Application of Niobium in Quenched and Tempered High-Strength Steels

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Abstract. This article offers an overview on the ways and means of the application of Nb in quenched and tempered high-strength steel plates. Thereby, the outstanding role of Nb to control the austenite microstructure during rolling or heat treatment and to contribute to effective precipitation hardening is discussed. It is shown, that Nb is very effective to retard the transformation processes during quenching. For high-strength constructional steels with up to 1100 MPa yield strength and for wear resistant steels, the improvement in strength and toughness properties in Nb microalloyed steels as compared to Nb-free steels is pointed out. A remarkable effect is the improvement in toughness and brittle fracture resistance due to a very fine microstructure and finely dispersed Nb carbonitrides in a martensitic microstructure. Fields of application for the new Nb microalloyed high-strength structural steels are presented too.

Introduction

The weight of the structure itself has a substantial effect on the working load and thus on the economy of heavy loaded steel constructions. A reduction of the weight of the construction itself but maintaining its loading capacity, given by the strength and safety of the construction, is of prime importance. Fig. 1 shows examples indicating that e.g. under tensile stresses the plate thickness can be reduced by around 60\% by using the steel grade S960 instead of S355 [1-3].

The steel industry fulfills the wishes for light-weight design by providing thermomechanically rolled and water-quenched plus tempered structural steels up to a minimum yield strength of 1100 MPa. Despite their high strength, these structural steels exhibit excellent toughness, good cold formability and good weldability. Fig. 2 gives an overview about the production process of water-quenched and tempered plates from the steelmaking to the final product.

Usually the quenching operation applies high-performance lines and starts with reheating to temperatures above $A_\text{c1}$, which have to be rather homogeneous distributed from the surface to the center. Then the plates are quenched by using pressurised water to obtain a transformation of the microstructure into martensite or bainite. Besides the chemical composition, also the tempering process, which follows the quenching operation, is a relevant factor controlling the mechanical properties [2]. Apart from the conventional reheat-quench plus tempering, quenching can done also directly from the rolling heat. This is known as direct quenching.

High-strength structural steels are applied in many fields of heavy machine building. Prominent examples include the construction of mobile cranes, of off-highway vehicles and pressure vessels. The chemical compositions of the steel grades get adapted to obtain the mechanical properties necessary for each specific application. High-strength quenched and tempered structural steels usually comprise a carbon content of less than 0.2\% and Mn contents of max. 2\%. These steels may contain also certain additions of elements, which retard the diffusion-controlled transformation process and thus increase the hardenability of the steels, such as molybdenum, chromium or nickel [3,4].
The high strength quenched and tempered steel grades often contain also certain quantities of the microalloying elements V and B. Being in solid solution, the latter is especially effective in retarding the transformation, since it restricts the diffusion of iron and carbon along grain boundaries. B can thereby partially replace the above-mentioned, more expensive alloying elements. Since B has a strong affinity to nitrogen, the formation of B nitrides must be prevented to make use of this effect [5]. Usually, Ti is added in quantities above the stoichiometric value (typically ≥ 0.04 %Ti) to fully fix the nitrogen. In this case coarse Ti carbonitrides will be formed, resulting in related unfavourable effects on ductility and toughness. Besides a certain effect in retarding the transformation, the addition of V mainly causes an increase in strength by precipitation hardening in the martensitic microstructure during the tempering process. However, the precipitation of V carbonitrides can lead to toughness impairment and has detrimental effects on the properties of the weldment. This is particularly observed after stress relieving, which is often employed in heavy-loaded structures [6].

Fig. 1. Reduction of plate thickness in relation to grade S355 by using high-strength steels

Usage of Niobium in Quenched and Tempered Steels

Niobium is not a rare element; its content in the Earth’s crust is 24g/t and thus it is more widespread than cobalt, lead or molybdenum and even ten times more common than tantalum. Even though it has many interesting applications as a metal and oxide, its dominant role is as a microalloying element in the steel industry. While the traditional application of Nb as a stabilising element in stainless steel remained almost constant, its usage as microalloying element in Europe in the last two decades increased drastically and the technology of thermomechanical rolling, originally developed for large-diameter pipes, spread to other steel products, such as for steel structures and for automobiles. When Nb is used in a microalloy, its typical proportion is below 0.10%.

