

**CHAPTER 1 INTRODUCTION**

The demand for high-performance line pipe steels has resulted in extensive research being conducted towards increasing, firstly, performance of high-strength low alloy steels (HSLA) and secondly, to improve large diameter forming processes to increase the capacity of pipelines used at higher operating pressures. The trends in the technology of line pipe are towards the use of thinner wall thicknesses and UOE pipe-forming, (plate-U-forming-O-bending and shrinking-E-expanding). These demands include the introduction of higher strength and higher toughness steels with lower ductile-to-brittle transition temperatures and higher impact energies. The grades of line pipe steels have, therefore, been developed from X65 grade towards X80 and X100 to meet these requirements.

**1.1 Strengthening mechanisms in line pipe steels**

The main strengthening mechanisms used in line pipe steels are strengthening by solid solution hardening, by dislocation substructure, by phase transformation strengthening, by precipitation hardening and by grain refinement. The solid solution strengthening result from elements such as manganese and molybdenum, the phase transformation from lower transformation temperature phases such as acicular ferrite and bainitic ferrite or martensite, resulting in finer microstructures with a higher dislocation density. On account of the micro-alloying element additions, carbonitrides of vanadium, niobium and titanium contribute to the precipitation strengthening. Besides dispersion hardening niobium has an added benefit on the refinement of the ferrite grains. Higher pass strains below the non-recrystallisation temperature during the controlled rolling process, also contributes to good ferrite grain refinement.

**1.2 Chemical composition of line pipe steels**

A special alloying design philosophy is used for line pipe steels. Micro-alloying element additions are necessary to obtain the high strengths, and raise the temperature

above which complete recrystallisation during hot rolling occurs and the recrystallisation of austenite is, therefore, retarded below this temperature. Generally speaking, the relatively low levels of the main chemical elements contribute to a low carbon equivalent (CE) for good weldability, and approximately an 0.15% total micro-alloying element content of vanadium + niobium + titanium is usual<sup>[1]</sup>. The micro-alloying elements may be only one of these three or a combination of any two or three of the micro-additions (V, Nb and Ti). Molybdenum and niobium are beneficial to the formation of acicular ferrite and they suppress the formation of pearlite<sup>[2, 3, 4]</sup>. Boron additions are used to form bainitic ferrite and also to suppress the formation of pearlite. Lower carbon contents (below 0.05% or less) are considered to improve weldability, increase the toughness, form less pearlite and increase the strength due to more effective dissolution of niobium.

### **1.3 Steel making of line pipe steel**

The main steel-making procedure for line pipe steels is a combination of converter blowing and ladle treatment<sup>[5]</sup> or the Electric Arc Furnace (EAF) or the Basic Oxygen Furnace (BOF) route. The cleanliness of the steel and the optimum chemical composition are important for obtaining the specified properties of the line pipe. The main considerations concerning the cleanliness of the steel are the requirements for a low sulphur content for high fracture toughness of the pipe body and the avoidance of clustered alumina inclusions in the vicinity of the weld line. CaSi ladle injection treatment ( $\sim 0.8 \text{ kg/t}$ <sup>[2]</sup> is often added for this purpose) is vital to reduce the sulphur content and to change the type and morphology of sulphide inclusions. The preferred inclusion composition and morphology is generated when the Ca:Al ratio in the steel is about 0.20<sup>[2]</sup>. The inclusion shape is also controlled by Ti and rare earth element additions. Vacuum degassing is another method to reduce the impurity content of these steels.

## **1.4 The controlled rolling of strip steel**

The continuously-cast slab is processed after melting by Electric Arc Furnace (EAF) or the Basic Oxygen Furnace (BOF). The major production route of strip for line pipe steels is that of controlled rolling and is most effective with line pipe steels containing micro-alloying elements that raise  $T_{nr}$ . Briefly, the entire process involves slab reheating, rough rolling, finish rolling, cooling on the run-out table and coiling.

### **1.4.1 Rolling schedule**

#### **1.4.1.1 Reheating**

Of importance here, are the reheating temperature and the presence of undissolved carbide particles: The objective of reheating is to achieve uniformly heated slabs with the complete dissolution of micro-alloyed carbonitrides (Nb,V)(C,N). Slabs are heated uniformly within either walking beam furnaces or pusher-type furnaces. The reheating temperature depends on which micro-alloying elements are present in the steel. It ranges generally from 1150 to 1250 °C for Nb-containing steels. TiN particles will remain undissolved at these temperatures and serve to inhibit the growth of  $\gamma$ -grains during reheating.

#### **1.4.1.2 Rough rolling**

The objective of rough rolling is to achieve the finest possible recrystallised austenite grain size before the  $T_{nr}$  is reached<sup>[6]</sup>. In this stage both recrystallisation and strain hardening will take place<sup>[7,8]</sup>. The rough-rolling phase is completed above the non-recrystallisation temperature ( $T_{nr}$ ), typically above about 1030 °C for X60 to X80 ERW line pipe steels<sup>[2, 9]</sup>. Specially developed reduction schedules together with TiN particles that inhibit growth of recrystallised austenite grains, are employed for this purpose<sup>[6]</sup>. For most line pipe steels the temperature of rough rolling is from 1200 down to about 950 °C<sup>[7, 9, 10, 11]</sup>. A minimum pass strain of 0.2% is needed for the required austenite grain refinement<sup>[12]</sup>.

### 1.4.1.3 Finish rolling

The objective of this phase is to accumulate rolling strain within the non-recrystallisation region of the austenite grains so that on subsequent ferrite transformation, ferrite nucleation sites are greatly multiplied in number and a very fine ferrite grain size can be achieved after rolling and during controlled cooling<sup>[6]</sup>. Finish rolling is, therefore, undertaken in the non-recrystallisation austenite region in the lower temperature range above the  $A_{r3}$  temperature (i.e.  $T_{nr} > T > A_{c3}$ )<sup>[9]</sup>. NbN also precipitates in this stage due to decreasing solubility of Nb in the austenite. The austenite grains elongate and become “pan-caked” in shape. The starting temperature for controlled rolling ranges from 1050 to 950 °C and finishes around 730 to 1000 °C<sup>[1]</sup> depending on alloying and processing conditions. The total finishing reduction below the  $T_{nr}$  should be about 64 to 80% when the initial and final thicknesses of the strip are 110 and 18mm respectively<sup>[1,6]</sup>.

### 1.4.1.4 Heavy reduction

The heavy reduction (60~85%) during controlled rolling increases the yield strength without an adverse effect on the Charpy ductile-brittle transition temperature (DBTT). Moreover, the heavy reduction followed by rapid cooling on the run-out table remarkably improves both the yield strength and the DBTT<sup>[10]</sup>. On their own, the heavy reduction results in grain refinement and the rapid cooling increases the fraction of bainitic structure. However, when the heavy reduction is followed by rapid cooling, the microstructure with the increased fraction of bainite becomes significantly grain-refined<sup>[10]</sup>. These results also showed that the volume fraction of martensite/austenite (M/A) constituents decreased on increasing the total deformation for a steel containing 0.03%C, 0.05%Nb and 0.024%Ti<sup>[13]</sup>.

### 1.4.2 Cooling rate

The cooling rate ( $V_c$ ) and the finishing temperature ( $T_c$ ) of accelerated cooling after finish rolling are important parameters of thermo-mechanically controlled processing for line pipe steels to achieve optimum strength through controlling the influence of transformation microstructure, ferrite grain refinement and precipitation hardening. The effect of  $T_c$  and  $V_c$  may be attributed to the control of the precipitation of carbonitrides during accelerated cooling<sup>[9]</sup>. The availability of high cooling rates immediately after finish rolling provides greater microstructural adjustment possibilities, especially for the case of Mo-Nb steel types. The possibilities for adjustment of the relative volume fractions of polygonal and acicular ferrite (and grain size) through the setting of the cooling rate and coiling temperature, are evident in principle<sup>[2]</sup>. Rapid cooling increases the volume fraction of bainite or M/A islands or acicular ferrite.

