

The Influence of Austenisation on the Kinetics of Tempering—Mössbauer Effect Study*

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The Mössbauer effect in ^{57}Fe is used to investigate the kinetics of carbide precipitation in plain carbon steel. The investigated carbides were extracted chemically after the steel had been treated at various austenisation and tempering temperatures. The relative amount of cementite precipitated after a certain heat treatment was determined from the spectral area. The activation energy of the process is found to be 0.3 eV. A formula is suggested for the dependence of carbide formation rate on the austenisation temperature.

It is found that in the process of the chemical extraction, amorphous iron gel or oxyhydroxide isomers form, rather than iron oxides. The effective internal field H_n and the isomer shift of the extracted carbides depend on the tempering temperature, while the carbide formation rate depends on the austenisation temperature as well.

1. Introduction

Many investigations have been made concerning the kinetics of carbide precipitation in plain carbon steel and α -iron [1, 2]. The results are often controversial due to differences in composition and treatment, as well as to the different methods used. For instance, X-ray diffraction [3] and electron microscopy [1] yield information about changes in carbide particle size and shape, rather than about the amount of carbon depleted from the matrix. At the same time, the internal friction method estimates the loss of carbon from solution during precipitation from α -iron [2], but this method cannot be used in the case of martensite [4].

The low tempering temperature (ltt) precipitates are usually identified by habit plane determination, for no diffraction pattern from the precipitates themselves could be obtained. Therefore it is sometimes hard to distinguish between the Johnson carbon clusters [4], α'' -precipitates on $(100)_\alpha$ planes [1] and the ϵ -carbide. The Mössbauer effect makes it possible to determine the number of Fe atoms in a certain carbide phase relative to that in other carbide phases in a mixture. The most direct method of identification is by a chemical extraction of the carbides.

However, transition carbides such as ϵ -carbide or ltt clusters, or α'' -precipitates may be dissolved in the extraction process [5-7]. Nevertheless, from a steel containing silicon, the ϵ and χ carbides have recently been obtained by chemical extraction, and their Mössbauer parameters have been reported [5]. The Mössbauer characteristics of the chemical decomposition products of the ltt precipitates are similar to those of amorphous (III) iron gel. This gel appears in the extract, together with the ϵ and χ carbides. It was recently reported [8] that (III)-iron gel or other iron (III) oxyhydroxides precipitate in the presence of high surface silica which serves as a nucleant. The unstable carbides seem to play a similar role in the process of chemical extraction.

2. Experimental

The samples studied in these experiments were prepared from an eutectoid steel and an Fe-C alloy. The composition and codes of the samples are listed in table I. Rods were cut into discs 4 mm thick, with a hole drilled at the centre. The specimens were treated at 950°C for 15 min (in a protective atmosphere of argon + 15% hydrogen) and quenched into water containing

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TABLE I Composition and codes of the materials.

Material	Sample code	C w.p.c.	Mn w.p.c.	Si w.p.c.	Cr w.p.c.
Eutectoid steel	B	0.7	0.62	0.22	0.1
Fe-C alloy	Fe-C	0.7	—	—	—

NaOH. From this starting stage samples were treated as follows:

(a) quenched after reheating to different austenitisation temperatures $-T_A$ - in the range 800 to 1350°C, then

(b) tempered for 1 h at different tempering temperatures $-T$, - in the range 220 to 740°C, or

(c) tempered for different times and temperatures. The loss of carbon as a result of the above treatments was found to be negligible. An aqueous solution of H_2SO_4 (30 wt %) was used for the dissolution of the steel matrix. The vessel was sealed and only gas at overpressure could leak out; thus a reducing atmosphere was maintained. The extraction process was carried out for 20 h at a constant temperature of 40°C. The residual material was separated by a centrifuge, flushed by distilled water and acetone and finally coated by collodion.