The most prominent and the outstanding role of Nb in steel is during austenite processing, where first the cubic carbonitrides of Nb are dissolved in the upper austenite region and then get re-precipitated again during rolling. Thereby, austenite grain coarsening as well as recrystallization processes are effectively influenced, resulting in a fine-grained microstructure. Grain refinement and precipitation hardening processes in the ferrite add to optimized property combinations, which is consequently used in the fabrication of thermomechanically rolled steels for line pipes, shipbuilding, bridges, automobiles, etc., with a domain in the range of yield strength between 350 and 700 MPa at the most [7].

In the course of intensive studies on high-strength, quenched and tempered structural steels, indications were found that the advantages of microalloying with Nb could also be used for this group of steels [5]. Nb has several positive effects on metallurgical mechanisms, which determine the properties of quenched and tempered steels, such as grain refinement the retardation of transformation and precipitation hardening [8]. A schematic assessment about the effects of Nb in comparison to other commonly used microalloying elements is given in Fig. 3.

During reheating to the quenching temperature the equilibrium condition for Nb(C,N) in austenite will be reached, promoted by the fact that the plate has already passed the transformation of α to γ and back from γ to α. Other than for vanadium, where a relevant amount will exist in solid solu-
tion in the lower austenite region of 900 to 950 °C, at these temperatures and the typical carbon level of quenched and tempered steel practically all the Nb will exist in form of Nb(C,N), Fig. 4.

<table>
<thead>
<tr>
<th>Microalloying</th>
<th>Affinity to C, N</th>
<th>Fine precipitates</th>
<th>Retardation of transformation</th>
<th>Grain refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>V</td>
<td>+</td>
<td>++</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Ti</td>
<td>+++</td>
<td>+ / - 1)</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

1) depending on Ti-content

> : positive effect
- : negative effect
o : no significant effect

Fig. 3. Metallurgical effect of Nb in high-strength steels

This is a role of Nb known from normalized steel [9]. The equally distributed and fine Nb carbonitrides of typically less than 20 nm diameter control successfully the austenite grain size and thus the microstructure after transformation. An additional effect is achieved in the boron containing quenched and tempered steels. In these steels the necessary fixing of nitrogen is usually made by microalloying Ti, which has a higher affinity to nitrogen than boron. Modelling [10, 11] of the thermodynamics of dissolution and precipitation of Nb(C,N), AlN and TiN in austenite is described generally by Eq. 1:

\[
\log([Me][C])^x[N]^{1-x} = A - \frac{B}{T}
\]

(A and B are constants, x specifies the C proportion in the carbonitride). Taking into account the Wagner interaction parameters \(\varepsilon_{\text{Nb}}^{\text{CrMoNi}}\), \(\varepsilon_{\text{C}}^{\text{CrMoNi}}\), and \(\varepsilon_{\text{Ni}}^{\text{CrMoNi}}\) Fig. 5 demonstrated that microalloying with Nb (≤ 0.03%) in combination with increased Al levels up to 0.10% develops both AlN and Nb(CN), but also results in a significantly higher content of free nitrogen at 900°C then known for TiN formation. However, it is remarkable that also in the Nb plus Al steel the content of dissolved nitrogen is below the solubility limit for the undesired development of B nitrides. Therefore this microalloy combination can be used to protect boron, which has the positive effect that it avoids the formation of coarse TiN. In steelpmaking a well-aimed sequence of adding the microalloying elements into the liquid steel is necessary during the secondary metallurgy operation.

In order to test the possibility of this approach, the transformation behaviour of boron-free steel was compared with this of boron-containing steels, and in the latter the nitrogen was either fixed by microalloying with Ti or with Nb. The results are shown in Fig. 6. The addition of B, together with
an adequate fixing of nitrogen, shifts the formation of ferrite to longer times and thus increase the hardenability. It is important to note that the microalloying with Nb has practically the same effect as the addition of Ti. Additional analytical investigations of the extracted phases showed that about 90% of the entire B content exists in solid solution in the steel, and this is true when either Ti or Nb is used as microalloy. However, due to the lower formation temperatures of the AlN and Nb(C,N) particles in the Nb microalloyed steel, a substantially finer particle dispersion exists compared to the TiN steels, with correspondingly more favourable effects on the material properties [5].

