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ON THE AGING OF Fe-Ni-C AND Fe-Mn-C MARTENSITES

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Abstract.

Virgin and aged martensites were studied by dilatometry and Fe^{57} Mössbauer spectroscopy. Dilatometric measurements were made between $-80^{\circ}C$ and $+100^{\circ}C$ with one high carbon manganese steel and three nickel steels with subzero M_s -temperatures. For nickel steels it was found that the aging curves, the change of length vs. $\log(t)$, were linear at temperatures below $+40^{\circ}C$, but at higher aging temperatures the curves were found to consist of two linear parts. The changing of the slopes occurred at shorter times the higher was the aging temperature. In case of the manganese steel the aging curves were not linear at any temperature. Some proposals concerning clustering and precipitation processes are made. The Mössbauer spectra were measured at liquid nitrogen temperature by transmission method. A new fitting model was developed based on the utilization of Fe-Ni reference spectra. The fitting function consists of a great number of these patterns corresponding to every possible neighbour configuration of the iron atom up to the third neighbour shell. Each pattern is modified by the changes in hyperfine interactions due to the carbon atoms. In virgin martensite the carbon atoms could be explained to be distributed apart from each other rather than randomly and to cluster during the aging. The present fitting model of Mössbauer spectra produces explicit values for carbon contents and the fractions of the cluster phases. Carbon contents well correspond to the structures, which are expected to be found according to the aging temperature. From the fitting results the volume changes of the martensite during the aging were calculated. The volume changes were compared with the values measured by dilatometry. Agreement was promising.

1. Introduction

The redistribution of carbon atoms due to aging in iron-base martensites has been the subject of many reports in recent years. Carbon atom clustering and early stages of tempering have been studied by different techniques e.g. hardness and resistivity measurements /1/, electron and atom probe ion field microscopy /2-3/, dilatometry /4/, internal friction /5/ and acoustic emission /6/. X-ray diffraction is widely used and interesting results have reported lately by Winchell et al. /7-8/. In case of Mössbauer spectroscopy there exist divergent views when interpreting the aging data. One conflicting point is whether carbon atoms occupy only octahedral sites, or are tetrahedral sublattices also involved /9-12/.

The aim of the present work was to study carbon atom clustering and early stages of tempering by using dilatometry and Mössbauer spectroscopy and to develop a new procedure to analyze the Mössbauer spectra of virgin and aged martensites.

11. Experimental procedures

The steels investigated were melted and chill cast under argon atmosphere. Then they were hot forged into plates 12 mm thick or rods \varnothing 15 mm. The austenitizing temperatures and compositions of steels (wt%) used in dilatometry are expressed in Table 1. Austenitizing temperatures were chosen so that the lowest M_s -temperature could be reached for each steel. These were determined by preliminary tests. The

austenitizing time was 30 min. The dilatometry samples were rods, 65 mm long and \varnothing 1,5 mm, and they were heat-treated in evacuated quartz capsules. The samples were quenched in dilatometer to liquid nitrogen temperature and held there for ten minutes. Then the samples were immersed into well stirred methanol or water baths and the measurements were made. Time was set to zero when the sample stopped expanding. The time the austenitic samples stayed at room temperature before quenching was not taken into account.

Table 1: The composition and austenitizing temperatures of steels which were used in dilatometry.

Steel	C	Ni	Mn	T_Y ($^{\circ}\text{C}$)
I	0.44	23.8	-	1050
II	0.71	18.0	-	1120
III	1.40	9.0	-	1120
IV	1.76	-	2.0	1150

In Mössbauer studies only steel III was used here. The developed fitting procedure of the Mössbauer spectra is valid for all of the previous materials. The measured spectra for the other steels will be reported later. The samples were mechanically thinned. The 25 μm thick austenite foils were quenched to liquid nitrogen temperature just before measurements. Carbonless reference samples were prepared by decarburizing the martensite foils in hydrogen atmosphere for several hours at 760 $^{\circ}\text{C}$. The Mössbauer measurements were made in transmission geometry. The radioactive source was $\text{Co}^{57}:\text{Pd}$. In all measurements the absorber was maintained at liquid nitrogen temperature. The Mössbauer spectra were measured from virgin and three differently aged martensites. The aging times were one hour at 35 $^{\circ}\text{C}$, further 30 hours at 38 $^{\circ}\text{C}$ and still 2.5 hours at 100 $^{\circ}\text{C}$. The Fe-9Ni reference spectrum was measured under the same circumstances as the martensite spectra.