### 1.4.3 Coiling temperature

There is no phase transformation during coiling, but it is very important for precipitation strengthening of these steels, so it requires careful control of the coiling temperature if the maximum degree of precipitation strengthening is to be attained.  $TiC$ <sup>[5]</sup>,  $NbC$ <sup>[12]</sup> and  $V(C,N)$  precipitate in the ferrite during coiling. The temperature should be sufficiently low (i.e. a high degree of under-cooling) for fine precipitation of these carbides and carbonitrides in the ferrite but not so low that the volume fraction of  $TiC$  is reduced through too slow diffusion<sup>[5]</sup>. When the coiling temperature is too low, precipitation is suppressed, resulting in low strength.

## 1.5 Pipe forming and welding process

The process of pipe making is through cold forming and cold expansion. There are two possible seam lines for the manufactured pipes, one is a spiral seam and the other longitudinal. Most of the pipelines manufactured globally belong to the former, but, as the quality of the plate has increased, pipelines with longitudinal seams have

increased lately in many manufacturing processes.

The last operation of pipe making is to either weld the seam by submerged arc welding, or by electrical resistance welding as has been preferred in the recent pipeline manufacturing process<sup>[6]</sup>. Low carbon equivalence improves the weldability.

## CHAPTER 2 MICRO-ALLOYING ELEMENTS AND THEIR EFFECTS ON PRECIPITATION

### 2.1 Vanadium

Vanadium is used in line pipe steels to form vanadium carbonitrides. Its content ranges from 0.03 to 0.05%V<sup>[14]</sup>. The main action of vanadium in these steels is dispersion hardening, refinement of ferrite grains and inhibiting grain growth of austenite up to 1050 °C, but it is detrimental to the formation of acicular ferrite<sup>[4]</sup>. As the solubility of vanadium in austenite is high there is a weak influence of vanadium on the non-recrystallisation temperature ( $T_{nr}$ ) of austenite. The solubility of vanadium in ferrite, however, is low, and its addition is extremely effective in the precipitation strengthening of ferrite.

The precipitation starting temperature of VN particles is 1005 °C through the solubility equation of the form  $\log(X\%)(Y\%)=(-A/T)+B$ , where X and Y in the equation are mass percentages of the dissolved micro-alloys, A and B are constants, (A and B are 8330 and 3.46 for VN, respectively), T is the absolute temperature<sup>[15]</sup>. The solubility limit of vanadium in typical line pipe steels is about 0.2% at 1150 °C<sup>[14]</sup>.

Vanadium carbonitrides will mostly dissolve in austenite at about 900 °C<sup>[9]</sup>. Vanadium also inhibits grain growth of austenite up to 1050 °C. It passes completely into solid solution above 1050 °C for typical line pipe compositions. Vanadium has no effect on the recrystallisation of hot-deformed austenite above 900 °C<sup>[16]</sup>.

### 2.2 Niobium

Niobium carbide is fully dissolved between 1225 and 1250 °C. It has a greater refinement effect on ferrite grain size, dispersion hardening and reduction of pearlite content. Niobium has a stronger effect on recrystallisation of hot-deformed

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austenite<sup>[17-19]</sup>. Niobium in solution is also considered to suppress the  $\gamma/\alpha$  transformation due to pinning of the  $\gamma/\alpha$  interfaces by NbC<sup>[20]</sup>. The solute niobium strongly segregates to  $\gamma/\alpha$  boundaries and reduces ferrite growth kinetics because of a solute drag effect. Accordingly, niobium additions suppress or delay the formation of polygonal ferrite and pearlite, and promote the formation of acicular ferrite<sup>[4]</sup> or bainite/martensite-austenite constituents and increases the bainitic hardenability<sup>[21]</sup>. The solubility temperature of niobium increases from about 1170 °C in a typical niobium steel to about 1250 °C, in a Nb-Ti steel. In relation to titanium, the presence of niobium leads to a higher amount of titanium precipitating in the low temperature range, up to the dissolution of complex Ti-Nb carbonitrides. Consequently, it can be concluded that high titanium concentrations present in Nb-Ti steels, exert a significant influence on the grain coarsening behaviour<sup>[22]</sup>. Some strengthening will result from NbN or Nb(C,N) precipitation in the austenite. However, the most effective precipitation strengthening comes from NbC precipitation in ferrite<sup>[12]</sup>.

The precipitation start temperature of Nb(C,N)<sub>0.87</sub> is 1181 °C. The solubility limit is about 0.05% at 1150 °C<sup>[14]</sup>. Higher niobium contents enable finish rolling to be carried out at higher temperatures because undissolved NbC provides a finer austenite grain<sup>[23]</sup> on soaking, which reduces the critical deformation for austenite to dynamically recrystallise. The most rapid precipitation of niobium occurs between 800 and 950 °C in austenite. The intermediate finish rolling temperature (FRT<sub>s</sub>) of 800~850 °C leads to lower soluble niobium levels than do lower or higher FRT<sub>s</sub><sup>[24]</sup>.

The content of niobium in line pipe steels is usually less than 0.05%. The main effects of niobium in these steels are as follows:

- (i) Much greater refinement<sup>[25,26]</sup> of ferrite grains due to increasing the inhibiting effect of the growth of austenite grains with Nb%;
- (ii) Dispersion hardening;
- (iii) Reduction of pearlite content due to the binding of carbon in Nb(C,N); and



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(iv) Stronger inhibiting effect on recrystallisation<sup>[27]</sup> of hot-deformed austenite below 950 °C<sup>[16]</sup>, thereby raising the non-recrystallisation temperature ( $T_{nr}$ )<sup>[12]</sup> due to the precipitation of Nb(C,N) during hot rolling<sup>[28]</sup>.

### 2.3 Titanium

Titanium can refine ferrite grains, suppress recrystallisation of hot-deformed austenite and reduce pearlite formation. Titanium will bind with free N during solidification of the steel. TiN is very stable at high reheating temperatures (such as 1250 °C), thus retarding grain growth during the reheating process. TiN will also retard grain growth between rolling passes. If it binds all of the free N, this will result in a significant increase in niobium available in the ferrite to precipitate as NbC. The stoichiometric ratio of Ti to N in TiN, is 3.4/1. Titanium can be used to control the sulphide inclusion shape, thus preventing MnS stringer inclusions. The stoichiometric value for Ti/S in TiS ratio is 1.5/1. Therefore, the titanium addition is calculated from<sup>[12]</sup>

$$Ti=3.4N+1.5S \quad (2.1)$$

The precipitation start temperature for TiN is 1633 °C<sup>[15]</sup> while that of TiC is less than that of TiN' (<1000 °C<sup>[5]</sup> for TiC). Therefore, the alloy needs sufficient titanium content for TiC to form ( $Ti>0.4N$ )<sup>[14]</sup>. The stoichiometric ratio Ti/N is 3.4/1 but it may change depending on several factors, such as the reheating temperature before hot rolling and the content of other micro-alloying elements<sup>[29]</sup>.

The main effects of titanium in high-strength low alloy steels are as follows:

(i) **Refining of ferrite grains**<sup>[30,31]</sup>: The optimum Ti/N ratio is close to 2 for Nb-free and V-free steels<sup>[29]</sup>. Titanium at levels of 0.02 to 0.03% has a much greater refinement effect on ferrite grain size. It inhibits the growth of austenite grains by the difficult-to-dissolve TiN and Ti(C,N) during heating<sup>[14]</sup>. It inhibits grain growth most effectively at 1150 °C and an addition of 0.015% Ti has a much greater refinement of austenite grains than the addition of the same amount of Nb<sup>[16]</sup>. Titanium in excess after binding with free nitrogen will be available to bind with sulphur.

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**(ii) *Suppression of recrystallisation of hot-deformed austenite:*** Titanium has a stronger inhibiting effect on recrystallisation at 1050 °C than niobium. There is a contradictory result, however, that 0.03% Ti does not have a substantial effect on the recrystallisation of the austenite of low alloy steels due to differences in the composition of these steels<sup>[16]</sup>.