![Graph showing N-fixation in boron containing high strength steels with Ti or Nb (results of thermodynamic calculations)](image1)

![Graph showing Effect of Ti and Nb on the transformation of S690QL with boron](image2)

![Graph showing Effect of Nb on transformation behaviour and precipitation hardening](image3)

When direct quenching from rather high finish rolling temperatures is applied, a certain amount of Nb will remain in solid solution, supported by the fact that under these conditions the equilibrium...
will not be reached. In this case the effect of Nb in retarding the transformation can be used effectively, which is much stronger than this of solute V or Ti, Fig. 7a [12]. Furthermore, Nb in solid solution also offers a higher precipitation hardening potential than V during the annealing process following the quenching operation. For example, a yield point increase of 100 MPa can be achieved with either 0.06% V or just around 0.02% Nb (Fig. 7b) [13].

The studies on the effect of Nb in quenched and tempered steels demonstrated that optimized results are already achieved with Nb levels of not more than 0.04%. This level corresponds to the Nb content, which could be dissolved during reheating to the rolling temperature.Nb in these steels is almost on the same order as in most of the thermomechanically rolled heavy plate steels.

**Nb in High-Strength Structural Steel Plates with Minimum Yield Strength up to 1100 MPa**

The high-strength, water-quenched and tempered structural steels N-A-XTRA and XABO® are suitable to fulfil severe requirements in strength and toughness, e.g. necessary for mobile crane construction. These steel grades range from a minimum yield strength of around 550 up to 1100 MPa.

With XABO® 1100, showing a minimum yield strength of 1100 MPa, actually a climax in the development of high-strength structural steels has been reached [1]. The most important alloying elements, the carbon equivalent CET and the specified mechanical properties of these high-strength structural steels are shown in Fig. 8.

Furthermore, also water-quenched and tempered structural steels with a minimum yield strength of 500 MPa and a low carbon equivalent CET are also available and get used e.g. in offshore engineering. The desired mechanical property combinations are adjusted by controlled tempering of the quenched plates at temperatures up to 700 °C. The characteristics of these steels include excellent combinations of high strength and good toughness. This is necessary because their use in heavy-loaded and sometimes safety-relevant structures often demands brittle fracture resistance at low subzero operating temperatures.

<table>
<thead>
<tr>
<th>Special steel</th>
<th>Quality acc. Euronorm</th>
<th>Alloying additions</th>
<th>Typ. CET (%) *)</th>
<th>Condition of delivery</th>
<th>Min Rmin (MPa)</th>
<th>Rm (MPa)</th>
<th>Min Ast. (%)</th>
<th>Min Av (J) -20°C</th>
<th>Min Av (J) -40°C</th>
<th>Min Av (J) -60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-A-XTRA 550</td>
<td>S550QL</td>
<td>CrMoB</td>
<td>0,31</td>
<td>QT</td>
<td>550</td>
<td>640 - 820</td>
<td>16</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-A-XTRA 620</td>
<td>S620QL</td>
<td></td>
<td></td>
<td></td>
<td>620</td>
<td>700 - 890</td>
<td>15</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-A-XTRA 700</td>
<td>S990QL</td>
<td></td>
<td></td>
<td></td>
<td>700</td>
<td>770 - 940</td>
<td>14</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XABO® 960</td>
<td>S990QL</td>
<td>CrMoNiV</td>
<td>0,36</td>
<td>QT</td>
<td>890</td>
<td>940 - 1100</td>
<td>11</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XABO® 1100</td>
<td>S1100QL</td>
<td></td>
<td></td>
<td></td>
<td>960</td>
<td>980 - 1150</td>
<td>10</td>
<td>27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) for a plate thickness of 10 mm

\[ \text{CET} = \text{C} + \frac{\text{Mn} - \text{Mn}_{\text{eq}}}{0.1} + \frac{\text{Cr} + \text{Ni}}{0.6} + \frac{\text{M}}{0.3} \]

