APPLICATIONS OF NIOBIUM MICROALLOYED FERRITE PEARLITE STEELS TO LINE PIPE AND PLATE

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Abstract

A variety of advanced controlled rolling techniques have been developed to improve toughness, strength and weldability of niobium-steels. To achieve optimum properties, control of prior stage rolling conditions and accelerated cooling are needed.

In low carbon steel, the addition of niobium results in a greater increase in tensile strength than that of vanadium without a loss of toughness. At the same strength level, niobium-steel has less susceptibility to weld cracking and good toughness in the HAZ of its weldments than similar vanadium steels.

Separation and formability of niobium steels are also discussed.

Introduction

The practical application of precipitation hardening to increase the strength of steel first began to attract attention in the 1950's. It can be said, therefore, that this is a very new area insofar as the history of steel is concerned.

As the precipitation or solution behavior of niobium in steel and their effects on mechanical properties of steel became evident, advances in control methods were made. The behaviors were systemized into modern thermomechanical treatment technology, a science which has made niobium-steel the most important steel for high grade linepipes.

This paper discusses both the technical subtleties of the manufacturing process and the mechanical properties of niobium-steel with a ferrite-pearlite structure. It further discusses the performance characteristics of this steel.

Steel Making and Casting

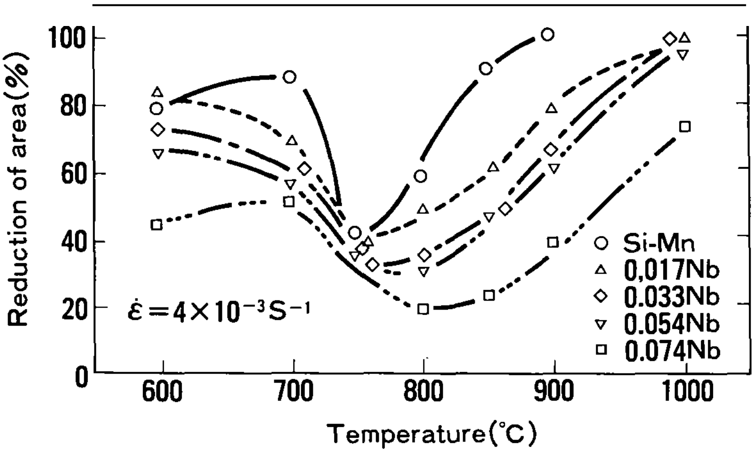
One of the advantages of using niobium for HSLA steels is that the low affinity of niobium for oxygen in molten steel enables both semi-killed steel as well as high yield, economical high strength steel to be manufactured (1, 2). In the 1960's in Japan and in the U.S.A., weldable, structural niobium-steel was manufactured in the semi-killed form (2). Subsequently, it was later recognized that silicon killed steel and, even more so, aluminum-killed steel were superior in quality to semi-killed steel in terms of toughness (3, 4). Thus recently, because of the improved internal quality and weldability, fully killed steel, including high strength line pipe material, has become predominant. At the same time, techniques for manufacturing clean steel, such as desulfurization of molten metal, vacuum degassing and ladle refining, and techniques for inclusion shape control using REM or calcium, have made rapid progress. These techniques improved the ductility of control-rolled niobium-steel and resistance to hydrogen induced cracking (5, 6).

With respect to casting, the technology for continuous casting has also advanced, greatly widening the range of applicable steel grades. Except for heavy plates, almost all grades of steel can be manufactured by the continuous casting processes. Niobium-steel, including X-70 grade line pipe (7-10) and other materials with plate thickness up to about 50 mm have been manufactured by continuous casting. Thus the manufacture of killed steel has been made possible with high yield.

Although transverse slab cracking was encountered in the process of development, (11-13) due to the low ductility of niobium steel just below the solidus line, there is no significant difference between a steel containing up to 0.05 percent niobium and ordinary steel (14, 15). However, hot ductility decreases in the temperature range where niobium carbo-nitride precipitates along grain boundaries, as shown in Figure 1 (16). Figure 1 shows reduction of area of steels with niobium content up to 0.07 percent, obtained by tensile tests at different temperatures after a solution treatment of niobium carbo-nitride by heating the steels to 1300 C. As is clear in the figure, a trough of ductility exists between 900 C and 700 C. The high temperature loss of ductility (in the austenite region: 800–900 C) is caused by grain boundary embrittlement resulting from precipiation of niobium carbo-nitride at austenite grain boundaries and that in the lower-temperature region (the austenite-ferrite region: 700-750 C), by strain concentration on pro-eutectoid ferrite. As a matter of course, the trough in the high-temperature region moves to the higher temperature as the content of niobium increases. As for measures to prevent transverse cracking which can be ascribed to this phenomenon, an effective method involves controlling secondary cooling so as to avoid slab straightening in the ductility reducing temperature range. It has also been reported that reduction of such elements as nitrogen (16) and soluble aluminum (11) improves this situation.

Rolling

Since niobium steel was commercially produced, it has been well established that the strength and toughness of the steel depend greatly on conditions of hot rolling. For the past two decades a considerable number of fundamental and applied studies have been conducted into the role of niobium in controlled rolling, or thermo-mechanical treatment of HSLA steel. These studies include comprehensive reports and surveys (2, 17-25) on the physical metallurgy in the fields of austenite recrystallization and recovery with niobium-steel and these have been reviewed in detail by A. J. DeArdo, J. M. Gray and J. L. Meyer in this conference.



Chemical composition of the steels(wt.%)

Steel	C	Si	Mn	P	S	Nb	sol.Al	total N
1	0.1S	0.29	1.36	0,01Ǝ	0.006	—	0,0ZZ	0.0066
Z	0.15	0,Ǝ0	1.36	0.01d	0.006	0.017	0.028	0.0059
Ǝ	0.13	0.29	1.32	0,01Ǝ	0.006	0,0ƎƎ	0,0ZS	0.0059
d	0.15	0.29	1.35	0.014	0.006	0,0Sd	0,0ZZ	0.0056
5	0,08	0,Ǝ0	1.56	0.01d	0.006	0,0ƎZ	0,0ZZ	0,0060
6	0,09	0.31	1.56	0,01Ǝ	0.006	0.074	0.024	0.007S

Nb

Conditions of rolling, on which the structure and properties of niobium-steel plates depend, include:

1. Slab reheating temperature,
2. The range of temperature for controlled rolling and amount of reduction, and
3. The cooling rate during and after rolling.

With an appropriate combination of these variables, it is possible to control strength and toughness of the steel. From the point of view of grain refining processes, controlled rolling in plate mills can be classified into the following three steps:

1. Refining of austenite grain size by repeated recrystallization in the high-temperature region,
2. Deformation bands and elongated grains introduced by rolling at temperatures where recrystallization does not occur, and
3. Rolling in the two-phase (austenite and ferrite) region.

Slab reheating temperature and roughing

In the process of plate rolling, the stage of rough rolling corresponds to the recrystallization region of austenite and in this range, greater reduction per pass is generally more effective in grain refining. As is well known with niobium-alloyed steel, however, dissolved niobium or niobium carbo-nitride precipitated by rolling, largely retards recrystallization. As shown in Figure 2 (21), the reduction needed to cause recrystallization, increases as the content of niobium increases or as the rolling temperature drops. Reduction at the stage of rough rolling in plate mills, on the other hand, depends on such conditions as the capacity (entry thickness, roll torque, roll force etc.) of rolling mills, and adjustment of plate width. In rolling wide plates for large diameter line pipes, generally, reduction per pass is at most around 10 percent, which is far less than the amount needed for recrystallization. Thus, at this stage, refining by static or partial recrystallization is to be expected by repeated reduction which is determined by the dimensions of slabs, products and the capacity of rolling mills. The grain size before the start of rolling, therefore, has a great effect on recrystallization in the high-temperature region and on the degree of refinement of austenite grain size, which is ultimately achieved.

An example of the relation between temperature for reheating niobium steel and the austenite grain size at the temperature is as shown in Figure 3 (26). As the figure shows, it is possible to vary greatly the grain size before the start of rolling, by controlling reheating temperature. Also, as a matter of course, it is important to optimize the amount of niobium in accordance with the reheating temperature. The effect of slab reheating temperature on strength and toughness of niobium-vanadium alloyed steel, is shown in Figure 4 (25). Here, consistent conditions are used for controlled rolling: the percentage of cumulative reduction above 900 C being about 50 percent, and that below 900 C in the non-recrystallized region, 70 percent. Under these conditions, strength is slightly lowered because the amount of dissolved niobium carbo-nitride decreases as the slab reheating temperature drops. Fracture appearance transition temperature (FATT, vTrs) in Charpy impact testing on the other hand, is effectively improved. This occurs because recrystallization is promoted when the grain size before the start of rolling is small and this causes a finer average grain size prior to rolling in the non-recrystallization region, which results in a decrease of the inhomogeneous mixed grains.

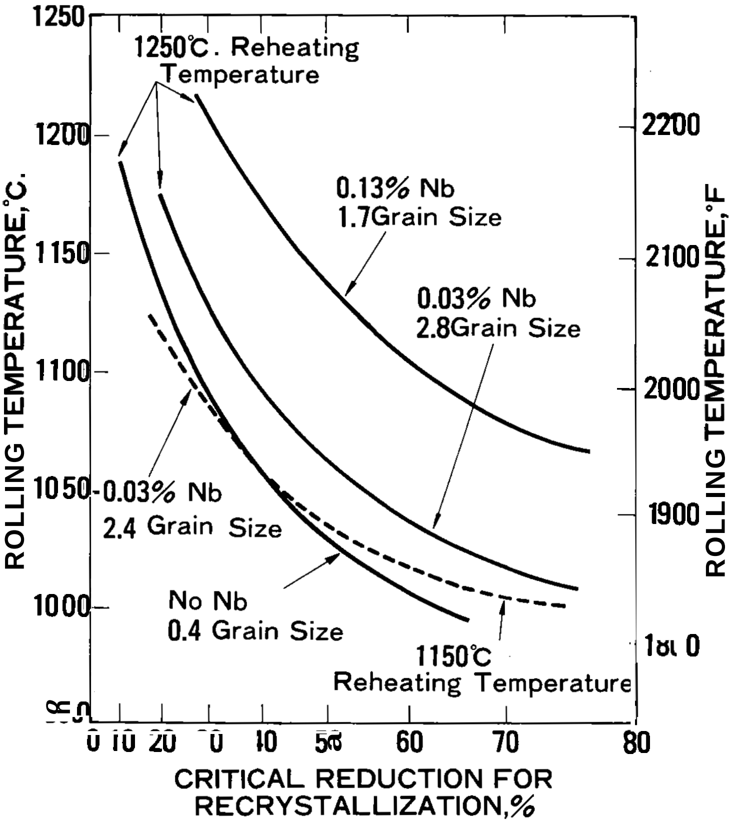


Figure 2. Effect of Nb on critical reduction for austenite recrystallization (21).

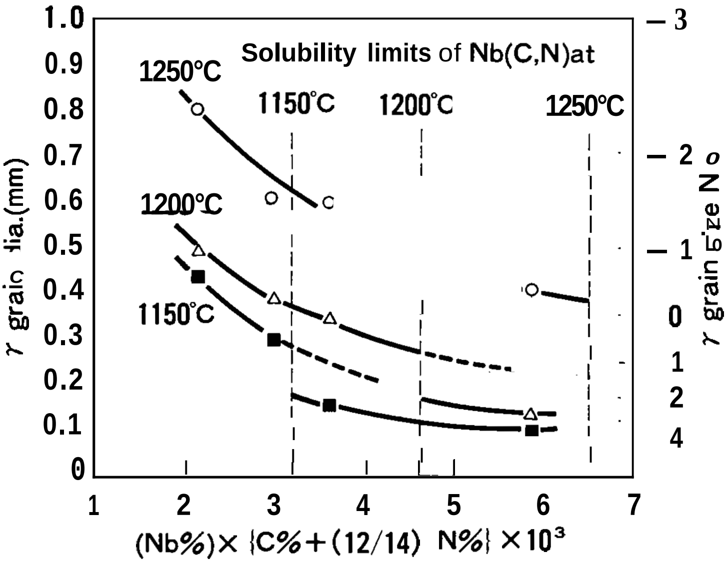


Figure 3. Relation between (Nb%) x {C% + 12/14)N%} and austenite grain size in steels heated at 1,150, 1,200 and 1,250 C for 2.5 hr (26).