**(iii) *Dispersion hardening:*** Because TiC forms at lower temperatures, the titanium content must exceed the bound content from TiN ( $Ti > 0.4N$ ).

**(iv) *Reduction of pearlite formation***

## 2.4 Molybdenum

The addition of molybdenum in Nb-containing steels can improve transformation hardening (increased volume fraction of acicular ferrite and M/A islands), grain refinement and precipitation hardening. It is mainly the metastable coherent carbide  $Mo_2C$  that provides hardening in Mo-containing steels, although the formation of this carbide requires relatively higher levels of addition. Molybdenum also greatly suppresses or delays the formation of polygonal ferrite and pearlite<sup>[4]</sup> and promotes the formation of acicular ferrite<sup>[32]</sup>. When the carbon content of the steel is sufficiently low, martensite formation is avoided and fine structures of bainite and acicular ferrite are formed during air-cooling after hot rolling. This will result in very good ductility. Line pipe steels with a discontinuous stress-strain curve lose some yield strength as a result of U-O pipe forming (U-bending and O-bending) and do not completely recover this loss after expansion of the pipe. For steel containing molybdenum, the stress-strain curve of the as-rolled plate is continuous without an upper yield point. This results in complete control of the detrimental Bauschinger effect during pipe forming and contributes to an increase in the yield strength from plate to pipe. The impact-transition temperature of traditional grades is raised by 10 to 20 °C after pipe forming, but does not change for steel with a molybdenum content<sup>[33]</sup>.

The addition of molybdenum in Nb-containing steels has the following purpose in line

pipe steels:

- (i) Transformation hardening due to increased acicular ferrite (AF) and martensite/austenite (MA) formation;
- (ii) Grain refinement; and
- (iii) Precipitation hardening<sup>[2]</sup>.

The addition of molybdenum provides a considerable strengthening advantage over Nb-V steels<sup>[2]</sup>.

## 2.5 Carbon

Carbon level in these steels is maintained below 0.06% for the following purposes:

- (i) Lowering the carbon equivalent (CE) for improved weldability: The maximum CE specification is 0.45;
- (ii) High toughness;
- (iii) Less micro- and macro-segregation;
- (iv) More effective dissolution of niobium: increasing the strength of steels; and
- (v) Less pearlite: improving toughness, formability, SSCC (sulphide stress corrosion cracking).

## 2.6 Manganese

An increase in the manganese content prolongs the incubation time for polygonal ferrite formation. The manganese addition extends the polygonal ferrite curve of continuous cooling transformation (CCT) diagrams. Accordingly, acicular ferrite structures can be obtained at a slower cooling rate with an increase in the manganese content. The addition of manganese delays the precipitation of titanium and niobium, and increases the solubility of NbC by decreasing the diffusivity of niobium in austenite<sup>[4]</sup>. Manganese also increases the solubility for nitrogen in austenite significantly.

**2.7 Copper, Chromium and Nickel**

These elements can improve resistance to HIC (hydrogen-induced cracking) and SSCC (sulphide stress corrosion cracking). Chromium and copper have little effect on the mechanical properties of as-rolled plate. Chromium and copper promote the formation of very fine precipitates when used in combination with niobium or vanadium<sup>[33]</sup>. Steels with a small amount of copper tend to have a somewhat higher corrosion resistance than alloys without copper. As little as 0.05 wt% Cu has been shown to have a significant effect and, usually, the addition of 0.2% Cu can provide increased resistance to atmospheric corrosion. Copper can increase the strength of ferrite through solid solution strengthening and, with 0.5% or more, is precipitated as elemental Cu-particles when the steel is aged within the temperature range of about 425 to 650 °C, thus providing a degree of precipitation hardening by virtue of ferrite strengthening<sup>[34]</sup>.

## **CHAPTER 3 THE CONTROLLED ROLLING PROCESS OF LINE PIPE STEELS**

Line pipe steels with high strength and good toughness properties are produced by using a controlled rolling process. Controlled rolling appears to be vital to produce these steels with optimum mechanical properties. The controlled rolling technique is most effective with steels containing micro-alloying elements that provide a region below which non-recrystallisation will take place during the finishing stages of hot rolling. Micro-alloying additions increase this temperature above where complete recrystallisation occurs and the recrystallisation of austenite below this temperature is retarded during deformation.

### **3.1 Three stages of deformation for controlled rolling process**

Controlled rolling may be divided in principle into three stages<sup>[11]</sup>:

- (1) Deformation in the austenite recrystallisation temperature region;
- (2) Deformation in the austenite non-recrystallisation region; and
- (3) Deformation in the two-phase austenite-ferrite region.

This is illustrated in figure 3.1<sup>[11]</sup> along with the structural changes, which occur during the controlled rolling process. Optimum mechanical properties of HSLA steels can be obtained only by the careful control of microstructural changes in each stage of controlled rolling. The principal variables are deformation temperature, amount of deformation and strain rate.

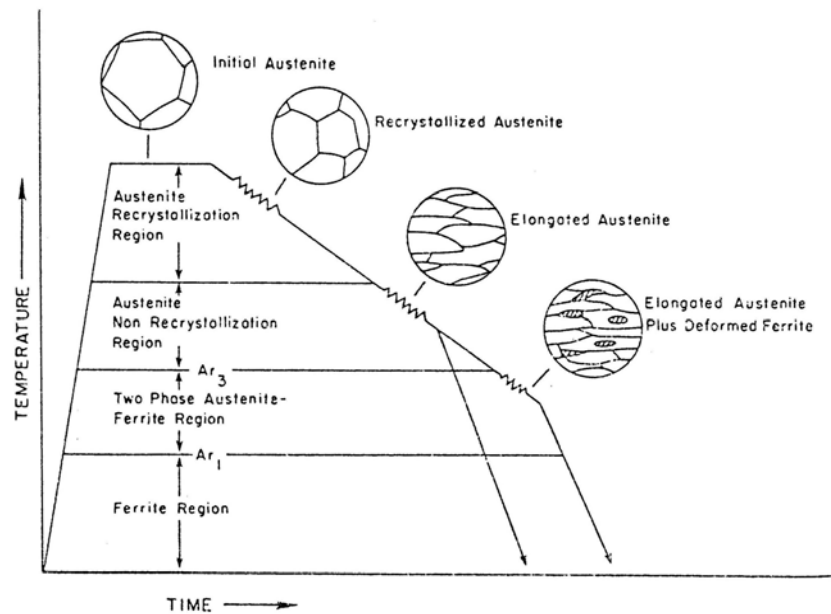


Figure 3.1 Schematic illustration of the three stages of the controlled rolling process<sup>[11]</sup>.

### 3.1.1 Deformation in the austenite recrystallisation region

The reheating temperature and the solubility of micro-alloying precipitates have a strong influence on the grain size of the initial austenite after reheating and the grain size of the recrystallised austenite before the  $T_{nr}$  is reached. The effects of micro-alloying elements depend on the reheating temperature<sup>[11]</sup>. The recrystallised grain size decreases rapidly as a function of both an increased reduction per pass and a decreasing deformation temperature. The smallest recrystallised austenite grain size can be attained by using deformations above the critical amount required for the initiation of dynamic recrystallisation during hot rolling.

### 3.1.2 Deformation in the non-recrystallisation region

It is commonly believed that micro-alloying elements retard the recrystallisation of austenite either by solid-solution effects through solute drag or by the pinning effect of strain-induced precipitation. Below the non-recrystallisation temperature, recrystallisation of austenite grains is sufficiently suppressed so that rolling produces deformed elongated austenite grains (also called ‘pancake’ grains) and deformation

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bands within the austenite. Deformation bands also serve as nucleation sites for ferrite<sup>[11]</sup>. With an increasing amount of deformation, the austenite grains become more elongated, thereby increasing their length-to-thickness ratio, and the number of deformation bands increases and their distribution becomes uniform, giving rise to a fine and uniform final austenite structure and also to the final ferrite structure after transformation on the run-out table.

