DEVELOPMENT OF HIGH STRENGTH QUENCHED AND TEMPERED SEAMLESS PIPES

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ABSTRACT

The technological evolution in the offshore sector exhibits a trend towards an increasing use of high strength steels. However, when increasing strength toughness is impaired. The results of studies on high strength quenched and tempered (Q&T) low-alloy steels for seamless pipes, performed to understand the relationships between microstructure and strength-toughness in complex tempered bainitic-martensitic microstructure, are discussed in this paper. Results have shown that toughness and strength of Q&T steels are governed by different microstructural parameters:

- the average cell size is the key factor in defining the yield strength;
- toughness is related to the inverse square root of the packet size;
- for a given prior austenite grain size, the increase of martensite volume fraction formed after quenching leads to a finer packet, enhancing toughness.

The role of chemical composition and Q&T process conditions on microstructure and precipitation are analyzed, together with their effect on strength and toughness. These results are exploited for the production of high strength seamless pipes for flowlines, steamlines, and risers for deepwater offshore fields.

KEYWORDS

Seamless pipes, quenching, tempering, high-strength, toughness, microstructure, precipitation.

INTRODUCTION

The technological evolution in the offshore sector seems to point out a trend towards an increasing use of high strength steels (grade X80 and higher) both for flowlines and risers, although the service conditions and the performance required for the two systems are significantly different. This trend is a consequence of both complex oil-gas field conditions, such as high pressure high temperature (HPHT) and developments in design criteria (i.e. limit state design), welding and laying technologies and is supported both by economical and technical reasons [1, 2].

Also technologies which improve the extraction rate of heavy oil, such as Steam Assisted Gravity Drainage, require high-strength pipelines to transport steam from a central production plant to the outlying wells. Because of the high temperature and pressures involved with transporting steam, the steel has to withstand temperatures up to 350 °C and pressures up to 810 bars. For this application, linepipes with outside diameter (OD) from 10” to 24” and grades up to X80 are required.
Seamless pipes of grade X80, with wall thickness (WT) greater than 16 mm, are also required for sour service applications.

On the other hand, also riser and flowline wall thickness (WT) is increasing to provide sufficient resistance for operating pressures. Often the requirements are close to the manufacturing limit of welded pipes, therefore seamless pipes that allow a higher WT/OD ratio will be preferred. Seamless pipes are considered the most suitable product for flowlines due to their size range and reliability compared with ERW pipes.

For large field developments employing floating production facilities, with many heavy risers attached directly to the surface structure, payload limitations are receiving higher consideration and the reduction of raiser weight is gaining importance. In this context the availability of higher-grade weldable steel risers, with a WT/OD ratio adequate to the expected collapse performance can be of engineering importance.

As a matter of fact pipe manufacturers are facing new challenges coming from new and/or more demanding material requirements, often related to specific performances and applications. New products and technologies have been developed in the field of quenched and tempered (Q&T) seamless pipe. Modern products combine high strength with good toughness properties and good girth weldability. Seamless Q&T pipes currently produced have wall thickness up to 44 mm and OD up to 24” and can reach grade X65 and higher after Q&T treatment. Results on X65-X70 heavy wall seamless pipes were presented elsewhere [3, 4].

In this paper, the metallurgical design of high yield strength (YS > 550 MPa) Q&T seamless pipes with WT < 30 mm is presented. This work is part of an on-going project on high performance Q&T seamless pipes, involving metallurgical modeling, laboratory tests, pilot and industrial trials and advanced metallographic examinations. The materials under consideration are grade X80, including sour service grade which sets limitations on maximum material hardness (e.g. HV10 < 248), and higher grades for non-sour service raisers and flowlines.

**EXPERIMENTAL PROCEDURE**

A rational approach to the design and production of high-strength (YS > 550 MPa) Q&T materials requires the quantitative knowledge of the effects of steel chemistry and heat treatment variables on the microstructure and final mechanical properties. The influence of alloying additions and Q&T practices on austenite grain, phase transformation and response to heat treatments of low-C steels for seamless pipes was investigated by dilatometry and pilot trials.