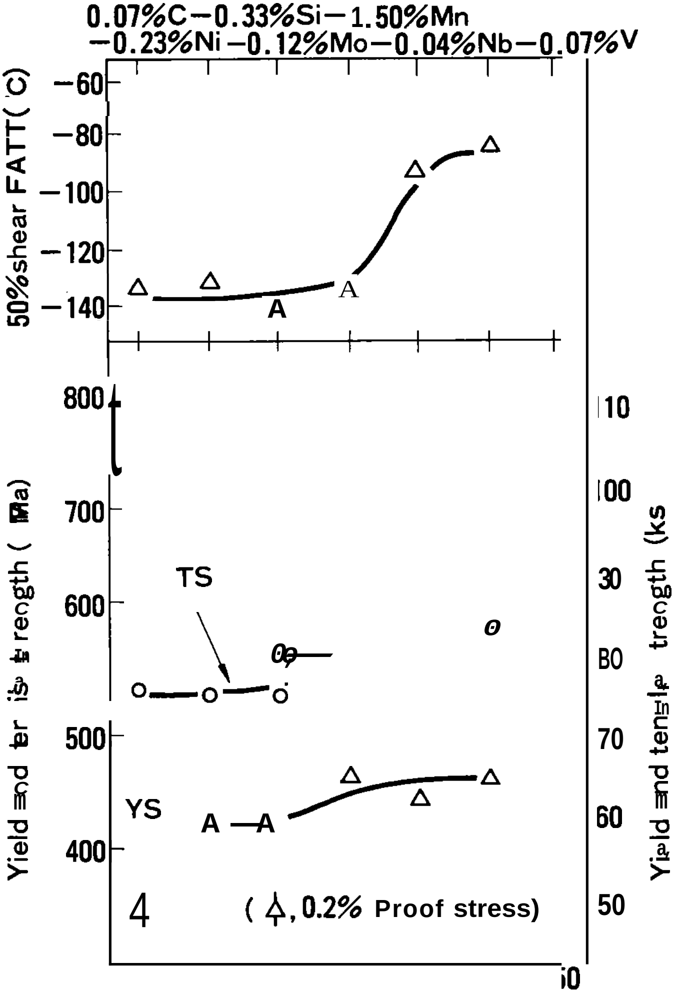


Figure 4. Effect of slab reheating temperature on the mechanical properties of Nb-V steel (25).

Cumulative reduction in the finishing stage

It has been empirically determined that, although it is difficult in rolling niobium-steel plates to obtain uniformly recrystallized austenite, an increase in cumulative reduction, below 850 - 950 C in the finishing stage (for one-stand rolling, in the latter half of rolling) will greatly increase toughness. Recently, the generation of deformation bands resulting from the reduction in this stage, and the mechanisms of phase transformation in non-recrystallized austenite, have been extensively studied (21, 23, 25) and have proved that reduction in this temperature range is very effective in increasing toughness. For niobium-steel, for example, assume that the grain diameter achieved by rolling in the recrystallized austenite region to be d and cumulative reduction in the non-recrystallized region to be ε. Then, the effective autenite grain boundary area Sv, as a ferrite nucleation site, is given by the following equation (27).

$$Sv\ (mm^2/mm^3) =$$

$$\left\{1.67(\varepsilon - 0.10) + 1.0\right\}\ (2/d) + 63(\varepsilon - 0.30)\ \ (\varepsilon > 0.30) \tag{1}$$

It is clear from this equation that the ferrite nucleation site increases in proportion to reduction in the non-recrystallized region ε. In other words, the structure can be refined by increasing cumulative reduction. Figure 5 (23) shows the relationship between a reduction in the non-recrystallized region and toughness for niobium steel. It indicates that although increases in reduction will largely increase toughness, starting temperature has only a modest effect in the non-recrystallized region. Also, with a constant reduction, variations in finishing rolling temperature, in the austenite range, will have little effect on toughness and strength. Figure 6 (25) shows the effect of finishing rolling temperature, on mechanical properties of niobium-vanadium steel. This was investigated by varying the number of passes with niobium-vanadium steel heated to 1100 C, and keeping the cumulative reduction below 900 C, consistently at 70 percent. Although changes in properties are rather mild due to reduction in the range above 740 C, (the transformation temperature of the steel), strength increases greatly as reduction is applied in the two-phase region, achieved by decreasing finishing temperatures.

Hot deformation strength of niobium steel

Recently, automation, using process computer control, is being promoted in plate rolling. This allows such important considerations as the determination of optimum pass schedules and the estimation of roll force needed for the control of plate thickness to be addressed (29). It is known that an increase in niobium content will result in an increase in resistance to deformation, as shown in Figure 7 (30). In addition, Figure 8 (30) shows a comparison of recrystallization and recovery between niobium steel and a conventional steel by applying a true strain of 0.7 at 900 C and 1000 C, redeforming after holding a time, and obtaining a softening degree from flow stress ratio. From this, it is clear that the degree of softening with niobium-steel, is only 20 percent implies an increase in resistance to deformation with the interval between plate mill passes about 10 sec. at 900 C. On the basis of this knowledge, studies have been conducted (28, 31, 32) to estimate optimum rolling schedules for niobium steel, with improved productivity of controlled rolling, and achievement of high and consistent quality.

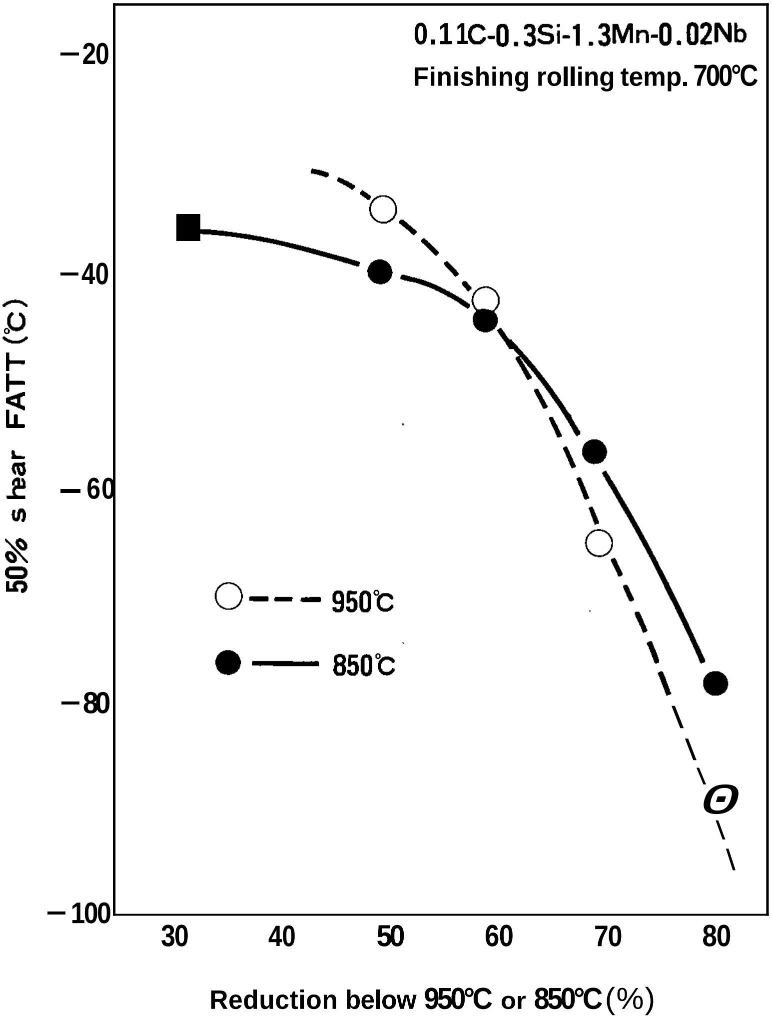


Figure 5. Relation between cumulative rolling reduction and fracture appearance transition temperature (FATT) in Charpy impact test (23).

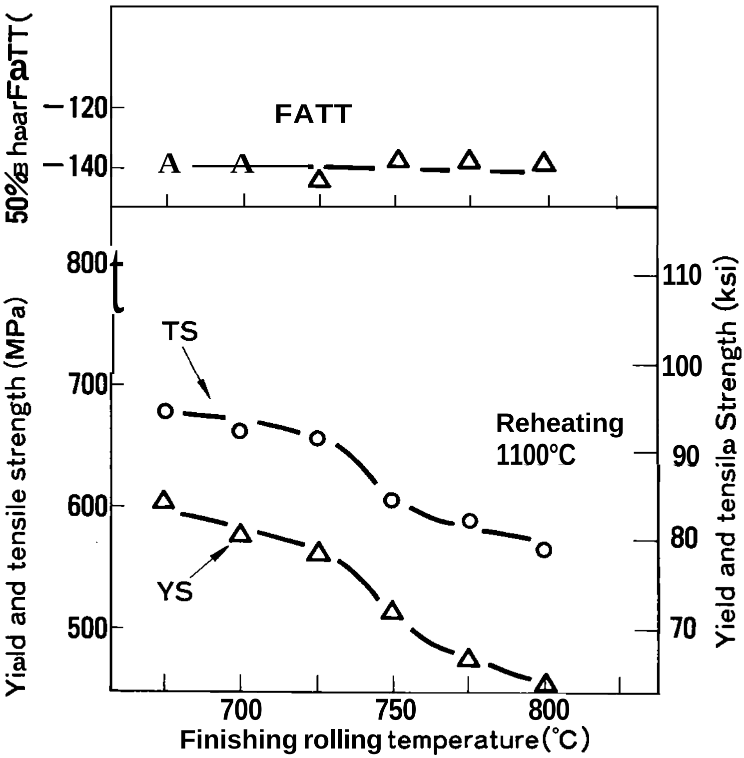


Figure 6. Effect of finishing rolling temperature on mechanical properties of Nb-V steel (25).

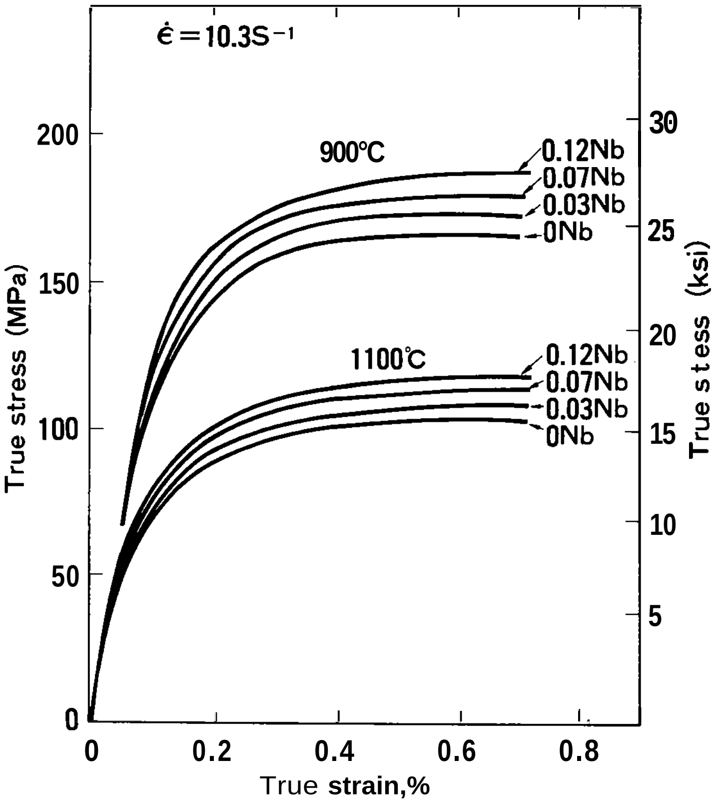


Figure 7. Effect of Nb content on the strength of austenite (30).

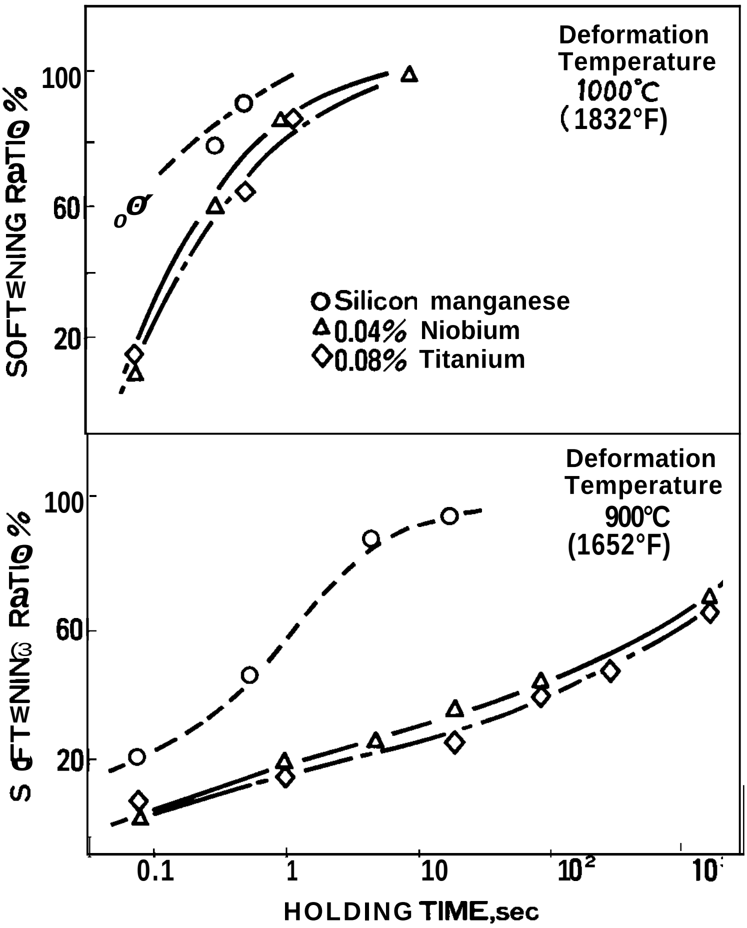


Figure 8. Change of softening ratio with holding time for the silicon-manganese, niobium and titanium steels (Base composition, 0.09% C-0.25% Si -1.50% Mn) (30).

