Microstructure-Composition Relationships and M_s Temperatures in Fe-Cr-Mn-N Alloys

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Microstructure-composition relationships and M_s temperatures have been determined in high purity nitrided Fe-Cr-Mn alloys, as part of a program to develop improved corrosion-abrasion resistant steels with unstable austenitic microstructures. Compositions in the range 8 to 12 pct Cr, 0 to 10 pct Mn, and 0 to 0.6 pct N were investigated by a resistivity technique to determine M_s temperatures and by X-ray diffraction and metallography to determine constitution. Hardness measurements were also made. At the low alloy end of the range, microstructures after annealing and air cooling are fully martensitic while at the high alloy end they are fully austenitic. At intermediate compositions, mixed martensite-austenite microstructures (with epsilon present as a minor phase in some cases) and unstable austenitic microstructures are obtained. The austenitic alloys contain a high density of stacking faults and the unstable austenitic alloys transform to martensite on deformation. At low N contents (up to at least 0.25 pct N) the M_s-composition relationship is linear and described by:

$$M_s = 555 - 9(\mathrm{Cr} - 8) - 40\mathrm{Mn} - 450\mathrm{N} \qquad [1]$$

where M_s is in °C and Cr, Mn, and N are the weight percentages of these elements. At higher N contents, the M_s generally falls more rapidly with increasing nitrogen content. Nitrogen solubility at 1050 °C exceeds about 0.3 pct in all alloys and increases with increasing Cr and Mn content. In commercial purity steels, unstable austenitic microstructures are expected to be obtained in compositions around 10 to 14 pct Cr, 8 to 12 pct Mn, and 0.1 to 0.3 pct N when the total level of these elements is selected to ensure the M_s is below room temperature.

I. INTRODUCTION

In recent years there has been considerable interest in austenitic stainless steels strengthened with nitrogen. As well as the strengthening effect, additions of nitrogen to an austenitic steel increase the stability of austenite. The nitrogen bearing austenitic steels which are now commercially available are therefore highly stable. This paper investigates steels in which the major alloying elements (Cr and Ni) have been reduced such that the austenite is unstable with respect to deformation despite the presence of significant quantities of nitrogen.

The work reported here was undertaken as part of a program to develop steels for the arduous conditions found in hard-rock mines. The steels need to be corrosion resistant, wear resistant, tough, formable, weldable, and relatively cheap. A conceptual steel which could meet these requirements is one comprising more than 8 pct Cr to confer corrosion resistance to typical mine waters, an austenitic microstructure to confer toughness and formability, instability of the microstructure under deformation combined with a high interstitial content to promote high work hardening and wear resistance, absence of carbon to safeguard weldability, and low levels of expensive alloying elements such as Cr and Ni to minimize cost. The Fe-Cr-Mn-N system was identified as promising, and unstable austenitic steels from this system with the required properties have been developed at Fulmer Research Laboratories.[1]

This paper describes the first stage of the develpment, which was to determine the microstructure-composition relationships and martensite start temperatures (M_s) in Fe-Cr-Mn-N alloys. Further developments in composition optimization and property determination followed, and these are reported in a companion paper.[2]

In order to obtain an austenitic microstructure, it is necessary that austenite forms at the annealing temperature and that the austenite is retained to room temperature; *i.e.*, M_s must be below room temperature.

Nickel, manganese, and nitrogen favor the formation of austenite at annealing temperatures but chromium does not. The first objective of this work was to ascertain whether fully austenitic structures could be obtained during annealing of low chromium (8 pct to 12 pct) alloys using manganese and nitrogen to replace nickel.

M_s temperatures are reduced by most alloying elements, including Cr, Ni, Mn, and N, and the effect of alloying elements on M_s temperatures has been widely investigated (*e.g.*, References 3 through 8). The reported M_s temperature-composition relationships differ widely and in general are valid only for the composition range for which they were derived. None of the published M_s-composition relationships specifically covers the Fe-Cr-Mn-N system and the second objective of this work was, therefore, to determine the M_s-composition relationship in this system.

If the austenite is to be unstable at room temperature, the temperature below which martensite forms under deformation, M_d, must be above room temperature. The M_d is generally 100 to 200 °C above the M_s, and a further objective of this work was to ascertain qualitatively whether martensite is formed by deformation in austenitic alloys with M_s temperatures up to 200 °C below room temperature.

The transformation from austenite to martensite under deformation can be expected to cause considerable work hardening, particularly if the martensite is hard. Since work hardening is expected to be beneficial to wear resistance, a

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further objective of this work was to determine the effect of nitrogen on the hardness of alloy martensites.

The composition range chosen for investigation was 8 pct to 12 pct Cr, 0 to 10 pct Mn, and 0 to 0.6 pct N. The chromium level was chosen to be as low as possible while providing some corrosion resistance (minimum 8 pct). Manganese was selected in preference to nickel since it is considerably less costly, enhances nitrogen solubility,[9,10] and lowers the stacking fault energy,[11] promoting work hardening.[12] Nitrogen was selected in preference to carbon since it is much less likely to lead to sensitization during welding.[13] Wide ranges of manganese and nitrogen were chosen because their effects both separately and together are relatively unknown. Low nitrogen contents have the advantage that they can be more readily incorporated during steelmaking whereas higher nitrogen contents reduce the M_s and further strengthen the alloy.

High purity alloys were used throughout the investigation to ensure that the effect of minor elements would not obscure the effects of the elements of interest, Cr, Mn, and N.

Although in commercial steelmaking practice nitrogen would be incorporated in the melt, it was decided to introduce nitrogen to solid Fe-Cr-Mn alloys by a gas nitriding technique, to minimize composition variations between samples. (The behavior of commercial purity alloys produced from nitrogen-bearing melts is discussed in the companion paper.[2]) Thus, six base Fe-Cr-Mn alloys were prepared and nitrided to give 22 compositions for investigation. M_s temperatures were determined by a resistivity technique, and the constitution of the alloys was investigated by X-ray diffraction and metallography. Hardness tests were also carried out.

II. EXPERIMENTAL DETAILS

A. *Preparation of Alloys*

Six 1 kg ingots with nominal compositions of 8 pct or 12 pct Cr and 0 pct, 5 pct, or 10 pct Mn were prepared from high purity Armco iron, low carbon ferrochromium, and low carbon ferromanganese alloys. The ingots were hot and cold rolled to give 1.0 mm thick strip. Chemical analyses of the six alloys are given in Table I. The amounts of elements other than those tabulated were negligible.

