

PRODUCTION CONCEPTS OF NIOBIUM MICROALLOYED STRUCTURAL HOLLOWS BY SEAMLESS PIPE ROLLING

H. Mohrbacher

NiobelCon bvba, Swaenebeecklaan 5, B-2970 Schilde, Belgium

Keywords: Structural Hollows, Seamless Pipe Rolling, Tubes, Niobium, Steel Processing, HTP, Precipitation, Recrystallization, Grain Size, Mechanical Properties, Charpy Toughness

Abstract

Seamless tubes are available with wall gages of up to 100 mm and outer diameters up to around 700 mm. Such tubes are typically used for oil country tubular goods, as well as for the automotive industry. Another large application area is that of structural hollows for buildings and construction applications. Due to weight and cost reduction efforts the demand for high strength seamless tubes is increasing. Many applications require high toughness in addition to high strength. The different rolling processes applied in production depend on wall gage and pipe diameter. The continuous mandrel mill is used to produce smaller gages and diameters; the plug mill covers medium gages and diameters; the pilger mill allows the production of larger diameters and heavy wall gage. In all these processes only a limited degree of thermomechanical rolling is possible. Therefore, strengthening and toughening by severe grain refinement, employing a conventional Nb-based microalloying concept are not easily achievable. Consequently, high strength and toughness seamless pipe is typically produced via a quench and temper process route. This route however is costly and constitutes a capacity bottleneck in the mill. An innovative low-C high-Nb alloy concept was identified to offer strength up to Grade X70 with very high toughness, off the rolling mill, ie. without a quench and temper treatment. The paper reveals the different functionalities of Nb in this concept based on the process of continuous mandrel mill rolling. In contrast the difficulties of obtaining a high strength and toughness combination with a more conventional alloy concept will be demonstrated.

Introduction

Seamless tubes are available with wall gages of up to 100 mm and outer diameters up to around 700 mm [1]. Such tubes are typically used for offshore pipelines and oil country tubular goods, as well as for the automotive industry and construction applications. Due to weight and cost reduction efforts, the demand for high strength seamless tubes is increasing. Many applications require high toughness in addition to high strength. The different rolling processes applied in production depend on wall gage and pipe diameter. The continuous mandrel mill is used to produce smaller gages and diameters; the plug mill covers medium gages and diameters; the pilger mill allows the production of larger diameters and heavy wall gage. The deformation and temperature schedule during pipe rolling in seamless tube mills naturally depend on the process type. However, for all processes it is typically necessary to apply a quench and temper treatment after rolling when tube strengths of Grade X65 (minimum yield strength of 448 MPa) or higher are to be produced.

The quench and temper treatment is an offline operation where the finished tube is heated above 920 °C for 30 minutes to austenitize the steel. The hot tube is then quenched in water producing a martensitic microstructure of high hardness and strength. In a subsequent tempering treatment the quenched tube is reheated to above 640 °C for a period of 30 to 60 minutes to reduce the as-quenched hardness and to increase toughness.

It is obvious that such a quench and temper treatment involves additional cost. Furthermore, in a market situation with increasing demand for high strength tubes the quench and temper treatment can become a bottleneck operation, either reducing the output of a plant or requiring additional capital investment to increase the production capacity. It should thus be of high interest to find a metallurgical solution enabling the production of 65 ksi strength without having to apply a quench and temper treatment. The cost saving that could be achieved is estimated to be around US\$60 per ton of tube produced.

Structural hollows are a variant of seamless tubes that come with round, square or rectangular cross-section. These are typically used for load-bearing applications in steel construction and mechanical engineering. According to EN10210-1 structural hollows are standardized for minimum yield strength levels of 235, 275, 355 and 460 MPa for wall thickness up to 16 mm. Higher wall thickness up to 65 mm is defined with a reduced minimum yield strength. Using increased strength in load-bearing applications has significant advantages with regard to sustainability as is highlighted by Table I.

Table I. Advantages of Using Higher Strength Structural Hollows

Criterion	S235JR	S355J2H	S460NH	Benefits of Strength Increase
Load-bearing capacity	100%	151%	197%	•Weight reduction •Material savings •Reduced welding effort •Less transport and handling •Leaner structure •More clearance •Architectural esthetics
Wall thickness for identical load-bearing capacity	100%	63%	44%	
Cross-section for identical load-bearing capacity and wall thickness	100%	65%	50%	

Besides strength, minimum elongation and impact toughness are specified. The toughness requirement is a minimum impact energy of 27 J at either 20 °C (JRH), 0 °C (J0H) or -20 °C (J2H). The NH grades require a minimum toughness of 40 J at -20 °C. The boundaries for alloy design and carbon equivalent are indicated in Table II. Additional restrictions may apply to the Si content if the structural hollow has to be galvanized.

Table II. Chemical Composition for NH-grades According to EN10210-1 (wt.%)

Grade	C	Si	Mn	P	S	Nb	V	Al	Ti	Cr	Ni	Mo	Cu	N
S275NH	≤0.20	≤0.40	0.50 1.40		≤0.030	≤0.05	≤0.05	≥0.02	≤0.03	≤0.30	≤0.30	≤0.10	≤0.35	
S355NH	≤0.20	≤0.50	0.90 1.65				≤0.12				≤0.50		≤0.35	
S460NH	≤0.22	≤0.60	1.00 1.70				≤0.20				≤0.80		≤0.70	
	CEV WT ≤16mm		CEV WT >16 ≤65 mm											
S275NH	≤0.40		≤0.40											
S355NH	≤0.43		≤0.45											
S460NH	≤0.53		≤0.55											

Continuous Mandrel Mill Process and Laboratory Rolling Simulation Schedule

The continuous mandrel mill process consists of different rolling steps as shown schematically in Figure 1. The reheated billet is hollowed in the piercing mill at high temperature, then elongated and further reduced in the continuous mandrel mill. The corresponding rolling temperatures are typically above the recrystallization stop temperature, T_{NR} , providing a recrystallized austenitic microstructure. After retraction of the mandrel the shell is transferred to a reheating furnace. During transfer, temperature drops to a level between 750 and 650 °C. The actual temperature at which the shell enters the furnace is however not strictly controlled. Sometimes several shells are collected and transferred in a group into the furnace. In this case the first shell is rather cold while the last shell is considerably hotter. It can thus occur that the temperature in individual tubes drops below the A_{F3} point. Finish rolling is done in the stretch reduction mill after reheating to temperatures between 930 and 900 °C for around 15 minutes. In this final processing step austenite pancaking may be possible, depending on the microalloy composition. It is, however, obvious that the degree of austenite conditioning is less severe compared to the possibilities prevailing in strip or plate mills. This implies that grain refinement, as a key mechanism for strengthening and toughening, is less prominent in seamless pipe rolling. The tube is air cooled after finish rolling.

