Effects of Niobium, Titanium and Nitrogen on the Microstructure and Mechanical Properties of Normalized Tank Car Steel Plates
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Abstract

The railroad tank car production industry is facing increasing safety requirements for pressure tank cars transporting hazardous materials such as chlorine and anhydrous ammonia. With this in mind, Mittal Steel USA continues to look for ways to improve mechanical properties and notch toughness of the normalized and stress relieved AAR TC128 Grade B steel that is specified for pressure tank car construction. A way to achieve the necessary improvement in the CVN notch transition temperature of this steel would be by grain refinement.

Previous work by Kyed et al showed that grain refiner additions of niobium to AAR TC128 Grade B steel did not have a significant effect on the normalized microstructure and mechanical properties of this steel. This paper presents the results of additional laboratory experiments with titanium additions directed at improving the CVN toughness of TC128 Grade B steel using niobium and titanium either singly or in combination.

Introduction

Since the mid-1990’s, there has been a continuing effort to increase the puncture resistance of Railroad Tank Cars that are used for the transport of hazardous materials. A number of options have been considered to achieve this increased puncture resistance. In late 1990’s, two methods were chosen to achieve the increase in puncture resistance: 1) set limits on carbon equivalent (CE) of TC128 Grade B steel to improve weldability and HAZ toughness and 2) increase plate thickness. Still further increases in puncture resistance are being sought. The addition of Nb to TC128 Grade B steel, already microalloyed with V was recommended as a possible way to increase strength and toughness. Even though Nb was shown to be detrimental to TC128 Grade B weld metal toughness (1), and simulated HAZ toughness (2), laboratory studies were conducted by Kyed et al (3), who studied the effect of Nb content on the base material strength and toughness (especially upper shelf) of laboratory-produced TC128 Grade B steel and concluded that adding Nb to this steel grade did not provide a meaningful benefit to the mechanical properties. It was subsequently suggested that small additions of Ti and N, singly or in combination, to an Nb bearing TC128 Grade B steel might be beneficial to the mechanical and impact properties. It was also thought that the addition of a small amount of Ti, by itself, to provide improved impact properties via increased grain refinement, would have merit. The proper dispersion of TiN particles has been shown to be an effective grain refiner. Even though Bodnar et al (4) reported that a 0.014% Ti addition to a normalized A516 Grade 70 plates actually lowered toughness, it was thought that the use of a lower slab reheat temperature, 1232°C instead of 1260°C might produce the desired grain refinement in a TC128 Grade B steel, thereby improving the notch toughness.

This work was carried out to determine whether the toughness and thereby, the puncture resistance of TC128 Grade B steel could be increased by adding Ti and N, in combination to an Nb bearing TC128 Grade B steel. In addition, this study was conducted to verify the
effectiveness of a small addition of Ti by itself to increase the notch toughness of TC128 Grade B steel.

**Experimental Procedure**

Six vacuum induction melted experimental 227 kg ingots of AAR TC128 Grade B steel containing about 0.013% Ti, three levels of Nb, and two levels of nitrogen were produced. Two 45 kg vacuum induction melted experimental ingots were also made. One of these ingots was a base grade TC128 Grade B steel. The second ingot had 0.010% Ti added to the base composition.

The 227 kg ingots were heated to 1260°C and rolled into 17 mm thick plates. The 45 kg ingots were heated to 1232°C and rolled into 16 mm plates.

