The Effects of Carbon Contents and M_s Temperatures on the Hardness of Martensitic Fe-Ni-C Alloys*

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Synopsis

The effects of carbon on the strength of martensite have been studied by using Fe-Ni-C alloys with three levels of M_s temperature of approximately 350°, 220°, and -25°C. The carbon content ranged from 0.012 to 0.34 wt%, while the nickel content was varied to adjust the M_s temperature. Vickers hardness measurements were made to evaluate the strength of martensite.

For a range of carbon content (X_c) below approximately 0.06 wt%, the hardness (H) is independent of M_s temperature, which is represented by $H = 164 + 757 \cdot X_c^{1/2}$. However, beyond this content the hardness becomes greater the higher the M_s temperature, which is represented by $H = 170 + 449 \cdot X_c^{1/3}$ for the martensite with M_s of -25°C, $H = 302 + 794 \cdot X_c$ for the martensite with M_s of 220°C and $H = 292 + 956 \cdot X_c$ for the martensite with M_s of 350°C, respectively.

Precipitation hardening contributes to the overall hardness of martensite with M_s of 350° and 220°C. The two major strengthening mechanisms, such as precipitation hardening and solid solution hardening for the martensite with M_s of 350° and 220°C, have been analysed by measuring the electrical resistivity changes of the martensite after tempering.

I. Introduction

A number of studies have been recently made on the strength of ferrous martensite, on the assumption that all the carbon atoms were dissolved interstitially in solid solution of martensite. However, there are many differences in the results achieved in these works. For example, Winchell and Cohen¹⁻⁴⁾ have suggested that the strength of martensite has a cube-root dependence on carbon content, whereas Owen,⁵⁾ Chilton and Kelly,⁶⁾ and more recently Speich and Warlimont⁷⁾ have suggested a square-root dependence, while Leslie and Sober⁸⁾ have suggested a simple linear dependence.

The debate concerning the dependence of martensitic strength on carbon content may be attributed to the segregation of carbon or carbide precipitation which occurs during quenching only in those martensites with high M_s temperatures. Thus, it is necessary to investigate the strength dependence on carbon content for the alloys with various levels of M_s temperature. Recently, Kelly⁹⁾ has suggested that precipitation hardening may be as great as or even greater than the hardening due to solid solution hardening. However, the strengthening mechanisms responsible for the higher strength exhibited by ferrous martensite have not yet been discussed quantitatively.

In the present paper, Fe-Ni-C alloys containing carbon from 0.012 to 0.34 wt% were prepared to three levels of M_s temperature, such as approximately 350°, 220° and -25°C, by addition of nickel, and the effects of M_s temperatures on the strength of martensite of

these alloys were investigated. Secondly, the contributions of the two major hardening mechanisms, being considered to be the solid solution hardening by carbon and the precipitation hardening by carbide or segregation of carbon, to the overall strength of martensite were estimated by measuring the changes of electrical resistivities of the martensite after tempering at 100° and 120°C respectively.

II. Experimental Procedures

The alloys were melted in air by means of a high frequency induction furnace or Tammann furnace, using pure electrolytic iron, electrolytic nickel, and Fe-5 wt% C alloy. The melts were cast in a metallic mould, and annealed at 1200°C for a considerable time. All the ingots were hot-worked to bars with 10 mm in dia. The M_s temperatures for the alloys with M_s of 350° and 220°C were determined using a Formastor made by Fuji Electronic Co., using the cylindrical specimens, 3 (dia.) × 10 mm, while the M_s temperatures for the alloys with M_s of -25°C were determined microscopically by the appearance of sur-

Table 1. Chemical compositions and M_s points of alloys tested

Alloy No.	Composition (wt%)				M_s (°C)
	C	Ni	Mn	Fe	
350-1	0.047	8.67	—	bal.	370
350-2	0.087	7.73	—	bal.	350
350-3	0.170	6.83	—	bal.	350
350-4	0.220	5.99	—	bal.	330
350-5	0.300	4.10	—	bal.	360
350-6	0.340	2.24	—	bal.	340
220-1	0.044	15.37	0.51	bal.	230
220-2	0.100	14.17	0.48	bal.	210
220-3	0.200	12.32	0.47	bal.	220
220-4	0.240	11.45	0.49	bal.	230
220-5	0.310	9.65	0.51	bal.	227
-25-1	0.012	30.62	—	bal.	-(20~22)
-25-2	0.021	30.35	—	bal.	-(20~24)
-25-3	0.028	29.82	—	bal.	-(22~24)
-25-4	0.055	29.07	—	bal.	-(22~24)
-25-5	0.120	27.84	—	bal.	-(26~28)
-25-6	0.240	25.19	—	bal.	-(24~26)
-25-7	0.310	24.09	—	bal.	-(34~36)

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face relief on polished specimens which were subjected to subzero-treatment. The temperature levels of subzero-treatment were chosen between 20° to -40°C with 2°C intervals in alcohol solutions refrigerated by liquid nitrogen. The chemical compositions and M_s temperatures of alloys used in this study are listed in Table 1.

