

Strengthening mechanisms in martensitic structures

MORGRIDGE A.R.

Mechanical Engineering Department of the University of Ibadan. Ibadan

ABSTRACT

During metal working, martensitic steels, in the form of duplex steels, possess the highest work hardening rate of all steels. This unique characteristic results from a combination of microscopic strengthening mechanisms in martensite during prior heat treatment and quenching. These strengthening mechanisms have been studied with reference to a plain carbon (C-Mn) steel and three microalloy (Nb, Nb-V, Nb-Mo) steels. Such mechanisms include:

- (i) Grain size effect
- (ii) Solid solution hardening
- (iii) Precipitation hardening
- (iv) Microalloy addition
- (v) Work hardening by movement of dislocation.

The contribution that each of these mechanisms makes to the overall strength is assessed. Tensile tests were performed on martensitic and non martensitic steels and their strength levels compared. A range of ultimate tensile strengths (U.T.S.), of 665-765 MPa was obtained for martensitic steels and 515-631 MPa for non martensitic steels. Hardening or strengthening of steel is very important because that imparts better mechanical properties i.e. better combination of strength and ductility (U.T.S., Work hardening rate, maximum uniform strain) on the steel. This leads to better performance of steels when subjected to higher design stresses and also has better fatigue strength. Nb, Nb-V, and Nb-Mo martensitic steels produced in the present work, possess 8-20% higher ultimate tensile (U.T.S.) than plain carbon or C-Mn steel. This means that parts made from these steels can be made lighter by as much as 20% and still carry the same load as C-Mn steel, with resultant less fuel consumption.

RÉSUMÉ

Dans un travail des métaux, les aciers martensitiques possèdent la vitesse d'écroutissage la plus élevée de tous les aciers. Cette spécificité est issue de l'effet combinatoire des mécanismes de consolidation qui se déroulent dans la martensite au cours des séquences de réchauffement et refroidissement préalable. Ces mécanismes de consolidation ont été étudiés sur l'acier au carbone ordinaire (C-Mn) et trois aciers micro alliés (Nb, Nb-V, Nb-Mo). Ces mécanismes sont: i) Effet de grosseur de grain, ii) Durcissement de solution solide, iii) Durcissement par précipitation, iv) Assition des aciers micro alliés v) Ecroutissage par déplacement de dislocation. Une évaluation est faite de la contribution qu'apportent chacun de ces mécanismes à la consolidation globale. Des essais de traction ont été effectués pour établir la limite d'élasticité des aciers martensitiques et celle des aciers non martensitiques et une comparaison faite. Il s'est avéré que l'élasticité verrait entre 665 à 765 Mpa pour les aciers martensitiques et 515 à 613 Mpa pour les autres.

INTRODUCTION

During metal working, martensitic steels are known to possess the highest work hardening rate of all steels. To this end, metallurgists have long sought to find out why martensite (upon transformation from austenite) imparts high strength to steels after quenching in water or other cooling medium. More recently, there has been an increase in research work in this field partly because of advances in techniques for metallographic examination and partly, because of attempts to develop a quantitative analysis of mechanisms that influence the strength of martensite which include: Grain size, Solid solution hardening, Precipitation hardening, Microalloy addition, Work hardening by movement of dislocations. It is necessary to know what mechanisms exists in a particular transformation combining to give overall strength, and how large a contribution each of these mechanisms make to the overall strength. Formation of austenite during intercritical annealing can be separated into 3 main stages. (i) Almost instantaneous nucleation of austenite at pearlite or grain boundary cementite particles, followed by very rapid growth of austenite until the carbide phase was dissolved. (ii) slower growth of austenite into ferrite at a rate that is controlled by carbon diffusion in austenite at high temperatures (850°C) and by manganese diffusion in ferrite at low temperatures (750°C) and (iii) very slow final equilibration of ferrite and austenite at a rate that was controlled by manganese diffusion in austenite¹. Martensitic structures may also contain microalloys such as vanadium, niobium, silicon, chromium, phosphorus or molybdenum in addition to manganese. These may lead to more complex effect on austenite formation. For instance, vanadium and niobium interact strongly with carbon and nitrogen to form a fine dispersion of VCN or NbCN. Upon intercritical annealing, this dispersion may be dissolved as the austenite phase grows into the ferrite. Also silicon widens the α and γ phase field and permits a wider range of intercritical temperatures to be used. Carbon and these microalloys are known to increase the hardenability of austenite upon transformation after annealing. Transformation in duplex steels occur at low temperature (750°C), so that the ferrite phase must