III. Experimental results and discussion

Dilatometry. The aging behaviour of nickel steels is presented in figure 1. Results are for 100% α' . It can be seen that only the steel with the highest carbon content did not shorten at the lowest test temperature, $T = -80^{\circ}\text{C}$. It was also found that at subambient temperatures steels I and II shortened more than steel III but the order was changed at higher test temperatures. The change of length vs. $\log(t)$ was found to be linear up to aging temperature +45 $^{\circ}\text{C}$, excluding the time before which the samples were found not to shorten, within the experimental accuracy, at the two lowest temperatures. At temperatures $T=+45^{\circ}\text{C}$ and higher, a deviation from linear behaviour was found. The deviation is not an abrupt one but it is stressed by two straight lines. It could be seen best with steel III. The high carbon manganese steel behaved in quite a different way (Fig.2). A dilation was found at every test temperature. Moreover there exists no linearity in the aging plots. A cause for this can be the competition of several different aging processes. When this steel was studied by transmission electron microscope (TEM) some diffraction patterns due to epsilon phase were found. This conflicts to earlier TEM observations for manganese steels /13/. A more detailed study of phases existing in this steel will be published elsewhere. In lack of exact knowledge of the microstructure of this steel the changes of length are not converted into 100% martensite.

It has been stated that before aging recovery takes place at temperatures below -50 $^{\circ}\text{C}$ /14/. Causes for the observed dilatations at low temperatures are unclear. Whether these are due to dislocation processes and/or carbon segregation to dislocations must be studied by techniques other than dilatometry or Mössbauer spectroscopy. A possible explanation for the aging behaviour of nickel steels is that carbon clusters at temperatures up to +40 - +50 $^{\circ}\text{C}$ and at higher temperatures clusters start to grow into precipitates. This might be the reason for the observed deviations from the linearity in the aging curves.

Mössbauer spectroscopy. A procedure for fitting the Mössbauer spectra of Fe-9Ni-1.4C martensite was developed. The procedure was based on the utilization of the Fe-9Ni reference spectrum. The Fe-9Ni reference spectrum was fitted by six independent Lorentzian lines with free parameters. It is assumed that the effect of nickel atoms on the hyperfine fields of Fe⁵⁷ is the same in the Fe-Ni system and in the corresponding martensite. Thus it would be unnecessary to use complicated physical fitting procedures here /15/. The fitting function of the martensite Mössbauer spectra consists of 135 six line Fe-9Ni patterns. Each pattern corresponds to a certain configuration of carbon atoms surrounding the probe Fe⁵⁷ atom and it is modified by the changes in hyperfine interactions caused by carbon atoms. It is supposed that carbon is randomly distributed in c-axis octahedral sites. Then every pattern is combined to the whole fitting function of martensite spectrum by binomially distributed weights. In this procedure three coordination shells are taken into account and so the weights are

$$P_{nml} = \binom{2}{n} \binom{4}{m} \binom{8}{l} C^{n+m+l} (1-C)^{14-n-m-l}, \quad (1)$$

where n, m, l express the number of carbon atoms on the first, second and third shells, and C is the occupation probability. A good approximation for the shifts in the effective hyperfine fields due to solute neighbours can be written as /16/

$$\Delta H = \sum_{n=1}^M m_n \Delta H_n, \quad (2)$$

where m_n is the number of solute atoms in the n th coordination shell, and M is the number of neighbour shells taken into account. Isomer shifts are assumed to obey the same kind of rules. To evaluate the effect of electric quadrupole interaction the effective magnetic field is assumed to be oriented along the c -axis. It is sufficient to take into account only the first coordination shell. If both sites are occupied, the quadrupole splitting is twice the amount produced by only one carbon atom. The absorption function used for fitting the Mössbauer spectra of the virgin martensite is /17/

$$f(v) = \sum_{i=1}^6 \frac{l_i P_{nml}}{1 + 4 \left(\frac{v-v_{inml}}{\Gamma_i} \right)^2}, \quad (3)$$

$$\text{where } v_{inml} = v_i + n\alpha_i + m\beta_i + l\gamma_i + nw + n\delta_1 + m\delta_2 + l\delta_3.$$