Saito et al (28) have developed a mathematical model for deformation resistance in the following specific regions: a strain-free austenite region, a low-temperature strain accumulated austenite region and an austenite ferrite region. With niobium-steel, the strain-free austenite region is determined by the rolling conditions of the pass interval over 60 sec. in the temperature range above 950 C. This mathematical model enables roll force to be controlled accurately from the beginning to the end of rolling for controlled rolling of API X-70 grade niobium-vanadium steel, as shown in Figure 9 (28).

Advanced rolling schedules

Rolling schedules in the early period of niobium-steel plate rolling, addressed only the control of rolling temperature for several finishing passes or stipulated a finish temperature inevitably in the non-recrystallized region because of thinner plate thickness. As increasingly greater demands were presented for toughness, strength and weldability, a variety of rolling methods have been developed. Typical schedules currently in use in rolling niobium-steel plates are schematically shown in Figure 10. For materials such as line pipe materials, which require especially high toughness, a controlled rolling process which uses lower slab reheating temperature and a cumulative reduction of around 50 - 80 percent in the non-recrystallized region is applied as shown in 2 of Figure 10 (33). Higher strength and toughness are achieved by lowering the finishing temperature down to the two-phase, austenite and ferrite region.

Two-phase rolling. From early times, attempts were made to use two-phase (austenite and ferrite) rolling for strengthening steel. However, while strengthening resulting from increase in dislocation density could be expected, a drawback of decreasing toughness was realized and it was generally believed that finishing rolling just above the Ar_3 transformation temperature, instead of two-phase rolling, was best for balanced strength and toughness. However, it was clarified (34-36) that if rolling conditions in the prior stages of controlled rolling of line pipe materials are optimized, toughness will not always decrease, when the finishing temperature is decreased into the ferrite transformation range. Also, Melloy et al (37) demonstrated to the possibility of increasing strength and toughness of steel, by rolling the steel in austenite, austenite plus ferrite and ferrite regions continuously.

Figure 11 shows the results of a survey of the effects of reduction in the two phase region subsequent to rolling a steel containing 0.07 percent C, 0.3 percent Si, 1.6 percent Mn and 0.03 percent Nb heated to 1100 C with a cumulative reduction of 50 percent in the temperature range above 900 C. The Ar_3 of this steel is around 740 C and the strength gradually increases, as reduction increases in the range below this temperature. Here, the 50 percent FATT in Charpy impact tests remains substantially the same, while shelf energy slightly decreases. This increase in strength is proportional to the ratio in volume of deformed ferrite, and is very prominant due to the recovery and recrystallization of deformed structures of niobium-steel being retarded by niobium carbo-nitride.

This two-phase rolling has achieved practicality for improving the strength and toughness of line pipe material in combination with optimized processing in the high-temperature ranges. It has also been applied to improving the toughness and weldability of high strength steel for shipbuilding (38, 39) and for improving the fracture toughness of aluminum-killed steel for low temperature service (40).

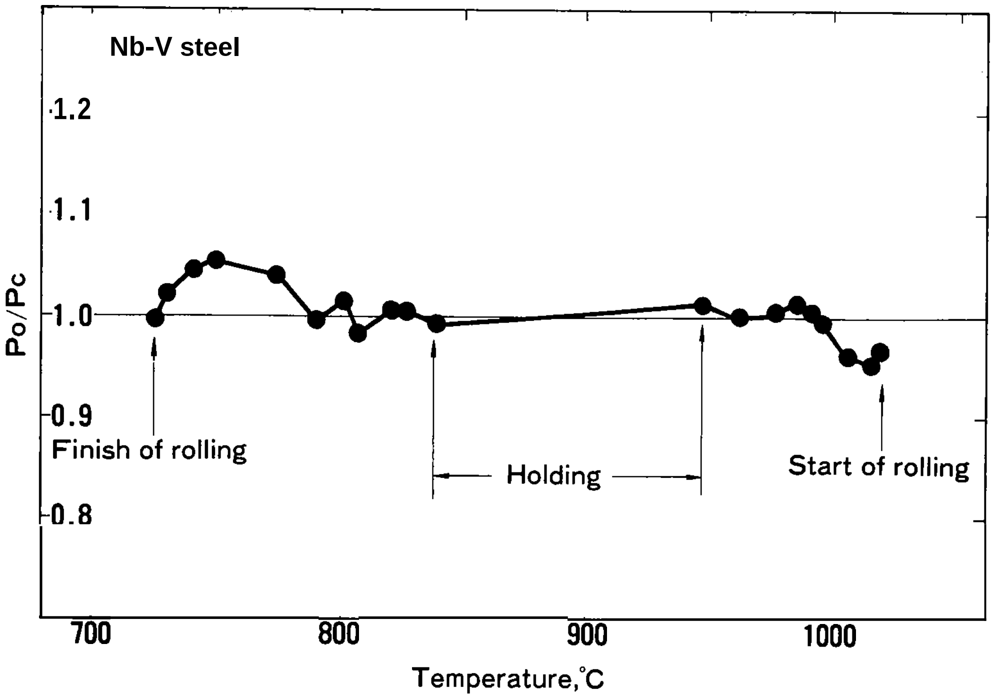


Figure 9. Accuracy of roll force model: variation in ratio of observed roll force Po to calculated one Pc with temperature in API x 70 class plate (28).

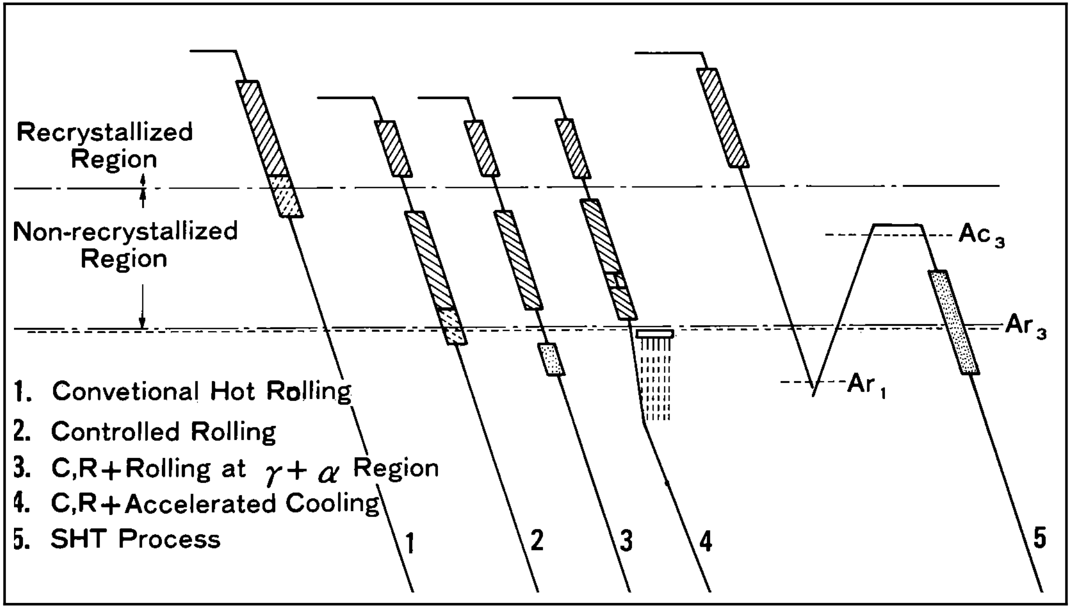


Figure 10 Schematic diagram of various types of controlled rolling process

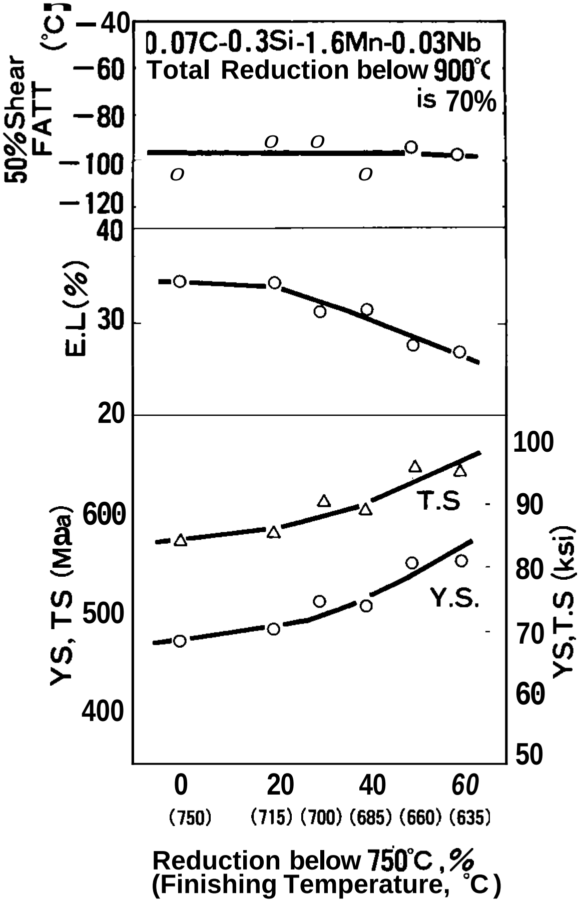


Figure 11. Effect of rolling reduction below Ar_3 temperature on mechanical properties of Nb steel.

Accelerated cooling. Accelerated cooling subsequent to controlled rolling is practical as a means of thermo-mechanical treatment in hot strip mills, bar mills and in wire rolling. The process is currently attracting attention as a method of increasing strength and toughness applicable to plate products. As distinct from the rolling of hot strip and bars, the rolling of plates has proven to have difficulties which have prohibited commercial production. These are (a) the difficulties of achieving uniform quality and (b) the difficulty regarding flatness control. Direct quenching *(41)* is an effective method to resolve these problems, but it requires a tempering process, and thus a loss of an advantage of controlled rolling: avoiding subsequent heat treatment.

The basic parameters for accelerated cooling, subsequent to controlled rolling, are the temperature at the start and end of cooling and the cooling rates. Figure *12 (25)* shows the effects of cooling rate on the strength and toughness of Si-Mn, *0.03* percent Nb and *0.04* percent Nb - 0.09 percent V steels with temperatures at the start and the end of cooling 780 C and 600 C respectively. As indicated in the figure, a moderate increase in strength can be expected without losing toughness, by increasing cooling rates. Variations in the strength and toughness of a 1.3 percent Mn steel and 0.03 percent Nb steel with a cooling rate of 6 - 8 C/sec. and a temperature at the end of cooling from 600 C to 500 C are shown in Figure *13 (42).* The strengths of the niobium-steel, follow a steady increase in the range from 600 C to *500* C, and then a sharp upward trend in the range below *500* C. In general, accelerated cooling subsequent to controlled rolling, is intended to obtain fine ferrite-pearlite or bainite structures. If the finishing temperature is too low, such structures transform partly into martensite at lower temperatures with a related increase in strength. Also, because accelerated cooling is intended to control transformation, an excessively low finishing temperature of rolling will cause ferrite to be produced before cooling starts. Thus results in a diminished effect of cooling on strength. Figure *14 (42)* shows the effects of finishing temperature of a niobium-vanadium steel, cooled at a rate of 8 C/sec., and with finishing temperature of cooling *550* C. The Ar_3 of this steel is around *750* C, and when the finishing temperature of rolling is below this, the effect of accelerated cooling will diminish, and the effect of two-phase rolling will be most noticeable on both strength and toughness. However, while in two-phase rolling, a low finish temperature results in a high incidence of separation, it is possible by accelerated cooling, to increase strength while controlling the generation of separations. Also, a combination of appropriate composition and rolling conditions may enable properties to be optimized by controlling the recovery of ferrite, subsequent to two-phase rolling, by applying accelerated cooling.