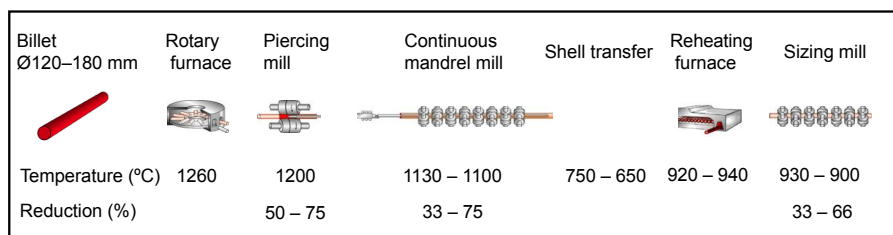


Figure 1. Schematic process flow of a continuous mandrel mill with typical temperatures and rolling deformations.

The process described above was simulated by a laboratory-scale rolling schedule, using flat samples, to analyze alloy concepts under various temperature and deformation schedules. Multiple-pass roughing in a reversing mill stand represents the piercing and the continuous mandrel mill deformations. Finishing is represented by a single pass reduction approaching the very short interpass time in the sizing mill. The simulation schedule, shown in Figure 2, summarizes the variation in conditions that were applied in rolling trials as discussed later. Thereby, also a temperature drop below A_{r3} before reheating was considered. After finish rolling all samples were subjected to natural air cooling at a rate of around 3.5 K/s.

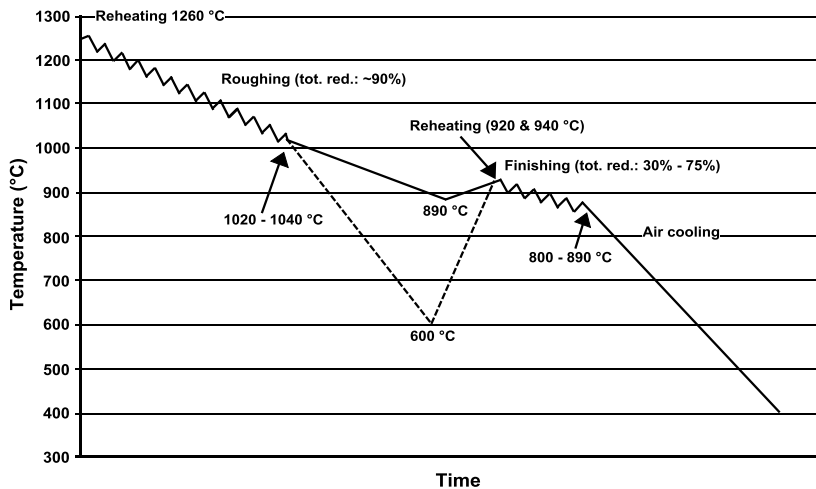


Figure 2. Simulation schedules of a continuous mandrel mill process for laboratory rolling.

Alloying and Processing Strategies for S460NH

Under the rolling and cooling conditions typical of seamless pipe production the final microstructure is expected to be ferritic-pearlitic. The yield strength of such material depends primarily upon the ferrite grain size and upon the content of Mn and Si in solid solution. One weight percent additions of Mn and Si increase yield strength by approximately 27 and 97 MPa, respectively [2]. By using the maximum amounts of Mn and Si permitted for S460NH by EN10210-1 (Table II) solid solution strengthening could deliver around 100 MPa increase in yield strength. This contribution is, however, insufficient to upgrade an as-hot rolled base grade (S235) to S460 strength level. Therefore, other strengthening mechanisms, such as precipitation hardening, have to be employed. The often used peritectic or over-peritectic alloy compositions have traditionally favored V as the microalloy addition for precipitation strengthening, as is clearly reflected by the EN10210-1 specification. Ti is limited to a low level by this specification and hence can not contribute much to strengthening. Nb has a precipitation strengthening potential only if the C content is clearly hypo-peritectic. The potential contribution of precipitation strengthening to yield strength is in the range of 50 to 200 MPa. It depends on the size, distribution and type of MC carbides precipitated. Nb has a very strong effect provided the

element is still in solid solution after finish rolling, which is the case in low-C steel. V on the contrary has good austenite solubility at all C contents applicable within EN10210-1. The formation of precipitates during or after the austenite-to-ferrite transformation is a kinetic process and is thus sensitive to cooling conditions. Accordingly, the strength increase indicated in Figure 3 should be considered as an upper limit while in industrial practice the effect might be considerably less.

The disadvantage of using a combination of solid solution and precipitation strengthening, particularly in hyper-peritectic steels, is that toughness is being reduced and the ductile-to-brittle transition temperature (DBTT) increases. As a result, the toughness requirements for S460NH may not be met. Hence existing V microalloyed concepts are often co-alloyed with Ni and Cu to improve low-temperature toughness. Nevertheless, it remains difficult to obtain a robust behavior in terms of required strength and toughness with such V-Ni-Cu alloy concepts.

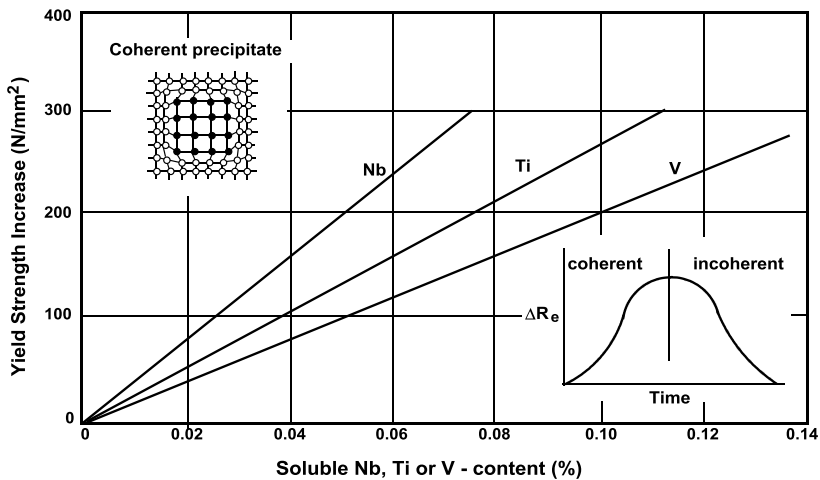


Figure 3. Precipitation strengthening potential of microalloying elements.