The Mössbauer spectra were taken by a constant velocity Mössbauer spectrometer described elsewhere [9]. The velocity scale was calibrated by means of an Armco iron absorber [10]. The line width of the ($\pm \frac{3}{2} \pm \frac{1}{2}$) transition lines (Nos. 1 and 6) of this absorber was about 0.32 mm/sec. A 15 mCi radioactive source of ^{57}Co in a copper matrix was used throughout the experiments.

3. Results

The Mössbauer spectra of the extracted carbides consist of two components: a six-line Zeeman splitting superimposed on a quadrupole doublet. The magnetic split component of the spectra is attributed to cementite of the composition $(Fe_{1-x}Mn_x)_3C$. The best fit for the doublet yields: I.S. = (0.39 ± 0.03) mm/sec relative to α -iron, and Q.S. = (0.33 ± 0.03) mm/sec (half the separation between the $m = \pm \frac{3}{2}$ and $\pm \frac{1}{2}$ levels [11]). These figures are close to those characteristic for iron (III) oxyhydroxide isomers and amorphous (III)-iron gel [5, 12]. The X-ray diffraction patterns show that the main phase is cementite. A detailed description of other phases present in the extraction residue is given in table VI of [5]. The reproducibility of the results

is satisfactory. By repeating the chemical extraction procedure with carbon-free iron, practically no residual material at all was left. Electrolytic extraction under protective atmosphere or extraction by means of HNO_3 at low temperature ($-15^\circ C$), described elsewhere [13, 14], was repeated and led to the same results as the chemical extraction used in this investigation. On the other hand, it was shown by Mössbauer spectroscopy and X-ray diffraction results [15] that the extract of well-tempered samples consists only of cementite. Such carbides held for two weeks in the H_2SO_4 solution did not decompose. From the results of these experiments and former reports [5, 15] it is concluded that the doublet represents a phase which forms in the presence of the unstable carbides. The unstable carbides probably serve as centres of nucleation for the precipitation of oxyhydroxide during the extraction process. It is difficult to determine the carbon content in this phase, since it is very hard, if not impossible, to distinguish between free and chemically bounded carbon.

For a given phase, the spectral area under the Mössbauer spectrum is related to the number of the resonant nuclei present in that phase. A quantitative analysis of phases can be done by relating that spectral area (corrected for background) to the amount of the phase [16]. The spectral area saturates less than the line intensity [17] does. The spectral area can be expressed by:

$$A = f_s \cdot \int_{-\infty}^{+\infty} dE \{1 - \exp[-nf_A \sigma(E)]\} \quad (1)$$

which is independent of the source line shape. n is the number of resonant atoms per unit area of the absorber, f_s and f_A are the recoil-free fractions of the source and absorber respectively, E is the energy of the gamma ray, and $\sigma(E)$ is the cross section for resonance scattering. It can be shown that in the case of a thin absorber ($t_A \ll 1$) the area can be expressed as:

$$A = \frac{1}{2} \pi I f_s t_A \text{ where } t_A = \sigma_0 f_A n$$

where σ_0 is the cross section at resonance.

In the case of a thin absorber, the ratio of the areas of two phases in mixture A_1 and A_2 , is given by:

$$\frac{A_1}{A_2} = \frac{t_{A_1}}{t_{A_2}} = \frac{f_{A_1} n_1}{f_{A_2} n_2} \quad (2)$$

where indices 1 and 2 refer to the two phases.

The spectral area was carefully measured. The

area of the six-line Zeeman split was unfolded from the area of the quadrupole split component. These two areas were designated F and P respectively. In the considered tempering temperature range the Mössbauer efficiency of the doublet is apparently constant. The efficiency of the cementite (phase F) is known from the measurements of the f -factor as a function of tempering temperature [18]. Counting for this change in f , the ratio $R_F = F/P$ was calculated for all samples. It is seen from the above definition that R_F is the relative number of Fe atoms in the stable carbide phase (cementite) precipitated during a particular heat treatment.