### 3.1.3 Deformation in the ( $\alpha+\gamma$ ) two-phase region

Deformation in this two-phase region is generally difficult to control because there is a differing deformation resistance in the two-phase region and this type of hot rolling is generally not considered for line pipe purpose. A time-temperature diagram indicating the microstructural processes during hot rolling is shown in figure 3.2<sup>[8]</sup>. Numerous metallurgical processes take place during hot rolling and subsequent cooling, which determine the final grain size and thus the mechanical properties of the strip.

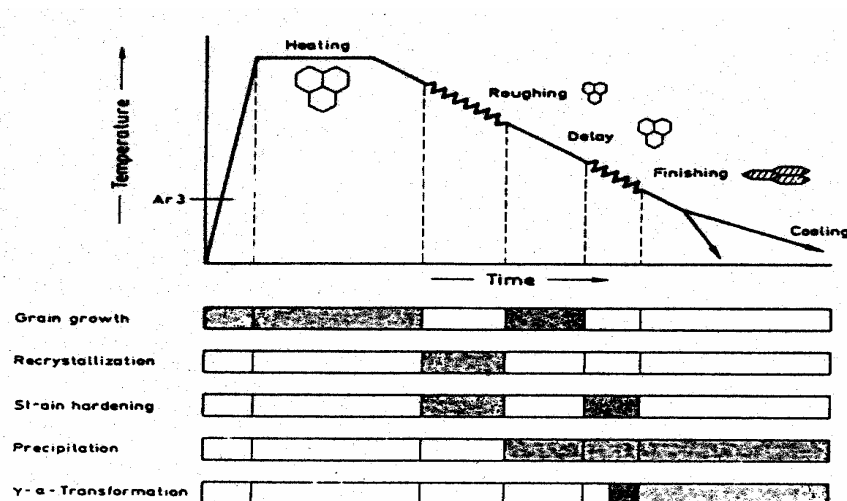


Figure 3.2 Metallurgical mechanisms during thermo mechanical hot rolling<sup>[8]</sup>.

### 3.2 Reheating temperature and undissolved particles

The objective of reheating is to achieve uniformly heated slabs with full dissolution of the micro-alloyed carbonitrides (Nb,V)(C,N). Continuously cast slabs are heated within walking beam furnaces or pusher-type furnaces. The reheating temperature depends on which micro alloying elements are present in the steel. It is generally from 1150 to 1250 °C for Nb-containing steels, so that most of the alloy carbides and nitrides (except for TiN) are dissolved in the steels in order to obtain maximum dispersion hardening later. The soaking time is usually from 30 to 60 minutes for a slab thickness of 26 to 110 mm<sup>[1, 10, 14, 35, 36]</sup>.

At higher reheating temperatures, most micro-alloying elements will be in solution in the austenite and will precipitate at lower temperatures both in the austenite and in the ferrite as carbides, nitrides, or carbonitrides, thereby increasing the strength of these phases (figure 3.3<sup>[24]</sup>). However, high reheating temperatures will allow considerable grain growth to occur. At lower reheating temperatures, a larger proportion of micro-alloying precipitates will remain undissolved in the austenite. These precipitates will act as barriers to grain movement. Precipitates formed during deformation will inhibit grain growth of the recrystallised austenite in the same manner as undissolved precipitates<sup>[11]</sup>.

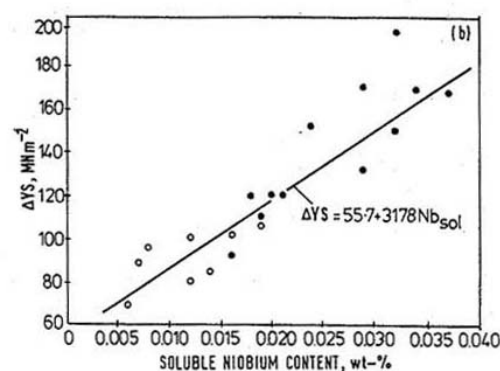


Figure 3.3 Correlation between the increase in yield strength  $\Delta YS$  and the content of soluble Nb<sup>[24]</sup> (0.075% C, 0.43% Si, 1.58% Mn, 0.013% P, 0.005% S, 0.51% Ni, 0.021% Al and 0.106% Nb, and 0.077% C, 0.36% Si, 1.56% Mn, 0.017% P, 0.005% S, 0.47% Ni, 0.020% Al and 0.130% Nb).



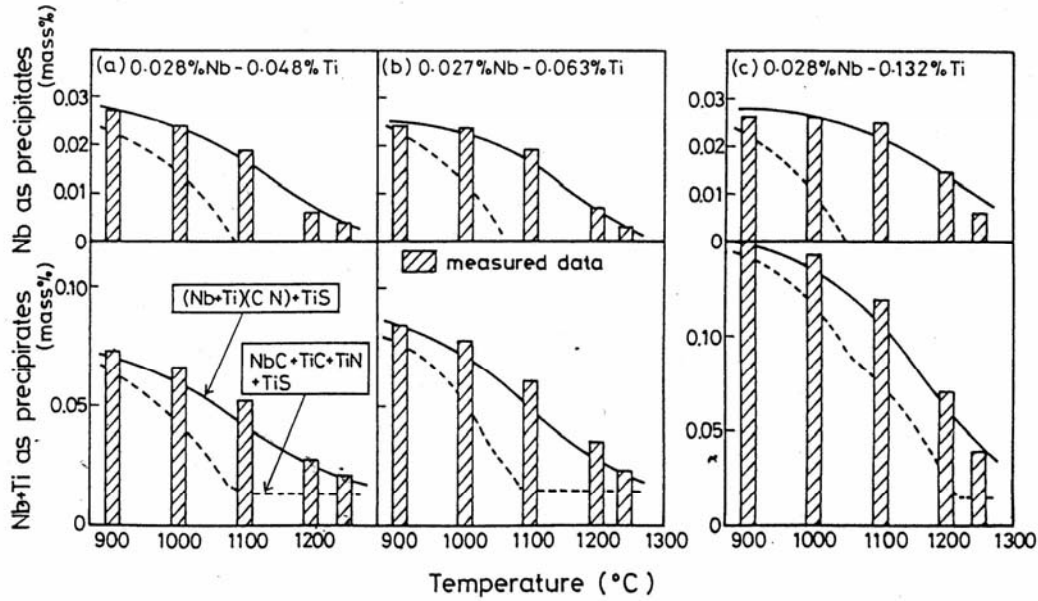


Figure 3.4 Comparison between the calculated and measured quantities of micro-alloying elements as precipitates<sup>[37]</sup>.

Vanadium carbonitride passes completely into solid solution if the reheating temperature is above 1050 °C<sup>[16]</sup>. Niobium carbonitride is not fully dissolved in austenite at 1250 °C and it has a fine spherical shape<sup>[38]</sup>. Figure 3.4<sup>[37]</sup> shows that the amount of Nb and (Nb+Ti) present within precipitates in three Nb-Ti bearing steels, decreases with increasing heating temperature<sup>[37]</sup>. It also shows that there are some undissolved Nb carbonitrides in the matrix even at ~1250 °C. The measurements also show that only 4 to 27% of Nb was dissolved in the austenite at 1100 °C for the Nb-Ti steel. This suggests that the mixing of niobium and titanium increases the stability of the precipitates, so that the solubility of precipitates decreases in Nb-Ti bearing steels through the formation of complex precipitates<sup>[35,37]</sup>. The complex (Nb+Ti) precipitates are more stable than binary Nb carbonitrides so that the coarse precipitates are not dissolved at 1250 °C<sup>[35]</sup>.

The austenite grain size increases and the quantity of undissolved precipitates decreases with increasing reheating temperature. Accordingly, the grain size after reheating is directly linked to the presence of micro-alloying elements, the dissolution

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behaviour of carbonitrides and the heating time and temperature (figure 3.5)<sup>[39]</sup>. The higher the quantity of undissolved precipitates, the more stable the carbonitrides are. So, the austenite grain size becomes finer due to the retarding effect of undissolved particles on the recrystallisation of austenite. The complex micro-alloying precipitates are more stable than binary precipitates. The reheating temperature may, therefore, have to be higher for those steels with complex precipitates.