Grain refinement is the only strengthening mechanism providing simultaneously increased strength as well as a DBTT reduction. With the process indicated in Figure 1 various rolling strategies are possible to obtain grain refinement:

- i. By recrystallization controlled rolling (RCR) carrying out reductions above the recrystallization-stop temperature (T_{NR});
- ii. Performing deformations during finishing below T_{NR} using an appropriate microalloying concept to produce austenite pancaking;
- iii. Under certain conditions dynamic recrystallization controlled rolling (DRCR) is possible [3];
- iv. An in-line normalizing treatment is possible by reducing the temperature below A_{r1} before reheating.

Conditions of RCR prevail during piercing and continuous rolling as the temperature in these processes is very high ($>1100\text{ }^{\circ}\text{C}$). Either dynamic recrystallization (DRX) or static recrystallization (SRX) can occur [3]. DRX is favored at lower strain rate and increased deformation temperature. These conditions exist during piercing. DRX is also possible during the initial continuous rolling passes whereas SRX is more likely during the final passes (higher strain rate, temperature drop). The austenite grain size produced is relatively independent of the applied strain once DRX has occurred. However, the application of low strains towards the end of continuous rolling can result in recrystallization induced grain growth. Unfortunately, low deformation strain is difficult to avoid in the last stands of a continuous mandrel mill especially at the positions of 45 degrees to the rolling axis. This phenomenon can lead to quite inhomogeneous austenite grain size around the tube circumference. The heterogeneity of austenite grain size can be reduced by the addition of Nb and reduction of the entry temperature to the continuous mill. Consequently SRX will be delayed and more strain will be accumulated.

Non-recrystallizing rolling with austenite pancaking is principally possible in the sizing mill. With an entry temperature in the range of 900 to 930 $^{\circ}\text{C}$ typical Nb-microalloyed steel concepts, providing a T_{NR} above 940 $^{\circ}\text{C}$, are suitable candidates. Figure 4 demonstrates the recrystallization-retarding effect of microalloying elements [4]. Nb has been shown to be a very effective element for microstructural refinement because of the combined effects of solute drag and strain-induced precipitation mechanisms. Mo may also contribute to austenite conditioning by its strong solute drag effect. It produces an increase in the non-recrystallization temperature, which allows the range of strain accumulation in the austenite to be extended [5]. A more severe degree of pancaking, ie. larger reduction in the sizing mill, leads to a finer final ferrite grain size (Figure 5). V, contrary to Nb, has a quite weak effect so that under the given conditions in the sizing mill austenite pancaking is not possible. Hence, the V-Ni-Cu alloy concepts that have been tried for S460NH do not prove suitable for non-recrystallizing rolling.

Jonas et al. [3] have reported that DRX is likely to occur in the stretch reduction (sizing) mill, especially when non-Nb-microalloyed steels are rolled with a relatively high entry temperature. After some initial strain accumulation DRX reduces the further increase of the mean flow stress. The repeated recrystallization of austenite grains and their inability to grow during the short interpass time is proposed as an effective means of refining the austenite grain size. However, the risk that only some of the austenite grains recrystallize by DRX can lead to an inhomogeneous grain structure, which is very detrimental to toughness. Recent experience with strip products has confirmed this [6]. Adapting the reduction schedule and lowering the finishing temperature can avoid the occurrence of DRX in a pancaking schedule.

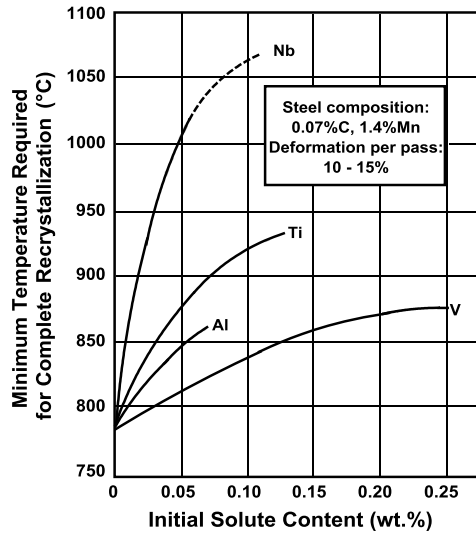


Figure 4. Retardation of austenite recrystallization by microalloying elements.

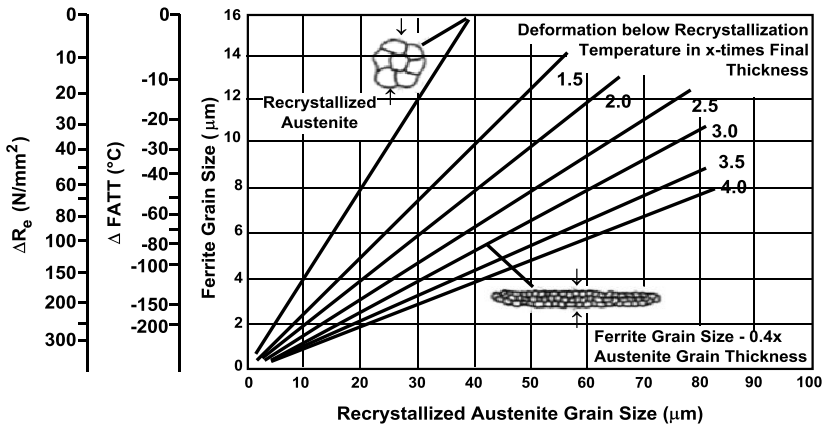


Figure 5. Correlation between austenite grain size and ferrite grain size after air cooling.

When the shell is cooled down to temperatures below A_{r1} before reheating to above A_{c3} a normalized microstructure is obtained. This treatment results in a rather homogeneous and fine-grained austenite microstructure. Solute microalloying elements precipitate during cooling below A_{r1} . Upon reheating Nb and Ti carbonitride particles are not re-dissolved and help in controlling the austenite grain size.

If the above-mentioned rolling conditions do not lead to complete precipitation of microalloying elements, the solute elements have the potential of lowering the austenite-to-ferrite transformation temperature irrespective of the cooling rate. Also in this respect, Nb has the strongest effect (Figure 6). It was shown [7] that the transformation temperature can be lowered by up to 100 °C depending on the amount of solute Nb and the cooling rate (Figure 7). The undercooling delivers a higher nucleation rate and limited grain growth so that the final grain size becomes refined. The addition of Mo to microalloyed steel delays the strain-induced precipitation of microalloying elements in austenite thus retaining a higher amount in solid solution to promote this effect.