B. *Nitriding*

Nitrogen was introduced into the base material by high temperature nitriding in high purity nitrogen-hydrogen gas mixtures as described elsewhere.[9,14]

The nitriding conditions and the analyzed nitrogen contents are given in Table II. The introduction of >0.4 pct N into 8 pct Cr and 8 pct Cr-5 pct Mn alloy was not attempted since the required reaction temperature was below 1000 °C, where formation of nitrides will inhibit nitrogen transfer.

Table I. Chemical Analyses of Base Alloys

Nominal Composition	Analysis (Wt Pct)			
	Cr	Mn	C	N
8Cr	8.1	0.12	0.017	0.017
8Cr-5Mn	7.8	4.95	0.014	0.011
8Cr-10Mn	8.19	10.24	0.022	0.014
12Cr	12.50	0.094	0.008	0.017
12Cr-5Mn	11.7	5.03	0.012	0.016
12Cr-10Mn	12.23	10.13	0.014	0.018

C. *M_s Determination*

Specimens for determination of M_s temperatures were prepared from the nitrided coupons. Standard resistivity techniques were used to establish the temperature at which the austenite-martensite reaction began during air cooling after austenitizing at either 900 °C or 1050 °C under a protective atmosphere. Experiments confirmed that nitrogen was not lost from the sample during annealing. An example of a potential difference *vs* temperature trace is shown in Figure 1.

Alloys for which no M_s temperature was observed above room temperature (5 in total) were cooled by holding above liquid nitrogen and then immersing in liquid nitrogen (temperature −196 °C). Resistivity measurements were generally unsuccessful in determining precise M_s temperatures between 0 °C and −196 °C, but testing with a magnet before and after cooling in liquid nitrogen confirmed whether specimens had transformed to martensite.

D. *Electropolishing*

Due to the expected unstable nature of the microstructures, samples for further investigation were prepared by electropolishing. The electropolishing solution was 20 pct perchloric acid in ethanol and conditions were 18 V and 15 to 35 °C.

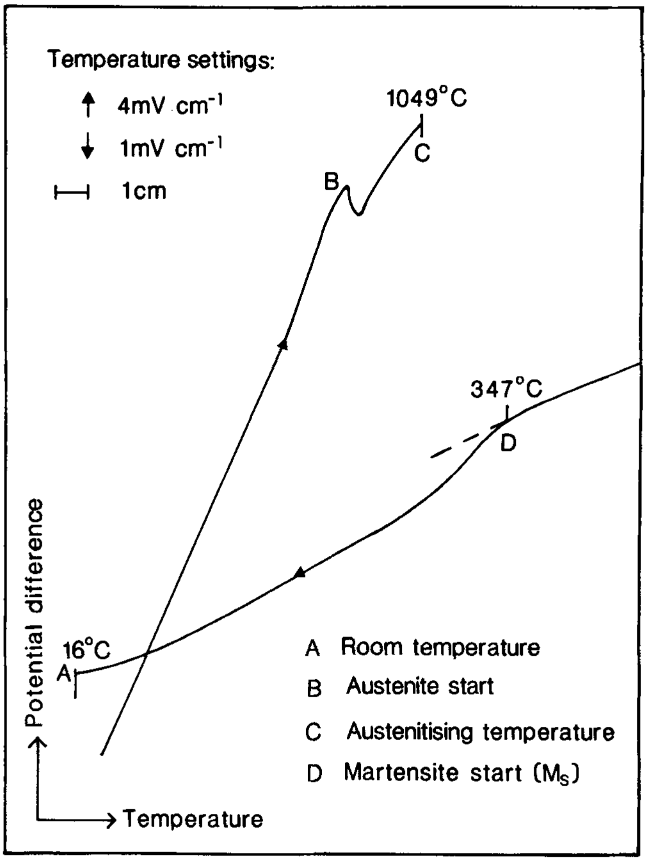

Fig. 1 — A trace obtained from a resistivity experiment, 8 pct Cr-0.293 pct N, annealed 1 h 1050 °C, and air cooled.

Table II. Nitrogen Contents and Processing Details for Nitrided Base Alloys

Base Alloy	Nitrogen Content (Wt Pct)	Nitriding Parameters		
		Atmosphere	Temperature (°C)	Time (Hours)
Fe-8Cr	0.206	90 N-10 H	1100	24
	0.293	90 N-10 H	1000	48
Fe-8Cr-5Mn	0.258	90 N-10 H	1100	24
	0.387	90 N-10 H	1000	48
Fe-8Cr-10Mn	0.206	25 N-75 H	1100	24
	0.340	90 N-10 H	1100	24
	0.575	90 N-10 H	1000	48
Fe-12Cr	0.257	25 N-75 H	1100	24
	0.416	90 N-10 H	1100	24
	0.596	90 N-10 H	1000	48
Fe-12Cr-5Mn	0.290	25 N-75 H	1100	24
	0.466	90 N-10 H	1100	24
	0.614	90 N-10 H	1050	48
Fe-12Cr-10Mn	0.212	5 N-95 H	1100	24
	0.374	20 N-80 H	1100	24
	0.546	50 N-50 H	1100	24

E. *X-Ray Diffraction*

Selected electropolished samples were examined by X-ray diffraction to determine the phases present. A Siemens D500 diffractometer was used with Fe filtered radiation from a Co target operated at 35 kV and 20 mA.

F. *Metallography*

All samples were examined by optical microscopy after mechanical polishing and etching, and selected samples were examined after electropolishing (see above). Specimens were etched in Vilella's reagent (1 g picric acid, 5 ml hydrochloric acid, 100 ml methanol). Etching in a color etch (3 g sodium metabisulfite, 1.5 g sulfamic acid, 0.75 g ammonium bifluoride in 100 ml water) distinguished between ferrite and martensite and confirmed that the only specimen which contained ferrite was the unnitrided 12 pct Cr alloy. Epsilon martensite was not distinguishable as a separate phase, and in mixed austenite-martensite microstructures the phases were not generally clearly distinguishable.

Selected specimens were examined by electron microscopy. Three-mm diameter discs with a thickness of 0.5 mm to 1 mm were punched from thin sheet. The discs were mechanically polished to a thickness of 0.08 to 0.12 mm and were electropolished in a Struers jet polisher in a solution of 5 pct perchloric acid, 25 pct glycerol, 70 pct ethanol at 60 V, 200 mA, and room temperature. The thin foils were examined in a Siemens Elmiskop 101 electron microscope operating at 100 kV.