Also an integrated metallurgical model, containing a thermal routine for simulating pipe quenching, coupled with a microstructural model, was applied for the design of both the chemical composition and Q&T conditions of seamless pipes. This model can calculate the fraction of microstructural constituents and hardness of a steel subjected to rapid continuous cooling after austenitisation (i.e. quenching). The calculation is carried out by an Artificial Neural Network (ANN) trained on a selected database of CCT diagrams of low-C low alloy steels [5, 6]. The program is able also to simulate a subsequent tempering treatment, predicting hardness, YS and ultimate tensile strength (UTS). The model is an effective tool in defining the optimum chemical composition and Q&T treatments for a given steel to match the required tensile properties of the final product. However, no information on toughness is available from modeling. Therefore, a specific experimental activity was designed and carried out to assess the effect of microstructure and precipitation on strength-
toughness combination, starting from promising chemical compositions identified by metallurgical modeling.

Specific investigations were carried out to understand the relationships between microstructure and strength-toughness combination in complex tempered bainitic-martensitic microstructures. Low-C Nb-V microalloyed steels with designed changes in chemical composition (e.g. Mn, Mo, Cr, Ni, Mo) were vacuum cast as 80 kg ingots. The carbon equivalent, Ceq (IIW), was below 0.5%, whilst Pcm parameter was ≤ 0.24%. The ingots were hot rolled by a pilot mill simulating the typical thermo-mechanical process of seamless pipes. All ingots were instrumented with thermocouples and the evolution of temperature during hot rolling was recorded. The hot rolled materials were quenched in stirred water and tempered under strictly controlled conditions, being each piece instrumented by a thermocouple embedded at mid-thickness. Various microstructures were formed acting on hardenability and heat treatment conditions chosen on the basis of the integrated metallurgical model. Tempering temperatures were usually in the range 590 °C to 650 °C.

In order to assess the effect of austenite grain size (AGS), formed after austenitizing before quenching, on final microstructure and mechanical properties, austenitizing temperatures higher than 920 °C were also used for promoting coarse AGS.

As-quenched and Q&T materials were examined by light and scanning electron microscopy (LM & SEM). A preliminary work was needed to compare images by light microscopy, SEM, and TEM to establish identification criteria of complex microstructures such as lath martensite, bainite, granular bainite (Fig.1).

![SEM and LM images showing bainite (B) and lath martensite (M)](image)

Fig. 1: Morphology of bainite (B) and lath martensite (M) in quenched steel. Light microscopy (LM) and Scanning Electron Microscopy (SEM) images.
Microstructures were observed on polished sections after 2%-nital etching. Volume fractions of martensite and bainite were measured by point counting on SEM images. The austenite grain boundaries were revealed by etching in a saturated aqueous picric acid solution containing a few drops of a wetting agent (teepol) and HCl. The AGS was measured according to ASTM E112 by LM.

Size of packets and cells, i.e. regions separated by high and low-angle boundaries respectively, were determined by Image Orientation Microscopy (OIM) using electron back-scattering diffraction (EBSD) patterns. By means of this technique, misorientations, types of grain boundaries, and crystallographic orientations can be determined in a fully automatic way. It is of great importance to correctly assess the crystallographic grain size, because this parameter greatly influences the strength and the cleavage fracture resistance of ferritic steels. EBSD is a very accurate method to measure the grain size, even for microstructures as fine as bainite and tempered martensite. In addition, it provides information about much larger areas than those investigated by TEM.

Information on nature and size of fine precipitates was obtained by transmission electron microscopy with scanning attachment and high spatial resolution EDS microanalysis (TEM/STEM-EDS) using extraction replicas.

Tensile tests were performed and Charpy V-notch transition curves were determined together with the fracture appearance transition temperature (50% FATT) on the most promising materials.

On the basis of the laboratory and pilot plant results, industrial heats were produced and seamless pipes with WT from 15 to 30 mm were manufactured using process conditions suitable to develop high strength levels. In addition to the microstructural and mechanical characterization, the industrial materials were assessed in terms of resistance to HIC and SSCC in the case of sour service, and weldability.