plastically deform to accommodate the volume expansion (2 to 4%) arising from the austenite to martensite transformation. As a result, both a high dislocation density and residual stresses are generated in the ferrite immediately surrounding the martensite particles. Martensite transformation substructures in duplex steels can vary from lath martensite substructure in low carbon martensite to internally twinned substructures typical of high carbon martensite². In this research work, individual mechanisms affecting strengthening in martensite will be discussed with reference to a plain carbon and three microalloy (Nb, Nb-V and Nb-Mo) steels, all of which have undergone martensitic transformation. An attempt will also be made to predict important combination of strengthening mechanisms which may have affected overall hardness of martensite in these steels. Hardening or strengthening of steel is very important because that imparts better mechanical properties i.e. better combination of strength and ductility (U.T.S, Work hardening rate, maximum uniform strain) on the steel. This leads to better performance of steels when subjected to higher design stresses and also has better fatigue strength. These martensitic or duplex steels, produced nowadays, are widely used in the car industry. Parts made from these steels are lighter in weight, compared with the conventional plain carbon or C-Mn steel, but possess greater strength. Cars made from these steels consume less fuel.

Also in the present work, comparisons will be made between the ultimate tensile strength (U.T.S.) of Nb, Nb-V, and Nb-Mo martensitic steels produced, and that of plain carbon or C-Mn steel and the resultant advantages.

EXPERIMENTATION

The four steels used were of the compositions listed in Table 1. They were hot rolled in four passes from 25mm to 4.5mm thick with initial rolling temperature 1200°C and final temperatures 780-950°C. The steel samples were then air cooled to room temperature. Scaled and decarburized surfaces were removed

Table 1: Steel Compositions

TYPE OF STEEL	COMPOSITIONS (WEIGHT%)										
	C	Mn	Si	S	P	Al	Nb	Mo	Gr	Ni	N ₂
(C-Mn)	0.1	1.44	0.35	0.005	0.006	0.35	-	<0.02	<0.02	<0.02	0.008
(Nb)	0.1	1.42	0.35	0.005	0.006	0.015	0.1	<0.02	<0.02	<0.02	-
(Nb-V)	0.1	1.40	0.29	0.005	0.006	0.030	0.045	<0.08 0.36	<0.02	<0.02	0.014
(Nb-Mo)	0.08	1.35	0.33	0.005	0.006	0.042	0.048		<0.02	<0.02	0.009

Table 2: Mechanical properties of C-Mn, Nb, Nb-V and Nb-Mo Steels, annealed at 700°C for 6 hours

Steel	C-Mn	Nb	Nb-V	Nb-Mo
Average U.T.S. (MPa)	515.0	543.0	586.0	631.0
Work hardening rate at 0.2% proof stress (MPa x 10 ³ per unit strain)	31.0	35.0	36.0	32.0
Range of strain hardening exponent, n	0.19-0.24	0.18-0.25	0.16-0.22	0.14-0.24
Maximum uniform strain	0.26	0.23	0.21	0.23

Table 3: Mechanical properties of C-Mn, Nb, Nb-V and Nb-Mo steels after intercritical annealing at 755°C for 10 mins.

Steel	C-Mn	Nb	Nb-V	Nb-Mo
Average U.T.S. (MPa)	615.0	741.0	665.0	691.0
Work hardening rate at 0.2% proof stress (MPa x 10 ³ per unit strain)	54.0	69.0	58.0	51.0
Range of strain hardening exponent, n	0.28-0.39	0.31-0.44	0.29-0.45	0.20-0.37
Maximum uniform strain	0.20	0.18	0.18	0.19
% Martensite	25.0	25.0	27.0	35.0