G. *Hardness Testing*

Standard Vickers hardness tests using a 5 kg load were carried out on selected samples.

III. RESULTS

The results of resistivity experiments, hardness testing, metallographic examination, and X-ray diffraction investigations are summarized in Table III.

A. *M_s Temperatures*

The variation of M_s temperatures with composition, as determined by resistivity experiments, is shown in Figures 2 to 5.

Figures 2 and 3 show the variation of M_s with manganese and chromium contents, respectively, in nonnitrided alloys after austenitizing at 1050 °C. The results indicate that in the composition range investigated, the M_s is lowered by about 40 °C for each 1 pct Mn and about 9 °C for each 1 pct Cr.

The variation of M_s with nitrogen content is shown after austenitization at 1050 °C in Figure 4 and after austenitization at 900 °C in Figure 5. The dotted lines in the figures refer to data which are uncertain, namely: the M_s temperature of the 12 pct Cr alloy which was obscured by formation of ferrite; the M_s temperatures of alloys containing 10 pct Mn and more than 0.2 pct N (12 pct Cr alloys) or 0.3 pct N (8 pct Cr alloys), in which M_s temperatures were either in the range 0 to −196 °C or below −196 °C.

M_s temperatures of nitrogen-free alloys were assumed to be independent of austenitizing temperature; the relevant

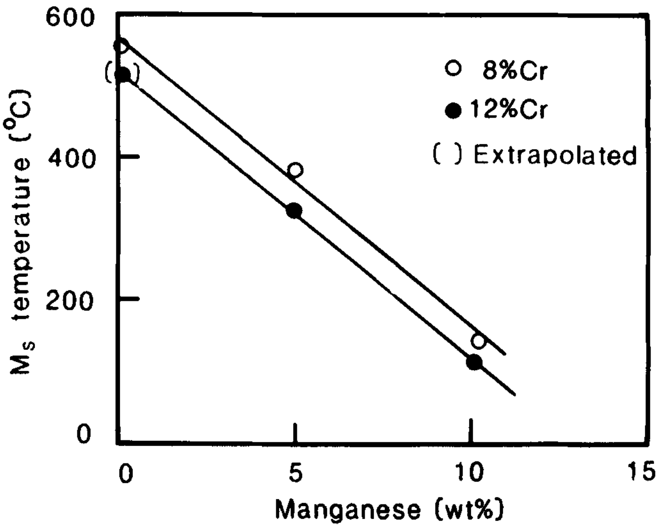

Fig. 2—M_s temperatures of nitrogen-free alloys as a function of manganese content.

Table III. M_s Temperatures, Hardness, and Microstructure of Experimental Alloys

					Microstructure		
		M_s Temperature (°C)			Metallography		
Base Alloy	Nitrogen Content (Wt Pct)	ST 900 °C	ST 1050 °C	Hardness (HV) ST 1050 °C	ST 900 °C	ST 1050 °C	X-Ray Diffraction ST 1050 °C
12Cr	0.017	—	—	188	—	F, M	—
	0.257	367	401	480	M, N	M	—
	0.416	372	285	549	M, N	M, N	α, 4 pct γ
	0.596	345	311	655	M, N	M, N	—
12Cr-5Mn	0.016	—	315	306	—	—	—
	0.290	160	187	473	M, N	M	α
	0.466	173	123	502	M, N	M	α, 6 pct γ
	0.614	192	−16	516*	—	M*	α, 34 pct γ
12Cr-10Mn	0.018	109	111	353	—	—	α, 6 pct γ, 6 pct ε
	0.212	<0	<0	277*	A, M*	A, M*	α, 53 pct γ, 3 pct ε*
	0.374	<−196	<−196	239*	A, N*	A*	γ*
	0.546	<−196	<−196	246*	A, N*	A*	γ, trace α*
8Cr	0.017	—	549	260	—	—	—
	0.206	465	458	447	M, N	M	—
	0.293	325	347	524	M, N	M, N	α, 4 pct γ
8Cr-5Mn	0.011	—	371	265	—	—	—
	0.258	262	272	460	M, N	M	—
	0.387	251	216	532	M, N	M, N	α
8Cr-10Mn	0.014	—	144	362	—	—	α, 10 pct γ, 5 pct ε
	0.206	50	58	401	M	M	α, 19 pct γ, 11 pct ε
	0.340	<0	<0	232*	A, N	A, N*	80 pct γ, α*
	0.575	<−196	<−196	268*	A, N*	A, N*	γ*

*After cooling in liquid nitrogen (−196 °C)
ST = Solution Treatment Temperature
A = Austenite, M = Martensite, N = Nitrides, F = Ferrite
α = α Martensite, γ = Austenite, ε = ε Martensite.

data for 1050 °C austenitization shown in Figure 4 are therefore repeated in Figure 5. The accuracy of the M_s data is estimated to be ±10 °C.

The variation of M_s temperature with composition is approximately linear at low nitrogen contents, the limit to linearity being between 0.25 and 0.55 pct N in 0 pct Mn and 5 pct Mn alloys and below 0.25 pct N in 10 pct Mn alloys. The M_s temperature in °C in the linear range is described by:

$$M_s = 555 - 9(Cr - 8) - 40Mn - 450N \qquad [1]$$

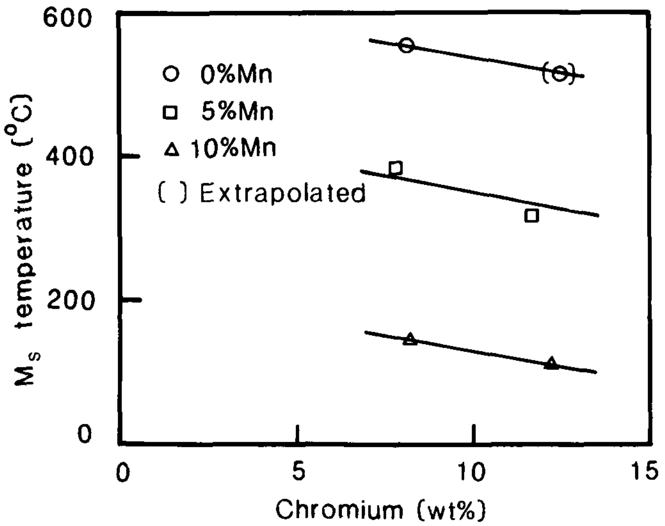

Fig. 3 — M_s temperatures of nitrogen-free alloys as a function of chromium content.