**RELATIONSHIPS BETWEEN MICROSTRUCTURE – PRECIPITATION AND STRENGTH – TOUGHNESS COMBINATION IN Q&T STEELS**

Mechanical properties of Q&T materials were practically not affected by the as-rolled microstructure. In order to relate the strength and toughness behavior of Q&T materials to their microstructure and precipitation, steels with various as-quenched microstructures, constituted of predominantly bainitic microstructure, mixed bainite-martensite and fully martensite, were produced acting on chemical composition and quenching conditions. These materials exhibited different toughness-strength combinations after tempering (Fig. 2). Both precipitation and microstructural contribution to strengthening were evaluated.

**Precipitation**

All Q&T materials exhibited amounts of precipitates larger than those of as-quenched materials. Particles located at grain boundaries were mainly of M₃C type, with size from 50 to 300 nm, whilst within laths and grains also small precipitates (size from 5 to 40 nm), rich in Nb, Mo, and V were revealed.

A different evolution of cementite was observed during tempering, depending on the as-quenched microstructures:
1. Low-C martensite: precipitation of M₃C at the boundaries of grains and laths;
2. Bainite: precipitation of M₃C at high-angle boundaries.
However, the M₃C precipitates seem too small to be initiation sites for cleavage.

The average size of fine precipitates ($d_p$) was measured by TEM to evaluate precipitation strengthening ($\sigma_p$) accordingly to the Orowan relationship:

$$\sigma_p = \frac{5.9}{x} \sqrt{VF_p} \ln \left( \frac{-x}{2.5 \cdot 10^{-4}} \right)$$

(1)

with $\bar{x} = d_p / 1.5$ ($\bar{x}$ is the average size referred to 2D-sections)  

(2)

Precipitation strengthening varied from 50 to 100 MPa in Q&T steels depending on volume fraction ($VF_p$) and average size of fine precipitates (see example in Table I). Such contribution is not able to explain the differences in terms of strength between the considered materials.

Table I  Strengthening ($\sigma_p$) due to fine precipitation estimated by TEM measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>C%</th>
<th>Nb%</th>
<th>V%</th>
<th>Mo%</th>
<th>Ti%</th>
<th>VF_p</th>
<th>d_p (nm)</th>
<th>$\sigma_p$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0.10</td>
<td>0.026</td>
<td>0.070</td>
<td>0.23</td>
<td>&lt; 0.0005</td>
<td>162 $10^{-5}$</td>
<td>13.5</td>
<td>94</td>
</tr>
<tr>
<td>T1</td>
<td>0.09</td>
<td>0.029</td>
<td>0.064</td>
<td>0.25</td>
<td>0.0080</td>
<td>1581 $10^{-5}$</td>
<td>23.1</td>
<td>63</td>
</tr>
<tr>
<td>D2</td>
<td>0.11</td>
<td>0.026</td>
<td>0.058</td>
<td>0.31</td>
<td>&lt; 0.0005</td>
<td>151 $10^{-5}$</td>
<td>13.2</td>
<td>93</td>
</tr>
<tr>
<td>T2</td>
<td>0.07</td>
<td>0.026</td>
<td>0.042</td>
<td>0.32</td>
<td>0.0080</td>
<td>127 $10^{-5}$</td>
<td>18.3</td>
<td>67</td>
</tr>
<tr>
<td>T3</td>
<td>0.10</td>
<td>0.025</td>
<td>0.004</td>
<td>0.25</td>
<td>0.0070</td>
<td>80 $10^{-5}$</td>
<td>19.8</td>
<td>50</td>
</tr>
</tbody>
</table>
Small Ti additions (0.008-0.012%), which are very effective in controlling grain growth at high temperatures typical of welding, made Nb rich precipitates slightly coarser, with a reduction in strengthening of 30-40 MPa (Table 1).

Microstructure

The above considered materials were examined by means of OIM technique, in order to outline the microstructural features affecting strength and toughness. Results show that Q&T materials coming from different as-quenched microstructures are characterized by different misorientation distributions (Fig. 3).