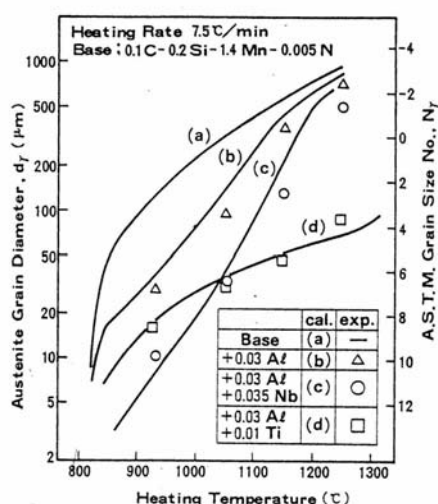


Figure 3.5 Change in austenite grain size during reheating process<sup>[39]</sup>.

### 3.3 Rough rolling

The objective of rough rolling is to achieve the finest possible recrystallised austenite grain size at the point where the  $T_{nr}$  is reached<sup>[6]</sup>. The rough-rolling stage is completed at a temperature above about 1030 °C<sup>[2]</sup>, i.e. in the recrystallised austenite region for the X60 to X80 ERW line pipe steels<sup>[9]</sup> where recovery and recrystallisation of austenite grains take place<sup>[7]</sup>. Specially developed reduction schedules together with TiN particle control to inhibit growth of recrystallised grains, are employed for this purpose<sup>[6]</sup>. The transfer bar thickness is typically about 26 to 30 mm for line pipe coils in the final strip thickness range of 5 to 10 mm and effectively sets the non-recrystallisation finish rolling reduction level at about 70 to 80%<sup>[2,6]</sup>. However, for most line pipe steels the temperature of rough rolling varies from 1200 to 950 °C<sup>[7,9-11]</sup>. Strain hardening also takes place besides recrystallisation in this stage<sup>[8]</sup>.

### 3.4 Finish rolling

The objective of this stage is to accumulate rolling strain within the austenite grains so that on subsequent ferrite transformation, ferrite nucleation sites are greatly multiplied in number and a very fine ferrite grain size can be generated during controlled cooling<sup>[6]</sup>.

The stage is confined to the non-recrystallised austenite region in the lower temperature range above  $A_{r3}$ <sup>[9]</sup>. The starting temperature for this stage is in the region of about 1050 to 950 °C and the finish rolling temperature is in the region of 850 to 950 °C<sup>[6,9,10]</sup>. The total finishing reduction is usually about 64 to 80% when the initial slab thickness and finishing thickness are 110 and 18 mm, respectively<sup>[1]</sup>. While further strengthening of the hot strip can be achieved when finish rolling is continued into the intercritical region of austenite and ferrite, there is little resultant benefit to the final pipe strength since the Bauschinger effect is increased in magnitude. Lowering the finish rolling temperature below  $A_{r3}$  was effective in one instance, in significantly increasing the strength of the hot strip (figure 3.6<sup>[22]</sup>). However, almost no further improvement in the corresponding pipe strength was recorded, suggesting that two-phase rolling exacerbates the Bauschinger drop<sup>[2]</sup>. This “diminishing return” effect led to the consideration of molybdenum additions as a means in which to comfortably reach higher strength levels in X70 and X80 line pipe steels whilst avoiding the use of an excessively high carbon equivalent in the interests of preheat-free welding<sup>[2]</sup>.

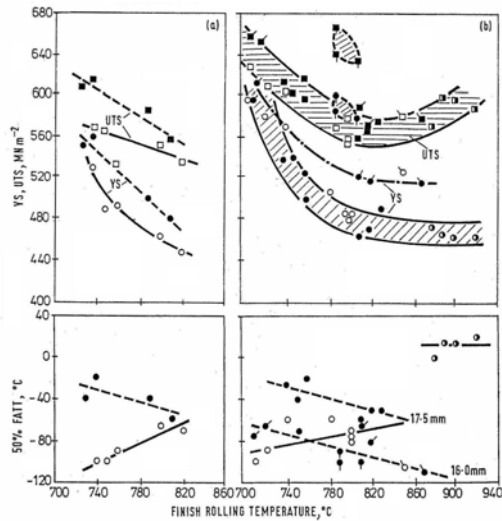


Figure 3.6 Influence of rolling conditions on the mechanical properties of plate and strip of different thicknesses<sup>[24]</sup>.

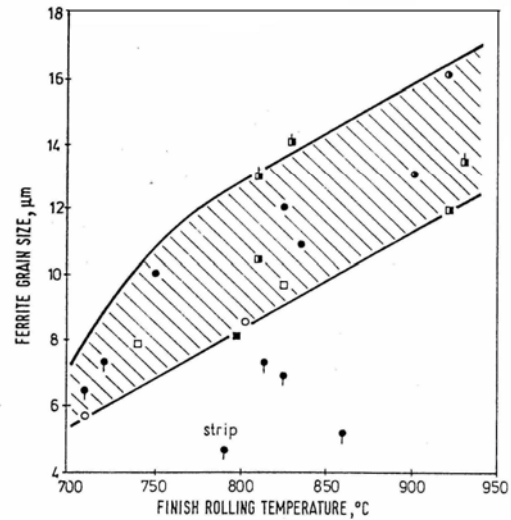


Figure 3.7 Influence of rolling conditions on the average ferrite grain size<sup>[24]</sup>.

The role of the finish rolling temperature on mechanical properties of the steel may be attributed to the acceleration of transformation to ferrite and the refinement of grains by the decrease in the finishing temperature<sup>[9]</sup>. Therefore, the decrease in finishing temperature will be beneficial to both strength and ductility as shown in the following regression equations determined for a steel of composition: 0.07%C, 0.25%Si, 0.9%Mn, 0.046%Nb, 0.04%V, 0.015%Ti and 40ppm N<sup>[9]</sup>:

$$\text{YS} = 0.508T_s - 0.231T_f - 0.334T_c + 1.905V_c + 323.6 \quad R^2 = 0.94 \quad (3.1)$$

$$\text{EL} = -0.002T_s - 0.064T_f - 0.086T_c + 0.325V_c + 121.8 \quad R^2 = 0.98 \quad (3.2)$$

where EL is the elongation in %,  $T_s$  is the start rolling temperature ( $^{\circ}\text{C}$ ),  $T_f$  is the finish rolling temperature ( $^{\circ}\text{C}$ ),  $T_c$  is the finish cooling temperature ( $^{\circ}\text{C}$ ),  $V_c$  the cooling rate ( $^{\circ}\text{C s}^{-1}$ ) and  $R^2$  is the regression coefficient. In such an approach, however, one needs to strictly control the lowering of the finish rolling temperature as higher mill loads are encountered. It has been reported<sup>[9]</sup> that when  $T_f$  is above a certain lower limit temperature, both the yield strength and the toughness of the steel increase with a decrease of  $T_f$ . If  $T_f$  is below this critical temperature, a banded microstructure appears which greatly reduces toughness.

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Figure 3.7<sup>[24]</sup> shows the effect of finish rolling temperature on the final ferrite grain size, showing that the ferrite grain size can be reduced at lower finish rolling temperatures<sup>[24, 36]</sup>. Some phenomena that appear are strain hardening, precipitation of micro alloying carbonitrides and/or  $\gamma$ - $\alpha$  transformation<sup>[8]</sup>.

### 3.5 Heavy reduction

A heavy reduction of 60 to 85% in total, increases the yield strength without adversely affecting the Charpy brittle to ductile transition temperature. Moreover, a heavy reduction followed by rapid cooling remarkably increases the yield strength and decreases the Charpy brittle to ductile transition temperature (figure 3.8<sup>[10]</sup>). The heavy reduction on its own results in a slight grain refinement and the rapid cooling again increases the fraction of the bainitic microstructure. However the two together, when the heavy reduction is followed by rapid cooling, the microstructure with the increased fraction of bainite becomes grain-refined<sup>[10]</sup>. The result also showed that the volume fraction of M/A constituents decreased on increasing the deformation for a steel containing 0.03%C, 0.05%Nb and 0.024%Ti (figure 3.9)<sup>[13]</sup>.