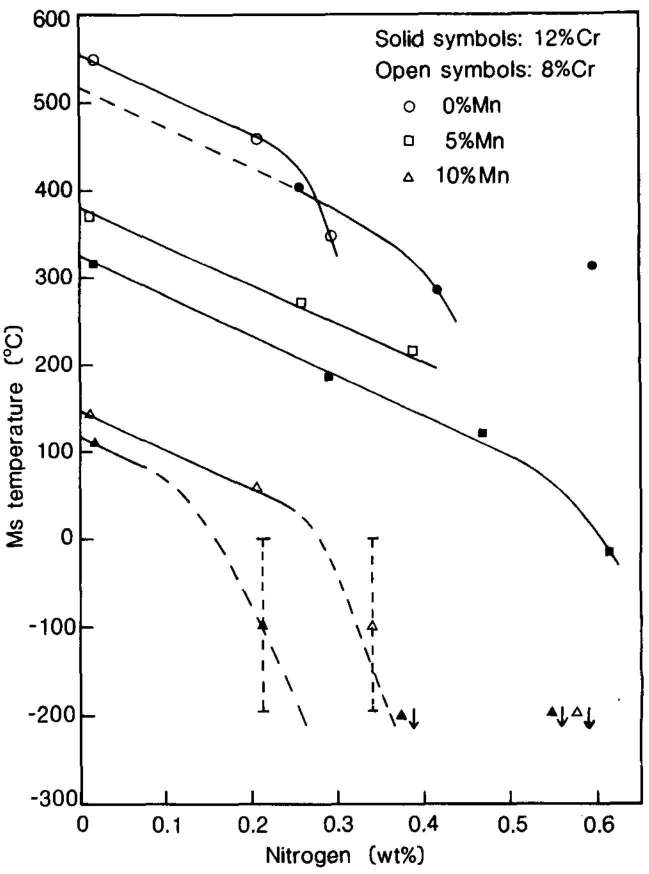

Fig. 4 — M_s temperatures as a function of nitrogen content after annealing at 1050 °C.

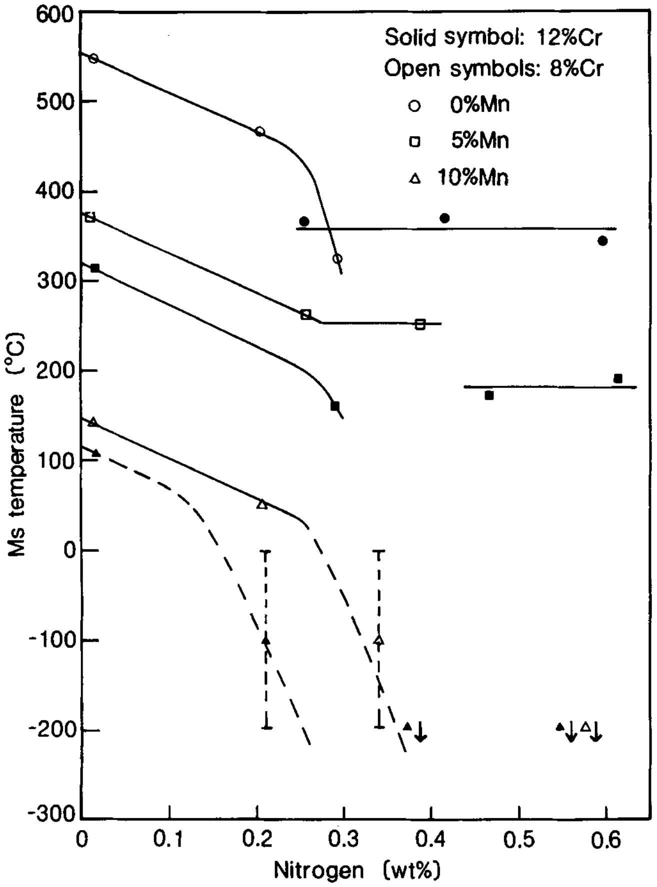

Fig. 5—M_s temperatures as a function of nitrogen content after annealing at 900 °C.

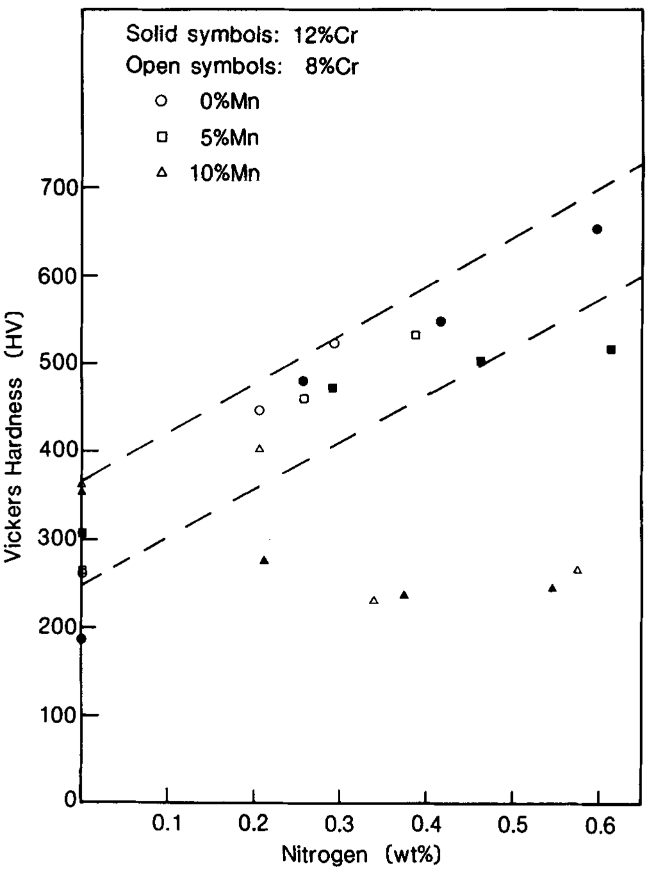

Fig. 6—Hardness as a function of nitrogen content after annealing at 1050 °C.

where Cr, Mn, and N are the weight percentages of the elements. At nitrogen levels beyond the linear range, the M_s temperature drops more rapidly with increasing nitrogen content, except in some samples containing nitrides (determined by metallography) in which the M_s remains approximately constant.