The thin plate specimens for hardness test, $2 \times 8 \times 15$ mm, were machined from the bars with 10 mm in dia., and the specimens for the measurement of electrical resistivity were cold extruded to wires with 1 mm in dia. All the specimens for hardness test and measurement of electrical resistivity were copper plated in order to prevent decarburization during heat-treatment, then austenitized for 15 min at 930°C in a vacuum-tube furnace, and violently quenched into iced brine. After quenching, the specimens with M_s of 350° and 220°C were immediately transferred into a liquid nitrogen bath and stored there to prevent any aging at room temperature. The plated copper on the hardness specimens was removed carefully by using a grinding machine operated under water supply just before performing hardness test, but the plated copper on the austenitic specimens with M_s of -25°C had been removed before they were subjected to subzero-treatment.

The hardness measurements were made at room temperature, using a Vickers hardness tester with a load of 10 kg. In the case of martensitic specimens with M_s of 220° and 350°C , it took about 15 min to finish the removal of the plated copper and the hardness test, while in the case of the specimens with M_s of -25°C , about 3 min were required to complete the hardness test. The measurement of electrical resistivity was made at 0°C using a wire, 500×1 (dia.) mm, by the potential drop technique. The specimens for

X-ray diffraction and microscopic examination were heat-treated under the same conditions as the hardness specimens. X-ray test was made by Shimadzu Diffractometer (VD-1A) using $\text{CoK}\alpha$ radiation. The lattice parameter of martensite was determined from diffraction line of (211) and half width of (211) line was also measured. The volume percent of austenite was estimated using the intensities of (110) martensite line and (111) austenite line as described later.

III. Experimental Results

1. Martensite with M_s of -25°C

The microstructures of Fe-Ni-C alloys with M_s of -25°C were examined before and after subzero-treatment at -196°C in liquid nitrogen. As shown in Photo. 1, before subzero-treatment the structures of alloys are completely austenitic, and after subzero-treatment at -196°C the structures are transformed into acicular martensite. Over the range of observed carbon content, it can be seen that the acicular mar-

Fig. 1. X-ray diffraction pattern of an Fe-Ni-C martensite with M_s of -25°C (Fe-29.07%Ni-0.055%C)

Photo. 1. Some microstructures of Fe-Ni-C alloys with M_s of -25°C , quenched to room temperature (above) and subjected to subzero-treatment at -196°C (below)

(a) Fe-27.84%Ni-0.12%C (b) Fe-25.19%Ni-0.24%C (c) Fe-24.09%Ni-0.31%C

tensite plates of the alloys are equal in size, independent of the level of carbon content.

The alloys were not transformed completely to martensite even by cooling in liquid nitrogen (-196°C), which contained a considerable amount of retained austenite, as shown in Fig. 1. Accordingly, various ratios of martensite-to-austenite were obtained for any given alloy by adjusting the cooling temperature below M_s temperature. Then the hardness of martensite-austenite aggregates was measured as a function of the volume percent of austenite. The hardness data are plotted in Fig. 2 as a function of the austenite content. The volume percent of austenite was determined by measuring the integrated intensities of X-ray diffraction lines, (111) austenite line, and (110) martensite line, using the following equations:

$$V_r = \frac{(R_a/R_r)I_r}{I_a + (R_a/R_r)I_r} \quad \text{.....(1)}$$

$$R = \frac{1}{V^2} \cdot F^2 \cdot P \cdot (L) \cdot e^{-2M} \quad \text{.....(2)}$$

where V_r is the volume fraction of austenite in mixture of austenite and martensite, I_r and I_a are the integrated intensities of austenite and martensite respectively, R_a and R_r correspond to R in Eq. (2) for martensite and austenite, which is determined by the following terms: V , the unit cell volume; F , the structural factor; P , the multiplicity factor; (L) , the Lorentz polarization factor and e^{-2M} , the temperature factor. As for the factors in Eq. (2), the values suggested by Cullity were assigned.¹⁰⁾ The unit cell volume was calculated from the measured lattice parameters of the martensite

Fig. 2. Hardness of martensite-austenite aggregates in the Fe-Ni-C alloys with M_s of -25°C

Table 2. Values used for the calculation of R_a and R_r corresponding to R in Eq. (2) (Fe-24.09%Ni-0.31%C alloy, $\text{CoK}\alpha$ radiation)

Plane	a_0 (Å)	$1/V^2$	θ	f	F^2	P	L	e^{-2M}	R (calculated)
M (110)	2.8684	1.795×10^{-3}	26.11	13.51	730	12	7.9	0.958	$R_a = 119$
A (111)	3.5862	4.7×10^{-4}	25.63	13.58	2951	8	8.25	0.96	$R_r = 87.9$

and austenite in the alloys. The values of some factors were slightly different, according to the composition of the alloys. The typical values used for the calculation of R are listed in Table 2.