Table 4: Average grain size of martensite in martensitic steels

Martensitic Steel	Average grain size (microns)
C-Mn	55.0
Nb	35.0
Nb-V	37.0
Nb-Mo	40.0

by grinding equal amounts from each side of the hot rolled material, to produce clean samples 4.0mm thick. They were cold rolled to 1mm thickness (80% reduction). Tensile test pieces were stamped out of the resulting strips and were all annealed in argon at 700°C for six hours in small batches. The pieces of all steels were then intercritically annealed in the martensitic region (755°C) in argon for 10 minutes, followed by water quenching, Metallographic samples were hot-mounted in plastic, ground under water on successively finer emery paper and polished on velvet covered wheels impregnated with diamond paste. Generally, microstructures were observed on longitudinal transverse sections after etching with nital. Martensite contents were determined by point counting (Table 3) and martensitic grain sizes by oxidation method (British Standard B54490) (Table (4)). Micrographs of martensitic structures obtained are shown in figure 1-3. Tensile test pieces of dimensions, gauge length 20mm, thickness 1mm, width 4.81mm were mechanically tested using Instron Universal Testing machine of 5 tonne capacity, at a nominal longitudinal strain rate of $3.8 \times 10^{-3} \text{ s}^{-1}$. Test results are presented in tables 2 and 3

RESULTS AND DISCUSSIONS

Grain Size

A correlation between the tensile properties of carbon-free martensite and the parent austenite grain size shows that the yield strength of the martensite is inversely proportional to the square root of the austenite grain size.³ The constant of proportionality in this Petch relationship is such that a decrease in prior austenite grain size from 1mm to 10mm would raise the yield stress of the corresponding martensite by 45 MPa. By extrapolating this relationship to $d^{1/2} = 0$, the value for the strength of an hypothetical single crystal of martensite is 40MPa. In this work, austenite grain size obtained varied between 35-55microns (Table 4). This corresponds to a strength of 78Mpa. Therefore the total contribution due to grain size is 27.4 MPa. This is a small contribution to the high yield stress of high carbon matensites.

Solid Solution Hardening

Substitutional elements such as nickel can lead to an increase in strength of ferrite and of carbon-free martensite⁴. The substitutional solid solution hardening of nickel at 10% is 30 MPa. However, when nickel is

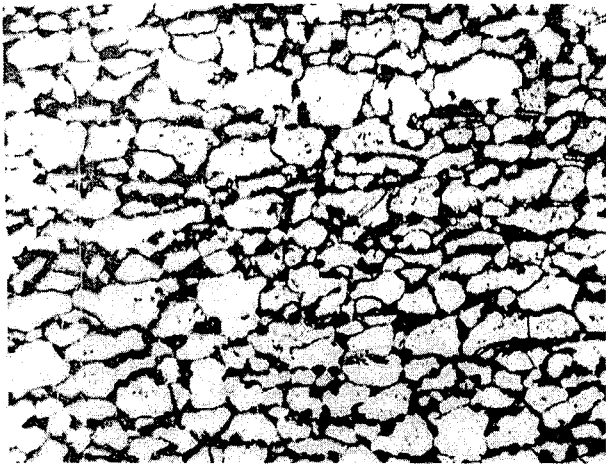


Fig.1: C-Mn steel. Intercritically annealed at 755°C for 10 minutes followed by water quenching. 25% Martensite. 650X.

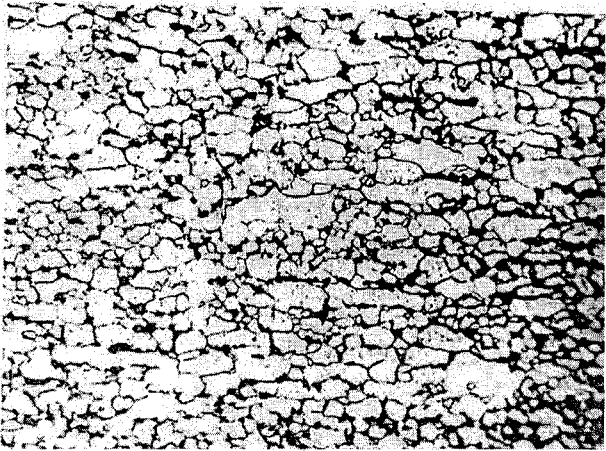


Fig.2: Nb steel. Intercritically annealed at 755°C for 10 minutes followed by water quenching. 25% Martensite. 650X.