B. *Hardness*

Hardness is plotted as a function of nitrogen content in Figure 6. The hardness of the predominantly martensitic steels, encompassed by the broad band in Figure 6, increases with increasing nitrogen content from around 300 HV at 0 pct N to about 650 HV at 0.6 pct N. The unnitrided 12 pct Cr alloy has a lower hardness due to a mixed martensite-ferrite microstructure. The other points lying below the band in Figure 6 refer to the samples which were predominantly austenitic after cooling in liquid nitrogen. Hardnesses of these materials were typical of austenitic steels at about 230 to 280 HV, except for the 12 pct Cr-5 pct Mn alloy containing 0.6 pct N. This alloy contained only about 35 pct austenite after cooling in liquid nitrogen and had a hardness of about 500 HV.

C. *X-Ray Analysis*

The X-ray analysis results in Table III refer to the phases α (ferrite or martensite), γ (austenite), and ε (epsilon martensite). The α phase was revealed by metallography to be martensite rather than ferrite in all cases. The ε phase was not found in the 0 pct or 5 pct Mn alloys and was found only as a minor constituent in 10 pct Mn alloys containing 0.2 pct N or less, where considerable amounts of α martensite (40 pct or more) were also present.

Where austenite is present as a minor phase the percentage quoted in Table III is a maximum. The detection limit is 3 pct austenite. Where austenite is a major constituent, the accuracy is about ±4 pct. The accuracy in the ε percentage figures is ±3 pct.

D. *Metallography*

The range of microstructures obtained in the alloys is illustrated in Figures 7 to 12. At the upper end of the Cr, Mn, and N ranges the microstructure is a stable austenite (see Figure 7) while at the lower end of the range the microstructure is fully martensitic (see Figure 8). At the lower Cr and Mn levels, nitrides formed in alloys containing high nitrogen levels, particularly when austenitized at the lower solution temperature of 900 °C (see Figure 9). At intermediate compositions mixed γ-α-ε or unstable γ microstructures developed.

In structures which X-ray diffraction showed to be mixed but predominantly martensitic, the phases could not be distinguished metallographically (see Figure 10). Optical microscopy revealed both austenite and martensite in predominantly austenitic mixed structures (see Figure 11). Unstable austenite structures appeared fully austenitic after electropolishing, but the deformation introduced by mechanical polishing caused transformation of the unstable austenite at the surface to martensite (see Figure 12).

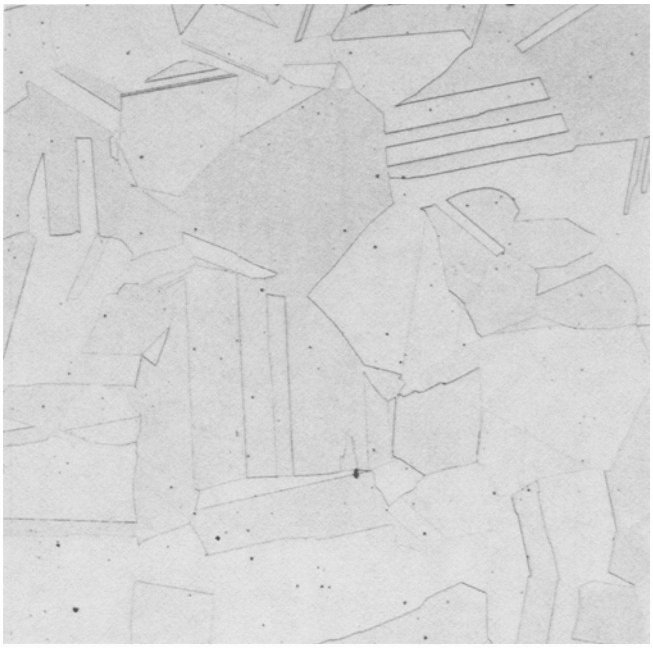

Fig. 7—Austenite in 12 pct Cr-10 pct Mn-0.546 pct N alloy, annealed 1050 °C, air cooled, and cooled in liquid nitrogen. Magnification 100 times.

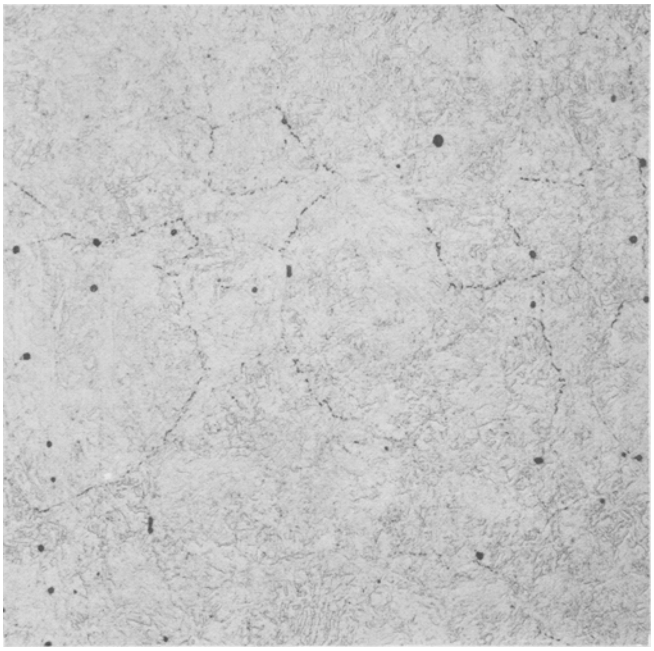

Fig. 9—Martensite and nitrides in 8 pct Cr-5 pct Mn-0.258 pct N alloy, annealed at 900 °C, and air cooled. Magnification 200 times.

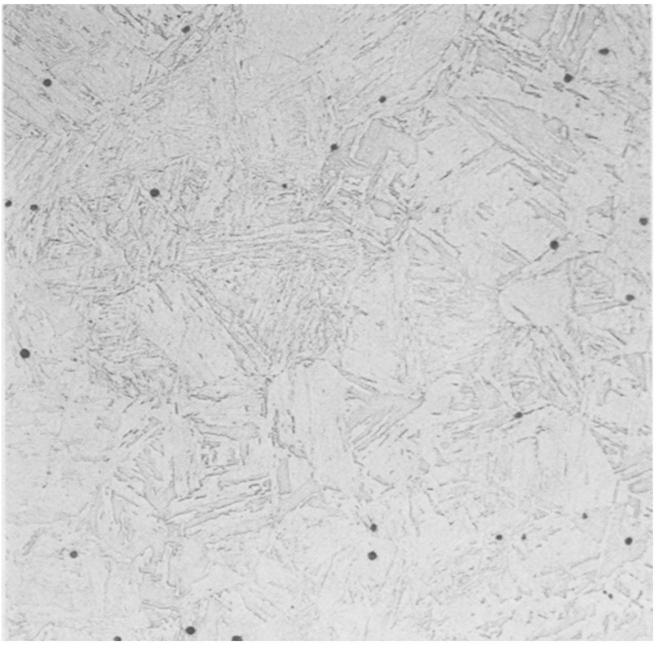

Fig. 8—Martensite in 8 pct Cr-5 pct Mn-0.258 pct N alloy, annealed 1050 °C, and air cooled. Magnification 200 times.