SHT process. As explained earlier, fine austenite grains before rolling are preferable for producing a homogeneous fine structure. The SHT process *(43, 44)* begins with normal rolling of slabs with given thickness, achieving the dissolution of niobium carbo-nitride. Rolling is interrupted when the plate is at an intermediate thickness corresponding to the reduction needed for secondary rolling. The slabs are allowed to cool down below the Ar_1. Then, the slabs are again heated to just above Ac_3 for secondary rolling. This promotes uniformity and refinement of the structure in the same way as normalizing. The toughness of steels manufactured by this process is largely influenced by the secondary reduction as shown in Figure *15.* Some of the rolling temperatures here, enable the effect of work hardening in two-phase rolling, to be utilized favorably. Although this system of controlled rolling requires, as plate mill equipment, a heating furnace for reheating medium-sized slabs near the rolling mill, and a secondary heating within the course of rolling, it is suited to the production of thick-wall line pipes and low-temperature steel with high toughness. The chemical compositions and mechanical properties of *X-65, X-70* grade line pipe manufactured by this process are shown in Table I.

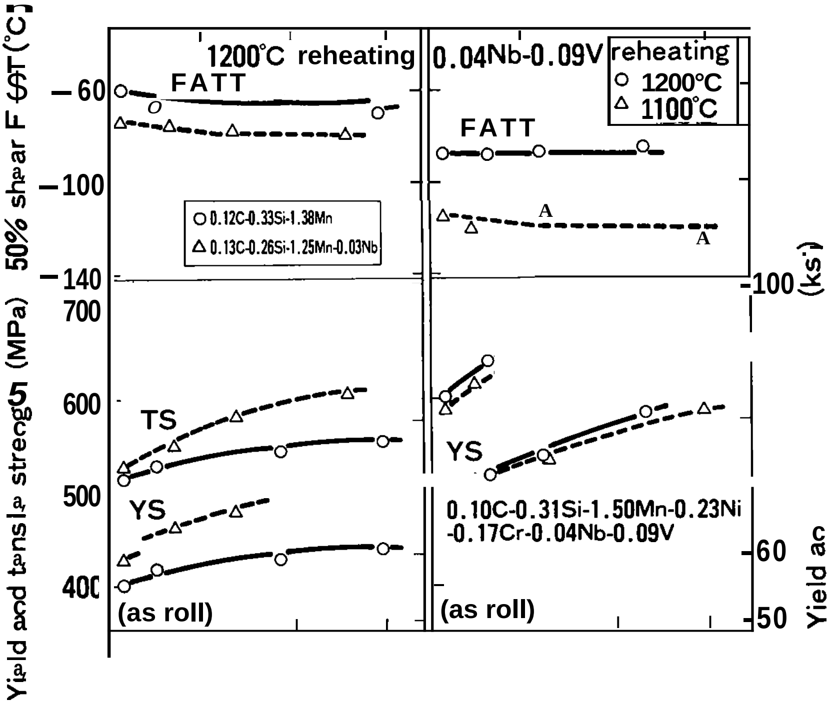


Figure 12. Effect of cooling rate on mechanical properties of controlled steels (25).

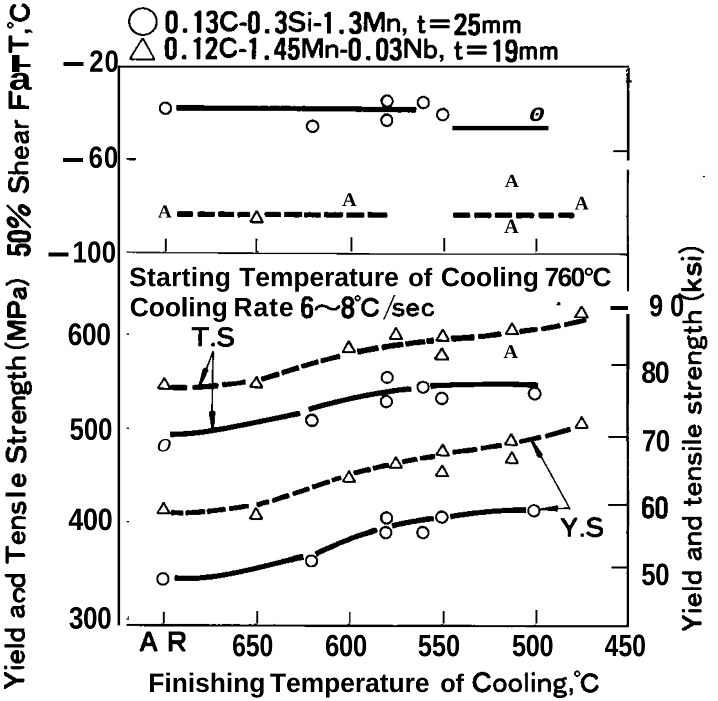


Figure 13. Effect of finishing temperature of accelerated cooling on mechanical properties of Si-Mn steel and Nb steel (42).

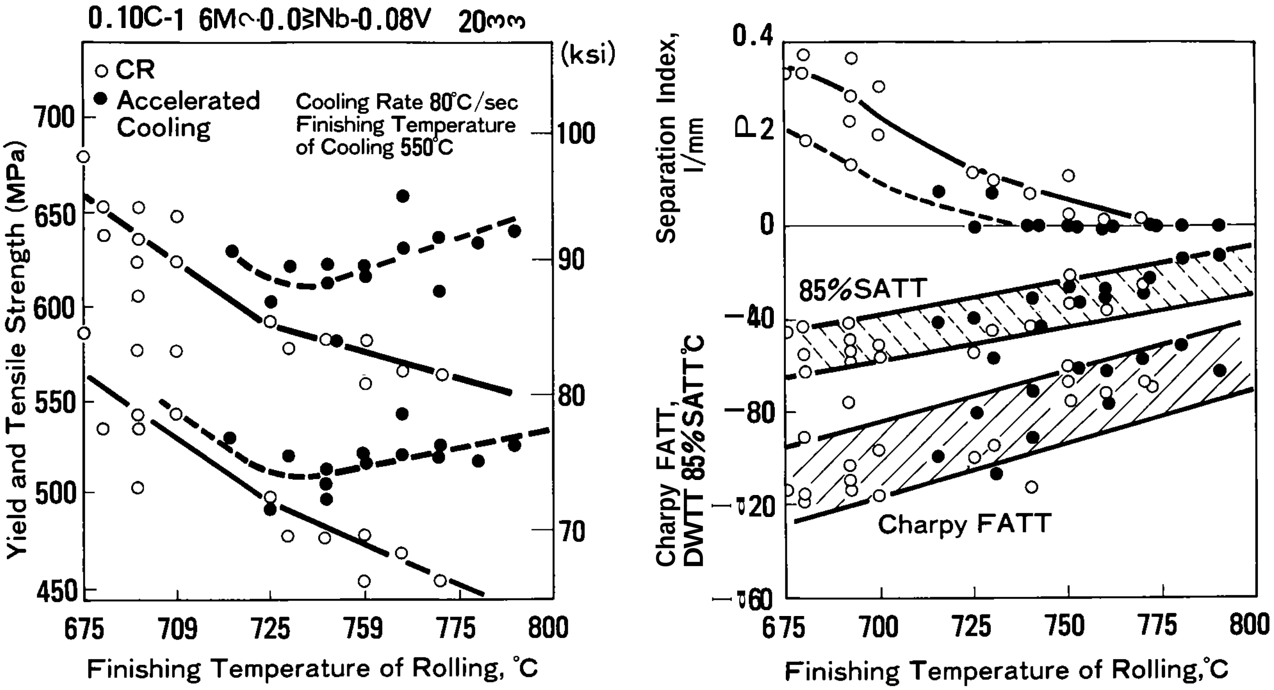


Figure 14. Effect of finishing rolling temperature on mechanical properties on accelerated-cooled Nb steel (42).

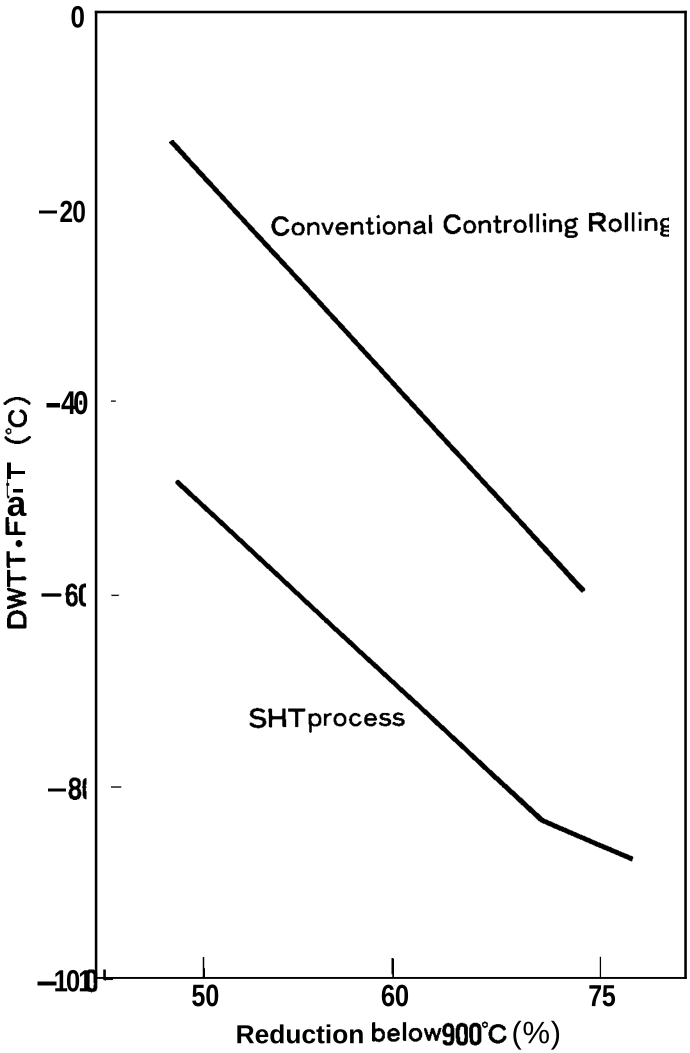


Figure 15. Relation between secondary reduction and fracture appearance transition temperature in DWTT in SHT process *(43)*.

Table I. Chemical composition and mechanical properties of X-70 grade line pipe steels (43).

Mark	Process: Plating	Process: Piping	Size: Dia. (mm)	Size: Wall thickness (mm)	C	Si	Mn	P	S	Nb	V	Al	Others
		UO	1220	18.3	0.09	0.28	1.26	0.019	0.005	0.027	0.08	0.045	Cu,Cr,Mo added(≦0.20)
		UO	1220	18.3	0.06	0.26	1.46	0.016	0.004	0.030	0.08	0.038	〃
1C	SHT	CFE	1220	18.3	0.07	0.35	1.51	0.011	0.004	0.011	0.09	0.046	Cu, Cr added(≦0.20)
		UO	1220	18.3	0.09	0.28	1.26	0.019	0.005	0.027	0.08	0.045	Cu,Cr,Mo added(≦0.20)
1C′	CR	CFE	1220	18.3	0.07	0.35	1.51	0.011	0.004	0.011	0.09	0.046	Cu, Cr added(≦0.20)

Mark	Tensile Properties(C-direction): Y.S (psi) {MPa}	T.S. (psi) {MPa}	Yield Ratio (%)	El. (%)	Notch Toughness(C-direction): V-Charpy 50%FATT (°C)	V-Charpy Absorped Energy −25°C	V-Charpy Absorped Energy −45°C	B-DWTT 85%FATT (°C)	NRL NDT (°C)
1A	77,700 {536}	94,600 {653}	81.4	30.0	−85	85	84	−57	−65
1B	74,500 {514}	87,800 {606}	84.8	34.0	−90	227	187	−52	−70
1C	71,500 {493}	88,700 {612}	80.5	35.1	−141	152	122	−68	—
1A′	84,300 {581}	100,500 {693}	83.9	29.6	−68	54	52	−31	−65
1C′	78,400 {541}	92,400 {637}	85.0	34.3	−82	222	156	−31	—

Normalizing

While losing the beneficial effects of precipitation hardening at normalizing temperatures because of coarsening of niobium carbo-nitride, these precipitates prevent the growth of austenite grains and produce a grain refined steel. If niobium is added in the range 0.02 - 0.05 percent to a 50 kg/mm^2 class aluminum-killed high strength steel, for example, grain refinement is advanced to 1/2 in terms of ASTM grain size number and to 3/4 when controlled rolling is employed (45). The product here shows improvement by about 20 MPa in terms of strength and about 15 C in terms of Charpy impact test FATT as compared with the aluminum-killed base material. Figure 16 (46) shows examples of the addition of niobium to 0.04 percent C - 1.4 percent Mn steel for low temperatures service. This indicates that the addition of niobium by more than 0.02 percent will result in a 20–30 MPa increase in tensile strength, 20 - 30 C improvement in terms of FATT and 15 - 20 C improvement in terms of NDT. Also, it is shown that the controlled rolled materials have their strength and toughness further improved. With normalized steel, controlled rolling as a preliminary treatment is effective for niobium steel in particular. In Europe, (48, 49) normalized niobium steel is being used as a steel with minimum tensile strength of 50 kg/mm^2 (47) (BS4360 Grade 50 or equivalent standards) for offshore structures which require low-temperature toughness and good "through thickness" properties, as EH36 steel for shipbuilding and as steel for low temperature service with applications down to –50 C.