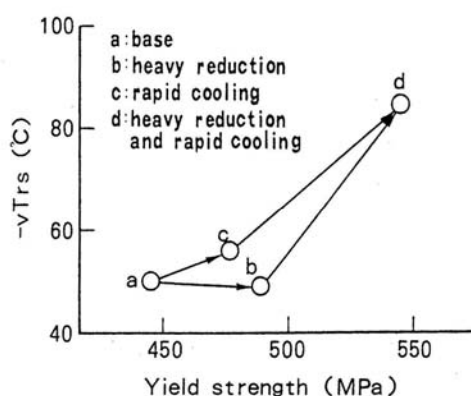


Figure 3.8 Improvement in yield strength and Charpy ductile to brittle transition temperature<sup>[10]</sup>.

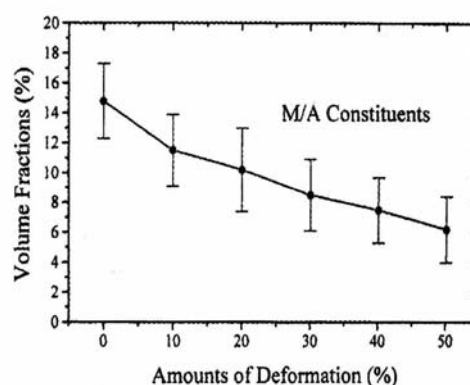


Figure 3.9 Plot of the volume fraction of M/A constituents versus the degree of prior deformation<sup>[13]</sup>.

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The total or cumulative reduction of HSLA steels in the hot rolling process is generally between 67 to 84%<sup>[1,6,9, 10,14,35,38]</sup>, while the maximum cumulative reduction is up to 95%<sup>[40]</sup>. The number of passes of thermo-mechanically controlled processing are generally between 4 to 6 with a maximum of 7 to 9 for an ~0.06%C steel<sup>[41]</sup>. Table 3.1 shows the typical reduction and passes of hot rolling for line pipe steels.

Table 3.1 Reduction/pass of hot rolling

Steel No	Reduction, %									Ref.
	Pass 1	Pass 2	Pass 3	Pass 4	Pass 5	Pass 6	Rough rolling	Finishing rolling	Total	
1	16	23	29	27	--	--			67	38,42
2	--	--	--	--	--	--	51	64	84	1
3	15	25	25	25	25	25	--	--	80	10
4	21	21	31	30	30	25	--	--	84	10
5	13	30	30	30	30	25	--	--	84	10
6	33	40	40	35	--	--	--	--	84	10
7	16	23	29	27	--	--	--	--	67	35
8	25	33.3	40	33.3	--	--	--	--	73	9

**3.6 Strip thickness**

The thickness of the final strip has a significant effect on the strength of these steels, especially on the ratio of yield strength to ultimate tensile strength or YS/UTS. Experimental results on X80 line pipe steels showed that the yield strength and tensile strength increased and the YS/UTS ratio also increased from 0.86 to 0.95 with decreasing strip thickness from 9 to 3 mm for an 0.07% C, 0.19% Si, 1.53% Mn, 0.045% Nb, 0.012% Ti and 0.20% Mo steel (figure.10)<sup>[6]</sup>. A similar relationship between the thickness and the YS/UTS ratio that dropped from 0.89 to 0.76 as the thickness was increased from 13.5 to 50 mm, was found in a X80 steel of composition: 0.075% C, 0.43% Si, 1.58% Mn and 0.106% Nb)<sup>[24]</sup>. The ratio also dropped from 0.80

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to 0.73 as the thickness increased from 10.3 to 32mm for a steel with composition of 0.09% C, ~0.20% Si, ~1.20% Mn, ~0.043% V, ~0.04% Nb and 0.007% Ti<sup>[38]</sup>.

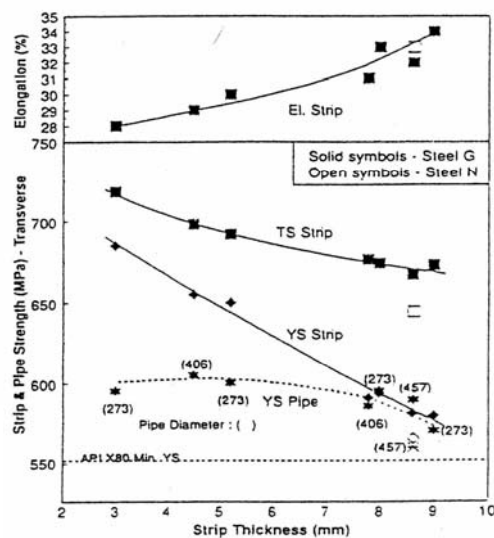


Figure 3.10 Strip and pipe properties for various X80 pipe sizes<sup>[6]</sup>. (Steel G: 0.075% C, 1.59% Mn, 0.31% Si, 0.057% Nb, 0.22% Mo, 0.013% Ti and 0.006% N; Steel N: 0.070% C, 1.53% Mn, 0.19% Si, 0.045 Nb, 0.20% Mo, 0.012% Ti and 0.0045% N.

### 3.7 Cooling rate after finish rolling

The cooling rate ( $V_c$ ) and the finishing temperature ( $T_c$ ) of the accelerated cooling process after finish rolling are important parameters to achieve optimum strength of thermo-mechanically controlled processing for line pipe steels. Controlling the  $T_c$  and  $V_c$  may lead to the control of precipitation of carbonitrides during accelerated cooling<sup>[9]</sup>. The availability of high cooling rates immediately after finish rolling provides greater microstructural adjustment possibilities, especially for the case of Mo-Nb steel types. The possibilities for adjustment of the relative volume fraction of polygonal and acicular ferrite (and grain size) through the setting of the cooling rate and coiling temperature are schematically evident in figure 3.11<sup>[2]</sup>. The rapid cooling increases the fraction of bainitic structure or M/A islands or acicular ferrite. This is because polygonal and pearlite transformations are governed by slow diffusion and have some difficulty in fully transforming during accelerated cooling. The austenite may remain as retained austenite or transform to an acicular ferrite structure because



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the transformation to acicular ferrite is a mixed mode of shear and diffusion<sup>[4,9,11,43]</sup>. The M/A islands are carbon-rich due to the replacement of pearlite by these small islands. The M/A islands also refine the ferrite grain size structure. The ferrite grain size becomes finer when a heavy reduction is followed by rapid cooling (figure 3.12<sup>[10]</sup>) because the nucleation rate increases and there is not enough time for growth of nuclei of ferrite grains due to increasing under-cooling at a rapid cooling rate. The heavy reduction during finish rolling results in more crystal defects and these provide the nucleation sites for the  $\gamma \rightarrow \alpha$  transformation.

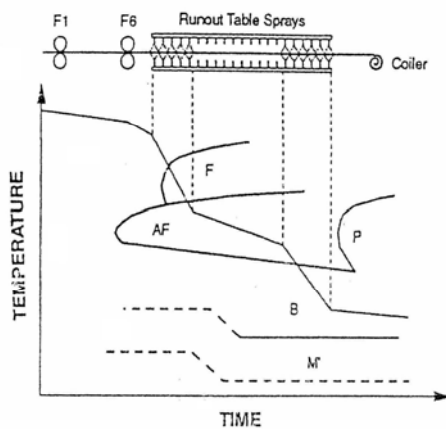


Figure 3.11 Schematic representation of the cooling pattern on the run-out table of a Hot Strip Mill<sup>[2]</sup>.