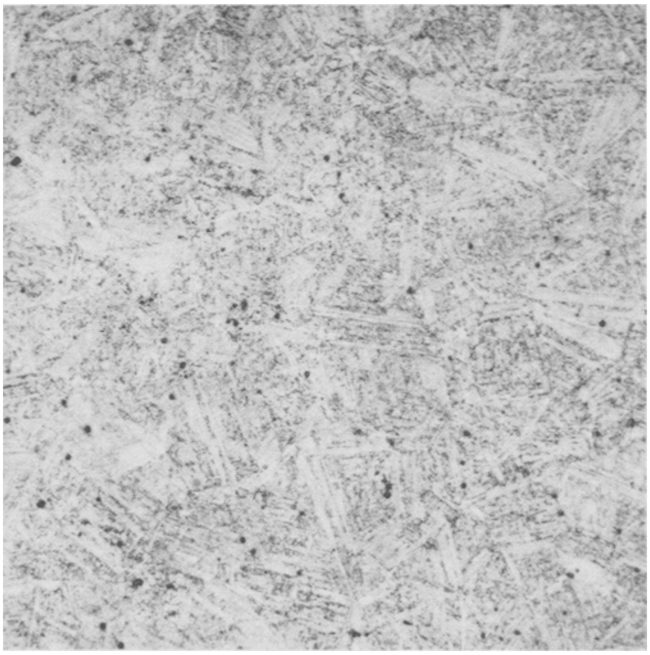

Fig. 10—Mixed martensite, austenite, and epsilon in 8 pct Cr-10 pct Mn-0.206 pct N alloy, annealed 1050 °C, and air cooled, electropolished. Magnification 100 times.

Electron metallography showed that the austenitic steels contained a high density of stacking faults, illustrated in Figure 13. The presence or absence of nitrides was also confirmed by electron microscopy.

IV. DISCUSSION

A. *M_s Temperatures*

Features of the M_s-composition curves presented in Figures 4 and 5 which require consideration include the effect of nitride precipitation on M_s; the linear relationship between M_s and composition, and deviations from linearity; and the higher M_s temperatures than predicted by earlier work.[3–8]

Three of the alloys (12Cr, 12Cr-5Mn, 8Cr-5Mn) displayed a constant M_s temperature at high nitrogen contents when austenitized at 900 °C (see Figure 5). All the above compositions contained nitride precipitates. The constancy of M_s indicates a constant level of nitrogen in solution in the austenite, which indicates that the nitrogen solubility limit

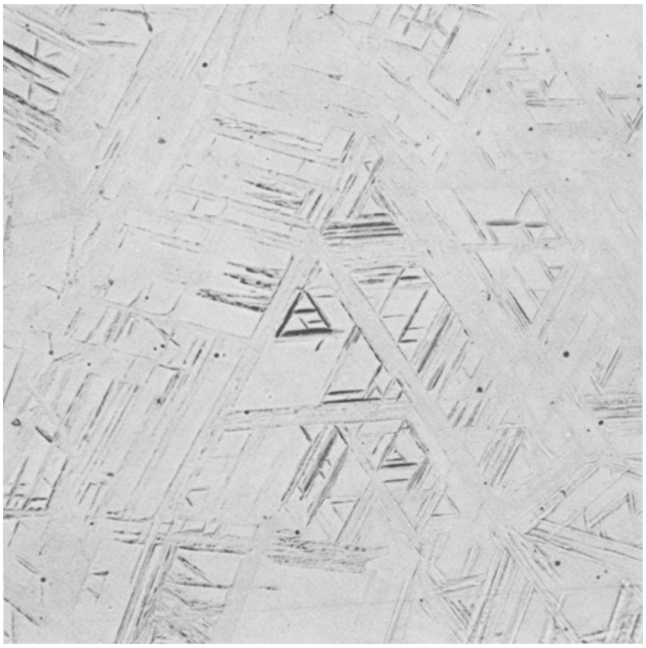

Fig. 11—Undeformed austenite and martensite in 12 pct Cr-10 pct Mn-0.212 pct N alloy, annealed 1050 °C, air cooled, and cooled in liquid nitrogen, electropolished. Magnification 200 times.

Fig. 12—Deformed austenite and martensite in 12 pct Cr-10 pct Mn-0.212 pct N alloy, annealed 1050 °C, air cooled, and cooled in liquid nitrogen, mechanically polished. Magnification 200 times.

has been exceeded. At compositions beyond this limit, excess nitrogen precipitates as nitrides or pre-existing nitrides do not fully dissolve.

Linear relationships between M_s and composition have been reported in the literature (*e.g.*, References 3, 4, and 5) and most of the alloys studied in this work obeyed a linear M_s-composition relationship at relatively low nitrogen levels, although at higher nitrogen levels, deviations from linearity occurred.

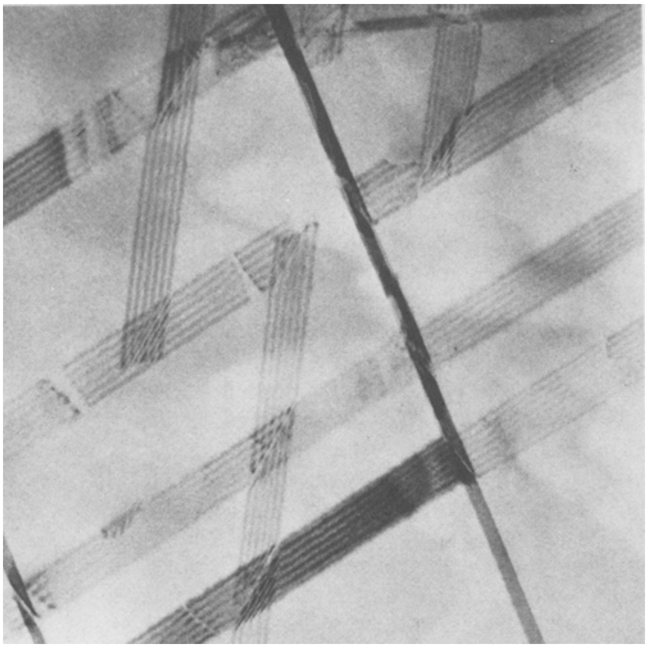

Fig. 13—Stacking faults in austenite in 12 pct Cr-10 pct Mn-0.374 pct N alloy, annealed at 1050 °C, and air cooled. Magnification 80,000 times.