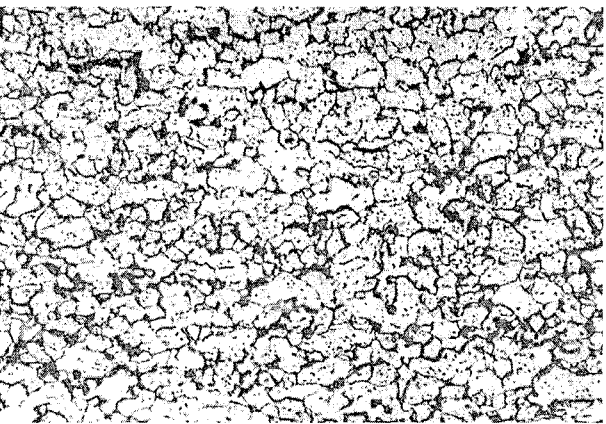


Fig.3: Nb-V steel. Intercritically annealed at 755°C for 10 minutes followed by water quenching. 27% Martensite. 650X.

added to carbon steels, so many other effects ((such as changes in Martensite transformation temperature (M_s) and in the amount of precipitation during quench)) are introduced that it is impossible to isolate the solid solution hardening effect of nickel. It seems likely that the effect of substitutional elements, particularly the non-carbide formers, will be independent of the presence of carbon and the overall effect will be small. Hardening by interstitial elements such as carbon on the other hand in solid solution, is by far the most popular of the strengthening mechanisms proposed for martensite. Owen et al⁵ showed that the strength of martensite varied linearly with the square root of the carbon content. They went on to show that interstitial carbon in solid solution is responsible for up to about half the strength of high carbon martensite. This means that a range of 30-100 MPa increase in yield stress for Nb-Mo and Nb steels respectively can be attributed to this source in the present work.

Precipitation Hardening

It is well known that quenched low-carbon steels contain precipitates which must have formed during the quench^{6,7}. The formation of these precipitates during a quench into iced brine serves to emphasize the high mobility of carbon atoms in low-carbon materials. In plain carbon steel, aging occurred during the quench while in alloy steel, aging was carried out after the quench. If it is assumed that the precipitation of carbon is dislocation nucleated, then during the quench, the dislocation will be moving and continually providing new nucleation sites as they sweep through the material. In steel aged after quenching, however, the dislocations will be stationary and consequently fewer sites will be available for nucleation. Thus a greater strengthening effect associated with the much higher precipitate density is to be expected in the steel aged during the quench. It has been estimated that a 30% increase in strength can be attributed to precipitation hardening after quench and as much as 45% increase associated with precipitation hardening during quench. From this source, a 45 MPa rise in strength for C-Mn and 20-60 MPa for Nb, Nb-V and Nb-Mo steels can be directly attributed to precipitation hardening.

Microalloy addition

During martensitic intercritical annealing, microalloys in carbide form such as chromium, molybdenum, vanadium and titanium tend to dissolve into the austenite phase in large amounts thereby creating coarse, homogeneous grains of austenite, hence increasing hardenability of austenite. Fine precipitates dissolve as

the austenite phases grow into the ferrite. Silicon is also observed to widen the γ and δ phase field thus permitting a wider range of intercritical temperatures to be used^{8,9}. Alloy contents exert a strong hardening effect on the austenite when the carbon content is low and when the cooling rate is high. They also decrease the rates of transformation of austenite at sub-critical temperatures thereby facilitating the attainment of low temperature transformation to martensite without prior transformation to 'unwanted higher temperature products'. The contribution to martensite strength from microalloy addition can be estimated once the effects of the other mechanisms have been taken into account. For Nb steel, a rise of 198 MPa is recorded over annealed steel strength. Of this, 27 MPa can be attributed to grain size, 99MPa due to interstitial carbon is solid solution hardening, 66MPa due to precipitation hardening and the rest 6MPa is due to 0.1% Nb microalloy addition. This is equivalent to 60 MPa increase in strength for 1% addition Nb. It appears that since molybdenum and vanadium are capable of dissolving in ferrite and also combining in carbide, this has 'diluted' the hardening effect of Nb in austenite and hence may be responsible for the 'low' values of strength obtained in Nb-V and Nb-Mo steels. It is therefore not possible to isolate the hardening effect of molybdenum and vanadium on martensite in this work. Vanadium is however known to contribute 80 MPa per 1% addition to the strength of martensite⁵.