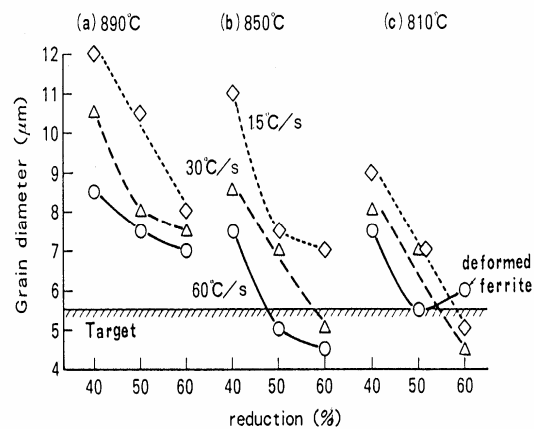


Figure 3.12 Influence of reduction and cooling rate on the ferrite grain diameter<sup>[10]</sup>.

The cooling rate after controlled rolling also has a significant effect on the degree of precipitation<sup>[11]</sup>. With slower cooling rates the coarsening of precipitates makes them less effective for strengthening while with faster cooling rates, no precipitation occurs and the micro-alloying elements remain in solution. Correctly designed accelerated cooling leads to fine precipitation of Nb(C,N) and also provides ferrite grain refinement<sup>[4]</sup>. Roberts<sup>[5]</sup> indicated that a higher yield strength can be obtained at a low carbon equivalent by employing accelerated cooling. In general, an increasing degree of precipitation hardening as the cooling rate is raised, has no detrimental effect on fracture toughness because of the simultaneous refinement of the microstructure and



the replacement of pearlite by small islands of bainite.

An increase in cooling rate from 15 to 30 °Cs<sup>-1</sup> in a Nb-bearing steel (0.1% C, 0.20% Si, 0.09% Mn, 0.046% Nb and 0.0018% N) enhanced the yield strength by 20 to 30 MPa<sup>[10]</sup>. This leads to a guideline equation (3.1) above. The yield strength of a line pipe steel can increase by an average of about 2 MPa for every increase of 1 °Cs<sup>-1</sup> in the cooling rate<sup>[9]</sup>.

The cooling rate on run-out tables for line pipe strip rolling in the laboratory is generally between 10 to 60 °C s<sup>-1</sup><sup>[9,10,44]</sup>.

### **3.8 Finish temperature of accelerated cooling**

The finish temperature of accelerated cooling ( $T_c$ ) is important in controlling the precipitation of carbonitrides during this cooling. At a temperature just above 500 °C,  $V_4C_3$  which is the main vanadium carbide in these steels, has the highest nucleation rate and its contribution to precipitation strengthening is most prominent<sup>[45]</sup>. Therefore, within a certain temperature range just above 500 °C, a lower  $T_c$  is beneficial to both strength and ductility as predicted by formulae (3.1) and (3.2). However,  $T_c$  cannot be decreased too low, because it will be detrimental to the fracture toughness of the steel<sup>[9]</sup>.

The pearlite transformation will also be retarded as the finish temperature of accelerated cooling is decreased. Optical microscopy showed that some pearlite is formed when  $T_c$  is at 781 °C, only a little pearlite is formed at 660 °C and no pearlite is formed below 580 °C in an 0.08% C, 0.007% Nb, 0.009% Ti steel<sup>[39]</sup>. When lowering the  $T_c$ , ferrite grains become finer and the volume fraction of acicular ferrite increases. Below 580 °C, however, the ferrite grain size remains largely unaffected because the ferrite transformation is already complete (figure 3.13)<sup>[39]</sup>.

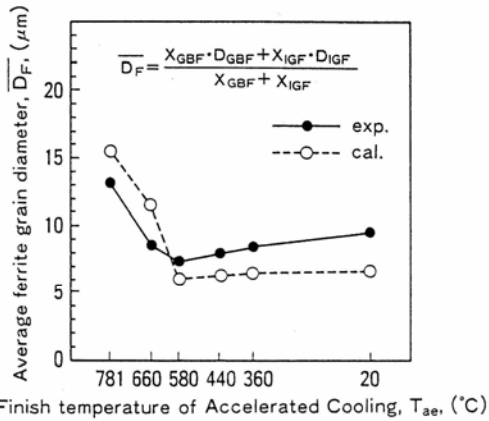


Figure 3.13 Effect of finish temperature of accelerated cooling on the average ferrite grain diameter<sup>[39]</sup>.

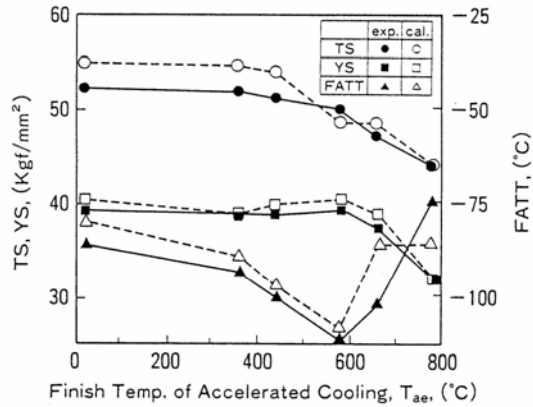


Figure 3.14 Comparison of mechanical properties between the observed and the calculated strengths of micro-alloyed steels<sup>[39]</sup>.

The relationship between  $T_c$  and the tensile strength is shown in figure 3.14<sup>[39]</sup>. It indicates that the yield strength and ultimate tensile strength increase with decreasing  $T_c$  until about 580 °C. But almost no further change in strength is found at  $T_c < 580$  °C.

The finishing temperature of accelerated cooling ( $T_c$ ) is, therefore, maintained generally between 550 and 670 °C<sup>[7,8,10,44]</sup> although sometimes it may even be as high as 800 °C ( $\sim 0.10\%$  C)<sup>[36]</sup> or even below 500 °C<sup>[9,10]</sup>.

From the above, it appears that the optimum mechanical properties for a line pipe steel can be obtained when the reheating temperature  $T_s$  is approximately 1100 °C, the finishing temperature  $T_f$  is about 890 °C, the finishing cooling temperature  $T_c$  is about 520 °C and the cooling rate  $V_c$  from the  $T_f$  to  $T_c$  is about  $30^\circ\text{C s}^{-1}$ <sup>[9]</sup>.

### 3.9 Coiling temperature

The coiling temperature will influence the effectiveness of Nb-precipitation but especially that of V(C,N) precipitation in the ferrite, thus controlling the precipitation strengthening of the steel. The coiling temperature requires careful control if the maximum degree of precipitation strengthening is to be attained. High coiling temperatures result in few and coarse precipitates, which will add very little to the strength, while lower temperatures should be sufficiently low for a fine precipitation, adding to the strength depending on the levels of micro-alloying additions, especially the vanadium and free N in solution. Low coiling temperatures will result in finer ferrite grains because of less ferrite grain growth taking place after transformation, adding to the strength and fracture toughness. Lower finish cooling and coiling temperatures, will suppress pearlite formation and microstructural banding<sup>[46]</sup>. The temperature, however, should not be too low so that the volume fraction of TiC is reduced by too slow diffusion<sup>[5]</sup>. Too low a coiling temperature results in low strength because precipitation may be retarded. The optimum coiling temperature for a given composition should preferably be determined experimentally.

Production experience with Nb-Ti-, Nb-V-Ti- and Mo-Nb-Ti-type line pipe steels shows somewhat different sensitivities of coiling temperature with strip strength properties as indicated in figure 3.15<sup>[2]</sup>. There was little effect in the relationship between coiling temperature and yield strength for these micro-alloying steels. The same tendency is that the yield strength increases with decreasing coiling temperature. Decreasing the coiling temperature has no effect on the yield strength below about 620 °C for a Ti-Nb-V steel with composition 0.085% C, 0.050% V, 0.045% Nb and 0.013% Ti<sup>[2]</sup>.