Strength and Toughness

Strength

The effect of niobium in increasing the strength of as rolled plate, varies according to the rolling conditions, C content, and added elements (50–54). Figure 17 shows this increase, with additions of niobium and vanadium, made to steels containing 0.05 percent and 0.18 percent C, 0.25 percent Si, and 1.2 percent Mn (50). In the figure, 5 niobium-vanadium shows the combined effect of adding vanadium to 0.05 percent niobium steel. An increase in strength by niobium saturates at an niobium content of 0.05 percent, and there is no major variation due to the carbon content. Figure 18 indicates the relationship between amount of fine niobium carbo-nitride precipitation (Δ Nb ppt wt%) and the increase in the yield strength (Δ YP). While the Δ Nb ppt changes with the carbon content, a large difference in yield strength is not noted. For low carbon steels this is attributable to the over aging due to growth of niobium carbo-nitride, even though there is an increase of precipitates in the ferrite because of a high transformation temperature. When compared with vanadium, niobium is more effective in obtaining an equivalent Δ YP. In the 0.18 percent carbon steel, there is no combined effect of niobium and vanadium on Δ YP. However, in the 0.05 percent carbon steel, a Δ YP greater than that of the total of an individual additions can be obtained. These facts suggest that niobium is an extremely advantageous additive, when the intention is to lower the carbon content for improvement of toughness and weldability.

Toughness

When comparing niobium with vanadium in quantities needed to produce equivalent Δ YP, the degree of embrittlement by niobium is much lower. Figure 19 indicates the relationship between the change of vTrs (Δ vTrs) in niobium and vanadium (54). As can be seen, the variation in toughness of

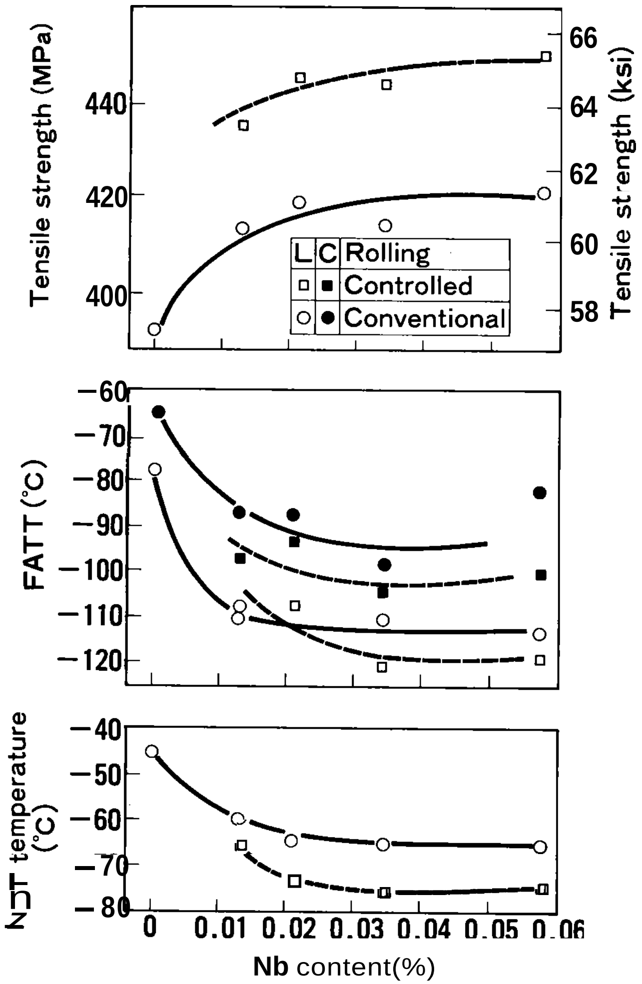


Figure 16. Effects of Nb content on mechanical properties of Al killed steel plates as normalized (46).

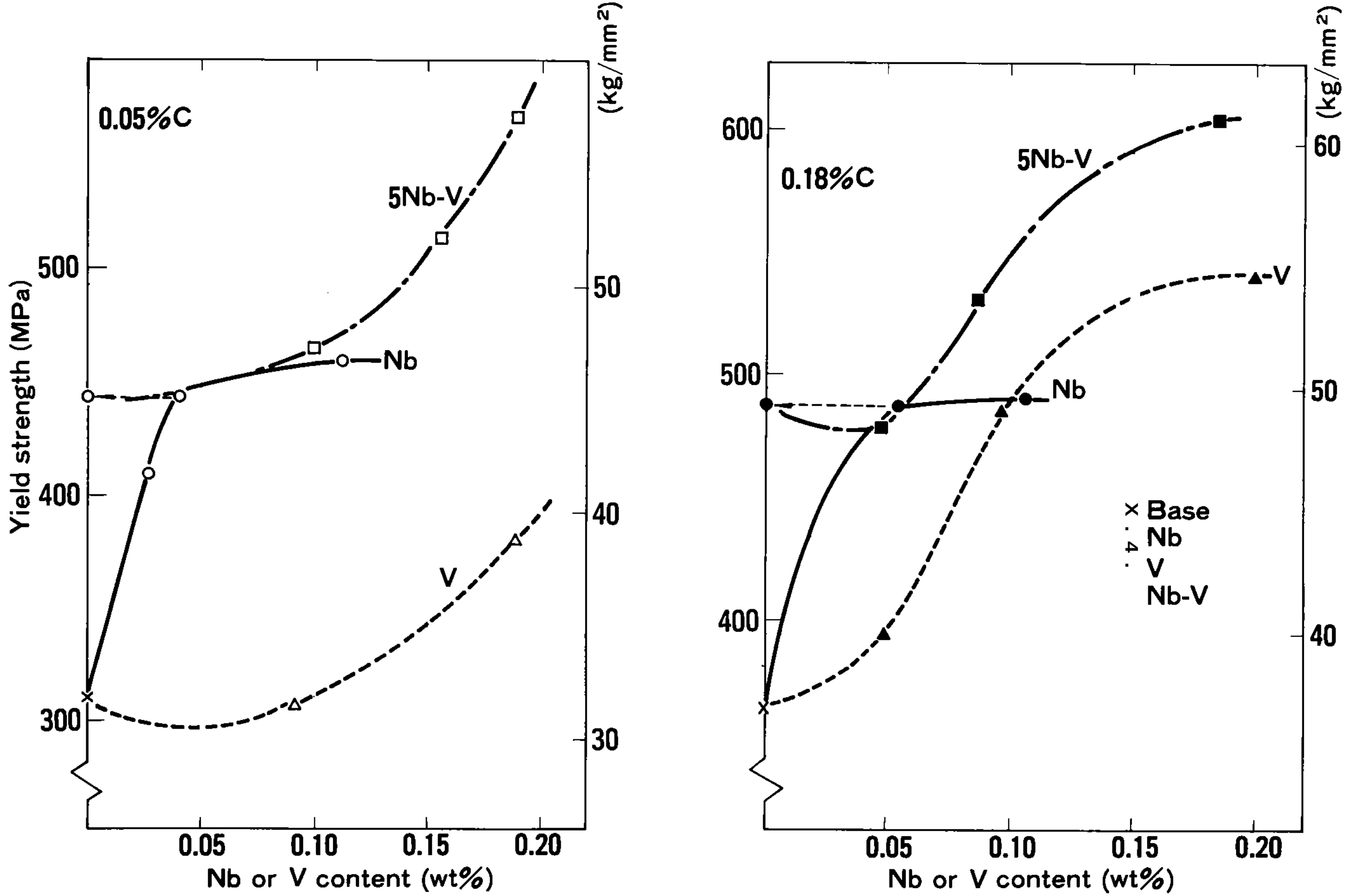


Figure 17. Effect of Nb or/and V addition on strength of as rolled steels (50).

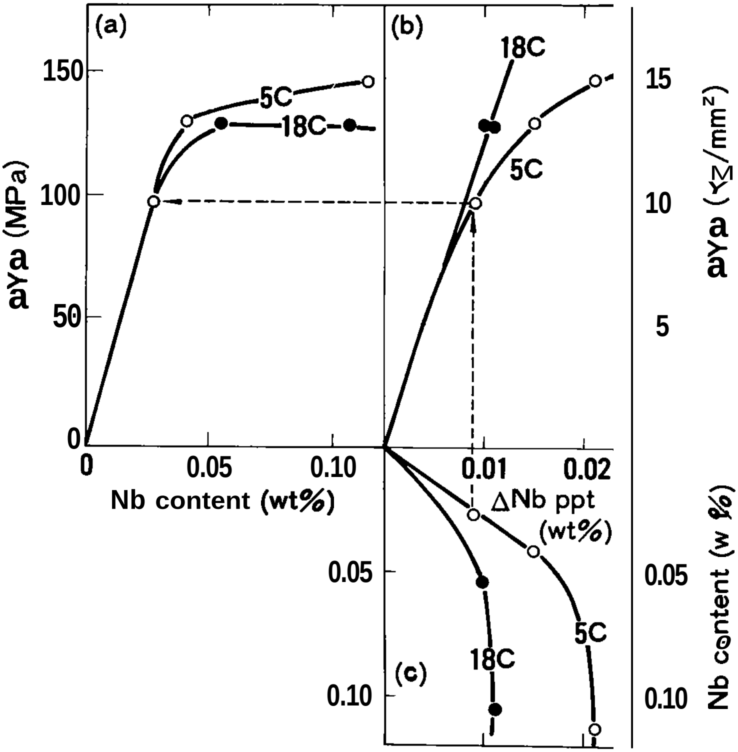


Figure 18. Effect of Nb addition and amount of Nb precipitates on strengthening of as rolled steels (50).

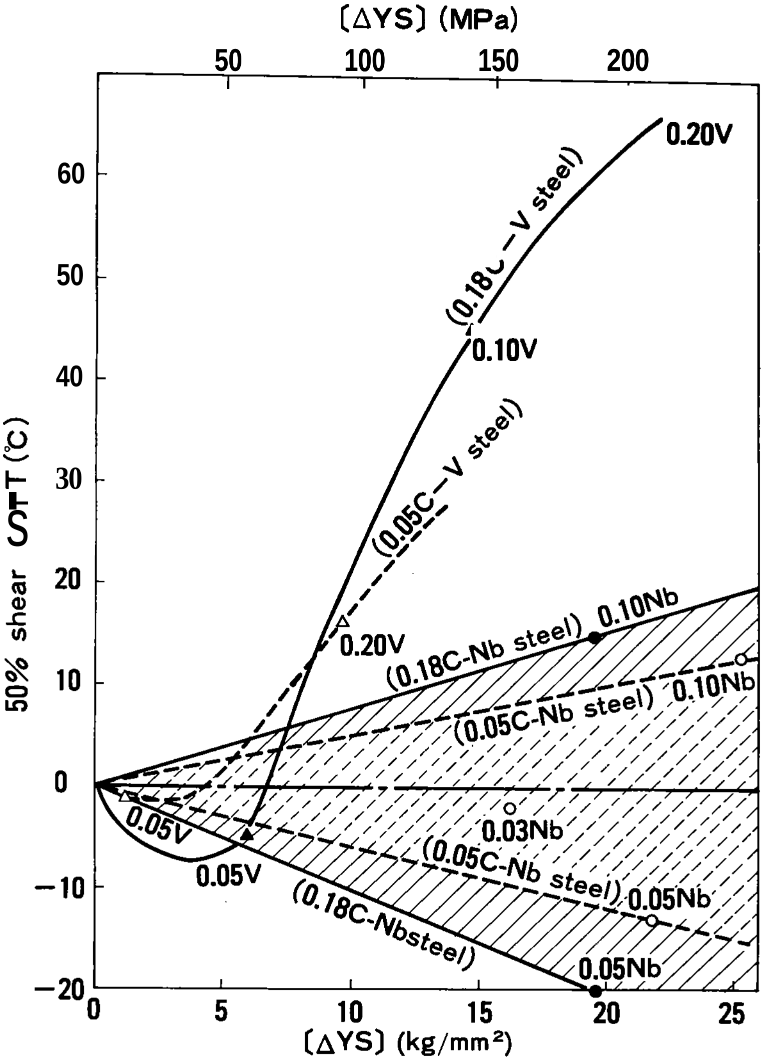


Figure 19. Increase of yield strength and change of vTrs temperature (FATT). Nb or V is added to two as rolled steels, one contains 0.05% C, the other 0.18% C. (0.25% Si, 1.2% Mn) (54).

niobium-steel is substantial, but if this is considered on the basis of the relationship between the carbon content and grain size, (N_α: ferrite grain size No.), we can obtain a satisfactory correlation by the following equation.

$$vTrs = 4.02\ TS\ (kg/mm^2) - 18.0\ N_\alpha + 196\ C\% - 125 \pm 14 \qquad (2)$$

Thus, we can see that grain refinement is important for the improvement in toughness of the base material.