In the considered tempering temperature range, both F and P appear on each spectrum; therefore $R = R_F/(1 + R_F)$ is restricted to $0 < R < 1$. The tempering kinetics for a constant austenisation temperature will be considered prior to that for a variable one.

3.1. Tempering Kinetics for Constant Austenisation Temperature $T_A = 950^\circ\text{C}$

The tempering temperature range considered here is between 220 and 740°C . The relative

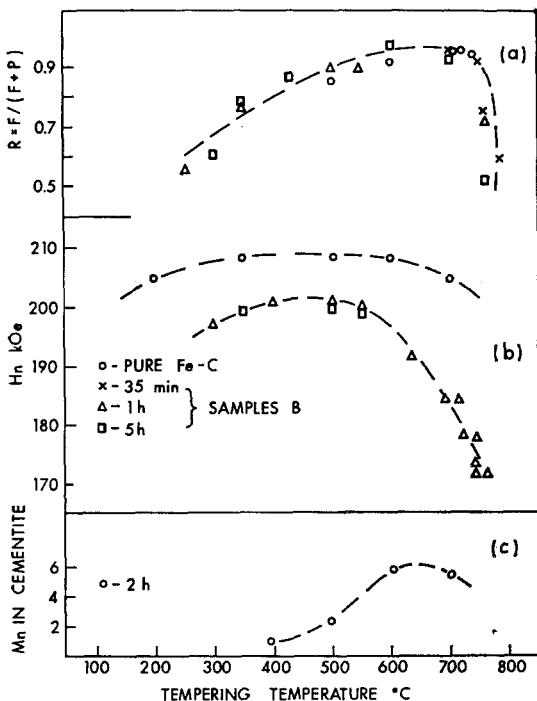


Figure 1 (a) The relative amount R of stable carbide (cementite). (b) The effective hyperfine field H_n at 300°K on the ^{57}Fe nucleus in cementite. (c) The Mn concentration (%) as calculated from [19].

amount of precipitated cementite R increases with increasing tempering temperature up to 700°C . Tempering at temperatures higher than 730°C results in a fall-off of R (fig. 1a). The dependence of R on T is qualitatively the same for the alloyed samples B and for the Fe-C samples. The effective internal field $H_n(300^\circ\text{K})$ of carbides, extracted from samples B, achieves its highest value of $H_n = 202$ kOe in the tempering temperature range: $350 \leq T \leq 550^\circ\text{C}$ (fig. 1b). The $H_n(300^\circ\text{K})$ of the Fe-C samples has a wider plateau: $300 \leq T \leq 630^\circ\text{C}$. The amount of Mn in carbides extracted from a similar steel is calculated from the chemical analysis results of Gurry *et al* [19], and plotted versus T in fig. 1c. From fig. 2 it is seen that the

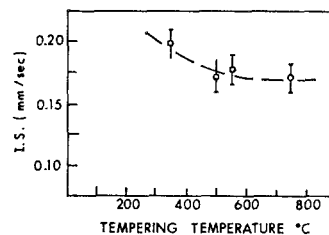


Figure 2 The mean isomer shift as a function of the tempering temperature. Samples labelled B.

I.S. decreases in the tempering temperature range between 250 and 450°C , and is practically constant for samples tempered at $T > 450^\circ\text{C}$. The Curie point of the carbides extracted from samples B tempered at 700 to 720°C is found to be $T_c = 100^\circ\text{C}$ (not shown in the figures).

The change in R_F with the tempering temperature yields a rate equation with a single activation energy Q :

$$R_F(T, T_A = 950^\circ\text{C}) = C \exp(-Q/kT), \quad (3)$$

where C is a pre-exponential factor (which is constant if the time of tempering is kept constant) T is the tempering temperature and k is the Boltzmann constant. A logarithmic plot of R_F versus $1/kT$ is shown in fig. 3. R_F is (defined as) the ratio F/P at each given tempering temperature- T . The tempering time was kept 1 h throughout all the experiments. The slope of the line in fig. 3 yields the value $Q \approx 0.3$ eV.