As shown in Fig. 2, the hardness of the alloys with relatively high carbon content decreases gradually as the volume percent of austenite increases up to about 25%, and beyond this the hardness decreases rapidly with austenite content. However, for the alloys with comparatively low carbon content, the hardness decreases gradually and linearly with increasing volume percent of austenite up to about 30%.

The hardness of 100% martensite for each alloy was obtained by extrapolating the hardness data to zero percent austenite in Fig. 2. The extrapolated results are shown in Fig. 3 as a function of carbon content and also the observed values of half width of the (211) martensite line in X-ray diffraction are plotted as a function of carbon content in Fig. 3. The two curves in Fig. 3 are completely parallel. Generally, it has been accepted that the broadening of X-ray diffraction line is attributed to particle size and microstresses in a crystalline material. However, the effect of particle size on the line width is neglected when the average linear dimension of the crystal is greater than 10^{-4} cm.¹¹⁾ In the case of this Fe-Ni-C martensite with M_s of -25°C , because martensite crystals are not only larger than 10^{-4} cm but equal in size over the range of observed carbon content, it is clear that the trend of the line width curve in Fig. 3 is due mainly to internal strain caused by carbon atoms dissolved interstitially in martensite. As a result, from the fact that two curves in Fig. 3 run parallel to each other, the martensite with M_s of -25°C may be considered to be the virgin martensite.

Fig. 3. Effect of carbon content on the hardness of 100% martensite and the half width of (211) line for the Fe-Ni-C alloys with M_s of -25°C

The hardness of 100% martensite can be plotted as a function of square-root of carbon content and cube-root of carbon content as shown in Figs. 4 and 5, respectively. As shown in Fig. 4, the hardness of as-quenched Fe-Ni-C martensite with M_s of -25°C varies linearly with the square-root of carbon content for a range of carbon content less than about 0.06 wt%. However, for the carbon content greater than about 0.06 wt%, the hardness varies linearly with cube-root of carbon content, as shown in Fig. 5.

The hardness of Fe-Ni-C martensite with M_s of -25°C is represented by the following equations:

$$H = 164 + 757 \cdot X_c^{1/2} \quad \text{.....(3)}$$

$$H = 170 + 449 \cdot X_c^{1/3} \quad \text{.....(4)}$$

Fig. 4. Hardness of 100% martensite of Fe-Ni-C alloys with M_s of -25°C as a function of the square-root of the carbon content

where H is Vickers hardness value and X_c is carbon content (wt%).

Equation (3) is applied for a range of carbon content less than approximately 0.06 wt% and Eq. (4) for a range of carbon content greater than approximately 0.06 wt%.

2. Martensite with M_s of 350° and 220°C

The alloys were quenched into iced brine from 930°C . Photograph 2 shows the microstructures of some alloys with M_s of 350° and 220°C . It can be seen that these structures are relatively fine and are independent of carbon content and of M_s temperature. In all the alloys with M_s of 350° and 220°C , it was found, using X-ray diffraction, that complete transformation to martensite was achieved as shown in Fig. 6.

The hardness values of these alloys are plotted as a function of carbon content in Fig. 7. For a range of

Fig. 5. Hardness of 100% martensite of Fe-Ni-C alloys with M_s of -25°C as a function of the cube-root of the carbon content

Photo. 2. Some microstructures of as-quenched martensite with M_s of 350° and 220°C

$M_s = 350^\circ\text{C}$: (a) Fe-7.73%Ni-0.087%C (b) Fe-5.99%Ni-0.22%C (c) Fe-4.1%Ni-0.30%C
 $M_s = 220^\circ\text{C}$: (d) Fe-14.17%Ni-0.10%C (e) Fe-12.32%Ni-0.20%C (f) Fe-9.65%Ni-0.31%C

carbon content greater than approximately 0.06 wt%, a good linear relationship exists between the hardness and the carbon content for the respective M_s temperature. The difference between the hardness values of both martensites with M_s of 350° and 220°C becomes larger with increasing carbon content. The hardness of martensite with M_s of 350° and 220°C in Fig. 7, can be represented by Eqs. (5) and (6), respectively:

$$H = 292 + 956 \cdot X_c \quad \text{.....(5)}$$

$$H = 302 + 794 \cdot X_c \quad \text{.....(6)}$$

Fig. 6. X-ray diffraction pattern of an Fe-Ni-C martensite with M_s of 220°C (Fe-11.45%Ni-0.24%C alloy)

Fig. 7. Hardness of Fe-Ni-C martensite with M_s of 350° and 220°C as a function of the carbon content

Fig. 8. Variation of the half width of (211) line with the carbon content for the Fe-Ni-C martensite with M_s of 350° and 220°C

where H is Vickers hardness value and X_c is carbon content (wt%).