Fracture Characteristics

Separation on a fractured surface

The separations observed on the fractured surface of the controlled-rolled niobium-steel plate in the Charpy test and DWTT appear at temperatures near the transition temperature as shown in Figure 20 (55). In steels which have a high sulfur content, manganese sulfide causes separation because of manganese sulfide elongation at low temperature rolling (56). However, since even at very low sulfur contents (10 ppm) the separations do not disappear, it must be concluded that other causes exist (57). For example, a reason for separation is considered to be the non-uniformity of the transition temperature as indicated in Figure 22. This is brought about by the ferrite crystallographic texture with {332} <113> and {311} <011> indicated in Figure 21 as its main direction. This orientation was formed from the austenite crystallographic texture by rolling through the phase transformation and satisfies the Kurdjumov-Sachs or Nishiyama's relation (58).

Separations have no appreciable effect on the tensile properties of the plate, other than the fracture appearance transition temperature as indicated in Figure 23. Figure 24 shows that the distinctive feature of a separation, which arrests the propagation of brittle fracture (60), is obvious by noting the high Kca value at the LPG temperature.

Unstable ductile fracture

The effect of separations on the unstable ductile fracture propagation of gas linepipe, has been widely discussed in the past. In Japan, four pipe makers jointly carried out burst tests on pipe 150 meters in length, X-70 grade, 1219 mm (48 inches) in OD, and 18 mm (0.72 inch) in thickness.

It was verified that the separation does not relate to the arresting of unstable ductile fracture propagation if the Charpy energy is sufficiently high (61).

Hydrogen induced cracking in hydrogen sulfide

The primary cause of blister cracking in linepipe steel under hydrogen sulfide atmosphere, is manganese sulfide (MnS) and can be removed by an extreme reduction in the sulfur content of MnS, or by making the inclusions discontinuous by the addition of calcium or Rare Earth Metals. A secondary cause of such cracking is a banded structure which forms more pronouncedly in niobium steel during controlled rolling (62).

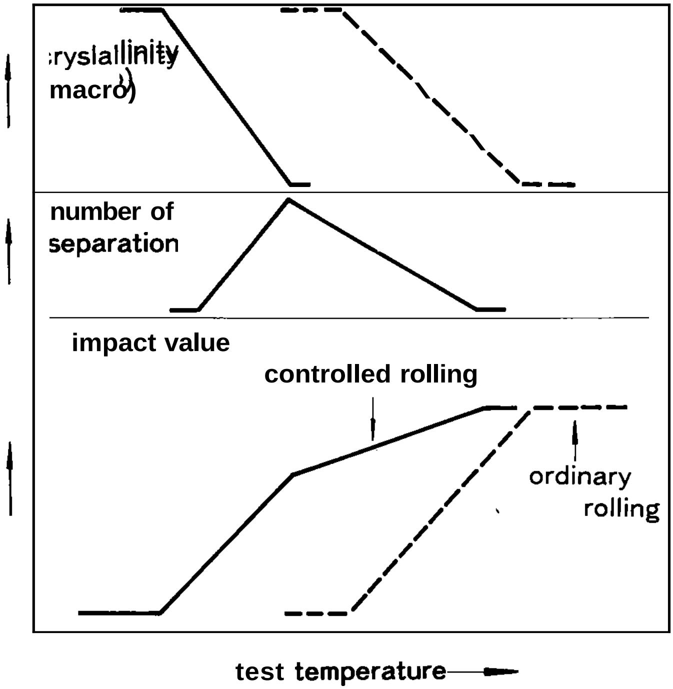


Figure 20. Relation between separation and Charpy transition curve in controlled steel (Schematic diagram) (55).

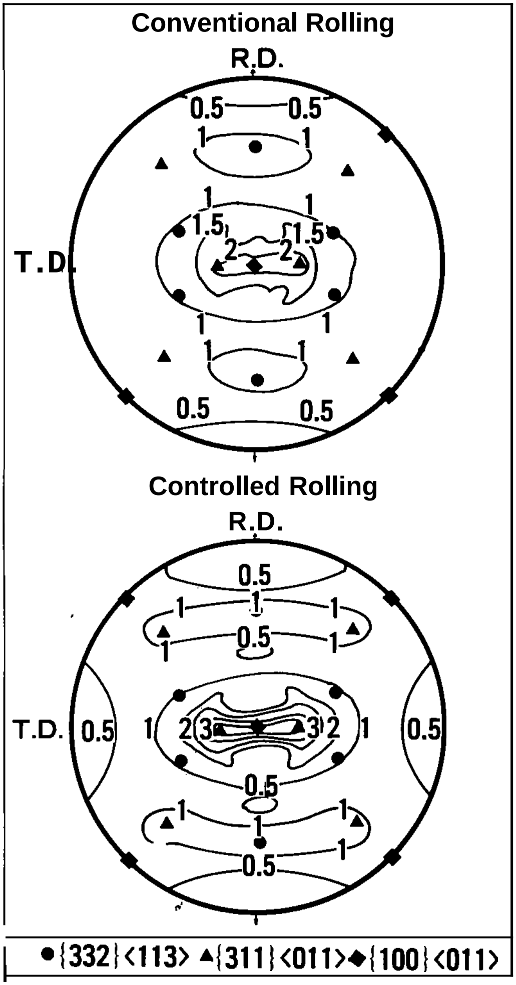


Figure 21. Formation of crystalline texture due to controlled rolling ({200} pole figure, 0.18C - 1.28Mn - 0.16Cr - 0.032Nb - 0.042V) (58).

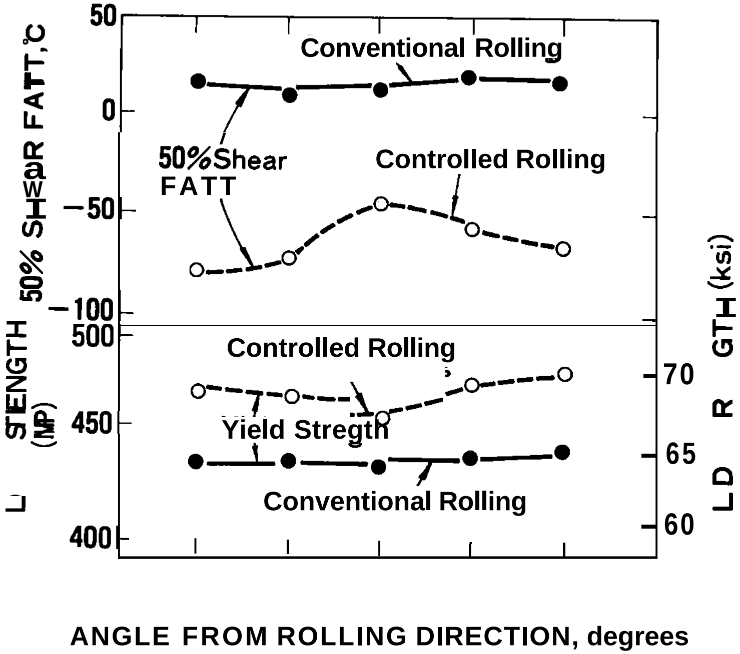


Figure 22. Change of mechanical properties by rolling direction of controlled rolled steel (58).

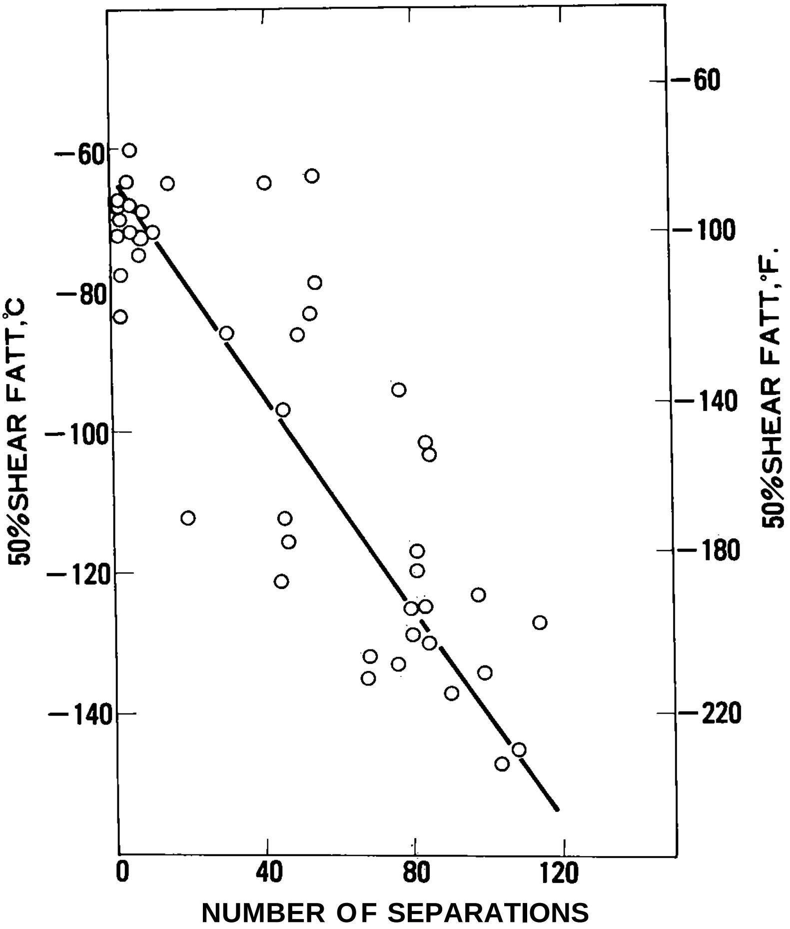


Figure 23. Effect of number of separation on Charpy vTrs Temperature of Nb steel (59).

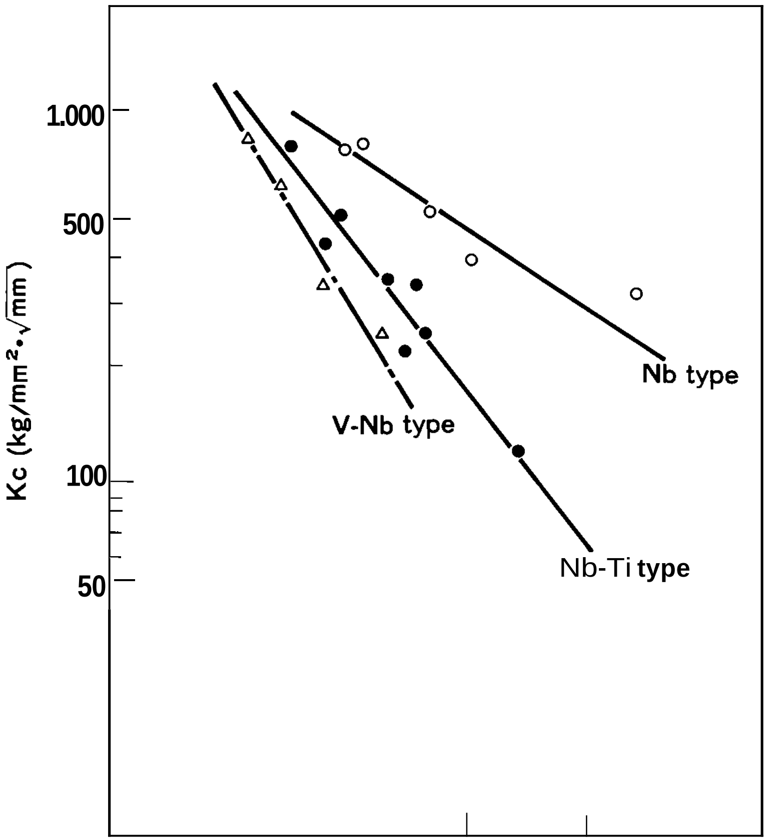


Figure 24. Kc value vs. temperature relationship of Nb steel (60).

Therefore, it is imperative that the foregoing treatment be carried out when subjecting the steel to hydrogen sulfide.