The compositions of the as hot rolled plates produced from the experimental steels are shown in Table 1 along with those of the Ti free steels, #4, #7 and #8, from a previous work.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>V</th>
<th>Al</th>
<th>Nb</th>
<th>Ti</th>
<th>N</th>
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<tr>
<td>#4</td>
<td>0.23</td>
<td>1.26</td>
<td>0.017</td>
<td>0.009</td>
<td>0.32</td>
<td>0.045</td>
<td>0.040</td>
<td>0.005</td>
<td>0.005</td>
<td>0.0063</td>
</tr>
<tr>
<td>#7</td>
<td>0.23</td>
<td>1.19</td>
<td>0.016</td>
<td>0.009</td>
<td>0.30</td>
<td>0.043</td>
<td>0.039</td>
<td>0.031</td>
<td>0.005</td>
<td>0.0070</td>
</tr>
<tr>
<td>#8</td>
<td>0.23</td>
<td>1.20</td>
<td>0.016</td>
<td>0.010</td>
<td>0.31</td>
<td>0.044</td>
<td>0.039</td>
<td>0.052</td>
<td>0.005</td>
<td>0.0072</td>
</tr>
<tr>
<td>#1</td>
<td>0.22</td>
<td>1.28</td>
<td>0.013</td>
<td>0.010</td>
<td>0.30</td>
<td>0.050</td>
<td>0.036</td>
<td>0.005</td>
<td>0.012</td>
<td>0.0063</td>
</tr>
<tr>
<td>#2</td>
<td>0.22</td>
<td>1.28</td>
<td>0.015</td>
<td>0.011</td>
<td>0.30</td>
<td>0.055</td>
<td>0.037</td>
<td>0.034</td>
<td>0.014</td>
<td>0.0067</td>
</tr>
<tr>
<td>#3</td>
<td>0.22</td>
<td>1.29</td>
<td>0.015</td>
<td>0.011</td>
<td>0.31</td>
<td>0.054</td>
<td>0.037</td>
<td>0.06</td>
<td>0.013</td>
<td>0.0062</td>
</tr>
<tr>
<td>#37</td>
<td>0.22</td>
<td>1.27</td>
<td>0.014</td>
<td>0.010</td>
<td>0.30</td>
<td>0.049</td>
<td>0.037</td>
<td>&lt;0.005</td>
<td>0.013</td>
<td>0.0089</td>
</tr>
<tr>
<td>#38</td>
<td>0.22</td>
<td>1.28</td>
<td>0.014</td>
<td>0.010</td>
<td>0.30</td>
<td>0.051</td>
<td>0.037</td>
<td>0.035</td>
<td>0.014</td>
<td>0.0095</td>
</tr>
<tr>
<td>#39</td>
<td>0.22</td>
<td>1.29</td>
<td>0.014</td>
<td>0.009</td>
<td>0.30</td>
<td>0.050</td>
<td>0.037</td>
<td>0.07</td>
<td>0.014</td>
<td>0.0096</td>
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<tr>
<td>#236</td>
<td>0.22</td>
<td>1.36</td>
<td>0.008</td>
<td>0.003</td>
<td>0.33</td>
<td>0.06</td>
<td>0.019</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.0047</td>
</tr>
<tr>
<td>#242</td>
<td>0.21</td>
<td>1.36</td>
<td>0.007</td>
<td>0.003</td>
<td>0.34</td>
<td>0.06</td>
<td>0.031</td>
<td>&lt;0.005</td>
<td>0.010</td>
<td>0.0049</td>
</tr>
<tr>
<td>TC128 Grade B</td>
<td>0.25</td>
<td>1.00/1.35</td>
<td>0.010</td>
<td>0.15/.40</td>
<td>≤0.08</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

The first three steels, #4, #7 and #8, in Table 1 are base TC128 Grade B steels containing three levels of Nb. The next three steels, #1, #2 and #3, in this table are base TC128 Grade B steels containing 0.013% Ti, 65 ppm nitrogen, and three levels of Nb. Steels #37, #38 and #39 have a higher nitrogen level, 95 ppm plus 0.013% Ti and the three levels of Nb. Finally, the last two steels #236 and #242, are base TC128 Grade B steels, and do not contain Nb. Heat No. 242 has a 0.010% Ti concentration.

All the plates were normalized at 900°C for 1 hour. Stress relieving was done at 620°C for 1 hour. The plates produced from steels #236 and #242 were tested in normalized and the normalized plus stress relieved conditions.

The heat treated plates were subjected to optical metallographic examination to determine the austenitic and ferritic grain sizes as well as the volume fraction pearlite. The grain sizes were determined by the intercept method. The 227 kg heats pearlite volume fractions were determined by manual point counting. The grain size and volume fraction determinations for the plate product from the 27 kg heats were done using Clemex image analyzing equipment.

Tensile and Charpy V-notch impact test data were obtained from the heat treated plates. When this work was started the AAR TC128 Grade B steel specification required 20 J minimum
at −34°C from longitudinal specimens. As a result, longitudinal CVN test data were obtained from steels in the Nb, Ti series.

In July 2005 the TC128 Grade B CVN test was specified to be in the transverse direction at −34°C. Transverse CVN data were obtained from steels #236 and #242.

Results and Discussion

Figures 1, 2, and 3 show the effects of Ti and N on the ultimate tensile strength, 0.2% offset yield strength and percentage elongations of the experimental TC128 Grade steel plates at three Nb levels. The data plotted in these figures were obtained from the plates rolled from the 227 kg ingots, Ht. Nos. 4, 7, 8, 1, 2, 3, 37, 38 and 39.