Work hardening by movement of dislocations

When martensite forms from austenite, a macroscopic change of shape as well as an inhomogeneous shear are involved. These two distortions, in particular the inhomogeneous shear, result in the formation of substructure within the martensite grains. When the inhomogeneous shear is compensated by internal twinning, the dislocation density within the martensite is not very high, but a large number of narrow twins are produced¹⁰. In low carbon steels, no internal twinning is observed. This implies that the inhomogeneous shear has been compensated by slip – a conclusion which is supported by the observation that the dislocation density in these low carbon martensite is high. By comparing the strength of finegrained low carbon ferrites with the strength of low carbon martensite, the contribution of this dense dislocation substructure to martensite strength is about 30MPa, a relatively small strengthening effect. When these steels are however subjected to plastic straining e.g. tensile test, they exhibit unique work hardening characteristics. Ferrite-martensite steels, in general, do not show a yield point

because the combination of high residual stresses and a high mobile dislocation density, due to transformation during cooling and differential thermal contraction, causes plastic flow to occur easily at low plastic strains. Because plastic flows begins simultaneously at many sites throughout the specimen, discontinuous yielding is suppressed. Work hardening processes in these steels are complex but can be separated and discussed in terms of three different regimes of behaviour during plastic flow. Initially (0.1-0.5% strain), rapid work hardening occurs because of the elimination of residual stresses and rapid build up of back stresses in the ferrite because of the high elastic stiffness of the martensite phase, hence plastic incompatibility of the two phases. Then (0.5-4% strain) work hardening rate of the material starts to decrease because the high stress promotes stress-aided cross-slip, even though plastic flow of the ferrite is constrained by the hard, undeforming martensite particles. Transformation of retained austenite may also occur here. Eventually, (4 to 18% strain) dislocation cell structures form and further deformation in the ferrite is governed by dynamic recovery and further stress aided cross slip and by the eventual yielding of the martensite phase¹¹. These factors are responsible for the high values of work hardening rate for duplex steels shown in table 3. An average rise of 25×10^3 MPa per unit strain is recorded over work hardening rate of non-martensitic annealed steels (Table 2).

Comparison of overall strengthening levels in martensitic steels over non martensitic steels.

Hardening or strengthening of steel is very important because that imparts better mechanical properties i.e. better combination of strength and ductility (U.T.S., Work hardening rate, maximum uniform strain) on the steel. This leads to better performance of steels when subjected to higher design stresses and also has better fatigue strength.

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In the present work, Nb, Nb-V, and Nb-Mo martensitic steels produced (Table2), possess 8-20% higher ultimate tensile strength (U.T.S.) than plain carbon or C-Mn steel. This means that parts made from these steels can be made lighter by as much as 20% and still carry the same load as C-Mn steel, with resultant less fuel

consumption.

CONCLUSIONS

1. Martensitic steels are characterized by
 - (i) High work hardening rate
 - (ii) High strain hardening exponent
 - (iii) Absence of a yield point
 - (iv) High yield stress

2. The various mechanisms giving rise to hardening in ferrous martensite appear to be, in descending order of effectiveness:
 - (i) Interstitial carbon in solid solution
 - (ii) Precipitation hardening
 - (iii) Grain size
 - (iv) Microalloy addition

3. Nb contributed 60MPa to martensite strengthening for every 1% addition

4. Nb, Nb-V, and Nb-Mo martensitic steels produced (Table 2), possess 8-20% higher ultimate tensile (U.T.S.) than plain carbon or C-Mn steel. This means that parts made from these steels can be made lighter by as much as 20% and still carry the same load as C-Mn steel, with resultant less fuel consumption.

5. Alloys like molybdenum and vanadium that readily dissolve in both ferrite and as carbides should not be combined with other alloys that only exist in carbide from e.g. Nb. Dilution of martensite strengthening could result.

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