Weldability

The niobium carbo-nitride dissolves in the weld heat-affected zone (HAZ), especially near the fusion line, since this region is heated to temperatures in excess of 1,400 C. The dissolved niobium raises the hardenability and enlarges the Hvmax (maximum hardness measured on the Vicker's scale) of the HAZ. However, since the undissolved carbides become the nuclei for transformation, they effect a grain refinement and restrict the grain coarsened region. The effect of niobium on Hvmax and weldability varies according to the carbon content and Δ T (cooling time from 800 C to 500 C after welding). An illustration of the effect of carbon and niobium on Hvmax when the Δ T is small, is indicated in Figure 25 (63). When Δ T is large or when post weld stress relief is carried out, the niobium provides resistance to softening.

As mentioned above, the addition of niobium between 0.02 and 0.05 percent, can allow a decrease in the carbon level by 0.07 to 0.1 percent. Therefore, when compared with the equivalent yield strength, the Hvmax is lowered by 20 to 40 points, and this exerts a marked effect on the prevention of weld cracking.

There are also many reports published on the toughness of niobium-steel at the weld fusion line (64-66). The effect of niobium on the Charpy value in the fusion line, is also greatly influenced by carbon content and Δ T. To estimate the vTrs, according to a simulated weld thermal cycle when Δ T is 17 seconds and about 80 seconds, the following equations have been proposed respectively (64).

$$\begin{aligned} vTrs(17) = &-148 + 1138\,C + 29\,Si + 20\,Mn + 502\,V \\ &+ 1670\,Nb + 1189\,N - 259\,C \times Mn \end{aligned} \tag{3}$$

$$\begin{aligned} vTrs\,(80) = &-141 + 818\,C + 50\,Si + 70\,Mn + 524\,V \\ &+ 601\,Nb + 1785\,P - 728\,N - 299\,C \times Mn \end{aligned} \tag{4}$$

(Note): Only information related to this report has been extracted.

In addition, there are reports concerned with the COD test. They all indicate that low-carbon steel far excells in toughness over other steels (67-69).

As these reports demonstrate, the simple addition of niobium to conventional steel does not have any effect on improvement of weldability. However, when a comparison is made at the equivalent strength level, the carbon content of the niobium-steel is reduced, and as a result, improvement in weldability can be expected. Few reports are available on the effect of niobium steel on weldability and strength at the same time. Accordingly, with the foregoing point of view in mind, an attempt has been made to estimate the effect of niobium when the YP is set at 35-36 kg/mm^2 (about 350 MPa), based on the results of the individual reports. The following 4 steels are given as typical examples. For steel 2, both the yield and tensile strength of as rolled (conventional rolling) is equivalent to Steel 1, but, if normalized, its tensile strength lowers by 1-3 kg/mm^2 (10-30 MPa).

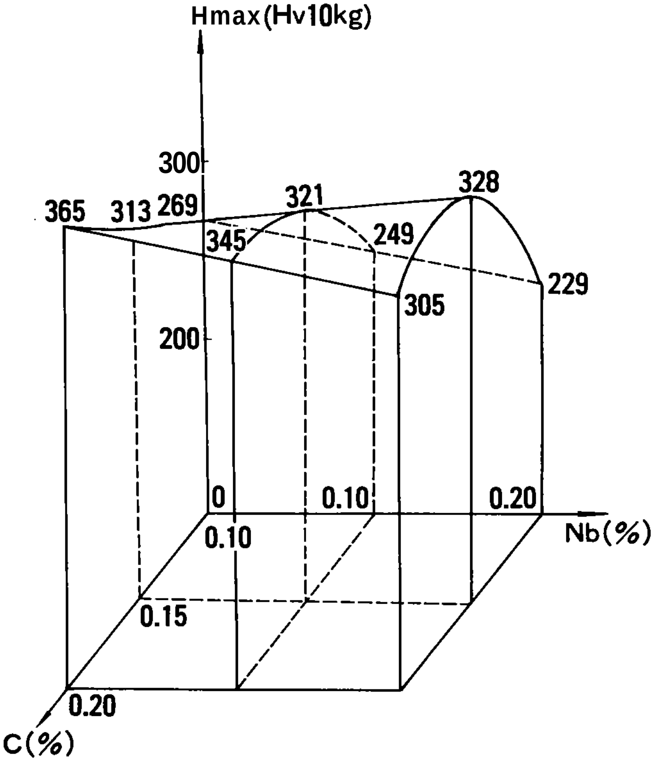


Figure 25. Relation between the maximum hardness and contents of C and Nb (63).

Steel 1: Carbon steel

C 0.17 - 0.19%, Ceq. 0.40 - 0.44%

Steel 2: Carbon steel + Nb

C 0.13 - 0.16%. Nb 0.02 - 0.04%. Ceq. 0.36 - 0.41%

Steel 3: Low-carbon steel + Nb (controlled-rolled)

C 0.09 - 0.11%, Nb 0.02 - 0.04%, Ceq. 0.33 - 0.35%

Steel 4: Ultra low-carbon steel + Nb (controlled-rolled)

C 0.03 - 0.05%, Mn 1.6 - 1.9%. Nb 0.03 - 0.05%, Ceq. 0.33 - 0.36%

$$\text{Ceq.} = C + \frac{1}{6}Mn + \frac{1}{24}Si + \frac{1}{14}V$$

An example of the change in Hvmax due to the Δ T in the HAZ is indicated in Figure 26. The Δ T 800 - 500 in the figure indicates the cooling time (in seconds) at the fusion line of the HAZ, ranging from 800 C to 500 C. As the heat input is increased, the Δ T increases also. In Steel 1, the Hvmax is high when the Δ T is small. When the Hvmax is $\geq$ 350, preheating becomes necessary, even if a low hydrogen type SMAW electrode is used.

In Steel 2, the Hvmax is lower because of the lower carbon content, but when the Δ T is in excess of 10 seconds the Hvmax becomes higher than that of Steel 1, due to the precipitation hardening of niobium. In Steels 3 and 4, the Hvmax is below 300 even at Δ T $\leq$ 10 seconds, and consequently, there is practically no concern over weld cracking.

At the fusion line, since the refining effect of an addition of niobium cannot be expected, low-carbon steel with the addition of niobium exhibits a combination of an improvement in toughness (which is brought about by the low carbon) and an embrittlement by niobium carbo-nitride. The tendency of vTrs by changing Δ T in the Charpy test of simulated HAZ is indicated in Figure 27. When the Δ T is small, the vTrs decreases as the carbon decreases, but when the Δ T becomes larger, embrittlement caused by precipitation of niobium carbo-nitride occurs, and raises the vTrs. The change in the vTrs when stress relieved (600 C x 1 - 2 hrs. furnace cooling) is carried out on these steels, is indicated in Figure 28. Steel 1 exhibits a significant recovery of toughness, because the martensite is subjected to tempering.

In the COD test, the merit of lowering the carbon content becomes much more obvious (Figure 29). As a general rule, this is indicated by higher COD values, as the hardness level declines. An example of the change in hardness with change of carbon content of respective steels due to Δ T and stress relief is expressed schematically in Figure 30.

The matter discussed here, is a consideration of the effect of niobium on weldability of steels with yield points in the 35 - 36 kg/mm^2 range. However, if additions of nickel, chromium, molybdenum and vanadium were carried out to obtain higher strength, further embrittlement would be promoted. Therefore, it would be impractical to apply these results to other steels.

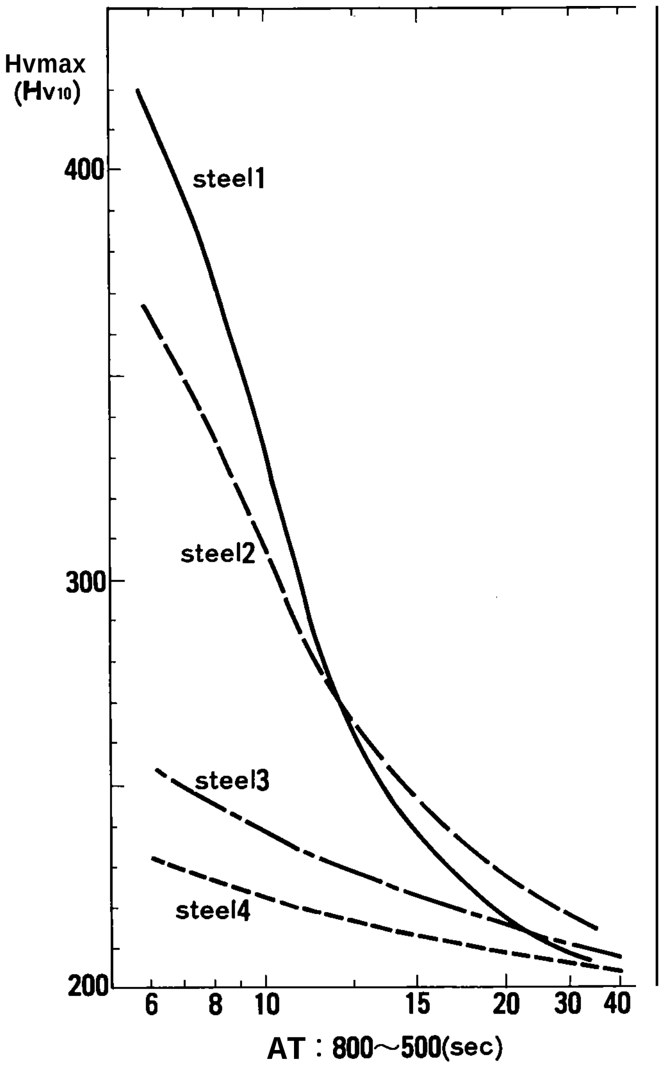


Figure 26. Relations between AT and Hvmax. of C steel and Nb steels (69).

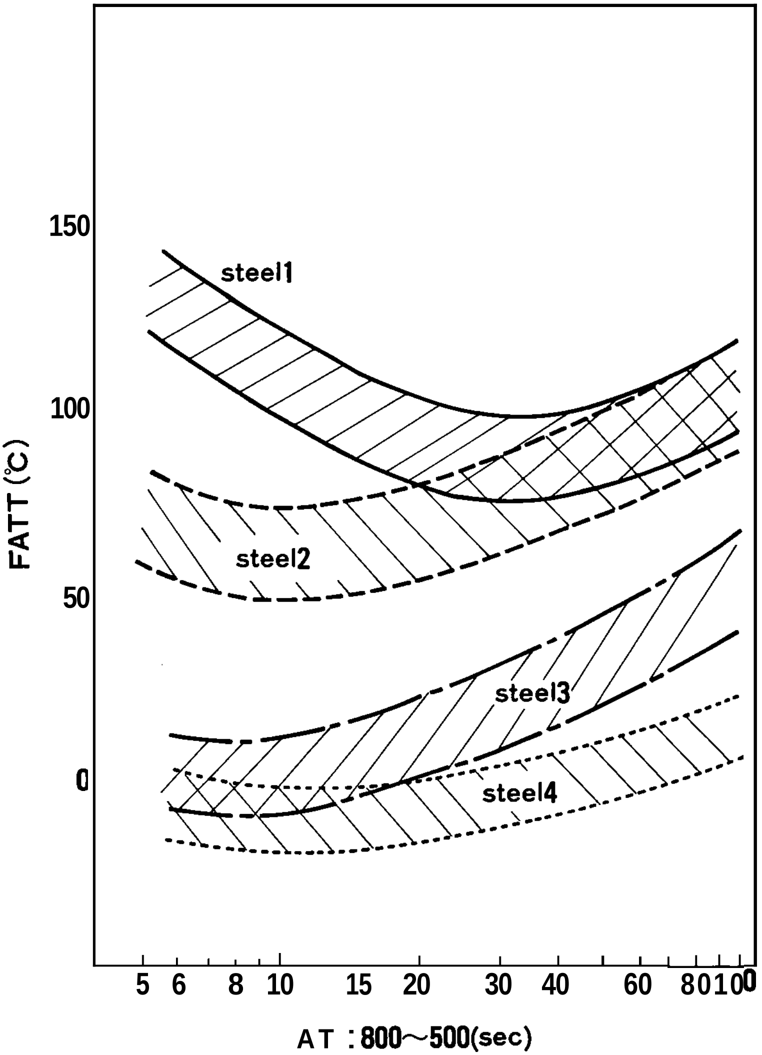


Figure 27. Relations between ΔT and Charpy vTrs temperature (FATT) of synthetic HAZ of C steel and Nb steels (69).