Considering the M_s data obtained after annealing at 1050 °C (Figure 4), the M_s-nitrogen relationship is linear in alloys containing less than about 0.3 pct N. Reference to Table III shows that in all alloys other than the 12 pct Cr-5 pct Mn and 12 pct Cr-10 pct Mn alloys, nitrides are present when the nitrogen level exceeds 0.3 pct. Considering these nitride-containing alloys, the M_s temperatures observed are generally lower than would be expected if the linear relationship were obeyed. If pre-existing nitrides had not fully dissolved during the solution treatment, the M_s temperature would be expected to be higher, since there would be less than the equilibrium amount of nitrogen in solution. Since this is not the case, the lower M_s must be due to stabilization of austenite for some reason. One possibility is that the nitrogen precipitates strengthen the austenite, thereby stabilizing it against transformation. Increases in yield strength of austenite are known to depress the M_s temperature.[15,16]

The 12 pct Cr-5 pct Mn and 12 pct Cr-10 pct Mn alloys do not contain nitrides after annealing at 1050 °C. At the highest nitrogen level in the 12 pct Cr-5 pct Mn alloy and at nitrogen levels above 0.2 pct in the 12 pct Cr-10 pct Mn alloy, M_s temperatures are lower than indicated by the linear relationship. In the latter alloy, it is clear that the M_s-nitrogen relationship does not obey the same linear relationship as the lower alloyed materials, but there are insufficient data to specify the actual form of the relationship. However, the data indicate that at the higher N levels, the M_s falls rapidly with increasing N content. Such rapid decreases in M_s with composition have been observed in other alloy systems.[17] Alloying elements influence M_s temperatures in several ways, including their effect on T_0, the temperature at which ferrite and austenite of the same composition have the same free energy, and their effect on T_m, the additional undercooling necessary to allow martensite to propagate, which is affected by strength.[15,16] Alloying elements affect both the magnetic and nonmagnetic components of the free energy change accompanying the γ-α transformation.[18,19] The effect of manganese in this respect does not seem to be straightforward, since manganese has been reported to act as an austenite former when present at low levels and as a ferrite former at higher levels (greater than about 6 pct,[20] 8 pct,[21] or 12 pct[22]). Furthermore, interactions between nitrogen and manganese in solution have been proposed in the literature,[23] and this may also affect M_s temperature.

The M_s temperatures obtained in this work differ from those predicted by previously published equations (*e.g.*, References 3 and 4), confirming that each relationship is valid only over the composition range for which it was derived. Generally, the values obtained in this work were higher, by up to 200 °C, than those predicted.

The experimental M_s results for nitrogen-free alloys are high compared to previously published data. For instance, the M_s temperature of the plain 12 pct Cr alloy obtained by extrapolating the experimental data to 0 pct N was 520 °C, whereas values in the range 350 °C to 450 °C have been reported previously.[3,24] A major difference is that the alloys investigated in this work were high purity, whereas commercial steels always contain significant amounts of residual elements such as C, Mn, Si, and Ni. The effect on M_s of these minor elements is quite considerable, and comparison of the experimental data with published data for a 12 pct Cr steel[24] yields quite good agreement (within 30 °C) when allowance for minor elements is made. In addition, it has been reported that cooling rate has a marked effect on the M_s temperature, slower cooling yielding lower M_s temperatures.[5] The cooling rate for the 1 mm thick samples in this work was relatively high and may explain the remaining difference in reported M_s temperatures.

B. *Nitrogen Solubility*

Limited data on the effect of composition and temperature on nitrogen solubility in austenite are available in the literature.[9,14] The experimental results show that in Fe-Cr-Mn alloys nitrogen is considerably less soluble at 900 °C than at 1050 °C and that solubility increases with increasing manganese content and, more markedly, with increasing chromium content. The maximum nitrogen solubility in the composition range investigated was obtained in the 12 pct Cr alloys austenitized at 1050 °C, for which the solubility limit lies above 0.3 pct N in alloys containing no manganese and above 0.6 pct N in alloys containing 10 pct manganese.

C. *Microstructure*

The microstructural investigations revealed that all the nitrogen-bearing alloys were fully austenitic (*i.e.*, contained no ferrite) at the annealing temperatures of 900 °C and 1050 °C.

All but one of the nitrogen-bearing alloys contained nitrides when austenitized at 900 °C, but most alloys were nitride-free when austenitized at 1050 °C. Therefore the preferred solution treatment temperature is 1050 °C.

M_d temperatures have not been determined directly, but the effect of mechanical polishing on austenitic microstructures revealed that all but the most highly alloyed austenites were unstable; *i.e.*, some transformation to martensite occurred on deformation, indicating that M_d temperatures in these alloys are above room temperature. Detailed investigations of instability are reported elsewhere.[2]

The microstructural investigations also revealed that the austenitic steels had a high density of stacking faults. High levels of stacking faults are known to increase work-hardening characteristics[12] and are found in highly work-hardening steels such as Hadfield's manganese steel.[25] The high density of faults observed can be attributed to the high manganese and chromium levels in the alloys investigated, since both elements are known to favor fault formation through lowering the stacking fault energy.[11,26]

D. *Composition Range*

M_s temperatures below room temperature and austenitic microstructures were obtained in several of the alloys investigated, namely:

12Cr-5Mn- > 0.6N

12Cr-10Mn- > 0.15N

8Cr-10Mn- > 0.3N

Bearing in mind that commercially produced steels would contain residual elements which may reduce the M_s temperature by around 50 °C, austenitic microstructures should be obtained in steels containing somewhat lower levels of Cr, Mn, and N than those given above.

In addition to the consideration of desired microstructure, selection of the optimum compositions for possible commercial production should take into account cost of steelmaking. Major considerations are incorporation of nitrogen into a steel melt and avoidance of ingot porosity; nitrogen can most readily be incorporated by blowing nitrogen gas through the melt. To avoid porosity the nitrogen level should not exceed the solubility limit of the melt. The solubility of nitrogen in molten iron alloys increases with increasing chromium and manganese contents,[10] but is unlikely to exceed 0.25 pct in the Cr-Mn steels of interest. Incorporation of higher levels of nitrogen would necessitate special steelmaking practices at higher cost.

