,  $\langle H \rangle$ . Their dependence on the aging time,  $t$ , can be seen in figure 4. One can observe there two kinds of curve: those which exhibit an immediate increase with  $t$  (for  $y \geq 19.2$ ) and those which have a flat dependence on  $t$  (for  $y \leq 19.2$ ). From previous Mössbauer-effect experiments [15, 24] as well as from theoretical expectations [10] it follows that the former behaviour can be taken as evidence for a spinodal mode of separation, while the latter should be indicative of nucleation and growth (with a long incubation time). If such an interpretation were correct, then the results presented in figure 4 could be used to determine the Fe-rich branch of the spinodal line in the miscibility gap. In the present case it should be located at  $16 \leq y \leq 18$  at 415 °C. This figure can be compared with the value of  $y = 15$  or  $y = 27$  as found from Monte Carlo simulations performed on the Fe–Cr system within the mean-field approximation

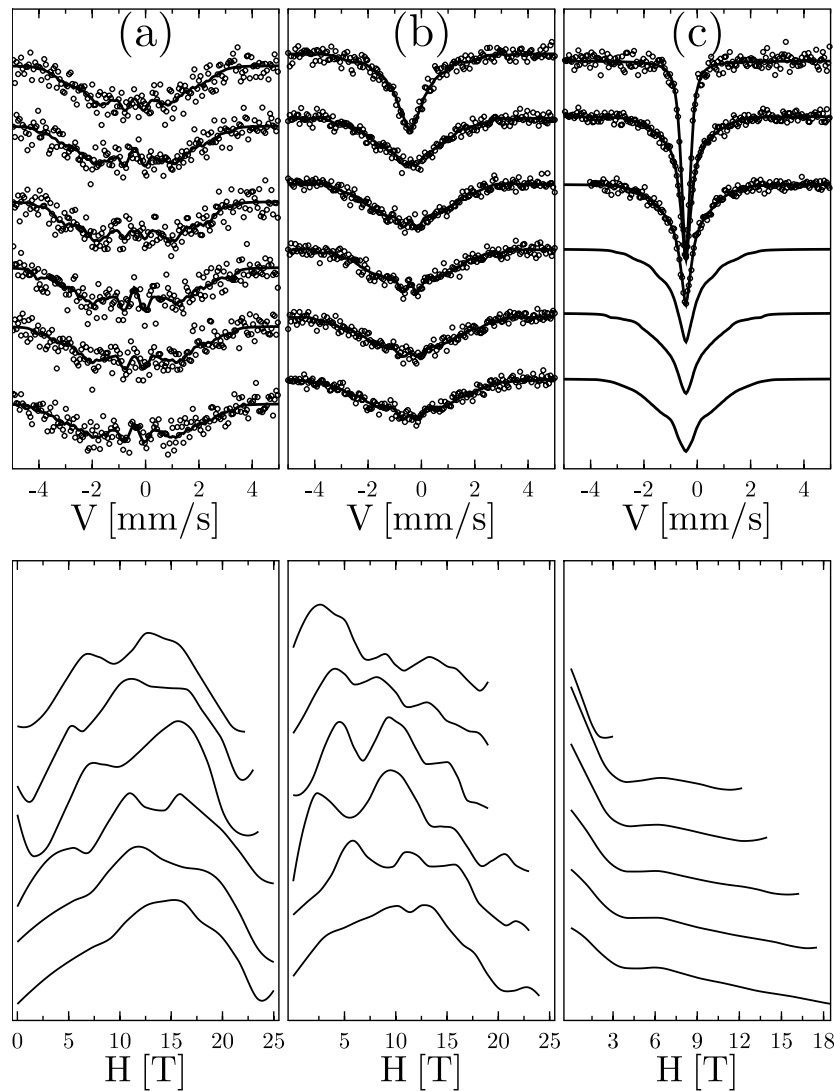


**Figure 2.**  $^{57}\text{Fe}$  Mössbauer spectra recorded at (a) room temperature and (b)  $415\text{ }^{\circ}\text{C}$  *in situ* for an  $\text{Fe}_{70}\text{Cr}_{30}$  sample as received (solid line) and after aging for 30 h (dotted line).

and using the ThermoCalc thermodynamic database, respectively [10]. On the other hand, the branch of the spinodal line for an Fe–Cr alloy doped with 5 at.% Ni was determined to lie between  $y = 16$  and  $y = 30$  at  $450\text{ }^{\circ}\text{C}$  [23].