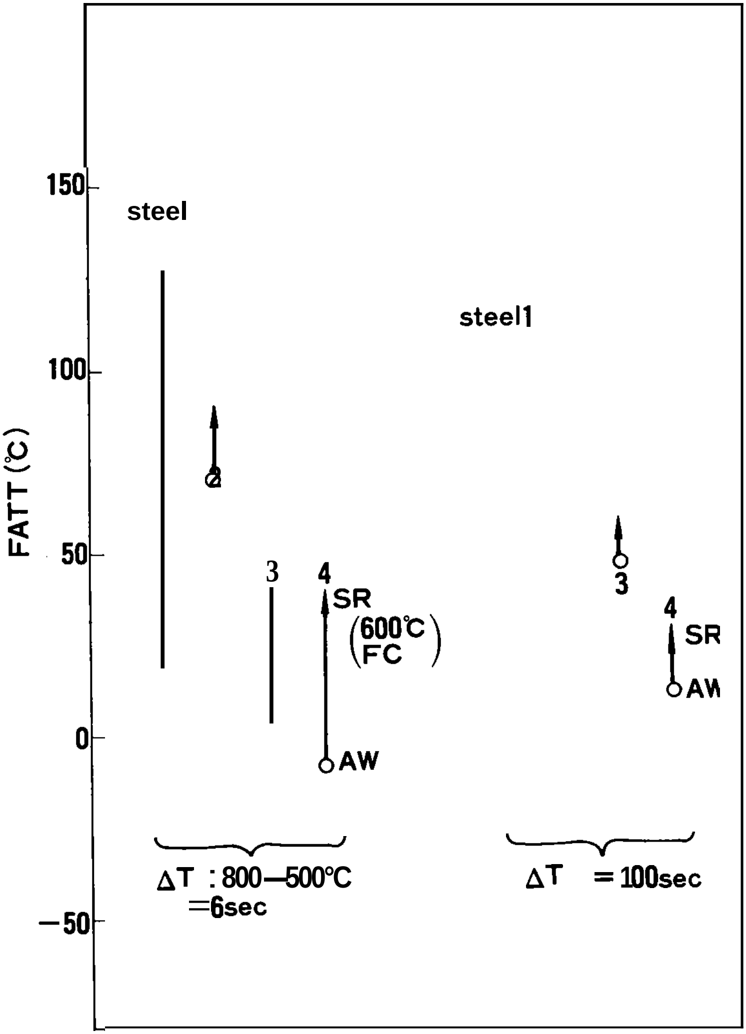


Figure 28. Effect of SR on Charpy vTrs temperature (FATT) or synthetic HAZ of C steel and Nb steels (69).

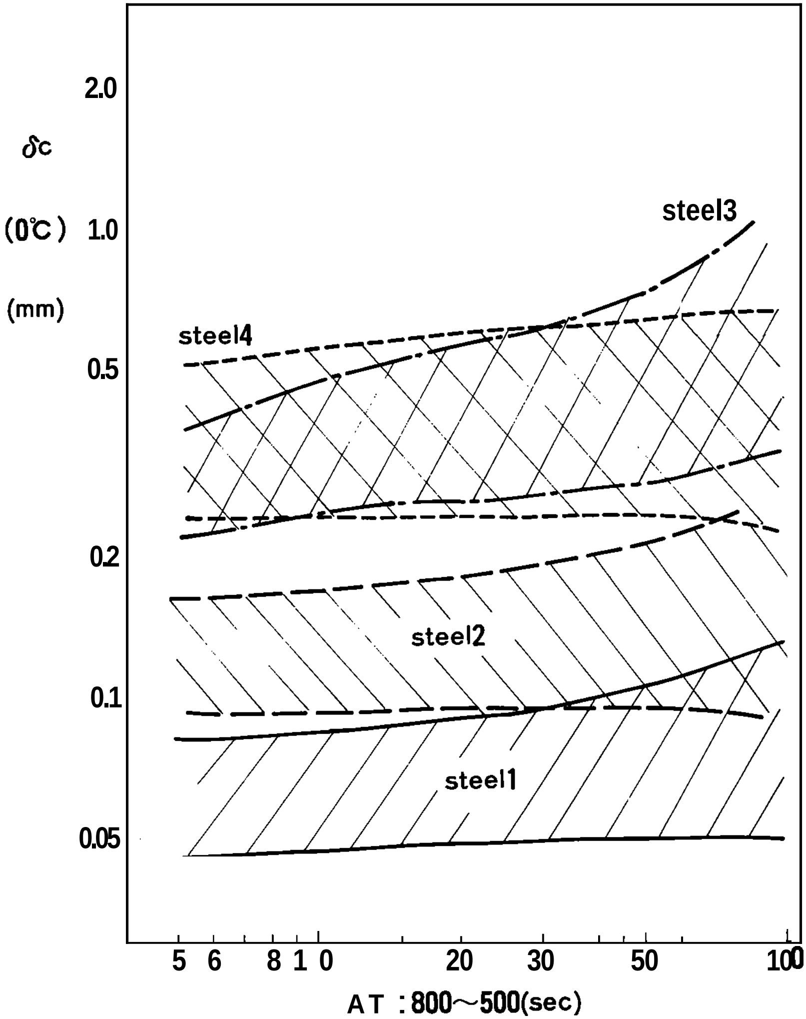


Figure 29. Relations between ΔT and COD value (at 0°C) of synthetic HAZ of C steel and Nb steels (69).

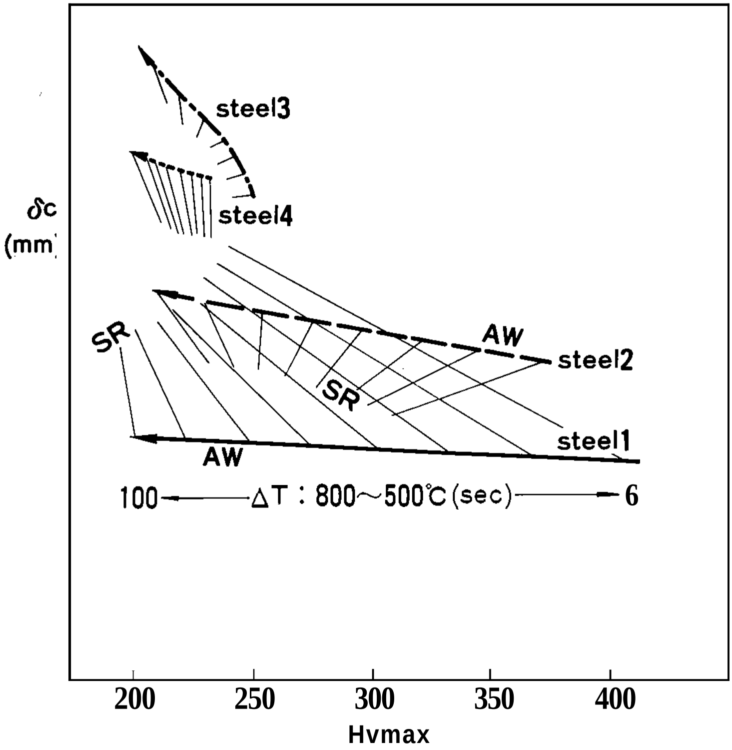


Figure 30. Change of hardness and COD value with ΔT and stress relief annealing (SR) of C steel and Nb steels (Schematic diagram) (69).

Formability

Bauschinger Effect

In bending a steel plate to form a pipe, the yield point of the formed pipe is generally different from that of the plate, prior to cold forming. Therefore, it is necessary to predict beforehand, the difference of the yield point at the time of manufacturing the plate and that of the formed pipe. Nakajima et al, in order to estimate this difference, have developed through experiments on several kinds of niobium and vanadium-steel (70) an equation of yield condition as shown below.

$$\sigma = f\,(\bar{\varepsilon} + \varepsilon) \cdot \left\{1 - \frac{\varepsilon}{K_1 + K_2\,\bar{\varepsilon}}\right\} \cdot \frac{(\bar{\varepsilon} + K_3)\,(\varepsilon/0.005)}{(K_3 + K_4\,\bar{\varepsilon})\,(e/0.005) + \bar{\varepsilon}\,(1-K_4)} \qquad (5)$$

Provided that $f\,(\bar{\varepsilon} + \varepsilon) = \sigma_0$ **when** $\bar{\varepsilon} + \varepsilon \leq \varepsilon_0$

$f\,(\bar{\varepsilon} + \varepsilon) = \sigma_0 + \lambda E(\bar{\varepsilon} + \varepsilon - \varepsilon_0)$ **when** $\bar{\varepsilon} + \varepsilon > \varepsilon_0$

where

σ = Flow stress of the 2nd forming (kg/mm^2)

σ_0 = Yield point of the 1st forming (kg/mm^2)

λ = Work hardening coefficient = $(\partial\sigma/\partial\varepsilon)/E$

ε = Strain of the 2nd forming

$\bar{\varepsilon}$ = Strain of the 1st forming

ε_0 = Yield point elongation of the 1st forming

K_1, K_2, K_3, K_4 = Coefficient of Bauschinger effect

From this equation, the following postulations can be made with respect to changes in mechanical properties in the circumferencial direction of "U" and "O".

1. The degree of the Bauschinger effect is not affected by the chemical composition of the steel, rolling conditions, or heat treatment.

2. The lower the yield point elongation of the plate, the smaller the Bauschinper effect.

3. The higher the work hardening coefficient of the plate, the more likely is the occurrence of a Bauschinger effect.

4. There is virtually no effect on the yield strength from the radius of curvature in the Uing operation.

5. Up-setting in the Oing operation does not affect the yield strength.

6. The greater the expanding ratio, the higher the yield stength.

7. In a flattened specimen taken from a pipe, the increase in the yield strength due to cold expansion is practically eliminated.

Strain aging

The degree of embrittlement due to cold forming was investigated by a strain aging test. The results are indicated in Figure **31 (71)**. According to the investigation, the degree of yield strength increase and embrittlement of niobium alloyed steel during straining are the same as those of a silicon-manganese steel. However, during the aging stage, embrittlement was more pronounced in the silicon-manganese steel, thus indicating that in total, toughness was better in the niobium steel after cold forming.

Conclusion

As the niobium content increases, the hot deformation strength increases. Research being carried out on the optimum reduction schedules for niobium-steel rolling, is providnp improvements in the efficiency of controlled rolling and consistency in the quality of the steel.

Many advanced rolling techniques have been developed for the purpose of making improvements in strength, touphness, and weldability. These have involved optimization of prior stage rolling conditions and accelerated cooling.

The effect of niobium on strength and toughness of steel varies according to the rolling conditions, carbon content and other elements. In low-carbon steel, niobium increases strength much more than vanadium. Furthermore, the toughness of niobium alloyed steel is better than other as rolled steels when compared at the same strength level. Separations observed in controlled-rolled steel, improve the ability to arrest brittle fracture propagation, but do not affect the arrest of ductile fracture propagation.

When compared at equivalent yield strengths, niobium steel excells in weldability since the carbon content can be reduced. The Hvmax in HAZ is low in the controlled-rolled niobium-steel. Therefore, the susceptibility to weld cracking is reduced. In addition, the toughness of HAZ (vTrs, COD value) is also satisfactory (50 kg/mm^2 class) for most common purposes.

In comparison with the carbon-manganese steel, the embrittlement of niobium steel due to strain aging is smaller.

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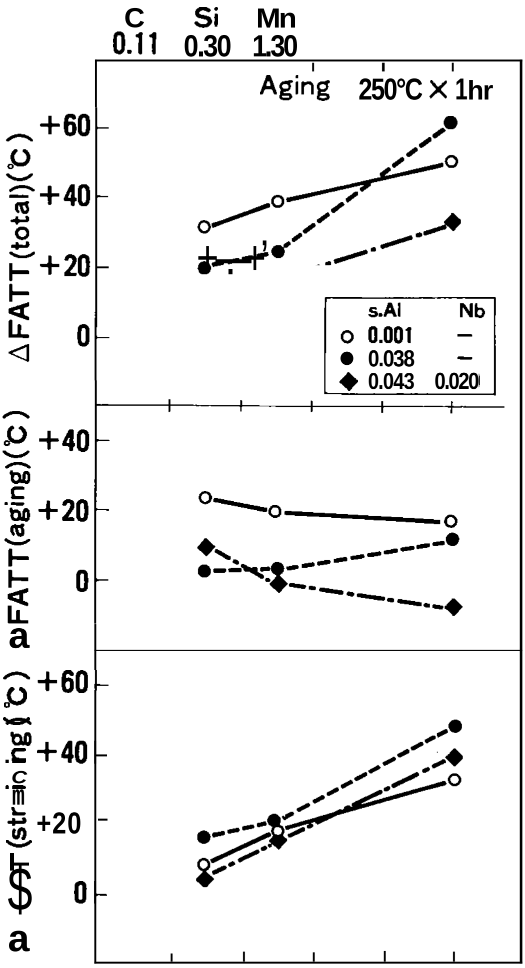

Figure 31. Increase of vTrs temperature (FATT) by strain aging (0.11C-0.30Si-1.30Mn) (71).

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