It can be seen from Figure 1 that in the normalized Ti free and Ti bearing plates, there was a slight increase in yield strength with increasing Nb content. This increase amounted to only about 28 to 34 MPa. Kyed et al (3) pointed out that at C levels of 0.22% found in TC128 Grade B very little Nb, ~0.0025%, would be in solution at the normalizing temperature, not enough to contribute much precipitation hardening to the modest increase in yield strength that was found.

![Figure 1](image_url)

Figure 1 0.2% offset yield strength values obtained from the normalized plates (900°C) of TC128 Grade B experimental steels with three levels of Nb and two levels of Ti + N.

From Figure 2, it can be seen that the ultimate tensile strength was not significantly affected by Nb content in the Ti free steels. However, in the Ti containing steels, a slight increase was found. Nitrogen was found to have no effect on the ultimate tensile strength. Finally at a given Nb concentration, the yield strength and tensile strength were not significantly affected by either the Ti addition or increased N.
Figure 2 The influence of additions of Nb with or without additions of Ti + N on the ultimate tensile strength of the TC128 Grade B experimental steel plates normalized from 900°C.

The results shown in Figure 3 indicate that there was no significant effect of Nb, Ti or N on total elongation.

Figure 3 Total elongation as a function of Nb or Nb + Ti + N additions to TC128 Grade B experimental steel plates normalized from 900°C.

Figures 4 and 5 depict the influence of Ti and N on the longitudinal CVN upper shelf energy and the longitudinal CVN energy found at −34°C, respectively, for the experimental steels. From Figure 4, it can be seen that the best CVN upper shelf values were obtained from the base steel. This steel did not contain Nb, Ti or higher levels of nitrogen. Longitudinal CVN data obtained at −34°C are plotted as a function of Nb, Ti and N in Figure 5. As in the case of the CVN upper shelf energy results, the base steel without Nb, Ti or higher N levels had the highest values. In all cases, energy absorption values decreased with increasing Nb.
The effects of Ti and N on the ferrite grain size (FGS), prior austenite grain size (PAGS) percentage pearlite (%P) and microstructure are shown in Figures 6, 7, 8, and 9, respectively. Referring to Figure 6, it can be seen that at constant Ti and N levels, the Nb addition resulted in a finer ferrite grain size. Figure 7 shows a similar trend in prior austenitic grain size with the 65 ppm N plates but not with the 95 ppm N plates. At a given Nb level, the Ti addition was seen to result in coarser ferrite and prior austenite grain sizes. Increasing the N in the Ti bearing plates was found to result in finer ferrite grains but coarser austenite grains.

The microstructures shown in Figure 9 confirm that the Nb addition produced a finer ferrite grain size at constant Ti and N levels.
Figure 6  Ferritic grain size variation found in experimental normalized (900°C) plates of experimental TC128 Grade B steels with additions of Nb or additions of Nb + Ti + N.

Figure 7  Prior austenite grain size values obtained from the experimental TC128 Grade B steels containing three levels of Nb and two levels of Ti + N. These values were determined at 900°C.

Figure 8  Influence of additions of Nb and Nb + Ti + N on the % pearlite in the normalized (900°C) experimental TC128 Grade B steel plates.

The most significant effect found from the presence of Ti in the experimental steel plates was the reduction in the percentage pearlite, see Figure 6. The base steel with no Ti or N had a pearlite percentage of 30. The Ti bearing experimental steels had a pearlite percentage of less than 20. This was not apparent in the micrographs shown in Figure 9. Apparently the use of quantitative metallographic methods are needed to distinguish the influence of Ti on the pearlite
volume fraction. This reduction in pearlite percentage would be expected to produce an increase in notch toughness, but no significant increase in notch toughness was found.

The tensile properties and the quantitative metallographic data obtained from steels #236 and #242 are given in Table 2. These steel plates were rolled from the 45 kg laboratory ingots.