The half width of X-ray diffraction line for the martensite with M_s of 220°C is greater than that with M_s of 350°C, as shown in Fig. 8. This means that the amount of carbon dissolved in martensite is greater in the lower M_s martensite than in the higher M_s martensite, provided the half width of X-ray diffraction line of martensite is a measure of carbon amount dissolved in the martensite.^{12,13)}

3. Comparison of the Hardness of Martensite with M_s of 350°, 220°, and -25°C

The hardness values of the martensite with M_s of 350°, 220° and -25°C are replotted as a function of carbon content in Fig. 9. The hardness of martensite for carbon content greater than about 0.06 wt% becomes higher with increasing M_s temperature and carbon content. For the relatively high carbon content, the hardness of martensite with M_s of 350° and 220°C is still higher than that of the virgin martensite with M_s of -25°C. Although Kelly⁶⁾ and Owen⁵⁾ have reported that, for the virgin martensite with carbon content below approximately 0.3 wt%, the yield strength of twinned martensite becomes slightly higher than that of lath martensite with increasing carbon content, the three lines in Fig. 9 will coincide with one another when any form of precipitation does not occur during quenching in the alloys with M_s of 350° and 220°C. Therefore, it seems that the hardening of martensite with the two higher M_s temperatures involves a contribution of precipitation hardening during quenching. This factor will be negligible when the carbon content is sufficiently low, but becomes significant when the carbon content is high.

The factors which seem likely to contribute to the hardness of martensite are:⁹⁾

(a) Interstitial solid solution hardening by carbon,

Fig. 9. Hardness of Fe-Ni-C martensite as a function of the M_s temperature and of the carbon content

- (b) Precipitation, segregation, or some other form of diffusional process involving carbon atoms,
- (c) The substructure of martensite (dislocation and internal twin),
- (d) The size of the martensite plates,
- (e) Elements in substitutional solid solution.

In this experiment, the nickel was used in order to adjust the M_s temperature of the martensite. Substitutional elements such as nickel can lead to an increase in hardness of ferrite and of carbon-free martensite.¹⁴⁾ The substitutional solid solution hardening due to the addition of nickel up to 10 at% increases with nickel content, but increasing the nickel content from 10 to 30 at% has virtually no effect on the strength of Fe-Ni martensite.^{2,14)}

It is necessary to investigate whether the addition of nickel to martensite containing carbon would have the same effect or not. However, when nickel is added to Fe-C alloys in order to determine the effect of nickel on the hardness of the corresponding martensite, the M_s temperature decreases with the addition of nickel, on which the precipitation of carbon during quenching is very dependent. Therefore, it is impossible to investigate the solid solution hardening effect of nickel in Fe-C martensite directly. Recently, Kelly⁶⁾ has suggested that the solution hardening effect of nickel in Fe-Ni-C martensite can be neglected.

The hardness of martensitic pure iron, obtained by extrapolating the straight lines to zero carbon content in Figs. 4 and 5, indicates 164 and 170 H_V respectively. These values are in good agreement with the value of 164 H_V observed directly using martensitic pure iron by Bibby and Parr.¹⁵⁾ Therefore, it may be concluded that the solution hardening effect of nickel in Fe-Ni-C martensite hardness can be neglected. The martensite grain size will be determined approximately by the prior austenite grain size, since a martensite crystal can never be larger than the austenite grain within which it forms. The correlation between the yield strength of carbon free-martensite and the parent austenite grain size will conform to the Petch type relation.³⁾ The crystal of martensite with M_s of -25°C was relatively larger than that of the martensites with M_s of 350° and 220°C . However, such a difference in size between their martensite crystals will not affect the relatively high hardness of martensite, particularly that containing carbon.

As a result, the hardness of Fe-Ni-C martensite can be represented by the following terms:

$$H = H_0 + \Delta H_{\text{sub}} + \Delta H_s + \Delta H_p \dots\dots\dots(7)$$

where H is the overall hardness of the martensite, H_0 the hardness of ferritic pure iron, ΔH_{sub} the increase in hardness due to the substructure introduced by the martensitic transformation, ΔH_s the solid solution hardening response due to carbon atoms, and ΔH_p the precipitation hardening response due to carbide or segregation of carbon atoms. In this study, the contribution of these hardening factors to the overall hardness of martensite, with M_s of 350° and 220°C respectively, was evaluated by measuring the changes of electrical

resistivity after tempering the martensite.