![Misorientation profile](image)

Fig. 3: Misorientation profiles of materials with different martensite content after quenching

The following observations can be drawn:

- In all cases very few boundaries are found with misorientation angle in the range 10°-50°.
- Bainitic microstructures exhibit preferential misorientations in the range 47°-60°. Such orientations are compatible with Nishiyama-Wassermann misorientation relationships for packets coming from different $\{111\}$ planes [7].
- Martensitic microstructures show a stronger peak at 60°. It is reported in literature [8, 9] that this aspect is typical of misorientation related twins associated with self-accomodating martensite variants.

Referring to the relationship between transgranular fracture and the presence of boundaries with a misorientation angle greater than 50° proposed by Watanabe [10], on the basis of the presently obtained results, bainitic or martensitic covariant packets and cells (i.e. regions separated by low-angle boundaries or subgrains) were defined as those regions misoriented more than 50° and more then 2° from their neigbourings, respectively.

Examples of inverse pole figure maps of microstructures with increasing amounts of martensite are reported in Fig. 4. From such maps both packet and subgrain average sizes were measured. Trend of packet size versus AGS is shown in Fig. 5.
Fig. 4: Inverse pole figure map of Q&T materials with predominantly bainite, mixed martensite and bainite, and martensite microstructures after quenching, respectively.

Fig. 5: Packet size versus prior austenite grain size (AGS).

Results indicate that:
- in predominantly bainitic microstructures (M < 20%), packet size tends to increase with AGS coarsening
- in martensitic microstructures (M > 60%), packet size slightly decreases as AGS increases.

Fig. 6 shows that average packet size in the Q&T microstructure decreases as the martensite content in the as quenched material increases.

In order to compare the toughness of materials with different strength levels, a normalized value of 50% FATT, referred to a same yield strength value of 600 MPa, was estimated using the relationship [11]:

\[
\frac{\Delta FATT}{\Delta YS} = 0.3 \ °C/MPa
\]  

(3)
Toughness resulted related to the inverse square root of the packet size (Fig. 7).

![Graph showing the relationship between packet size and martensite content.](image)

**Fig. 6:** Packet size versus martensite content after quenching.

![Graph showing the relationship between packet size and normalised FATT.](image)

**Fig. 7:** Toughness versus packet size for the considered Q&T materials.

According to the classical theoretical model for cleavage fracture, which dictates that the critical stage for cleavage cracking is the propagation of a small crack originated in a single packet to the adjacent one, high-angle boundaries delimitating packets are effective barriers to crack propagation. Moreover, the finer the packet the smaller the incipient crack, that is the smaller the possibility for such crack to reach the “critical” size for propagation.
On the other hand, sub-grain (low-angle) boundaries delimitating cells are effective barriers to dislocation movement, thus determining the yield strength.

Based on the above proposed mechanisms, the yield strength of the materials was plotted versus the inverse square root of subgrain size \(d\), according to a Hall-Petch relationship [12]:

\[
YS = YS_0 + k_y d^{-\frac{1}{2}}
\]

(4)

Results, reported in Fig. 8, show that:
- \(YS\) follows equation (4) with \(k_y = 21.5\) MPa mm\(^{1/2}\). This coefficient appears to be independent on microstructure and similar to that found on ultra-fine grained steel [13].
- The cell size decreases as the martensite content in the as-quenched material increases, with consequent strengthening.

\[
\Delta YS/\Delta(d_{\text{subgrain}}^{-1/2}) = 21.5\text{ MPa mm}\(^{1/2}\)
\]

\(R^2=0.93\)

Fig. 8: YS dependence on subgrain size in the considered Q&T materials

METALLURGICAL DESIGN OF HIGH STRENGTH Q&T SEAMLESS PIPES

From the results shown in the previous section, in order to develop a Q&T materials with YS greater than 550 MPa and good toughness (e.g. 50\%FATT < – 40 °C) a volume fraction of martensite > 30\% shall be formed during the quenching process.

In addition to effective quenching facilities for seamless pipes (i.e. external and internal cooling in a water tank with rotating pipe), adequate hardenability of the steel is needed, depending on WT, i.e. minimum cooling rate, to reach this target. Both judicious additions of Mn, Cr, Mo and Ni, and also AGS of 15-25 µm will promote martensite formation without increasing packet size, i.e. introducing a detrimental effect on toughness.
This target as-quenched microstructure, tempered at temperatures in the range 600 °C to 650 °C, is able to develop subgrains with an average size smaller than 2 \( \mu \text{m} \), required to achieve final YS levels greater than 550 MPa, also exploiting the precipitation hardening that can be varied in the range 50 to 100 MPa, acting on typical Nb, Mo, and V additions.