To achieve austenitic microstructures at nitrogen levels of 0.25 pct or less, the Cr and Mn levels would have to be at the upper end of the range investigated, *i.e.*, toward 12 pct Cr and 10 pct Mn. Given that commercial purity steels would have M_s temperatures somewhat lower than those measured here and that some latitude in nitrogen contents may be available, a suitable composition range may be 10 to 14 pct Cr, 8 to 12 pct Mn, and 0.1 to 0.3 pct N, provided the total of these elements is sufficient to ensure that the M_s is below room temperature.

V. CONCLUSIONS

Investigation of nitrided high purity alloys in the composition range 8 to 12 pct Cr, 0 to 10 pct Mn, and 0 to 0.6 pct N, balance iron, has led to the following conclusions:

1. All alloys except the unnitrided 12 pct Cr alloy were fully austenitic (*i.e.*, contained no ferrite) at annealing temperatures of 900 °C and 1050 °C.
2. In the solution-treated and air-cooled condition, fully martensitic structures are obtained at the low alloy end, and fully austenitic structures at the high alloy end, of

the composition range investigated. At intermediate compositions, mixed martensite-retained austenitic structures (with epsilon phase present as a minor phase in some cases) and unstable austenite microstructures are obtained.

3. Austenitic microstructures are obtained in 12 pct Cr-10 pct Mn alloys containing more than about 0.2 pct N, and in 8 pct Cr-10 pct Mn alloys containing more than about 0.3 pct N. The production of austenitic microstructures in alloys containing 5 pct Mn or less would require impractical amounts of nitrogen (>0.5 pct).
4. Some of the austenite and martensite-austenite microstructures obtained are unstable under deformation, leading to transformation of austenite to martensite and refinement of the microstructure.
5. The hardness of nitrogen-bearing martensites is generally over 400 HV at nitrogen levels of 0.2 pct or more and reaches 650 HV at 0.6 pct N.
6. Nitrogen is more soluble in austenite at 1050 °C than at 900 °C and solubility increases with increasing Cr and Mn content. Solubility of nitrogen at 1050 °C exceeds 0.3 pct in Mn-free 12 pct Cr alloys and exceeds 0.6 pct in 12 pct Cr-10 pct Mn alloys.
7. In the composition range 8 to 12 pct Cr, 0 to 10 pct Mn, and at low N contents in high purity alloys the M_s temperature is linearly related to composition as follows:

$$M_s = 555 - 9(Cr - 8) - 40Mn - 450N \quad [1]$$

where M_s is in °C and Cr, Mn, and N are the weight percentages of these elements. The limit to linearity lies between 0.25 and 0.5 pct N in alloys containing 0 pct or 5 pct Mn and below 0.25 pct N in alloys containing 10 pct Mn. At higher nitrogen levels, the M_s generally falls more rapidly with increasing nitrogen content.

8. In commercial purity steels, unstable austenitic microstructures are expected to be obtained in compositions around 10 to 14 pct Cr, 8 to 12 pct Mn, and 0.1 to 0.3 pct N when the total level of these elements is selected to ensure that the M_s is below room temperature.

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REFERENCES

1. Patent Application No. 85115253.8, European Patent Office, 1986.
2. U.R. Lenel and B.R. Knott: *Metall. Trans. A*, 1987, vol. 18A, pp. 847-55.
3. K.J. Irvine, D.J. Crowe, and F.B. Pickering: *J. Iron Steel Inst.*, 1960, vol. 195, pp. 386-405.
4. F.B. Pickering: ASTM STP672, American Society for Testing and Materials, Philadelphia, PA, 1978, pp. 263-95.
5. E.P. Klier and A.R. Troiano: *Trans. AIME*, 1945, vol. 162, pp. 172-85.
6. P. Payson and C.H. Savage: *Trans. ASM*, 1944, vol. 33, pp. 261-75.
7. G.H. Eichelmann and F.C. Hull: *Trans. ASM*, 1953, vol. 45, pp. 77-95.
8. W. Stevens and A.G. Haynes: *J. Iron Steel Inst.*, 1956, vol. 183, pp. 349-59.
9. D. Kumar, A.D. King, and T. Bell: *Met. Sci.*, 1983, vol. 17, pp. 32-40.
10. R.D. Pehlke and J.F. Elliott: *Trans. AIME*, 1960, vol. 218, pp. 1088-1101.
11. R.E. Schramm and R.P. Reed: *Metall. Trans. A*, 1975, vol. 6A, pp. 1345-51.
12. C.H. White and R.W.K. Honeycombe: *J. Iron Steel Inst.*, 1975, vol. 200, pp. 457-66.
13. J.J. Eckenrod and C.W. Kovach: ASTM STP679, American Society for Testing and Materials, Philadelphia, PA, 1977, pp. 17-41.
14. E.T. Turkdogan and S. Ignatowicz: *J. Iron Steel Inst.*, 1958, vol. 188, pp. 242-47.
15. T.Y. Hsu (Xu Zuyao): *J. Mater. Sci.*, 1985, vol. 20, pp. 23-31.
16. E. Hornbogen: *Acta Metall.*, 1985, vol. 33, pp. 595-602.
17. H. Warlimont: [Iron Steel Inst. Symposium on] Physical Properties of Martensite and Bainite, Scarborough, 1965, pp. 58-67.
18. H.K.D.H. Bhadeshia: *Met. Sci.*, 1981, vol. 15, pp. 178-80.
19. C. Zener: *Trans. AIME*, 1955, vol. 203, pp. 619-30.
20. F.C. Hull: *Welding J.*, 1973, vol. 52(5), pp. 192s-203s.
21. R. Franks, W.O. Binder, and J. Thompson: *Trans. ASM*, 1955, vol. 47, pp. 231-59.
22. M. Fujikara, K. Takada, and K. Ishida: *Trans. Iron Steel Inst. Jpn.*, 1975, vol. 15, pp. 464-69.
23. T. Gladman and F. Pickering: *J. Iron Steel Inst.*, 1965, vol. 203, pp. 1212-17.
24. R.L. Rickett, W.F. White, C.S. Walton, and J.C. Butler: *Trans. ASM*, 1952, vol. 44, pp. 138-68.
25. K.S. Raghavan, A.S. Sastri, and M.J. Marcinkowski: *Trans. AIME*, 1969, vol. 245, pp. 1559-75.
26. H.M. Otte: *Acta Metall.*, 1957, vol. 5, pp. 614-27.