The wire specimens of the prepared alloys with various M_s temperatures, austenitized at 930°C for 15 min, were quenched into iced brine and immediately transferred into liquid nitrogen. The electrical resistivity of as-quenched martensite was measured at 0°C by means of the potential drop technique, and then the specimens were tempered for one hour at various temperatures up to 200°C . The results obtained for the martensite (about 0.22 wt% C) with three levels of M_s temperature are shown in Fig. 10. The magnitude of the resistivity change is the greater the lower the M_s temperature. These results mean that the amount of carbon dissolved in martensite is the greater the lower the M_s temperature, because at relatively low tempering temperatures the decrease in resistivity is due to the depletion of the carbon atoms in the solution of martensite. Therefore, the amount of carbon dissolved in as-quenched martensite with M_s of 220° and 350°C can be estimated by comparing their electrical resistivity changes with that of the martensite with M_s of -25°C . Figure 11 shows the electrical resistivity changes for the martensite with M_s of -25°C , which are those for 100% martensite corrected for retained austenite. The magnitude of the resistivity change is greater the higher the carbon content dissolved in the martensite at a given tempering temperature.

The relationship between the magnitude of electrical resistivity change and the dissolved carbon content for the martensite is represented by a straight line at relatively high tempering temperatures, whereas at lower tempering temperatures the relationship is represented by a curved line. In this study, the straight line of 120°C tempering and the curved line of 100°C tempering were selected to estimate the carbon content dissolved in the martensite from the change of electrical resistivity. The magnitude of electrical resistivity changes ($\Delta\rho$) of the martensite with the two high M_s temperatures, after the tempering of one hour at 100° and 120°C , is given in the third column of Table 3. The carbon content (X_s) dissolved in the as-quenched martensite with the two high M_s temperatures can be determined as the point corresponding to the measured electrical resistivity change of this martensite in the

Fig. 10. Change in electrical resistivity of the Fe-Ni-C martensite with the tempering temperature and with the M_s temperature. Tempering time: 1 hr

Table 3. Estimated values of the contributions of the hardening factors to the overall hardness of as-quenched martensite with M_s of 350° and 220°C

(a) Estimation from the change of electrical resistivity after tempering at 120°C

M_s (°C)	X_c	$\Delta\rho$	X_s	X_p	H	$H_o + \Delta H_{sub} + \Delta H_s$	ΔH_s	ΔH_p	$(\Delta H_s)\%$	$(\Delta H_p)\%$	$(\Delta H_{sub})\%$
350	0.22	6.5	0.134	0.086	502	405	241	97	48.0	19.3	16.7
	0.30	9.0	0.184	0.116	590	429	265	161	45.0	27.3	14.2
	0.34	11.5	0.236	0.104	604	448	284	156	47.0	25.8	13.9
220	0.20	8.0	0.164	0.036	452	420	256	32	56.6	7.1	18.6
	0.24	9.0	0.184	0.056	485	429	265	56	54.6	11.5	17.3
	0.31	11.0	0.226	0.084	550	446	282	104	51.3	18.9	15.3

(b) Estimation from the change of electrical resistivity after tempering at 100°C

M_s (°C)	X_c	$\Delta\rho$	X_s	X_p	H	$H_o + \Delta H_{sub} + \Delta H_s$	ΔH_s	ΔH_p	$(\Delta H_s)\%$	$(\Delta H_p)\%$	$(\Delta H_{sub})\%$
350	0.22	6.0	0.150	0.070	502	414	250	88	50.0	17.5	16.7
	0.30	7.0	0.176	0.124	590	426	262	164	44.0	27.8	14.2
	0.34	8.0	0.200	0.140	604	436	272	168	45.0	27.8	13.9
220	0.20	6.0	0.150	0.050	452	414	250	38	55.0	8.4	18.6
	0.24	7.0	0.174	0.066	485	425	261	60	54.0	12.4	17.3
	0.31	9.5	0.242	0.068	550	451	287	99	52.0	18.0	15.3

Fig. 11. Change in electrical resistivity as a function of the carbon content for the 100% martensite of Fe-Ni-C alloys with M_s of -25°C , after tempering of 1 hr at the temperatures indicated

corresponding tempering line in Fig. 11.