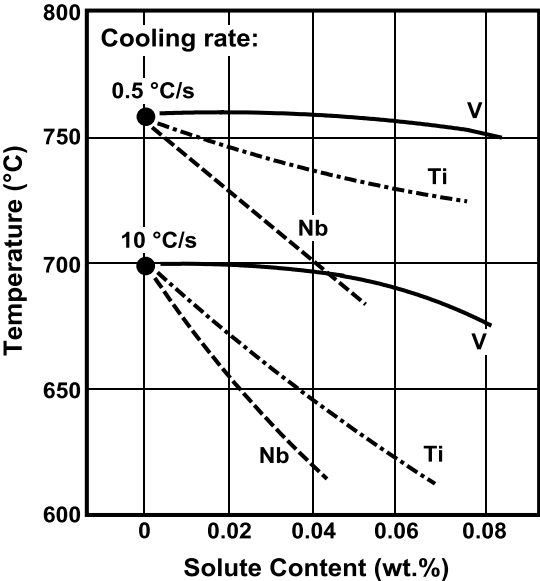


Figure 6. Effect of solute microalloying elements on the austenite-to-ferrite transformation temperature.

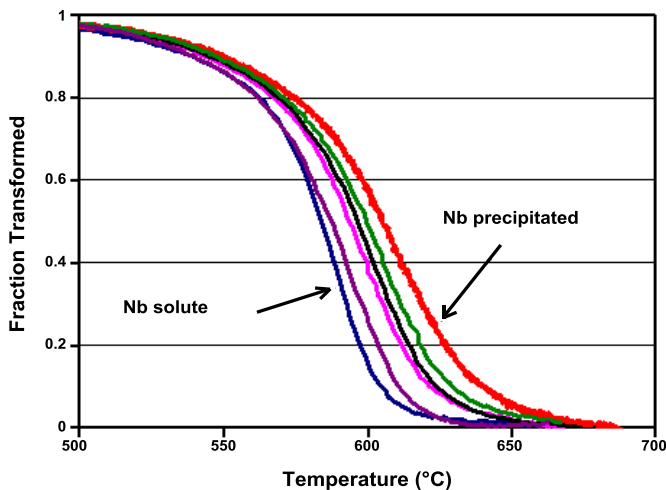


Figure 7. Effect of 0.04%Nb in solution on austenite decomposition kinetics in steel with a prior austenite grain size of 26 μm cooled at 1 $^{\circ}\text{C/s}$.

Based on the effects described above, a trial heat was designed to make better use of grain refinement as a strengthening method. The concept uses 0.10%C, 1.7%Mn, 0.2%Si, 0.25%Cr and 0.07%V, together with Nb and Mo additions at the upper limit allowed by EN10210-1. The CE was significantly reduced to a value of 0.47, as compared to 0.15%C V-Ni-Cu concepts having a CE of around 0.51. Rolling trials achieved a yield strength that was close to S460NH grade. Toughness for this concept did not reach the required 40 J at -20°C . The reason for these unsatisfactory properties can be derived from the microstructure (Figure 8). This consists of about 63% ferrite, 32% bainite and 5% martensite. The grain size is a mixture of fine and coarse ferrite grains. Low impact toughness may be associated with the presence of Widmannstätten ferrite and high-C martensite. The presence of martensite has also an effect on the yielding as it generates mobile dislocations in the ferrite phase. The yield ratio of the material was around 0.65 and thus rather low. It can be assumed that solute V, Cr and Mo promote the formation of C-rich martensite islands. Tempering of this alloy (650 $^{\circ}\text{C}$, 0.5 h) leads to a yield strength increase of more than 100 MPa. Toughness is, however, still insufficient. On the other hand, slow cooling of the as-rolled product from 650 $^{\circ}\text{C}$ brings the properties just into the specified range, albeit with little margin, see square symbols in Figure 15.

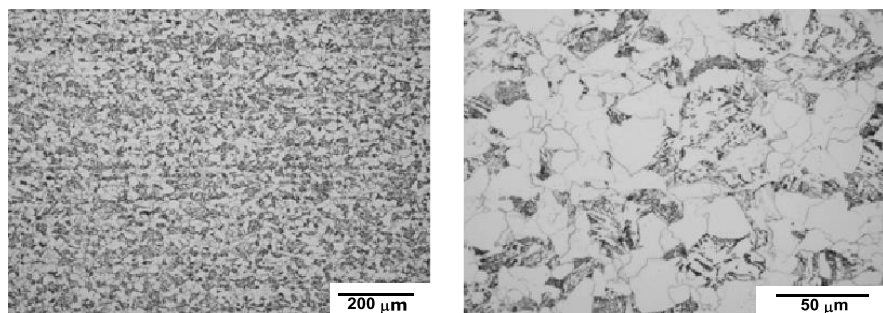


Figure 8. Final microstructure of 0.1%C-1.7%Mn-Cr-V-Nb-Mo concept after rolling simulation.

The strength gain can be related to precipitation of solute microalloying elements. In both cases 650 °C is a suitable temperature for this metallurgical process.

As a consequence of this trial, a modified alloy concept should reduce the C and V contents to eliminate the formation of martensite. A mixture of ferrite and bainite with fine grain size is aimed for, to achieve sufficient strength and toughness.

HTP Alloy Design

In recent years, the so-called HTP (High Temperature Processing) alloying concept has been developed successfully by several steel producers [8-11]. The HTP alloying concept is characterized by low C content (0.03-0.05%) and high Nb content (0.08-0.10%). The use of such a Nb content does not meet the EN10210-1 specification. However, it has been well established in the production of pipe plate and strip. In several projects this steel was processed to longitudinally welded pipe, as well as spiral pipe, fulfilling API 5L specifications up to a strength level of X80.

The current study investigated the possibility of applying the HTP alloying concept under seamless tube rolling conditions. Based on a typical rolling schedule of a continuous mandrel mill, laboratory rolling simulations were carried out according to the parameters shown in Figure 2.

The investigated HTP alloy design based on the chemical composition shown in Table III has a CE of only 0.34. A small addition of Ti adjusted to be substoichiometric with respect to N (<3.4) is meant to provide high-temperature stable particles limiting austenite grain coarsening during reheating.