3.2. Tempering Kinetics for Austenisation Temperatures from 800 to 1350°C

A surprisingly strong dependence of R on T_A is observed from the present results. From figs. 4

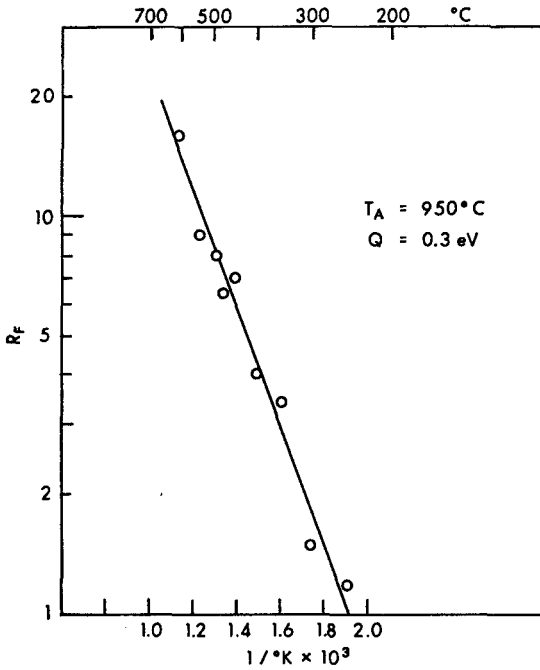


Figure 3 A logarithmic plot of $R_F = F/P$ versus $1/KT \times 10^3$ as a function of the tempering temperature. Samples labelled B.

and 5 it is evident that the relative amount of the ferromagnetic cementite $[Fe_xC \text{ or } (Fe_{1-x}Mn_x)_3C]$ increases with the austenisation temperature T_A . If T_A is changed from 800 to 1350°C, R changes from 0.4 to 0.6 for $T = 350^\circ\text{C}$, and to 0.8 for $T = 550^\circ\text{C}$. On the other hand, if $T = 740^\circ\text{C}$, the change in T_A from 800 to 1300°C results in a decrease of R , from 0.97 to 0.55 (fig. 6). Plots of R versus T_A for the three different tempering temperatures 350, 550 and 740°C are shown in fig. 7. The difference in the rise of $R(T_A)$ in curves I and II illustrates the dependence of R both on T and T_A . The fall of $R(T_A)$ in curve III is attributed to the dissolution of the carbides at $T = 740^\circ\text{C}$.

If the dependence of R_F on T_A is introduced, then equation 3 may be re-expressed in the form:

$$R_F(T, T_A) = R_0 f(T_A) \quad (4)$$

where $f(T_A)$ describes the dependence of R_F on T_A , and $R_0 = R_F(T, T_A^\circ)$ yields the dependence of R_F on T for a particular austenisation temperature T_A° . Empirically it is found that $f(T_A)$ can be expressed in the following form:

$$f(T_A) = 1 - A \exp \left\{ - \left(\frac{n}{n_0} \right)^\gamma \right\} \quad (5)$$