The absorption l_i , the linewidth Γ_i and the peak position v_i of the i th line are obtained from the Fe-9Ni fits. Three sets of parameters $\alpha_i, \beta_i, \gamma_i$ are the magnetic hyperfine shifts of the line i and they are related to ΔH_i as $\alpha_i = S_i \eta \Delta H_1$, $\beta_i = S_i \eta \Delta H_2$, $\gamma_i = S_i \eta \Delta H_3$, where S_i is a real number depending linearly on velocity. For the line $i=1$ it is 1 and for the line $i=6$ it is -1. The symbol η is a conversion coefficient and its value is $\eta = -0.01652$ (mm/s)/kOe. The electric quadrupole splitting is denoted by $2w$. Isomer shifts for the three shells are $\delta_1, \delta_2, \delta_3$. To evaluate the electric quadrupole splitting and the isomer shift R . Kaplow's results /10/ were utilized after scaling to larger effective fields due to nickel atoms. The scaled parameters in mm/s are $\delta_1 = -0.046$, $\delta_2 = 0.149$, $\delta_3 = 0.032$ and $2w = 0.34$. Only parameters $\Delta H_1, \Delta H_2$ and ΔH_3 were determined by minimizing the mean square deviation between the computed and experimental points. The fitted Mössbauer spectrum of the virgin Fe-9Ni-1.4C martensite is shown in figure 3a. The best fit was achieved with the parameter values $\Delta H_1 = -63$ kOe, $\Delta H_2 = -40$ kOe and $\Delta H_3 = 15$ kOe. The accuracy achieved even without fitting the intensities of the virgin martensite spectrum shows that the orientation of the magnetic fields are the same in the binary Fe-9Ni and in the virgin martensite systems. The orientation is fairly random, as expected. The positions of the

lines were not quite correct. The spectrum ought to be slightly broader. There would be at least two ways to get a better result: one is to take further coordination shells into account and the other is to assume that the distribution of carbon atoms is not quite random. The latter assumption is supported by the fact that the carbon distribution in virgin martensite is inherited from austenite, where it was found to be nearly ordered /17/.

When aging martensite carbon atoms are assumed to form clusters and thus minimizing the strain energy. Obviously the carbon atom distribution is ordered in clusters. It is seen, however, that exact knowledge of the structures of the clusters is not necessary for fitting the Mössbauer spectra of aged martensite quite well, because the fraction of the cluster phase and so its contribution to the spectrum is small. In the fitting procedure carbon distribution in clusters is supposed to be, for the sake of simplicity, the same as in virgin martensite, although the carbon content is higher. In figure 4 the function (3) is simulated with different carbon contents. The absorption function $\bar{f}(v)$ of the Mössbauer spectra of aged martensite is achieved by combining two terms of the form (3), one belonging to the matrix and the other to the cluster phase with weights P_1 and $P_2=1-P_1$ and carbon contents C_1 and C_2 , respectively. Carbon contents are connected to each other by $C_2=(C-P_1C_1)/(1-P_1)$. The spectra were fitted by varying only three parameters, the fraction P_2 and the carbon content C_2 of the cluster phase and an extra parameter K for the intensities of the lines 2 and 5. The fitted spectra are expressed in figure 3b-d. The orientation of the effective field obviously changes during aging to favour the direction of the foil surface remaining, however, random in a sufficient accuracy. The maximum value of K (Fig.3d) is only 1.22(1). In measurements made in external magnetic field of 3 kG oriented along the foil surface, K was 1.83 /17/.

In figure 5 the accuracy of fitting is expressed as a function of carbon content of the cluster phase. After the first aging treatment (1h at 35°C) the carbon content of the cluster phase seems to be 22 at% (Fig. 5a) and its fraction is $P_2=7.4(4)\%$. The obtained carbon content 22 at% is quite close to the stoichiometry of Fe_4C , which is shown to be an energetically favourable structure to be formed at the present aging temperatures by R. Kaplow et al./10/. When the sample was aged at 100°C (Fig. 5c) the best fit was achieved with the carbon content 32 at% and with the phase fraction $P_2=11.5(2)\%$. This phase could be identified with ϵ or some other transition carbide /18/. The carbon content 32 at% corresponds to the composition $Fe_{2.2}C$. The value 25 at% obtained from fig. 5b might be explained by the combination of the previous phases, e.g. the portion 2.9(2)% $Fe_{2.2}C$ carbide and 6.7(2)% the structure Fe_4C .