The metallurgical model indicates that to develop a volume fraction of martensite \( \text{M} > 30\% \), for a cooling rate > 35 °C/s, typical of pipes with WT < 30 mm, a steel with \( \text{Ceq} = 0.48\% \) and AGS > 15 \( \mu \text{m} \) is required (Fig.9a). In the case of WT = 15-25 mm and AGS = 20 \( \mu \text{m} \), a steel with \( \text{Ceq} = 0.37-0.40\% \) appears suitable (Fig.9b).

![Graph a)](image1)

![Graph b)](image2)

Fig. 9: Calculated effect of Ceq, cooling rate and AGS on Martensite amount.

These results were confirmed by pilot trials on laboratory steels with Ceq = 0.46\% and 0.50\%, respectively, designed to achieve YS = 560-620 MPa and YS = 620-690 MPa, which gave also indications on the achievable strength-toughness combination (Fig.10).
Fig. 10: Toughness-strength combination for two laboratory steels with Mo contents of 0.17% (0.46%Ceq) and 0.29% (0.5%Ceq), respectively, processed under various Q&T conditions.

YS values can be tuned in the range 560 MPa to 690 MPa, maintaining good toughness levels (50%FATT < −45 °C) acting on chemical composition, AGS (i.e. austenitizing temperature, T aust), and tempering temperature. As expected, strength is improved increasing the cooling rate (very effective quenching, WT < 30 mm), rising the austenitizing temperature from 890 °C to 940 °C, i.e. larger AGS, and decreasing tempering temperature. Toughness tends to slightly improve when increasing the tempering temperature from about 600 °C °C to 650 °C.

EXAMPLES OF INDUSTRIAL PRODUCTION

On the basis of the acquired metallurgical knowledge on high-strength Q&T steel pipes, seamless pipes with OD = 219 to 609.6 mm and WT = 15 to 28 mm were manufactured at Tenaris works by the seamless process, using the steel chemistry range and heat treatment conditions identified as promising by the metallurgical design. Water quenching was carried out on pipes with OD ≤ 406.4 mm by dipping the rotating pipe in a tank containing stirred water. Also an internal water jet is used to increase heat transfer at the inner surface. In the case of large diameter pipes (OD > 406.4 mm) an external water quenching ring was used. All pipes were manufactured according to specific customer requirements for production risers and flowlines/steamlines.

The characterization of selected pipes from the production was carried out by extensive metallography and mechanical testing, which included hardness measurements, longitudinal and transverse tensile testing, Charpy-V impact testing, crack tip opening displacement (CTOD) testing. The industrial production confirmed the effect of main process parameters and metallurgical factors on microstructure and strength-toughness combination, as outlined by the laboratory experiments and pilot trials, and allowed to identify the actions for a fine tuning to develop a good combination of strength and toughness.
High-strength risers

The tuning of Mn, Mo, Cr, V and Ni additions was done on the basis of the results from the metallurgical model which gives reasonable predictions (Table II). A Nb-V microalloyed steel containing Mn, Cr, Mo, and Ni, with carbon equivalent, Ceq (IIW), in the range 0.37% to 0.40% and maximum Pcm parameter below 0.21% was selected for grade X80 pipes with WT = 15 – 25 mm. The sizes and mechanical properties of the risers produced are shown in Table III.

Table II  Comparison between predicted and experimental strength for a Nb-V linepipe steel submitted to laboratory tempering at various temperatures for 60 min after industrial quenching (WT = 22 mm).