### 3.3. Kinetics of the phase separation

A characteristic feature of the  $\langle H \rangle = f(t)$  curves shown in figure 4 for  $y \geq 19.2$  is not only their instant and steep increase with  $t$  (in the case of the sample annealed at  $440\text{ }^{\circ}\text{C}$  and  $480\text{ }^{\circ}\text{C}$  the initial part of the curve has the form of a plateau, which follows from the fact that the sample at these temperatures is in its paramagnetic state at the beginning of the annealing process), but also a saturation-like behaviour. Can the latter feature be taken as indicative of the termination of the separation process? In order to answer this question, *in situ* measurements were performed on an  $\text{Fe}_{53}\text{Cr}_{47}$  sample at various temperatures. A selection of the spectra recorded can be seen in figure 5. As before, they were analysed to yield the values of  $\langle H \rangle$ . Their dependence on the aging time,  $t$ , can be seen in figure 6. To get insight into the kinetics of the phase separation and to eventually answer the question posed, the spectra for the three samples were also recorded at room temperature after the aging process was completed. The spectra obtained in that measurement are presented in figure 7. They were analysed in terms of the hyperfine-field distribution, assuming that they each consist of a magnetic subspectrum, with a broad distribution of the hyperfine field, and a paramagnetic subspectrum. The former



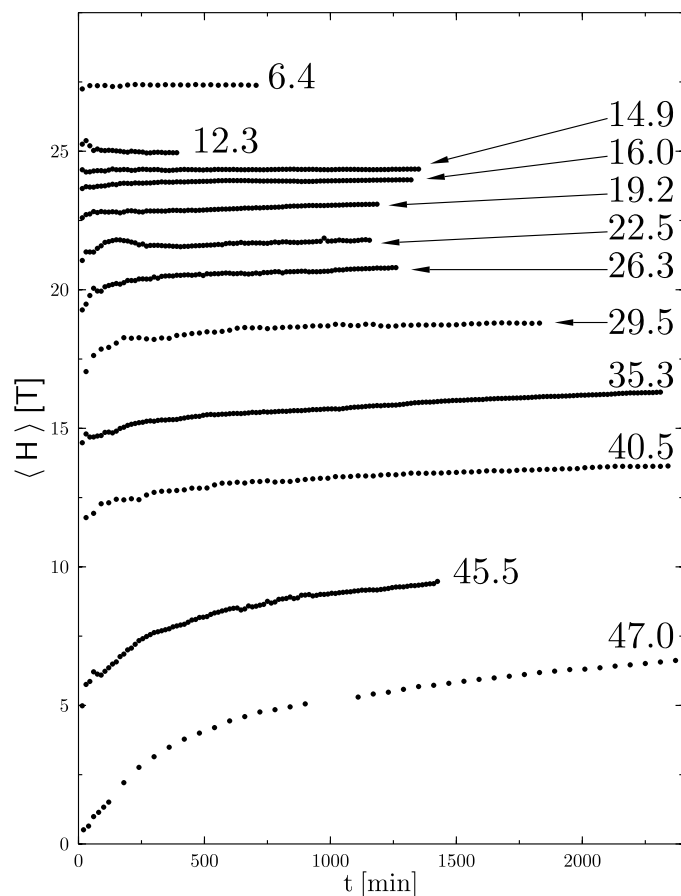
**Figure 3.**  $^{57}\text{Fe}$  Mössbauer spectra and the corresponding hyperfine-field distribution curves as recorded *in situ* at 415 °C for  $\text{Fe}_x\text{Cr}_y$  samples for: (a)  $y = 40$ , (b)  $y = 45$ , (c)  $y = 47$ . The spectra shown were measured in the following time intervals (from top to bottom): 0–30, 120–180, 240–300, 480–540, 720–780, 1080–1140 minutes.

was ascribed to the Fe-rich phase, while the latter was ascribed to the Cr-rich one. Knowing the values of  $\langle H \rangle$  for the ferromagnetic subspectrum and using the  $\langle H \rangle = f(y)$  plot shown in figure 1, the composition of the Fe-rich phase,  $x^\alpha$ , was uniquely determined with an accuracy of about 2%. The values of  $\langle H \rangle$  and  $x^\alpha$  obtained in that way are displayed in table 1.