Table III. Nominal Chemical Composition (CEV: <0.38)
of HTP Steel for Seamless Pipe Trials (wt.%)

C	Si	Mn	P	S	Al	N	Nb	Ti
0.04	0.25	1.70	0.015	0.002	0.025	0.005	0.100	0.015

Hot torsion testing has indicated that T_{NR} of the HTP alloying concept is approximately 1060 °C, which significantly exceeds that of conventional Nb-microalloyed low C steel which are around 950 °C. This can be due to the precipitation of NbC particles pinning the austenite grain boundaries, but also to the solute drag effect of Nb in solid solution.

A microstructure consisting of polygonal ferrite and low C bainite will be formed according to the CCT diagrams shown in Figure 9 even under the condition of slow cooling in air [7]. The amount of bainite formed depends on the cooling speed and also on the amount of accumulated strain. Low C bainite is characterized by a high dislocation density and a small effective grain size. The presence of this phase in a fine-grained matrix of polygonal ferrite is responsible for the favorable combination of high strength and good toughness. The diagram suggests that if strain accumulation is low due to a high finishing temperature and DRX, the proportion of bainite should be in the order of 90 percent. At lower finishing temperatures and significant pancaking with strain accumulation, ferrite nucleation is promoted and accordingly the bainite proportion should range between 20 and 30 percent.

Figure 10 shows the equilibrium solubility of NbC in 0.04%C-0.10%Nb steel. The total amount of 0.10% Nb is fully dissolved at a reheating temperature of 1250 °C. Roughing is finished slightly below T_{NR} . Two samples were quenched after roughing and analyzed by chemical extraction to determine the amount of Nb precipitated. This analysis revealed that 0.08% Nb is still in solid solution at the quenching temperature of about 920 °C. This quantity is considerably higher than the maximum solubility under equilibrium conditions. The precipitation kinetics may not have been fast enough to bring the system into equilibrium.

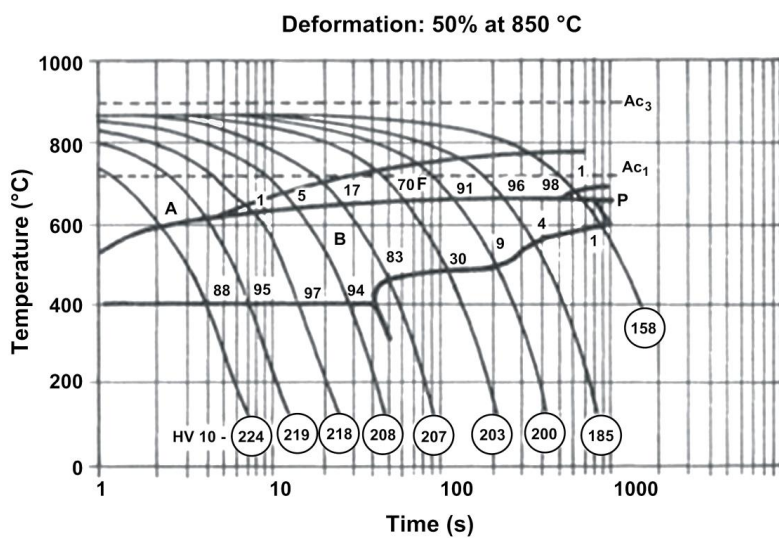
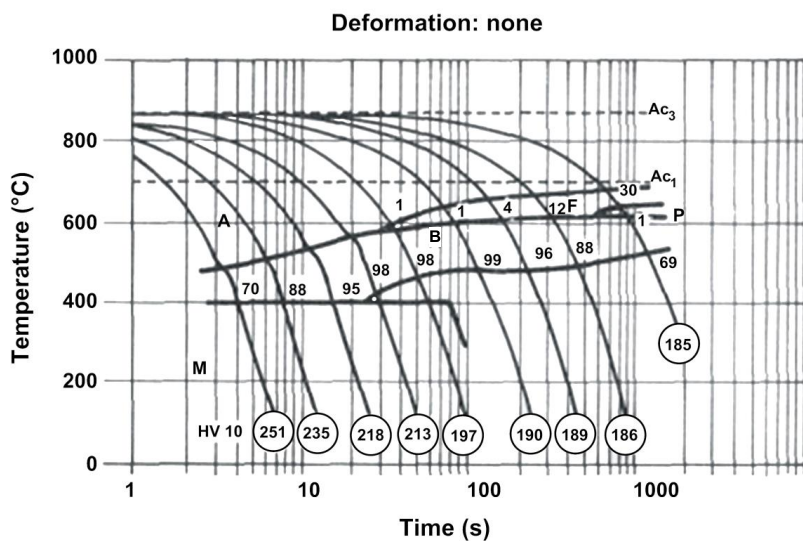


Figure 9. CCT diagram of HTP steel (soaking at 1250 °C) [12].

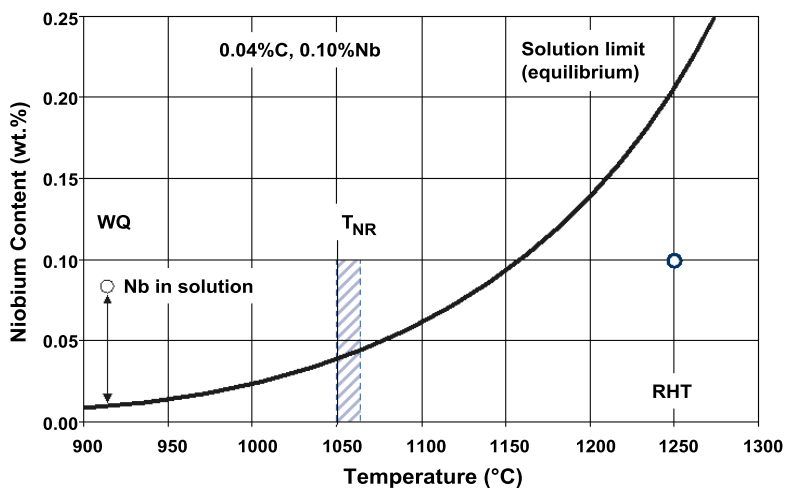


Figure 10. Nb in solid solution before and after roughing.

The pre-rolled samples were transferred to the reheating furnace at temperatures above A_{r3} . The finish rolled material was machined into tensile test specimens and Charpy V-notch samples. From the tensile curve the yield strength ($R_{p0.2}$) and the tensile strength (R_m) were determined. Both quantities are shown as a function of the total reduction during finish rolling and the finish rolling temperature in Figure 11. The data indicate that even at the lowest reduction ratio ($\lambda = 1.3$) the minimum strength for S460NH is exceeded. With increasing final reduction the yield strength increases. Reducing the finishing temperature also results in a yield strength increase as expected.