<table>
<thead>
<tr>
<th>Tempering Temperature (°C)</th>
<th>HV Calc</th>
<th>HV Exp</th>
<th>YS (MPa) Calc</th>
<th>YS (MPa) Exp</th>
<th>UTS (MPa) Calc</th>
<th>UTS (MPa) Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>620</td>
<td>229</td>
<td>229</td>
<td>617</td>
<td>605</td>
<td>695</td>
<td>706</td>
</tr>
<tr>
<td>640</td>
<td>219</td>
<td>225</td>
<td>585</td>
<td>576</td>
<td>670</td>
<td>681</td>
</tr>
<tr>
<td>660</td>
<td>210</td>
<td>221</td>
<td>558</td>
<td>586</td>
<td>647</td>
<td>665</td>
</tr>
<tr>
<td>680</td>
<td>202</td>
<td>217</td>
<td>530</td>
<td>561</td>
<td>624</td>
<td>637</td>
</tr>
<tr>
<td>700</td>
<td>194</td>
<td>209</td>
<td>503</td>
<td>516</td>
<td>603</td>
<td>615</td>
</tr>
</tbody>
</table>

Table III  Sizes and average mechanical properties of the produced risers.

<table>
<thead>
<tr>
<th>Pipe</th>
<th>OD x WT (mm x mm)</th>
<th>Ceq (IIW)</th>
<th>HV max</th>
<th>YS (MPa) Longitudinal</th>
<th>UTS (MPa) Longitudinal</th>
<th>EI (%) Longitudinal</th>
<th>FATT (°C) Longitudinal</th>
<th>YS (MPa) Transverse</th>
<th>UTS (MPa) Transverse</th>
<th>EI (%) Transverse</th>
<th>FATT (°C) Transverse</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>323.9 x 16</td>
<td>0.38</td>
<td>243</td>
<td>575-622</td>
<td>645-712</td>
<td>40-43</td>
<td>−60</td>
<td>583-608</td>
<td>659-689</td>
<td>25-26</td>
<td>−50</td>
</tr>
<tr>
<td>B</td>
<td>298.5 x 22</td>
<td>0.40</td>
<td>248</td>
<td>587-628</td>
<td>674-728</td>
<td>40-42</td>
<td>−50</td>
<td>593-608</td>
<td>674-690</td>
<td>25-26</td>
<td>−40</td>
</tr>
</tbody>
</table>

* full strip specimen; ** round specimen

The pipes exhibited very good mechanical properties in terms of strength, with YS from 575 to 628 MPa (83-89 ksi) for longitudinal full strip specimens and CVN toughness with low 50%FATT values (longitudinal: −50 to −60 °C; transverse: −40 °C to −50 °C). An interesting feature found is that there are no significant differences between the longitudinal and the transverse tensile properties at room temperature. This is due to the high isotropy which is typical of seamless pipes.

The materials exhibited an absorbed energy value above 140 J up to −60 °C. This is a consequence of the microstructure promoted after external/internal quenching and tempering, characterized by an uniform austenite grain (average AGS = 15 µm) and a predominant microstructure of bainite-martensite with very low ferrite content.

Also high CTOD values (> 1.2 mm) were measured at −20 °C on these high strength Q&T seamless pipes.

Usually, hardness near the internal surface is higher because a high-pressure water jet blows the steam generated inside the pipe during the immersion in the water tank, promoting a higher heat transfer coefficient, thus increasing the effectiveness of quenching. However, it is important to mention that suitable hardness values can be obtained adjusting the tempering treatment parameters.
Because all hardness values were below 250 HV\textsubscript{10}, (Table III) these pipes can be used for sour service applications. In fact, specific testing showed that the material develops very high:

- resistance to HIC in accordance with NACE standard TM-02-84/96: CLR = 0, CTR = 0, CSR = 0;
- SSC cracking resistance by four point bent test: coupons were crack-free when stressed at both 100\% of AYS and 100\% of the SMYS;
- SSC cracking resistance by NACE standard TM-01-77/96, method A: all specimens survived longer than 720 hours.

Weldability trials proved that the selected chemical composition combined with proper welding procedure assures hardness values lower than 280 HV and satisfactory toughness levels both in the weld metal and heat affect zone.

Other Q&T treatments performed on 375 mm OD and 28 mm WT pipe, having a chemical composition slightly enriched in C, Mn and Cr (Ceq = 0.48\%), showed the possibility to achieve adequate strength levels (average YS of 620 MPa and UTS of 723 MPa) with enough toughness (50\%FATT = – 30 °C) also for relatively heavy pipes.