Using next the phase diagram of the Fe–Cr system [5], we were in a position to determine the degree of separation,  $d$ , for the three samples as follows:

$$d = \frac{x^\alpha - x'}{x_0^\alpha - x'} \quad (1)$$

where  $x_0^\alpha$  stands for the content of Fe in the Fe-rich phase as taken from the phase diagram [5]

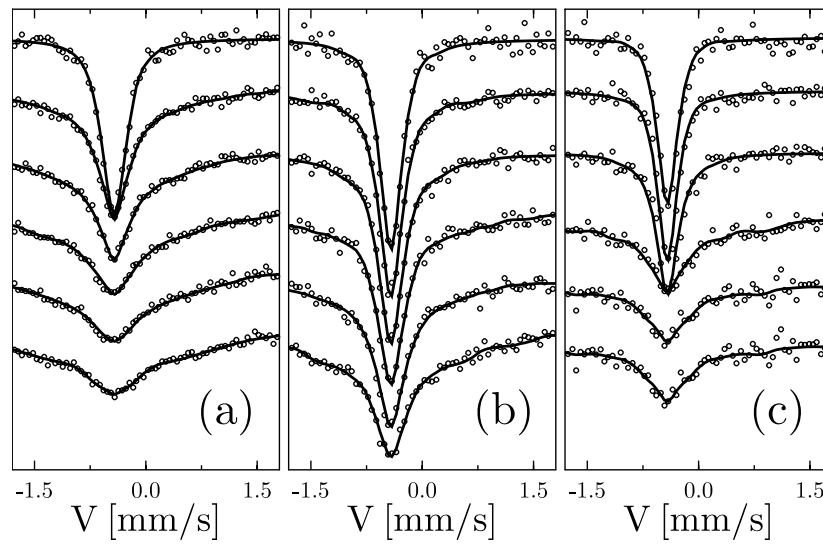


**Figure 4.** The average hyperfine field,  $\langle H \rangle$ , versus aging time,  $t$ , as derived from the spectra recorded *in situ* at 415 °C for samples with the various contents of chromium indicated.

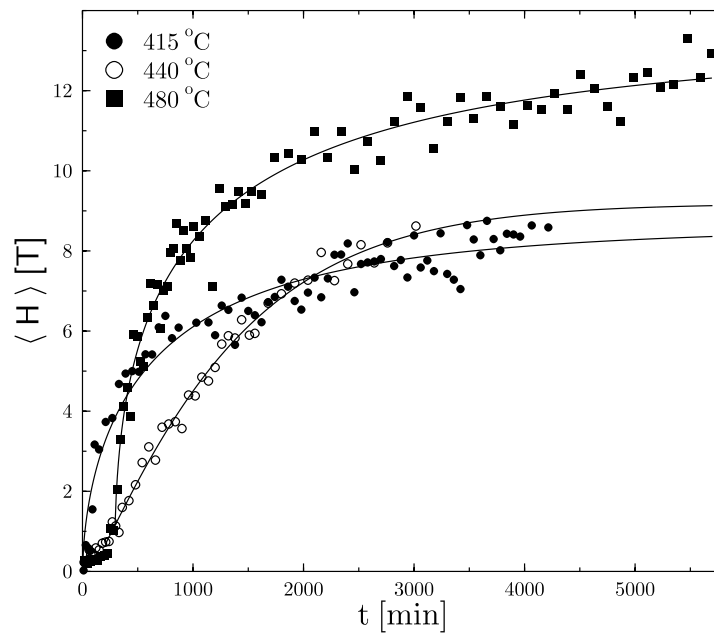
**Table 1.** The aging temperature,  $T$ , the average hyperfine field,  $\langle H \rangle$ , the Fe content in the Fe-rich phase,  $x^\alpha$ , and the degree of separation,  $d$ , as derived from the spectra shown in figure 7 and using the formula (1).

$T$ (°C)	$\langle H \rangle$ (T)	$x^\alpha$ (at.% Fe)	$d$
415	21.8	58	0.2
440	22.0	60	0.2
480	25.5	78	0.8

and  $x'$  for the initial Fe concentration ( $x' = 53$  in this case). The  $d$ -values obtained in the above-described way are included in table 1, too. It is obvious that the saturation of the  $\langle H \rangle = f(t)$  plot does not indicate the termination of the separation process. Adequate information in that respect can, however, be obtained from the room temperature spectra by calculating the  $d$ -values. Their dependence on  $t$  would yield appropriate information on the kinetics of the phase separation. From the data displayed in table 1 it is also clear that the separation process strongly depends on  $T$ : the higher the temperature is, the faster the separation process proceeds. In particular, the same degree of separation, namely  $d \approx 20\%$ , requires 4290 min at 415 °C