**Fig. 8. Mechanical properties of high-strength steels**

Consequent optimisation of the analytical concepts including the usage of Nb < 0.04%, allowed to further improve the property combinations of these steels. A substantial increase in toughness could be achieved by refining the microstructure as a result of the fine distribution of carbonitrides. Fig. 9 compares the Charpy-V-notch impact energy of steels with and without niobium microalloying. It is obvious that e.g. the impact energy in all steel grades up to the high strength of the B alloyed steel N-A-XTRA 700 gets improved by around 70 J when replacing Ti by Nb microalloying, while the strength properties remain unchanged. This applies to both conventional reheat-quenching plus tempering as well as to direct quenching from the rolling heat, followed by tempering. A doubling of the impact energy is also observed in the steels with strength levels up to 1100 MPa.

Besides the Charpy-V-notch impact energy also the transition temperature T27, which is the temperature, where the impact toughness of 27 J is obtained and is a characteristic value to describe brittle fracture, is shifted to more favourable values by Nb microalloying as shown by the example in Fig. 10. According to the brittle fracture concepts of EUROCODE 3, a lower transition temperature reduces the growth of cracks and thereby improves the susceptibility of the construction to brittle fracture. Furthermore, this has a simultaneously positive effect on the fatigue properties of welded structures, which are often exposed to cyclic loading. Experimental investigations and mathematical approximation of the fatigue properties of the high-strength structural steels XABO®
1100 demonstrated [3] that an improvement in the impact toughness by Nb addition (see Fig. 10) results in an improvement of the service life of the cyclic loaded structure of a welded crane component by about 10 to 20%.

Of particular importance for the application of high-strength structural steels is their behaviour during fabrication. Structural components are usually manufactured by cold forming and/or welding. Due to the low carbon content, these steels can be easily welded using common welding processes. They also exhibit a high resistance towards cold cracking due to their low carbon equivalent, when high-quality welding additives are used. More data about this are summarised in EN 1011. Of course, the welding conditions for high-strength structural steels also influence the mechanical properties of the welded joint. In this context one usually defines a suitable cooling time $t_{\alpha/5}$, since this characteristic value combines various welding parameters including the heat input into one number. This characteristic value has a direct influence on the toughness of the welded joint. Fig. 11 shows with the example of N-A-XTRA 700, that microalloying with Nb allows a significant improvement in the properties of welded joint, similar as the results in the base metal. This is particularly true for high $t_{\alpha/5}$ times, corresponding to high heat input welding. The achieved optimisation of the microstructure shifts the characteristic transition temperature $T_{27}$ for the characteristic cooling times $t_{\alpha/5}$ from 10 to 25 s to values being approximately 20 K lower.

Niobium in Wear-Resistant Steel Plates

Machines and other equipment in industry, agriculture and for constructions often apply heavy plate, which has to guarantee a high wear resistance. The trade name of this group of plates at Thyssen Krupp Stahl AG (TKS) is XAR, available in various strength levels and thicknesses. Typical fields of application are machines to excavate raw materials such as coal, ores, stone etc. Fig. 12 provides an overview about the chemical composition of heavy plate made from wear-resistant special structural steels XAR. These steels comprise as characteristic alloy elements Mn, Cr, Mo and Ni.

![Fig. 9. Toughness properties of high strength steels after quenching and tempering](image)

![Fig. 10. Charpy-V toughness and transition temperature of N-A-XTRA 700](image)

![Fig. 11. Influence of welding conditions on the toughness in the HAZ of N-A-XTRA 700](image)
and are based on a carbon content up to 0.40%. Consequently they attain high hardness values of 400 to 600 HB. Typical plate thicknesses range up to 100 mm [14].

In the most important fields of application for wear-resistant steels, the characteristic wear type is ploughing leading to abrasive wear. Thereby usually the plate surface gets scratched when exposed to an abrasive and hard material such as sand or minerals and is finally removed - this wear mechanism is called abrasion. A high hardness of the material is one important for good wear resistance. Furthermore, also a higher toughness of the material improves the wear resistance and thus reduces the material loss, because it changes the wear mechanism from micro-ploughing into micro-machining [14, 15].