The same steel, heat treated in the laboratory showed the possibility to develop a 90 ksi grade material with YS = 670 to 696 MPa, still maintaining a high toughness. However, the weldability of this steel is more critical than that of the 0.4\%Ceq steel.

**High-strength steam lines**

The steam line grades have to meet a specific set of requirements in terms of yield and tensile strength both at room temperature (RT) and at 350 °C (Table IV) [14]. For the Grade 550, there are no Ceq and toughness requirements, but the maximum hardness allowed is 30 HRC.

**Table IV** Tensile and Ceq requirements for steamlines.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Test T</th>
<th>SMYS (MPa)</th>
<th>SMTS (MPa)</th>
<th>Min. Elongation in 2”</th>
<th>Max. Hardness HRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>RT</td>
<td>551</td>
<td>675</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>350 °C</td>
<td>520</td>
<td>675</td>
<td>18</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

RT = Room Temperature

On the basis of the laboratory investigations and predictions by metallurgical modeling, the chemical composition range reported in Table V was selected for the industrial production of large diameter seamless pipes (406.4 mm OD x 23 mm WT, and 609.6 mm OD x 25.4 mm WT), which are externally quenched (Table V).

**Table V** Chemical composition range (mass %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>0.09</td>
<td>1.3</td>
<td>0.15</td>
<td>0.04</td>
<td>0.020</td>
</tr>
<tr>
<td>Max</td>
<td>0.14</td>
<td>1.6</td>
<td>0.30</td>
<td>0.10</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Hardness values were always less than 27 HRC (270 HV\textsubscript{10}).
A comparison of the strength values in terms of YS and UTS at RT and at 350 °C for two pipes of WT = 25.4 mm, manufactured from heats with different Ceq contents, is presented in Fig.11. The target strength levels, even at high temperature, were always achieved using adequate tempering temperatures.

![Fig. 11: Average YS and UTS values at room temperature (RT) and at 350 °C for two pipes of 25.4 mm WT, manufactured from two heats (pipe1: Ceq = 0.43%; pipe 2: Ceq = 0.34%).](image)

**CONCLUSIONS**

Significant progress was achieved in the metallurgical design of high strength Q&T seamless pipes as a result of an extensive investigation on laboratory steels and application of metallurgical modeling, as well as well-focused industrial trials. Moreover, basic aspects were clarified, in particular those concerning:

- microstructure evolution as a function of heat treatment conditions
- relationships between microstructure/precipitation and strength/toughness properties.

The following conclusions can be drawn:

- AGS has an important role in determining steel hardenability and as-quenched microstructure, for a given chemical composition and cooling rate;
- bainite and martensite show different misorientation profiles;
- bainite exhibits a larger packet (7-9 µm), compared with martensite;
- toughness (50%FATT) is related to the inverse square root of the packet size;
- for a given AGS, the increase of martensite volume fraction formed after quenching leads to a finer packet, enhancing toughness;
- in bainitic microstructures, coarsening of AGS leads to larger packets with possible detrimental effects on toughness;
- in microstructures predominantly constituted of martensite, the packets appear always fine (< 5 µm), independently from AGS;
- the average cell size is the key factor in defining the yield strength according to a “Hall-Petch” law;
• subgrain is refined when martensite formed in quenching is increased, with consequently strengthening of the material;
• typical precipitation strengthening is estimated 50 to 100 MPa, depending on volume fraction and average size of fine precipitates.

This work showed that high strength Q&T pipes can be developed with adequate toughness levels, using steels with low-C content and suitable hardenability (proper additions of Mn, Cr, Ni and Mo), when:

• the austenitizing conditions and the microalloying additions (e.g. Nb, Ti) allow to form uniform and relatively fine austenite grains (AGS = 15 to 20 µm);
• the effectiveness of the quenching system is able to develop a bainitic-martensitic microstructure with M > 30%;
• tempering temperatures are in the range 620 to 650 °C.

New chemistries and optimized Q&T conditions were identified for the production of seamless pipes for flowlines and risers with WT from 15 mm to 28 mm and YS from 550 to 690 MPa. Adequate strength levels were also achieved at 350 °C in Q&T steamlines of grade X80.

REFERENCES

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