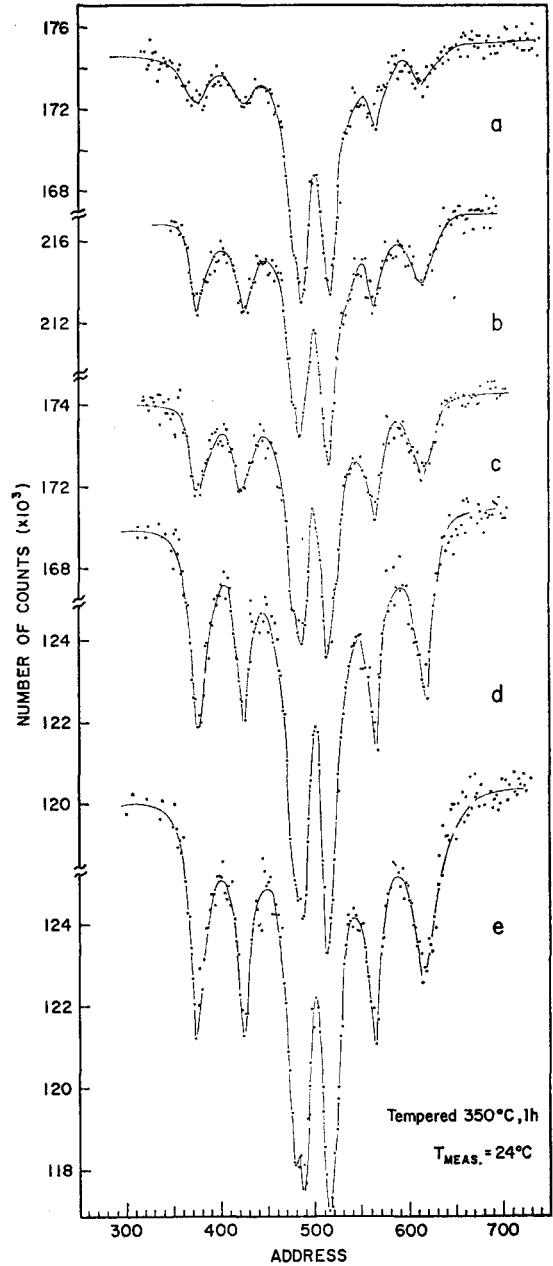


Figure 4 Mössbauer spectra of carbides extracted from samples labelled B. The samples were austenised at 950°C for 20 min, reheated and quenched from: (a) 800°C (b) 950°C (c) 1050°C (d) 1200°C (e) 1300°C.

where $n = n(T_A)$ is the equilibrium vacancy concentration at an austenisation temperature T_A , and is given by $n = \exp(-E_v/kT_A)$; E_v is the vacancy formation energy; A is a constant of the order of unity ($A \gtrsim 1$); n_0 and γ are constants.

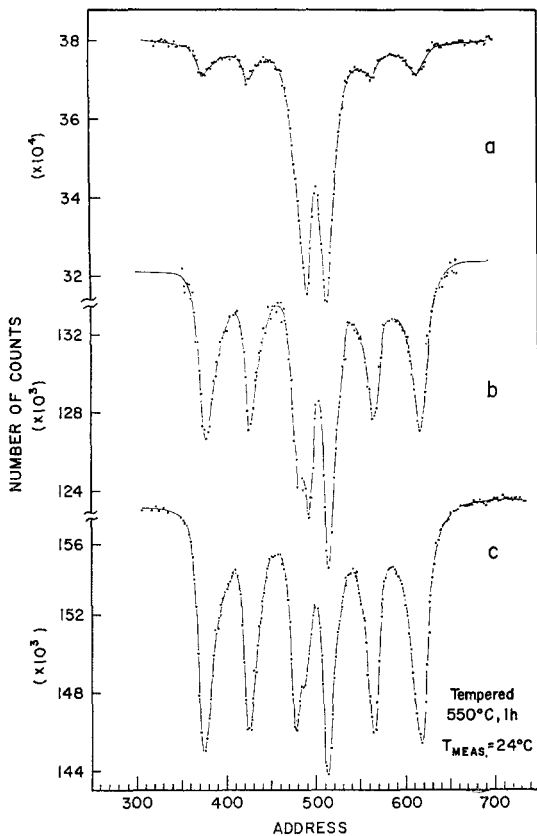


Figure 5 Mössbauer spectra of carbides extracted from samples labelled B. The samples were austenised at 950°C for 20 min, reheated and quenched from: (a) 800°C (b) 950°C (c) 1200°C. Finally they were tempered at 550°C for 1h.

The log log plot of R_F (not shown here) yields the product $E_{\nu\gamma} \approx 0.7$ eV.

4. Discussion

The kinetics described in part (a) (with constant T_A) obey the rate equation 3.