The solution hardening response due to the measured value of carbon content, ΔH_s , was determined by subtracting the hardness of martensitic pure iron, $H_o + \Delta H_{sub} = 164 H_V$, from the hardness value ($H_o + \Delta H_{sub} + \Delta H_s$) corresponding to the measured carbon content (X_s) in the hardness-carbon curve of the martensite with M_s of -25°C in Fig. 9. The values of ΔH_s for the alloys are listed in the eighth column of Table 3. Then, the precipitation hardening response, ΔH_p , was evaluated from Eq. (7), as shown in Table 3. The value of H_o was determined as $80 H_V$ experimentally,

Fig. 12. Precipitation hardening response in the martensite with M_s of 350° and 220°C as a function of the cube-root of the precipitated carbon content

and hence the value of ΔH_{sub} became $84 H_V$.

The estimated values of the contributions of the hardening factors to the overall hardness (H) of as-quenched martensite with M_s of 350° and 220°C, respectively, are listed in Table 3. From the Table 3, it can be seen that the effect of precipitation hardening on the as-quenched hardness becomes predominant in the alloys which contain higher levels of carbon or have higher M_s temperature. The precipitation hardening response, ΔH_p , is plotted as a function of cube-root of precipitated carbon content in Fig. 12. The carbon content precipitated or segregated during quenching (X_p) is plotted as a function of total carbon content (X_c) in Fig. 13. It can be seen that X_p is greater in the martensite with M_s of 350°C than in the martensite with M_s of 220°C.

IV. Discussion

Hardness and yield strength data for low carbon martensite and iron-nickel alloys with various carbon

Fig. 13. Relationship between the total carbon content and the precipitated carbon content produced during quenching for the Fe-Ni-C martensite with M_s of 350° and 220°C

contents were accumulated by Speich and Warlimont.⁷⁾ A good linear relationship exists between the Vickers hardness (H_V) and the 0.2% yield strength (σ_y) of as-quenched martensite, and the yield strength thus can be represented by the following equation:

$$\sigma_y = 375.88(H_V - 26.3) \times 7 \times 10^{-4} \text{ (kg/mm}^2\text{)} \dots\dots(8)$$

Therefore, the measured hardness values for the martensite in this study can be compared with the yield strength in the following discussion of the strength of martensite referring to the results of other previous papers.

The yield strength of virgin martensite is usually represented by the equation:

$$\sigma_y = \sigma_i + m(X_c)^n \dots\dots\dots(9)$$

where σ_y is the yield strength defined at some strain, σ_i the yield strength of martensitic pure iron, m a constant which is a measure of the strength of the interaction of the carbon atoms with the dislocations responsible for plastic flow, X_c the carbon content in solution, and n an exponent of which value depends on the strengthening mechanism being considered.

σ_i is composed of the three terms:

$$\sigma_i = \sigma_o + \sigma_{\text{sub}} + kd^{-1/2} \dots\dots\dots(10)$$

where σ_o is the friction stress of the basic lattice, σ_{sub} the strengthening increment due to substructural defects such as dislocations, twins, and cell walls arising from the martensitic transformation, k the Petch constant, and d the martensitic grain size.

The effect of martensitic plate size on the yield strength is very small except in the cases of special thermomechanical treatments, so that the last term ($kd^{-1/2}$) can be neglected.

The value of n in Eq. (9) depends upon the value chosen for the intercarbon distance along the dislocation line. Thus, in the theory of Fleischer,^{16,17)} it is assumed that the dislocation only interacts with the carbon atoms adjacent to the slip plane and a value of n equal to 1/2 is obtained. In the theory of Winchell and Cohen,^{2,4)} it is assumed that the dislocations can cross slip or bend out of the slip plane and thus in-

teract also with other carbon atoms which are not on the slip plane, and value of n can be taken as 1/3. If the ordering of carbon atoms occurs uniformly along the dislocation line as proposed by Schoeck and Seeger,¹⁸⁾ a value of n will be unity which may be applied to ferrite.

In Figs. 4 and 5, it is obvious that the measured hardness shows square-root dependence on carbon content below approximately 0.06 wt%, and cube-root dependence on carbon content above approximately 0.06 wt%. In the case of relatively low carbon content, such as below 0.06 wt% C, because the carbon atoms are homogeneously distributed in martensitic lattices and, further, the driving force for the carbon atoms to segregate at dislocations is very small, each distortion dipole caused by interstitial carbon atoms will be independent and stable up to the strain corresponding to the yield strength. Therefore, all the carbon atoms in the solution of martensite contribute to the strengthening by Fleischer model. Thus, the hardness (0.2% yield strength) is proportional to square root of carbon content. However, in the case of relatively high carbon content, such as above approximately 0.06 wt% C, some carbon atoms initially lie so close together that the dipole stress fields may perhaps overlap one another. Further, the driving force for carbon atoms to diffuse to dislocations is relatively so high that the carbon atoms around the moving dislocations are rearranged to lower free energy of the martensite. During this rearrangement, some carbon distortion dipole stress fields may overlap one another, or some carbon atoms may diffuse into the dislocation cores due to the interaction of carbon atoms with dislocations. As a result, because the number of effective distortion dipoles is reduced, the hardness (0.2% yield strength) is not proportional to the square-root of carbon content as predicted by the Fleischer model.