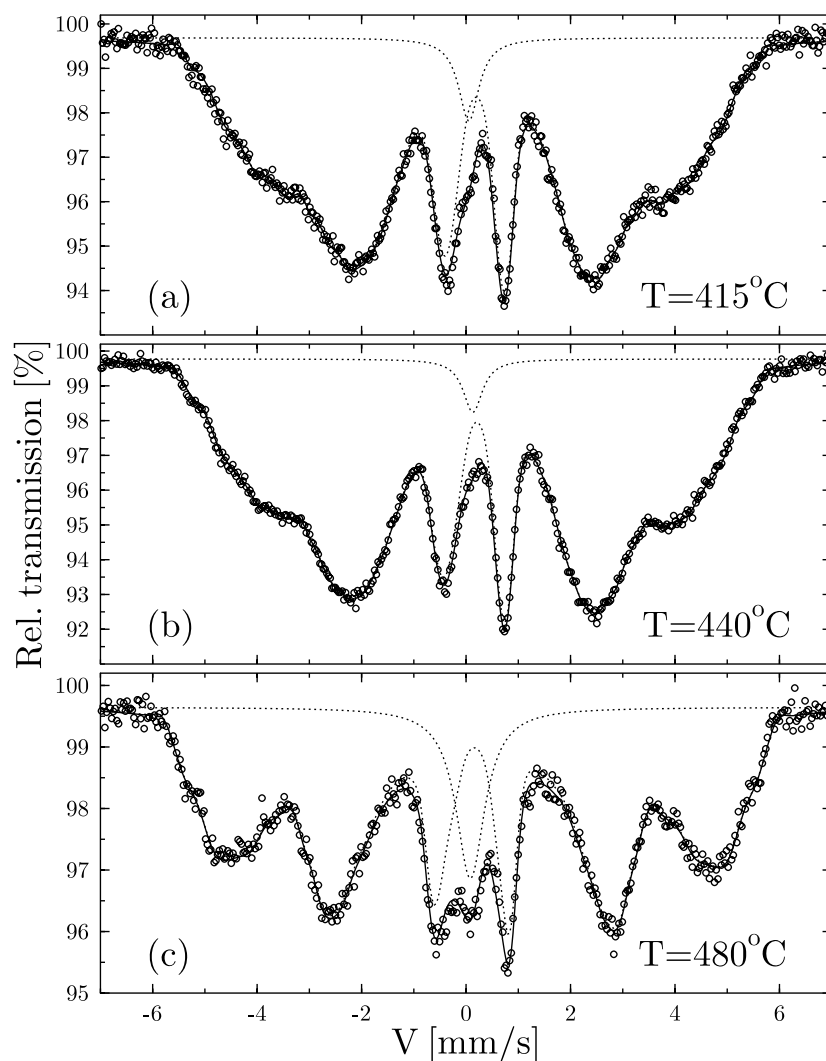
**Figure 5.** Examples of the Mössbauer spectra recorded *in situ* for the  $\text{Fe}_{53}\text{Cr}_{47}$  sample at: (a) 415 °C, (b) 440 °C, (c) 480 °C. The spectra shown were measured in the following time intervals (from top to bottom): 0–30, 120–180, 240–300, 480–540, 720–780, 1080–1140 minutes.



**Figure 6.** The average hyperfine field,  $\langle H \rangle$ , versus the aging time,  $t$ , derived from the spectra measured *in situ* for the sample of  $\text{Fe}_{53}\text{Cr}_{47}$  at the various temperatures shown. The solid lines are to guide the eye.

and only 3020 min at 440 °C. This means that the process at the higher  $T$  is faster by a factor of 1.4 while the difference in temperature is only about 8%.





**Figure 7.**  $^{57}\text{Fe}$  Mössbauer spectra recorded at room temperature for the sample of  $\text{Fe}_{53}\text{Cr}_{47}$  aged at the temperatures shown for (a) 4290 min, (b) 3020 min and (c) 5735 min.

#### 4. Conclusions

The results obtained in this study enable the following conclusions to be drawn:

- (1) A distinction between (i) nucleation and growth and (ii) spinodal mechanisms of the phase separation can be made based on the *in situ* Mössbauer-effect measurements.
- (2) The Fe-rich branch of the spinodal line is located as lying between 80.2 and 84 at.% Fe at 415 °C.
- (3) Saturation of the average hyperfine field versus the aging time cannot be taken as an indicator of the termination of the separation process.
- (4) The kinetics of the separation strongly depends on the aging temperature.

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