The toughness was measured by Charpy V-notch testing at -20°C . The data points shown in Figure 12 are average values of three individual measurements for each rolling condition. The data population shows rather high scatter, between 180 and 400 J. It is reasonable to assume that a minimum level of 200 J can be safely maintained under more reproducible industrial rolling conditions. Again, the requirements of S460NH are safely met.

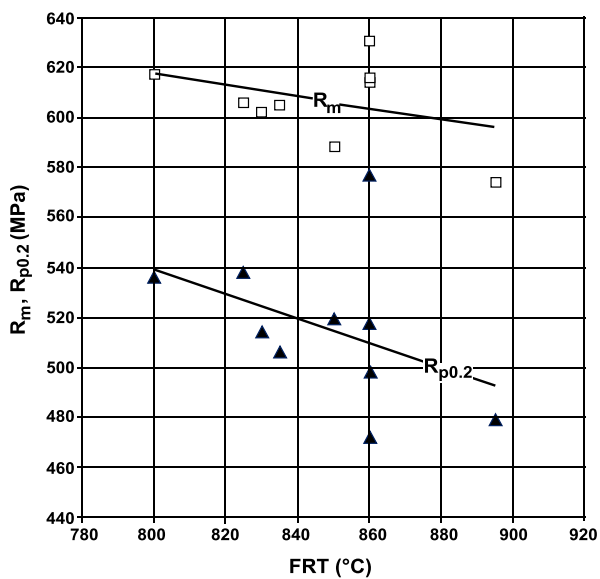
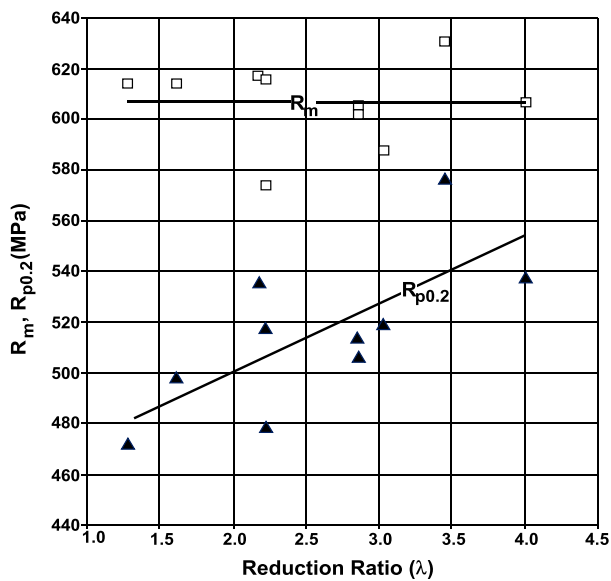


Figure 11. Yield and tensile strength dependence on finish rolling conditions.

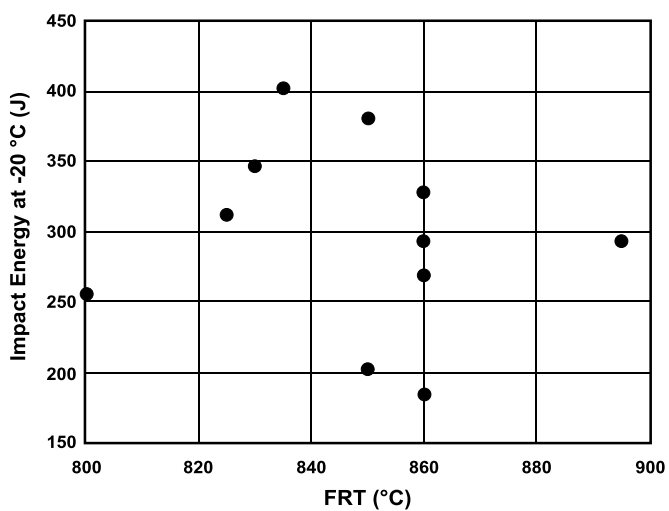
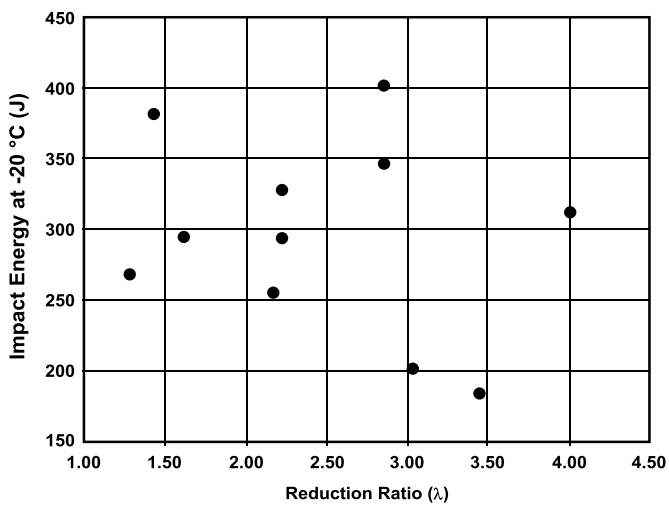
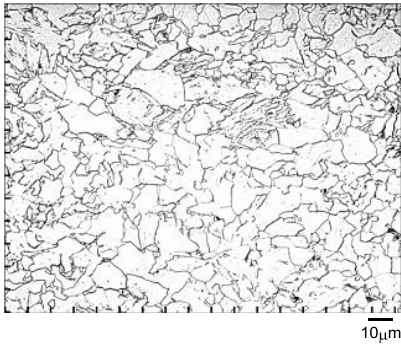


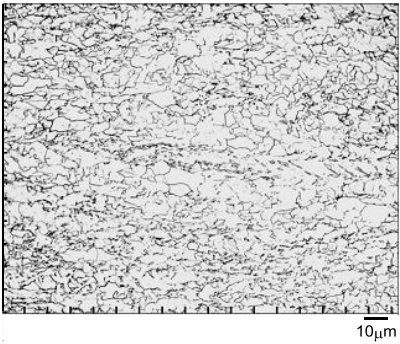
Figure 12. Charpy V-notch toughness at -20 °C for different finish rolling conditions.