<table>
<thead>
<tr>
<th>TKS steel grade</th>
<th>Hardness (HB)</th>
<th>Plate thickness (mm)</th>
<th>Chemical composition (%)</th>
<th>typ. CET, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAR 400</td>
<td>360 - 440</td>
<td>100</td>
<td>C max. 0,20 Mn max. 0,80 Cr max. 1,50 Ni max. 1,00 Mo max. 0,50</td>
<td>0,26 0,37</td>
</tr>
<tr>
<td>XAR 450</td>
<td>410 - 490</td>
<td>100</td>
<td>C max. 0,22 Mn max. 0,80 Cr max. 1,50 Ni max. 1,00 (1,50) Mo max. 0,50</td>
<td>0,38 0,38</td>
</tr>
<tr>
<td>XAR 500</td>
<td>450 - 530</td>
<td>100</td>
<td>C max. 0,28 Mn max. 0,80 Cr max. 1,50 Ni max. 1,00 (1,50) Mo max. 0,50</td>
<td>0,41 0,41</td>
</tr>
<tr>
<td>XAR 600</td>
<td>550 - 630</td>
<td>40</td>
<td>C max. 0,40 Mn max. 0,80 Cr max. 1,50 Ni max. 1,50 Mo max. 0,50</td>
<td>0,55 0,55</td>
</tr>
</tbody>
</table>

Extensive and systematic studies at the Mannheim Technical College on the wear resistance of a variety of steels [14] demonstrated that the addition of Nb is very favourable, since it increases substantially the toughness of the material by refining the microstructure and improving the precipitation state of the carbonitrides, similar as described for the water-quenched plus tempered structural steels. One result of toughness data is shown in Fig. 13 by the example of the XAR 400 steel. The studies on the abrasive wear properties showed that the increase in toughness connected with Nb microalloying results in an improvement on the wear behaviour due to the explained changed in the wear mechanism. In fact, the results with the XAR 450 steel indicate that the service life under the abrasive wear by hard minerals can be increased by around 20% using Nb microalloying (Fig. 14).

As a result of these systematic studies on the wear properties of various steels, the model PROWEAR, based on a computer-aided correlation and regression analysis, was developed to predict the wear resistance and the resulting service life [14]. This model defines the combined effects of the chemical composition of the steel, the hardness and the environmental conditions on the wear behaviour and allows an economical, time-saving and praxis-oriented support of steel selection exposed to abrasive wear. A comparison of the predicted wear properties with the results measured under practical conditions demonstrates good correlation. This is shown in Fig. 15, where the mean
abrasion data determined for a skip made of the niobium micro-alloyed XAR 450 and XAR 500 steel grades after use in the Chino Mines in New Mexico are compared with corresponding calculated values. The computer program PROWEAR thereby permits a good, integral determination of the wear properties in real abrasive systems.

Fig. 15. Calculated and measured wear rates in a truck dump body used in Chino Mines/New Mexico

Summary and Future Trends

The use of Nb as a microalloying element in high-strength, water-quenched and tempered steels for heavy machine construction and other application is worthwhile. In general, the advantageous effects of Nb applied in normalised and thermomechanically rolled steels can also be exploited in quenched plus tempered steel grades. In particular, it refines the grain size and thus improves the toughness of the material guaranteeing a high resistance against brittle fracture. Furthermore, in boron microalloyed steels it allows to substitute Ti, improving the cleanliness of the steel. Also the performance after welding and the resistance against wear are improved. Generally said, one achieves a higher quality level for high-strength quenched and tempered steels when microalloying with Nb.

Actual developments have to consider even higher requirements in toughness at increasingly lower temperatures, e.g. for pressure vessel constructions. To comply with this demand, the use of Nb in quenched and tempered steels will further increase in the future. A limiting factor for this solution can be seen in specifications of the actually valid standards DIN EN 10137 and also the ASTM/ASME regulations.

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Microalloying for New Steel Processes and Applications
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