Microalloying with Niobium in TRIP Steels

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Introduction

An important step towards steel grades with a high strength level and excellent formability was the development of low-alloyed thin sheet TRIP steels (TRIP = TRansformation Induced Plasticity). TRIP steel grades are characterized by a ferritic matrix with bainite and retained austenite inclusions (Figure 1). In these grades, metastable austenite transforms into martensite during plastic deformation, which results in an outstanding elongation and formability at a very high strength level.

The first observation of an unexpected increase in formability, due to the austenite to martensite transformation in Fe-Ni alloys, was observed in 1937 by Wassermann [1]. In 1967 Zackay et al. [2] described how a phase transformation in highly-alloyed homogeneous metastable austenitic steels was the reason for the ductility enhancement. This effect of Strain-Induced Martensite (SIMT) leads to TRansformation Induced Plasticity, usually abbreviated as TRIP. Researchers at Nippon Steel Corporation showed that austenite stabilization also occurred during an isothermal bainitic transformation (IBT), a process often referred as “austempering”, which followed an intercritical $\alpha+\gamma$ annealing of low alloy Si-bearing medium-C (0.12 - 0.55 %) CMn steel [3-6]. In this new class of low-alloyed TRIP steels the austenite is present as a disperse phase. Since C hardening is much higher for the martensite than for the austenite phase and the volume expansion due to this transformation results in plastic deformation and work hardening of the surrounding ferrite, a localized strengthening is obtained. These effects postpone further deformation in this area and move the martensitic transformation to neighbouring areas (Figure 2), leading to a delay in the onset of macroscopic necking and consequently, to higher values of uniform and total elongation.
Two factors determine the TRIP effect, causing enhancement of mechanical properties of TRIP steels:

The volume fraction and the stability of the retained austenite. The optimal volume fraction of retained austenite for a significant TRIP effect to occur is reported to be in the range of 10-20 vol. %.

The stability of retained austenite being determined by the C content and the grain size of the retained austenite.

The C content lowers the Ms temperature and therefore stabilizes retained austenite. The optimal C content in the retained austenite has to be in the range of 0.5-1.8 wt. % in order to provide the desirable TRIP effect. The Ms temperature of the retained austenite is above room temperature. Smaller austenite particles contain less potential nucleation sites for transformation to martensite and consequently require a greater total driving force for the nucleation of martensite. This will lower the Ms temperature to below room temperature. It has been suggested that the grain size of the retained austenite must be in the range of 0.01 to 1 mm to ensure the TRIP effect in low-alloyed multiphase TRIP steels. Larger retained austenite particles may already be partially transformed into martensite at the early stages of straining.

**Hot rolled TRIP steels**

Typical hot-rolled residual-austenite steels are based on a mere aluminium concept or on a mixed SiAl concept. On the basis of a 0.19%C-MnAlSi-concept three niobium-contents between 300 to 700 ppm have been studied (Table 1) [7].

<table>
<thead>
<tr>
<th>Nb</th>
<th>RA-content</th>
<th>RA-diameter</th>
<th>Lattice parameter $a_i$</th>
<th>$C_{RA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>µm</td>
<td>nm</td>
<td>%</td>
</tr>
<tr>
<td>0</td>
<td>7</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>13</td>
<td>1.8</td>
<td>0.36236</td>
<td>1.036</td>
</tr>
<tr>
<td>0.04</td>
<td>16</td>
<td>1.8</td>
<td>0.36218</td>
<td>0.996</td>
</tr>
<tr>
<td>0.07</td>
<td>13</td>
<td>1.6</td>
<td>0.36212</td>
<td>0.952</td>
</tr>
</tbody>
</table>
The residual austenite content and the lattice constant of the retained austenite were determined by radiography. The carbon content can then be calculated by:

\[ C_{RA} = \frac{a_i - 0.3578}{0.0044} \]

\(a_i\) = lattice constant, \(C_{RA}\) = carbon content of retained austenite
At 0.03% niobium the ferrite grain is already clearly refined, as shown in the Figure 3.

Figure 3. Grain refinement by Nb in hot-rolled retained austenite steels

The addition of 300 to 400 ppm niobium increases yield and tensile strength roughly 100 MPa by grain refinement and precipitation hardening (Table 2). The product of tensile strength and elongation improves. An addition of up to 700 ppm niobium does not further enhance the strength level but increases elongation values. One reason for this may be the slightly finer size of the retained austenite particles and a more homogeneous distribution in the microstructure. The smaller they are the greater is their geometric stability against strain induced transformation to martensite as mentioned before. This means that the transformation to martensite is delayed until higher stresses are applied, shifting the onset of the reduction of area to higher elongation values. Depending on the finishing temperature only part of the niobium precipitates as rather coarse particles during finish rolling. Especially in the case of the highest niobium content of 700 ppm more than 50% stays in solid solution (Figure 4).