Table 2 Tensile and Quantitative Metallographic Data Obtained from the Experimental TC128 Grade B Steels With and Without Ti

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Condition</th>
<th>0.2% Yield Strength MPa</th>
<th>Ultimate Tensile Strength MPa</th>
<th>Percent Elongation GL=36 mm</th>
<th>Ferrite Grain Size ASTM</th>
<th>µ</th>
<th>% Pearlite</th>
</tr>
</thead>
<tbody>
<tr>
<td>236 Base</td>
<td>N900°C</td>
<td>420</td>
<td>602</td>
<td>38</td>
<td>11.2</td>
<td>(7.5)</td>
<td>40</td>
</tr>
<tr>
<td>236 Base</td>
<td>N900°C SR620°C</td>
<td>396</td>
<td>578</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>242 Base + Ti</td>
<td>N900°C</td>
<td>404</td>
<td>592</td>
<td>40</td>
<td>11.4</td>
<td>(7)</td>
<td>43</td>
</tr>
<tr>
<td>242 Base + Ti</td>
<td>N900°C SR620°C</td>
<td>379</td>
<td>575</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The AAR tensile strength requirements for TC128 Grade B steel are 345 MPa minimum for the yield strength and 558 MPa minimum for the ultimate tensile strength. As can be seen from Table 2 the two experimental steels meet the tensile strength requirements for TC128 Grade B steel.

Quantitative metallographic data are also given in Table 2. The measured ferritic grain size for the Ti bearing experimental steel was ASTM 11.4 which is slightly finer than the ASTM 11.2 determination made on non Ti containing steel. This difference is not thought to be significant, however. The pearlite volume fractions found for the two experimental steels did not differ significantly. The Ti bearing steel had a 44% pearlite content while the non Ti experimental steel had a 45% pearlite content. These values are considerably higher than reported earlier in this paper.

The full curve transverse Charpy V-notch impact data can be seen plotted in Figure 10. Charpy impact data were obtained from the Ti bearing and non Ti bearing experimental TC128 Grade B steels in the normalized (900°C) and normalized (900°C) plus stress relieved (1 hr at 620°C) conditions. Two separate groupings of the data can be seen. The Ti bearing experimental TC128 Grade B steel has better impact properties than the non Ti steel over the temperature range tested. For both steels, the impact properties in the normalized (900°C) and normalized (900°C) plus stress relieved 1 hour at 620°C) conditions were essentially the same.
<table>
<thead>
<tr>
<th></th>
<th>No Nb</th>
<th>Medium Nb</th>
<th>High Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No Ti</strong> 65 ppm N</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td><strong>0.013% Ti</strong> 65 ppm N</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td><strong>0.013% Ti</strong> 95 ppm N</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

*Figure 9 Typical microstructures obtained from no Nb, medium Nb and high Nb TC128 Grade B experimental steel with and without Ti and N additions 4% Nital + 2% Picral etc.*
These results differ from those reported by Bodnar et al\(^4\). Hicho and Harne\(^5\) reported that stress relieving at 633°C improved the fracture toughness of normalized TC128 Grade B steel plate.

The Charpy V-notch toughness improvements found for the Ti bearing experimental steel cannot be explained on the basis of ferrite grain refinement since no significant ferritic grain size difference exists between the two experimental steels. The pearlite content is not a factor in improving the notch toughness either, since both experimental steels have essentially the same pearlite volume fraction.

Further studies are needed to explain the mixed effects of stress relieving on notch toughness.

**Summary and Conclusions**

For given Ti and N levels, Nb additions were found to increase the 0.2% offset yield strength by about 28 MPa.

At constant Ti and N levels, Nb appeared to result in a finer ferrite grain size. A similar trend is seen in the prior austenite grain size with the 65 ppm N steel, but not with the 95 ppm N steel. The addition of Ti and N to the TC128 Grade B experimental steels did not produce finer ferrite or prior austenite grain sizes compared to the base TC128 Grade B steel.

In the Nb, Ti, N steels, the most significant effect of the 0.013% Ti addition was to lower the pearlite content. This reduced pearlite volume fraction would be expected to result in a toughness increase, however, none was found.

With regard to the CVN toughness measured at −34°C and at the upper shelf, it was found that the base TC128 Grade B steel containing no Nb or Ti, exhibited the best toughness.
Little difference was found between the CVN upper shelf energy values measured for the base TC128 Grade B steel and the Nb + Ti + N containing TC128 Grade B steels. In fact, with regard to the CVN toughness measured at both −34°C and at the upper shelf, it was found that the base TC128 Grade B steel containing no Nb or Ti, exhibited the best toughness.

A single addition of 0.010% Ti to an experimental TC128 Grade B steel resulted in improved Charpy v-notch properties. It is thought that the Ti addition coupled with a slab reheat temperature of 1232°C apparently enabled this improvement.

With the base TC128 Grade B steel and its companion, Ti bearing steel, stress relieving after normalizing did not result in any deterioration in Charpy V-notch impact toughness.

The combination addition of Nb and Ti to TC128 Grade B steel did not provide any meaningful benefit to the mechanical properties in the normalized condition at both N levels tested.

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References