Next it will be speculated that the clustering obtained from the fitting results of the Mössbauer spectra of aged martensite could cause the observed shrinking of martensite. By using the empirical relations between the lattice parameters and carbon contents for binary Fe-C systems neglecting the effect of Ni and the changes due to aging in lattice parameters /19/ a simple calculation shows that the volume change of the unit cell is -0.0217 \AA^3 after aging one hour at 35°C/17/. Hence, the relative length decrease is $-2.9 \cdot 10^{-4}$, which seems to be in accordance with the value measured by dilatometry (Fig.1c)

Acknowledgement

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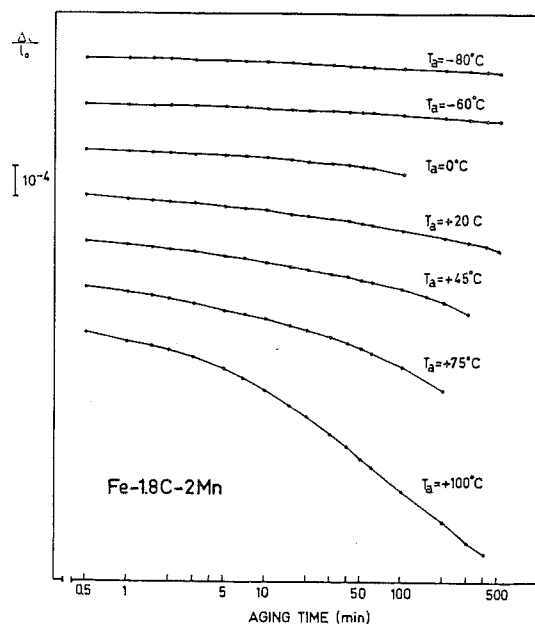
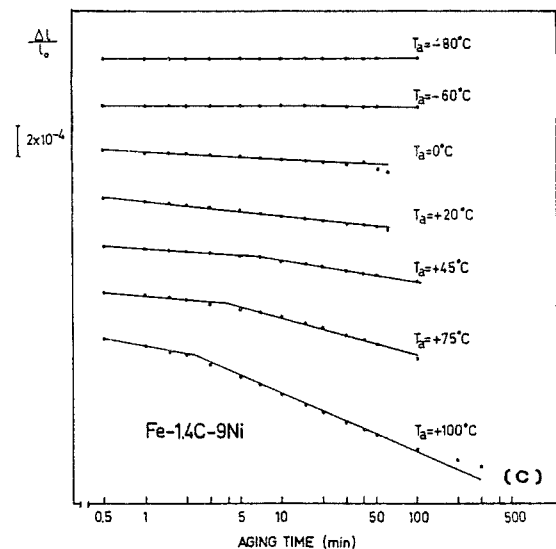
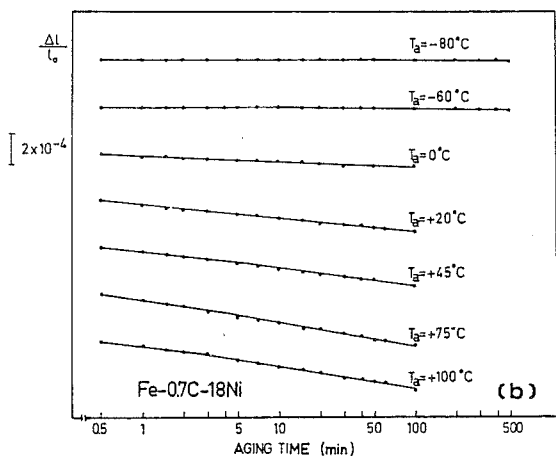
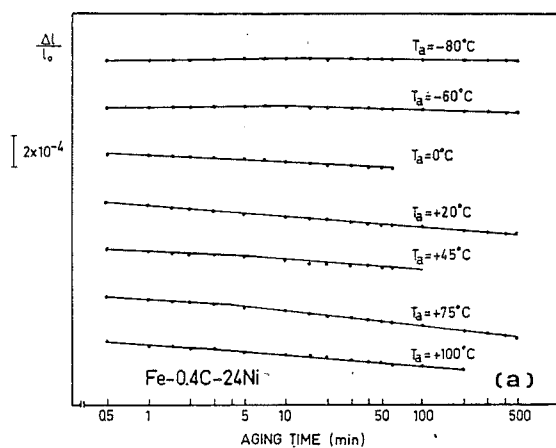


Fig.2. Relative length changes vs. time at different aging temperatures (T_a) for manganese steel. ($\Delta l/l_0$ not for 100% martensite)

Fig.1.a-c Relative length changes vs. time for 100% martensite at different aging temperatures (T_a) for nickel steels.