Richman¹⁹⁾ investigated the plastic deformation modes at room temperature in Fe-Ni-C martensites with M_s between -30° and -35°C as a function of carbon content, and has reported that at very low carbon levels deformation occurs by wavy slip, at about 0.05 wt% C the deformation begins to accompany mechanical twinning, and beyond approximately 0.4 wt% C the mechanical twinning becomes effectively the only plastic mode. As shown in Fig. 4, the change of slope in hardness-carbon curve has been observed at approximately 0.06 wt% C. It seems that this content of 0.06 wt% C corresponds to the composition at which mechanical twinning begins to appear during deformation. Converting the hardness data into 0.2% yield strength by Eq. (8), Eq. (3) is changed into the following equation:

$$\sigma_y = 36.23 + 199.2X_c^{1/2} \text{ (kg/mm}^2\text{)} \dots\dots\dots(11)$$

The value of 36 kg/mm² for the strength of martensitic pure iron is somewhat smaller than the value of 42 kg/mm² found by Speich and Warlimont,⁷⁾ but is in agreement with 37.8 kg/mm² obtained by extrapolating strength of Fe-N martensite on a square-root basis to zero percent nitrogen by Roberts,²⁰⁾ and also

with the value obtained directly from the martensitic pure iron by Bibby and Parr.¹⁵⁾ From Eqs. (9) and (11), the value of m becomes 199 kg/mm² for the martensite with M_s of -25°C . This value is nearly equal to the value of 175 kg/mm² found by Speich and Warlimond⁷⁾ for Fe-C martensite.

The hardness in the range of carbon content less than about 0.06 wt% is just the same value for the martensite with different M_s temperatures in this study. These results may indicate that (1) autotempering does not occur during quenching in those martensites containing carbon less than about 0.06 wt% and having M_s between -25° and 350°C , (2) even if some form of precipitation occurs during quenching, the increment of the hardness due to the precipitation corresponds to the loss in the hardness of solid solution due to the removal of the carbon from the solution. As shown in Fig. 13, extrapolating the data to zero percent precipitated carbon, the total carbon content becomes about 0.06 wt% C for the martensite with M_s of 220°C and about 0.02 wt% C for the martensite with M_s of 350°C . These results show that the martensite with M_s of 220°C corresponds to the case (1) mentioned above, and the martensite with M_s of 350°C to the case (2). As a result, it may be concluded that the martensite with M_s temperature below 350°C containing carbon less than about 0.06 wt% can be treated in the same way as virgin martensite in relation to the hardness of martensite without considering any component of precipitation hardening during quenching.

However, the precipitation hardening response appears clearly in the range of carbon content greater than approximately 0.06 wt% for the martensite with M_s of 350° and 220°C . As shown in Fig. 12, the relationship between the precipitation hardening response (ΔH_p) and the cube-root of precipitated carbon content is linear, and the precipitation hardening response is thus represented by the following equation:

$$\Delta H_p = 790 \cdot X_p^{1/3} - 240 \quad \text{.....(12)}$$

where X_p is the precipitated carbon content above approximately 0.04 wt%. The precipitation hardening response ($500 H_V$) obtained by Kelly⁹⁾ for the plain carbon martensite with 0.8 wt% C ($X_p = 0.6$ wt% C), can be obtained from Eq. (12) by neglecting the solution hardening effect of nickel ($75 H_V$).

Conrad²¹⁾ has proposed that the strength of tempered martensite can be represented by the equation:

$$\sigma_f = \sigma_f(T) + \alpha_1 \mu b \rho^{1/2} + \alpha_2 \mu b \frac{1}{\lambda} + \alpha_3 f / b a_o^3 + k d^{-1/2} \dots \text{.....(13)}$$

where $\sigma_f(T)$ is the thermal component, α_1 , α_2 and α_3 , are constants, μ the shear modulus, b the Burgers vector, ρ the dislocation density, λ the precipitate spacing, f the atomic fraction of carbon in solution, and a_o the lattice constant of the solvent. As well known, the second, third, and fourth terms in Eq. (13) represent the strengthening response due to the dislocation, precipitation, and carbon solution, respectively.