Microstructural evaluation (Figure 13) of the samples confirmed the expectations from the CCT diagram (Figure 9). The ferrite fraction is approximately 75% and that of bainite around 22%. A small amount of MA phase was also detected. The ferrite grain size was ASTM 9 for the lowest rolling reduction and ASTM 11 for the most severe rolling conditions. It is thus reasonable to assume that the strength variation observed in Figure 11 is due to differences in the grain size.

Several samples were subjected to air-cooling to room temperature after roughing, ie. without a reheating and finishing treatment. These samples still meet requirements for S460NH. The yield strength is between 465 and 500 MPa. The microstructure shows a higher fraction of bainite (around 35%) and less ferrite (around 63%). However, the grain size is coarser (ASTM 8) due to limited finishing deformation. Therefore also toughness at -20 °C is reduced to a level of 130 to 150 J.

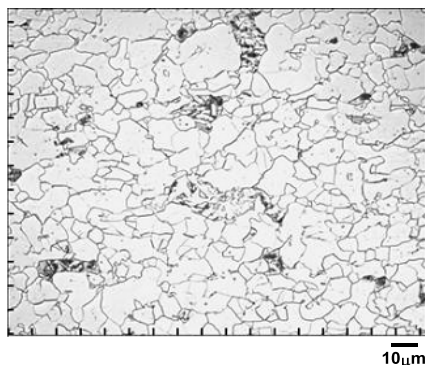


1.3 x / 860 °C
Microstructure:
73% Ferrite
25% Bainite
2% MA
ASTM grain size: 9

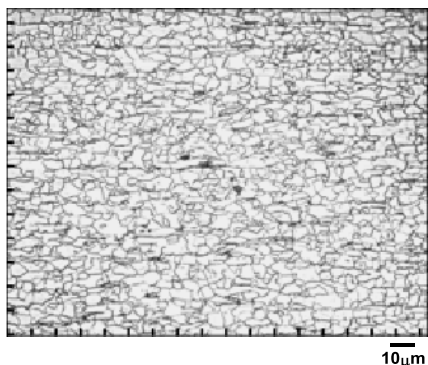


4.0 x / 825 °C
Microstructure:
75% Ferrite
22% Bainite
3% MA
ASTM grain size: 11

Figure 13. LOM of selected samples with finishing reductions of 1.3x and 4.0x, without in-line normalizing giving ferrite grain sizes of ASTM 9 and 11 respectively.



Microstructure:
91% Ferrite,
6% Bainite,
3% MA
ASTM grain size: 9



Microstructure:
93% Ferrite,
2% Bainite,
5% MA
ASTM grain size: 12

Figure 14. LOM of selected samples after in-line normalizing.

In a second set of trials the effect of an in-line normalizing treatment was investigated using a HTP alloy concept with a reduced Nb content (0.08%). After roughing, the temperature dropped to between 600 and 620 °C before reheating to 920 °C. The yield strengths after the different finishing conditions range between 360 and 430 MPa. This is considerably lower than the series without a normalizing treatment. Again, the more severe are the finishing conditions the higher is the yield strength. Toughness values are in the same scatter band as the non-normalized series. Consequently, the in-line normalizing with the current HTP alloy would produce an S355NH grade. Analyzing the microstructure readily explains the lower strength level. The ferrite fraction is now between 90 and 95% and the remaining phases are bainite and MA. The ferrite grain size is between ASTM 9 and 12 depending on the severity of finish rolling (Figure 14). The reduced amount of bainite must be directly related to a lower content of solute Nb after the normalizing treatment. A substantial fraction of the Nb precipitates after the temperature drop below A_{r1} and the subsequent reheating. Apparently these precipitates are still functional in retarding recrystallization and thus providing some degree of austenite pancaking during finish rolling.

Metallurgical Recommendations

The present trials have identified several metallurgical effects that can be used to improve product properties of structural hollows, despite the sometimes unfavorable and uncontrolled conditions in seamless pipe rolling:

- i. Toughness is improved by reducing grain size and developing a homogeneous grain size distribution. Either of these features is difficult to guarantee in seamless pipe rolling. The current trials indicate that reducing the C content to a low level, such as 0.04 wt.%, provides a high toughness under all rolling conditions;
- ii. Reducing the average grain size from 16 μ m (ASTM 9) to 8 μ m (ASTM 11) brings about a yield strength increase of around 60 MPa (Figure 5). The actual final grain size depends on several factors but the severity of finish rolling has the major contribution;
- iii. Non-recrystallizing rolling resulting in austenite pancaking is possible in the sizing mill. Due to the relatively high finishing temperature in seamless pipe rolling, higher Nb containing alloy concepts are favorable since these increase T_{NR} to a suitable temperature level;
- iv. If strain induced precipitation is not feasible in the early stands of the sizing mill, a prior normalizing treatment will force Nb precipitation. These precipitates can control austenite grain size during reheating and at least partially suppress recrystallization during finish rolling;
- v. Solute Nb delays the austenite-to-ferrite transformation after finish rolling. It also suppresses pearlite formation and promotes bainite or acicular ferrite formation. The higher the amount of solute Nb the larger are these effects;
- vi. A fraction of around 20% bainite appears to be necessary to safely fulfill the strength requirements of S460NH;
- vii. More severe pancaking and strain accumulation at the end of finish rolling enhances ferrite formation. Thus higher-Nb steels with little austenite conditioning exhibit a higher fraction of bainite and a larger grain size;
- viii. Solute Nb will partly precipitate as fine particles during cooling. The mechanism of interphase precipitation should be more effective after severe austenite conditioning since the ferrite-start temperature is higher and the two-phase field is wider. However, precipitation cannot be expected to be complete without isothermal holding in the temperature range favorable for precipitation. Therefore, the contribution of precipitation strengthening is limited to an estimated 40 MPa, although the potential could be in the order of 200 MPa (Figure 3);
- ix. Precipitates generated during the normalizing treatment are too coarse for particle strengthening;
- x. Sub-stoichiometric Ti addition with respect to N (Ti/N <3.4) is beneficial for limiting austenite coarsening during the very hot stages of the process.

Figure 15 benchmarks different alloy concepts (and process modifications) with respect to the minimum requirements for S460NH. It is obvious that the HTP concept delivers the best performance by far. All other concepts either fail or are close to the minimum requirements. Thus, they cannot be considered to be sufficiently robust for industrial mass production.