The ltt-carbide phases are described in the literature as “Johnson clusters” [4], α'' – an intragranular phase having the $(100)_\alpha$ habit [1] – and ϵ -carbide. They grow to a limited extent and are coherent or partially coherent with the matrix. The phase P , represented by a central doublet in the Mössbauer spectra, results from these unstable carbides after the matrix is dissolved during chemical extraction.

According to the model given by Johnson [4], a C-atom moves in α -iron with a migration energy $E_m = 0.86$ eV and becomes elastically bound with a binding energy $E_b = 0.3$ eV when

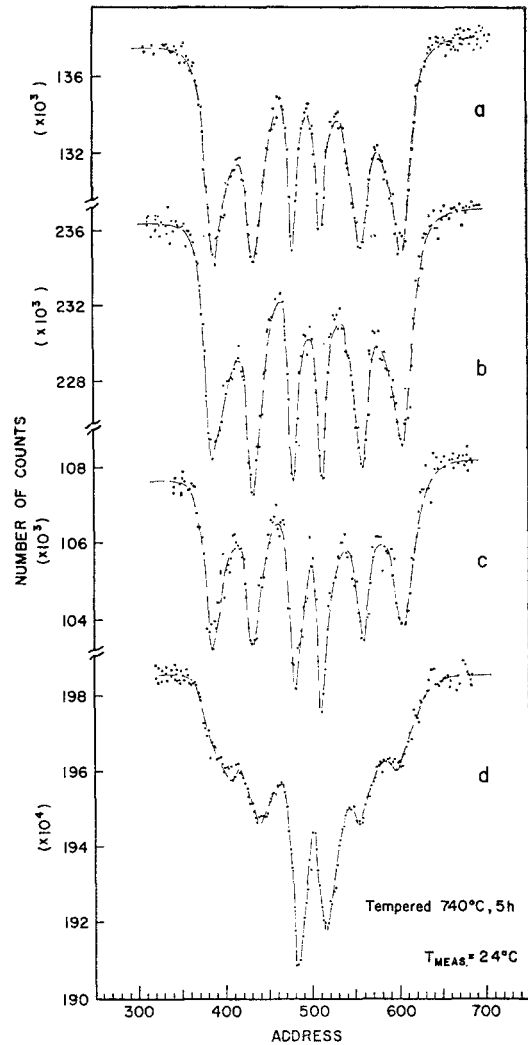


Figure 6 Mössbauer spectra of carbides extracted from samples labelled B. The samples were austenised at 950°C for 20 min, reheated and quenched from: (a) 800°C (b) 950°C (c) 1200°C (d) 1300°C. Finally they were tempered at 740°C for 5 h.

approaching a cluster of several C-atoms. Values close to 0.3 eV have also been obtained for the energy of a C-atom in α -iron relative to metastable carbide phases [2, 20].

The migration energy E_m of a carbon atom in martensite increases with concentration – C_m . The initial migration occurs in regions where the carbon concentration C_m is relatively low ($C_m \sim C_\alpha$). The persistence of transition carbides at higher tempering temperatures is, therefore, explained as being due to new regions of the martensitic matrix which lower their carbon

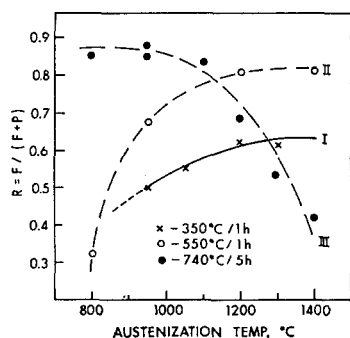


Figure 7 The relative amount, R , of the stable carbide (cementite) as a function of the austenisation temperature. Samples labelled B.

concentration. This is supported by findings that the transition carbides persist at higher tempering temperatures if C_m is increased [1, 2].

Butler [2] has found that practically all the carbon is depleted from the matrix in the stage of formation of the unstable carbides.