Equation (12) is qualitatively in agreement with the

precipitation hardening term, $\alpha_2 \mu b 1/\lambda$, in Eq. (13) because, if there are n precipitated carbon atoms in unit volume of as-quenched martensite, which are changed into N carbide particles, then N is proportional to n , and the mean distance between carbide particles λ is $(1/N)^{1/3}$, thus $1/\lambda$ is $N^{1/3}$, accordingly $1/\lambda$ is proportional to $n^{1/3}$. Therefore, the precipitation hardening for the martensite with M_s of 220° and 350°C in this study is considered not to be attributable to some form of segregation of carbon due to diffusion of carbon to dislocations, but to some form of carbide such as ϵ -carbide or cementite in the tempered martensite. The relationship between the precipitated carbon content (X_p) and the total carbon content (X_c) is linear, as shown in Fig. 13. According to Cottrell and Bilby,²²⁾ the carbon amount diffusing to the dislocations due to the interaction energy of carbon atoms with dislocations in the cold worked alpha-iron is represented by the equation:

$$C_t = 3C_o L \left(\frac{1}{2\pi} \right)^{1/3} (Adt/kT)^{2/3} \quad \text{.....(14)}$$

where C_t is the number of carbon atoms migrated to dislocation per unit volume of the material in time t , L the total length of edge dislocation per unit volume, C_o the number of carbon atoms dissolved initially in unit volume, A the constant estimated as approximately 1.4×10^{-20} dyne·cm² for carbon or nitrogen in alpha-iron, and D the diffusion coefficient at the absolute temperature T . Hillert has suggested the following relationship for approximating the diffusion coefficient of carbon in martensite:²³⁾

$$\begin{aligned} D_c^M &= D_c^s \cdot \exp \left[-\frac{6700 \cdot X_c}{2RT} \right] \\ &= 0.02 \exp \left[-\frac{20100 + 3350 \cdot X_c}{RT} \right] \quad \text{.....(15)} \end{aligned}$$

where D_c^M is the diffusion coefficient of carbon in martensite, X_c the carbon content in wt%, R the gas constant, and T the absolute temperature. The Eqs. (14) and (15) can be applied to the martensite with M_s of 350° and 220°C in this study. Thus, when the required time from M_s to M_f during quenching (t) and the dislocation density (L) are assumed to be constant for the respective martensite with the same M_s temperature, the relationship between C_t and C_o is represented by curve similar to parabola for the martensite with M_s of 350° and 220°C . However, the experimentally determined relationship was linear as shown in Fig. 13. This supports further the opinion that the precipitation hardening in the martensite with M_s of 350° and 220°C in this study is due to the type and amount of carbide. The previous workers²⁴⁻²⁶⁾ have reported that cementite is formed in low carbon martensite due to autotempering during quenching. However, in this study, it has been considered that ϵ -carbide may be formed rather than cementite during quenching, considering that the alloys contain a considerable amount of nickel which prevents the formation of cementite.

For the martensite of 0.3 wt% C with M_s of 350°C ,

the precipitation hardening response (ΔH_p) was measured as the values of 161 and 164 H_V (about 36 kg/mm² in yield strength), as shown in Table 3. If the spacing of precipitates (λ) can be estimated by the equation $\sigma_y = 2\mu b/\lambda$, λ becomes about 1 000 Å when put $\sigma_y = 36$ kg/mm², $\mu = 8$ 000 kg/mm² and $b = 2.5 \times 10^{-8}$ cm. This value of λ may be acceptable for a tempered martensite.

V. Conclusions

Results obtained in this study are summarized as follows:

(1) For a range of carbon content (X_c) below about 0.06 wt%, the hardness (H) of martensite is independent of M_s temperature, which is represented by $H = 164 + 757 \cdot X_c^{1/2}$. However, beyond this content, the hardness increases with the M_s temperature and is represented by $H = 170 + 449 \cdot X_c^{1/3}$ for the martensite with M_s of -25°C , $H = 302 + 794 \cdot X_c$ for the martensite with M_s of 220°C , and $H = 292 + 956 \cdot X_c$ for the martensite with M_s of 350°C , respectively.

(2) The half width for (211) martensite line becomes broader with decreasing M_s temperature and likewise the magnitude of electrical resistivity change of martensite after tempering becomes also greater.

(3) The precipitation hardening contributes to the overall hardness of the martensite with M_s of 220°C as well as 350°C .

As an example, for the martensite of 220°C M_s with carbon content ranging from 0.20 to 0.31 wt%, the contribution of precipitation hardening (ΔH_p) is measured from 8 to 18% and the contribution of solid solution hardening (ΔH_s) from 51 to 57%, and for the martensite of 350°C M_s with carbon content ranging from 0.22 to 0.34 wt%, the ΔH_p is measured from 17 to 28% and the ΔH_s from 45 to 50%.

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