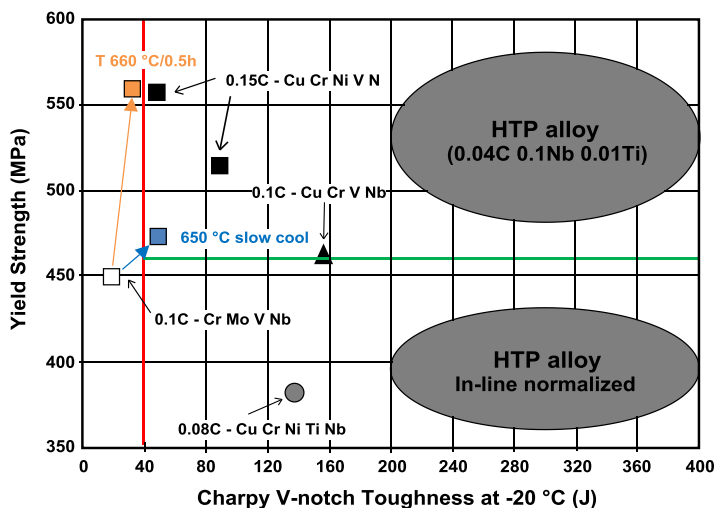


Figure 15. Benchmarking diagram indicating the performance of different alloy concepts with respect to the minimum requirements of S460NH.

Since Nb additions higher than 0.05% are not permissible according to EN10210-1 an alternative alloy concept with similar metallurgical performance is desirable. A modified HTP alloy concept (Table III) involving reduction of Nb to the maximum of 0.05 wt.% and adding Mo to about the allowable maximum of 0.10 wt.% is likely to deliver this performance. In this concept synergies of Nb and Mo are being used as follows:

- i. Mo will be completely in solution in such low C steel but strongly supporting, by solute drag, the recrystallization retarding effect of Nb [5];
- ii. Mo (and to a lesser degree Mn) delay strain induced precipitation of Nb [13]. Thus an increased amount of Nb will be in solution after finish rolling favoring the formation of bainite;
- iii. Mo strongly delays the formation of pearlite and also supports bainite formation;
- iv. This effect of Mo would even work when the temperature before the reheating furnace accidentally drops below A_{r1} since Mo does not precipitate in this case;
- v. Consequently, in-line normalizing becomes an option for the modified HTP steel. The normalizing treatment refines and homogenizes the grain structure. Nb is forced to partially precipitate. The precipitates are then available to provide non-recrystallizing conditions during finish rolling. Mo in solid solution promotes partial bainite formation.

It is certainly worth also considering some process modifications:

- i. The billet reheating temperature could be reduced by 50-70 °C due to good solubility of microalloys in low C steel. This could shift part of the upstream rolling process in to the non-recrystallizing regime and provide grain refinement;
- ii. Likewise it would be advisable to reduce the intermediate reheating temperature;
- iii. Moderate accelerated cooling by forced air or water spray after finish rolling would enhance the formation of bainite (Figure 9) and thus strength.

Conclusions

The proposed low C alloy concept is cost-efficient compared to all alternative and prior concepts. Furthermore, it offers additional benefits due to its extraordinarily low CE value, particularly with regard to welding [14]. Existing experience with such HTP-like alloy concepts also revealed superior performance in continuous casting in terms of avoiding slab cracking and thus reducing flame scarfing requirements.

To enable all these benefits to be realized the current EN10210-1 should be revised allowing Nb additions higher than 0.05%, especially for steel with low C content (<0.1%). As an example, the API 5L specification for PSL 1 pipe does allow increased Nb additions (Nb+Ti+V: max. 0.15%) in linepipe steel.

Acknowledgements

The author would like to thank Ch. Wintermann, C. Stallybrass, J. Konrad and M. Frommert (Salzgitter Mannesmann Forschung GmbH) for valuable discussions and performing part of the experimental work.

References

1. K.H. Brensing and B. Sommer, Steel Tube and Pipe Manufacturing Processes, http://www.mrw.de/downloads/stahlrohre_engl.pdf.
2. B. Engl and Th. Gerber, "Microalloyed Vacuum Degassed High-strength Steels with Special Emphasis on IF Steels," *Steel Research*, 67 (10) (1996), 430.
3. L.N. Pussegoda and J.J. Jonas, "Comparison of Dynamic Recrystallization and Conventional Controlled Rolling Schedules by Laboratory Simulation," *ISIJ International*, 31 (3) (1991), 278.
4. L. Cuddy and J. Raley, "Austenite Grain Coarsening in Microalloyed Steels," *Metallurgical Transactions A*, 14 (10) (1983), 1989.
5. P. Uranga, B. Lopez and J.M. Rodriguez-Ibabe, "Microalloying and Austenite Evolution During Hot Working in Near Net Shape Processed Steel," *Materials Science and Technology*, 25 (9) (2009), 1147.

6. C.L. Miao et al., "Recrystallization and Strain Accumulation Behaviors of High Nb-bearing Line Pipe Steel in Plate and Strip Rolling, *Materials Science and Engineering A*, 527 (2010), 4985.
7. F. Fazeli and M. Militzer, "Effect of Nb on Austenite Formation and Decomposition in an X80 Linepipe Steel," *Journal of Iron and Steel Research International*, 18 (May 2011), 658.
8. K. Hulka and J.M. Gray, "Niobium Science & Technology," *Proceedings of the International Symposium Niobium 2001*, TMS, (2001), 587.
9. D. Stalheim, "The High Temperature Processing (HTP) Steel for High Strength Oil and Gas Transmission Pipeline Applications," *Proceedings of the 5th HSLA Steels 2005*, Volume 40, China (2005), 699.
10. W.J. Fazackerley, P.A. Manuel and L. Christensen, "First X-80 HSLA Pipeline in the USA," *Proceedings of the 5th HSLA Steels 2005*, Volume 40, China (2005), 711.
11. S. Bremer, V. Flaxa and F.M. Knoop, "A Novel Alloying Concept for Thermo-Mechanical Hot-Rolled Strip for Large Diameter HTS (Helical Two Step) Line Pipe," *Proceedings of 7th International Pipeline Conference*, Volume 3, ASME (2008), paper IPC2088-64678, 489.
12. K. Hulka, J.M. Gray and F. Heisterkamp, Niobium Technical Report 16/90, CBMM 1990, 53.
13. M.G. Akben, I. Weiss and J.J. Jonas, "Dynamic Precipitation and Solute Hardening in a V Microalloyed and Two Nb Steels Containing High Levels of Mn," *Acta Metallurgica*, 29 (1981), 111.
14. J.M. Gray, "Weldability of Niobium-Containing High-Strength Low- Alloy Steel," *Welding Research Council Bulletin*, No. 213, February 1976, 1-19.