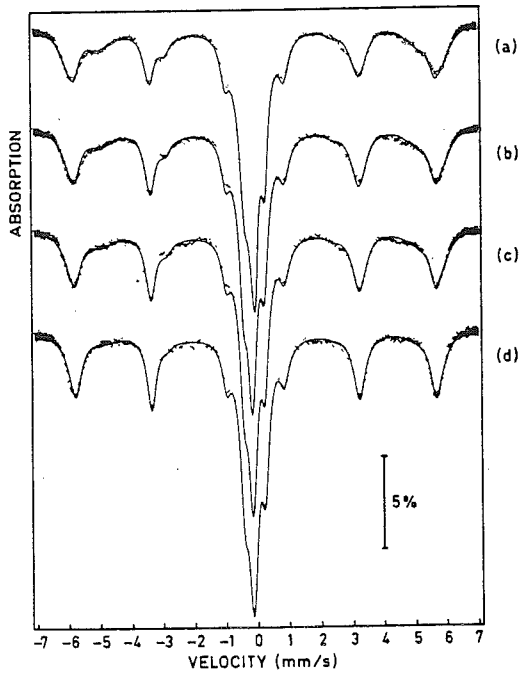


Fig.3. Mössbauer spectra of Fe-9Ni-1.4C martensite measured at 77K. The source is $\text{Co}^{57}:\text{Pd}$. (a) virgin martensite, (b) aged one hour at 35°C , (c) further aged 30h at 38°C and (d) still further aged 2.5h at 100°C . The central lines are due to retained austenite.

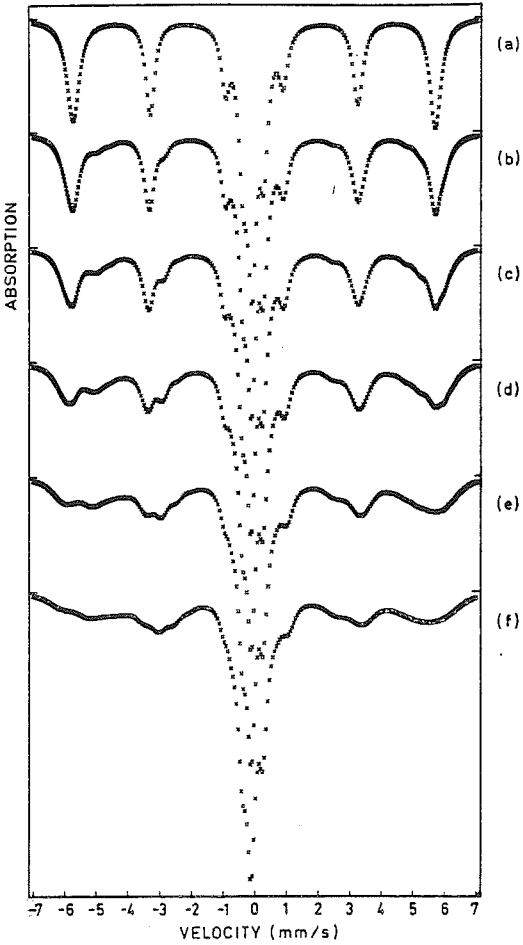
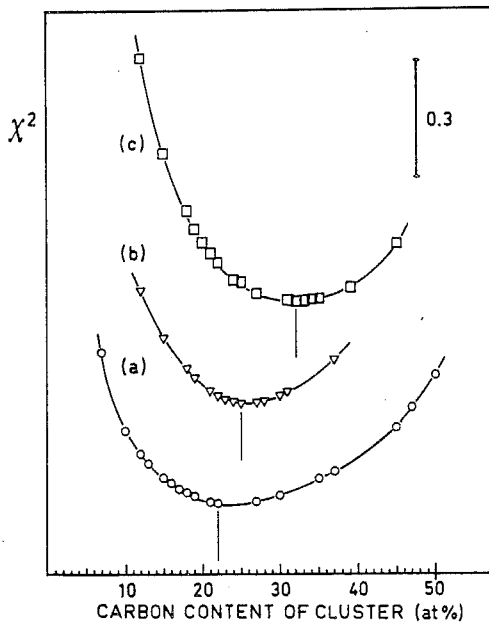


Fig.4. The simulation of the Mössbauer spectra of virgin martensite. The carbon contents are supposed to be: (a) 0at%, (b) 3at%, (c) 6at%, (d) 10at%, (e) 15at% and (f) 20at%. The other parameter values are the same as in the fitted spectrum shown in figure 3a.

Fig.5. The fitting accuracy of the Mössbauer spectra of aged Fe-9Ni-1.4C martensite as a function of the carbon content of the cluster phase. Aging times: (a) 1h at 35°C , (b) 30h at 38°C , (c) 2.5h at 100°C cumulatively as in figure 3.