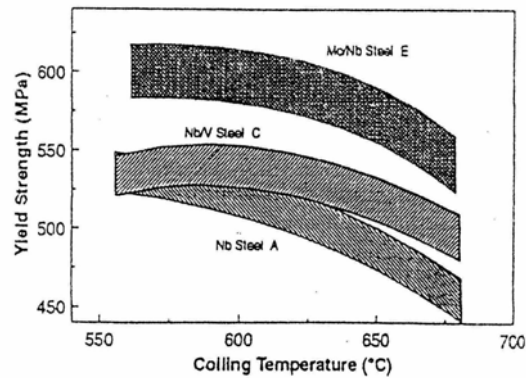


Figure 3.15 Effect of coiling temperature on the YS of hot rolled strip for various types of alloys<sup>[2]</sup>.

### 3.10 Non-recrystallisation temperature ( $T_{nr}$ )

The non-recrystallisation temperature ( $T_{nr}$ ) is also an important parameter for the controlled rolling process of line pipe steels. The rough-rolling process is generally carried out above the  $T_{nr}$  temperature, which is associated with the finishing temperature of the rough-rolling stage. During finishing below the  $T_{nr}$ , a total of at least 0.8 strain should be applied for effective grain refinement (effective controlled rolling)<sup>[46]</sup>.

A coarse, polygonal ferrite plus pearlite microstructure can be ascribed to insufficient strain below  $T_{nr}$ , coupled with higher coiling temperatures, while a coarse acicular ferrite can be ascribed to insufficient strain below  $T_{nr}$  coupled with lower coiling temperatures<sup>[46]</sup>.

#### 3.10.1 Effect of alloying elements

Micro-alloying elements have some effect on the  $T_{nr}$ . Niobium binds with free nitrogen and precipitates as niobium nitrides at higher temperatures, e.g. during rough rolling. Thus, most of the niobium then becomes ineffective in retarding austenite recrystallisation during finish rolling at lower temperatures. Titanium is, therefore, often used in combination with niobium to tie the free nitrogen in Nb-Ti

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micro-alloyed steels and this generally forms (Ti,Nb)N precipitates. Thus, titanium will increase the effect of the niobium on the  $T_{nr}$ . Thus titanium and niobium micro-alloying elements will raise the  $T_{nr}$  (inhibiting recrystallisation)<sup>[47]</sup>, and cause more effective grain refinement. Titanium appears to accelerate the precipitation of Nb(C,N), and therefore, contributes to the retardation of recrystallisation. Titanium is only 0.31 times as effective as niobium in retarding recrystallisation and aluminium 0.15 times<sup>[48]</sup>. The  $T_{nr}$  temperatures at a strain rate of  $3.63 \text{ s}^{-1}$  were found to be 918 and 937 °C for a V-micro-alloyed (0.075% V) and a V-Ti (0.055% V+0.024% Ti) micro-alloyed steel, respectively, while the  $T_{nr}$  was about 1042 °C for a Nb (0.026%) steel deformed at the same strain rate<sup>[47]</sup>. The  $T_{nr}$  decreases with decreasing super-saturation ratio or the [Nb][C] solubility product<sup>[48,49]</sup>. The addition of Mo, Nb, and (Mo+Nb) increases the  $T_{nr}$  in this order<sup>[48]</sup>. The  $T_{nr}$  is increased by boron additions because it accelerates the precipitation kinetics of Nb(C,N), but a maximum in the  $T_{nr}$  at a boron concentration of 48 ppm occurs. The results showed that increasing the boron content beyond 48 ppm leads to a decrease in the  $T_{nr}$ <sup>[48]</sup>. This decrease in the  $T_{nr}$  was possibly due to an acceleration in the rate of coarsening of the Nb(C,N), as precipitate coarsening of Nb(C,N) is accelerated by the presence of boron<sup>[48]</sup> and such coarsened particles lose their effectiveness with regard to retarding the recrystallisation. When less than 48 ppm boron was added, the equilibrium segregation of boron to austenite boundaries and the acceleration of Nb(C,N) precipitation can both contribute to increasing the  $T_{nr}$ .

**3.10.2 Effect of the controlled rolling process**

At the same solution reheating temperature, the non-recrystallisation temperature was found to decrease with an increase in the strain rate from 1.09 to  $3.63 \text{ s}^{-1}$ . This is because a higher strain rate and strain will cause a consequent increase in the density of dislocations, which are beneficial to the onset of recrystallisation through increasing its driving force. Increasing the pass strain and strain rate was found to lead to a decrease in the  $T_{nr}$  for Nb-containing, (Nb+Ti)-containing,

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(Nb+Ti+Mo)-containing and B-containing steels. The strain rate had a smaller effect on the  $T_{nr}$  than the pass strain. These relationships were found to be as follows<sup>[48]</sup>:

$$T_{nr} \propto \varepsilon^{-0.12} \quad (3.3)$$

$$T_{nr} \propto \dot{\varepsilon}^{-0.01} \quad (3.4)$$

The effect of inter-pass time on the  $T_{nr}$  is complicated by the transition from a solute drag effect to retardation by precipitation. In a short inter-pass time range (generally less than 12.5 seconds), the  $T_{nr}$  decreases with increasing inter-pass time because niobium solute drag appears to be responsible for the retardation of recrystallisation<sup>[48]</sup>. The full  $T_{nr}$  relationship to process conditions can be expressed as:

$$T_{nr} = A \varepsilon^{-0.12} t_{ip}^{-0.1} \dot{\varepsilon}^{-0.01} \quad (t_{ip} < 12.5 \text{ s}) \quad \text{or} \quad (3.5)$$

$$T_{nr} = (A \log[\text{Nb}]_{eq} + B) \varepsilon^{-0.12} t_{ip}^{-0.1} \dot{\varepsilon}^{-0.01} \quad (3.6)$$

where  $[\text{Nb}]_{eq}$  is the equivalent niobium content given by  $[\text{Nb}]_{eq} = [\text{Nb} + 0.31\text{Ti} + 0.15\text{Al}]$ ,  $A = 88.1 \text{ }^\circ\text{C per wt\%}$  and  $B = 1156 \text{ }^\circ\text{C}$ .

At long inter-pass times, however, the  $T_{nr}$  increases with increasing inter-pass time. This is because the volume fraction of precipitates that are formed is time dependent, so that the retardation effect increases with the holding time before precipitate coarsening sets in. The effect of the deformation parameters on the  $T_{nr}$  is then as follows:

$$T_{nr} = A' \varepsilon^{-0.12} t_{ip}^{0.04} \dot{\varepsilon}^{-0.01} \quad (12.5 \text{ s} < t_{ip} < 30 \text{ s}) \quad \text{or} \quad (3.7)$$

$$T_{nr} = (A' \log([\text{Nb}][\text{C}]) + B') \varepsilon^{-0.12} t_{ip}^{0.04} \dot{\varepsilon}^{-0.01} \quad (3.8)$$

where  $A' = 63.5 \text{ }^\circ\text{C per wt\%}$ ,  $B' = 885 \text{ }^\circ\text{C}$

Strain has the following effect on the  $T_{nr}$ <sup>[47]</sup>:

$$T_{nr} = T_s - P \varepsilon^a \dot{\varepsilon}^b D^c \quad (3.9)$$

where  $T_s$  is the solution temperature,  $\varepsilon$  is the strain,  $\dot{\varepsilon}$  is the strain rate and  $D$  is the austenite grain size. From the equation above, it appears that a smaller grain size

contributes to raising the  $T_{nr}$ .

The effect of micro alloying elements on the  $T_{nr}$  is described by the following solute retardation parameter (SRP):

$$SRP = \log\left(\frac{t_x}{t_{ref}}\right)\left(\frac{0.1}{X}\right)100 \quad (3.10)$$

where  $t_x$  is the time required for the start of static recrystallisation in the steel containing the element  $x$ ,  $t_{ref}$  is the equivalent time for a reference plain carbon steel and  $X$  is the alloy content of  $x$  in at%. The SRP of V, Mo and Nb is 10, 37 and 409, respectively for a static condition or 8.4, 25 and 135, respectively for a dynamic condition with  $\dot{\epsilon}=2 \text{ s}^{-1}$  at  $1000 \text{ }^\circ\text{C}$ <sup>[50]</sup>.