Duggin [21] has considered the structural similarities of the iron carbides, suggesting mechanisms by which regions of carbides may transform in the transformation sequence $\epsilon \rightarrow \chi \rightarrow \theta$. If there is a difference in composition, e.g. excess of C-atoms in the $\chi \rightarrow \theta$ transformation, then the transformation rate would depend upon the rate of diffusion of the excess C-atoms. Duggin makes a reservation from his proposed mechanism as far as the $\chi \rightarrow \theta$ transition is concerned, taking into consideration the preferred growth of cementite at dislocation sites. The θ -carbide precipitates on dislocations with a rate which is enhanced by stress assisted diffusion [22]. Nevertheless, a study by Leslie [1] shows clearly that in α -iron the type of precipitated carbide is independent of the site where it appears (matrix or dislocation); only the rate of precipitation is affected. Thus Duggin's mechanism is also applicable to the $\chi \rightarrow \theta$ transformation, at least in regions where the dislocation density is not very high.

The value of 0.3 eV obtained for Q is sufficient for the process of cementite formation in the sense of mechanism given by Duggin [21].

It should be emphasised here that coagulation of carbide particles will not affect the results as long as no transformation to cementite occurs. Therefore the Mössbauer analysis is not sensitive to ripening of cementite particles.

The representation of the dependence of R_F on T_A (equation 4) implies a vacancy mechanism.

The connection between the ltt precipitation and vacancies has already been suggested elsewhere [1, 2]. Vacancy-carbon couples or higher complexes may provide the onset of nucleation embryos. Butler [2] reported a rise in the number of nucleating particles of ltt carbides in α -iron as the quenching temperature was increased. Leslie [1] pointed out that the reason for the anomalous high rate of precipitation of ltt carbides originates in the nucleation on intragranular matrix sites, where there may be single or multiple vacancies.

It is definitely shown that the rate of the tempering process increases with T_A . Also it was found that T_A influences the retransformation to austenite (through the dissolution of cementite). This is seen from the decrease in R (and R_F) in the isothermal heating at 740°C (figs. 6, 7).

The dependence of R (or R_F) on T and T_A is qualitatively the same for the Fe-C alloys as for the alloyed samples (B). The effective internal field H_n (300°K) of the pure Fe-C carbide is almost constant (208 kOe) in the whole range of tempering temperature. It deviates from this value only by 2% in the tempering temperature range of $T < 350^\circ\text{C}$ and $T > 650^\circ\text{C}$. It seems reasonable to relate these variations in H_n to changes in carbon concentrations in the carbides. The alloyed carbides $(\text{Fe}_{1-x}\text{Mn}_x)_3\text{C}$, where x increases with the tempering temperature, have the cementite structure. The effective internal field, H_n (300°K) and the Curie temperature, decrease with increasing tempering temperature above 500°C. This is in reasonable agreement with former Mössbauer results [15, 23]. According to the results reported by Huffman [23], $T_c = 100^\circ\text{C}$ corresponds to a Mn concentration of 3%. The $T_c = 100^\circ\text{C}$ is found for carbides of 700°C tempering.

The isomer shift of the iron carbide Fe_xC may be described in the frame of the donor theory [23, 24]. Below T_c the addition of Mn to the carbide $(\text{Fe}_{1-x}\text{Mn}_x)_3\text{C}$ with tempering temperature should decrease the I.S. by decreasing the number of d -electrons and changing the s -electrons [23] a little. However, the results show that in the range of tempering temperature of 400 to 700°C the I.S. remains unchanged. The Mn, the concentration of which increases in this range up to 3%, prefers to enter General Sites (Fe_G - according to Fasiska and Jeffrey [25]). In this way the average d -electron density of an Fe_G -atom is lowered and is closer to the average d -electron density of the cementite as given by

Huffman [23]. Below T_c , no quadrupole interaction can be measured within the accuracy of these experiments.

Acknowledgement

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