Table 2. Influence of Nb on the mechanical properties of retained austenite steels

<table>
<thead>
<tr>
<th>Nb [%]</th>
<th>YS [MPa]</th>
<th>TS [MPa]</th>
<th>U.EL [%]</th>
<th>T.EL [%]</th>
<th>TS x T.EL [MPa x %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>539</td>
<td>623</td>
<td>16.5</td>
<td>35.8</td>
<td>22303</td>
</tr>
<tr>
<td>0.03</td>
<td>655</td>
<td>705</td>
<td>19.3</td>
<td>34.9</td>
<td>24605</td>
</tr>
<tr>
<td>0.04</td>
<td>623</td>
<td>718</td>
<td>18.3</td>
<td>33.4</td>
<td>23981</td>
</tr>
<tr>
<td>0.07</td>
<td>644</td>
<td>717</td>
<td>23.5</td>
<td>38.6</td>
<td>27676</td>
</tr>
</tbody>
</table>

Niobium retained in solid solution prevents carbide precipitation in the temperature range of bainite formation and lowers at the same time the martensite transformation start temperature [3]. This widens the process window of the coiling temperatures for the production of retained austenite steels and increases the stability of properties.
Cold rolled TRIP steel

The most important steps during heating and soaking of the as-cold-rolled material at an intercritical temperature (in the ferrite-austenite range) are the recrystallization, the dissolution of cementite and the formation of austenite. Depending on the soaking time and particularly the annealing temperature, the amount of austenite and the resulting carbon content in the austenite are adjusted [8, 9]. In contrast to dual-phase grades, the annealing temperature is much less important, even though it must be kept in mind that too low temperatures or an insufficient soaking time can result in an unrecrystallized microstructure and in undissolved cementite. Very decisive for the final properties is the growth of existing ferrite and the resulting enrichment of carbon in the austenite during cooling. At low cooling rates, enrichment and therefore stabilization of the austenite is very efficient in the temperature range between 600 and 700°C. Formation of pearlite during cooling and thus a loss of carbon must be avoided.

The last step is the enrichment of the austenite with carbon during the bainite transformation (overaging). Proper amounts of alloying elements such as Si, Al and/or P prevent the precipitation of C as Fe₃C. According to [10], the carbon content in the retained austenite is then about 1.4 - 1.8 mass %. At higher overaging temperatures, an enhanced transformation kinetics and a reduction of the amount of bainite formed are observed. At low overaging temperatures, the transformation kinetics is delayed and within overaging times typical of a continuous annealing line or a hot-dip galvanizing line the transformation is not completed. During this step, precipitation of cementite may occur if the annealing temperature is too high. A very strong influence on the amount of transformed bainite stems from the cooling rate due to the enrichment of carbon in austenite during cooling. Low cooling rates result in a marked reduction of the amount of bainite formed. During final cooling, transformation from insufficiently stabilized austenite into martensite may take place.

At present, TRIP grades with minimum tensile strength levels of 600, 700 and 800 MPa are common in the automotive industry. The mechanical properties of TRIP grades are determined by the fraction and strength of ferrite, bainite and austenite and in particular, on the stability of the retained austenite against strain induced martensitic transformation. Therefore, the properties of TRIP steels are mainly controlled by a well adapted thermal treatment of the alloy design. For the alloy design the most important elements are C, Mn and Si, Al and P or a combination of the last three. These additions control the phase transformations and therefore, the basic mechanical properties. Microalloying additions are
therefore not as important for TRIP grades as for mild and conventional high strength steel grades. Nevertheless, an overall control of the microstructure and the size of the different phases seem to be additional key factors for optimizing the final mechanical properties.

Particularly interesting is the addition of Nb as a microalloying element strengthening the ferritic matrix by means of grain refinement and precipitation hardening [11-15]. An increase of the yield and the tensile strength by approximately 15 MPa per 0.01 % of Nb is reported and this can be of particular interest for Al-based TRIP steel grades. According to [14, 15], the coiling temperature has to be considered when alloying TRIP-steels with Nb, since it determines the precipitation state of Nb. When applying low coiling temperatures (500°C), Nb likely remains partly in solid solution or assists the formation of very fine and hardly detectable carbonitrides. For high coiling temperatures (700°C), however, coarse Nb precipitates are formed and a smaller influence of Nb on the mechanical properties is reported. Using coiling temperatures between 600 and 650°C, small precipitates are formed being very effective in refining the microstructure by particle pinning and consequently the highest tensile strength levels can be reached.

Besides its effect on grain refinement, a delayed bainite formation is reported for Nb-alloyed TRIP-steels. The retarded bainite formation is attributed to an enhanced ferrite formation during cooling as a consequence of the fine grained microstructure. The ferrite formation results in a carbon enrichment of the remaining austenite delaying the austenite transformation to bainite [15]. In addition to the enhanced ferrite formation, a deactivation of nucleation sites for bainite by the very fine dispersed carbonitrides could be made responsible for the delayed bainite formation kinetics [15]. Small amounts of Nb staying in solid solution are reported to retard the bainite formation kinetics [14].

The influence of Nb additions on the phase transformations during annealing in a continuous annealing line or hot dip galvanizing line were investigated for Al and Si based TRIP materials by Traint et al. [16]. Concerning the dissolution of cementite and the formation of austenite, a significant impact of Nb was not detected. However, a delayed recrystallization kinetics was observed for the grades with Nb. Furthermore, the addition of Nb results in an increase of the ferrite formation kinetics during cooling.

The mechanical properties show a more continuous and smooth decrease of the strength for the Nb alloyed material (Figure 5) [17]. For the material without Nb (alloy A) only a minor decrease of the strength is observed until quenching temperatures of 700°C. Further decreasing the quenching temperature results in a marked decrease of strength. As the strength level of the material is related to the fraction of ferrite and martensite the figures reflect the increase of the ferrite fraction during cooling. As the transformations are gradual due to the existing ferrite after intercritical annealing, a detection of the difference is quite challenging in dilatometric investigations. Nevertheless, careful comparison of the length changes during cooling for the different grades additionally supports the proposed increased ferrite formation kinetics in grades with Nb additions.

Dilatometric experiments proved that the transformation behavior of the austenite is nearly the same for these two alloys [16]. The austenite transformation is characterized by a one step transformation for temperatures between 350 and 450 °C. In this temperature range the amount of austenite transforming decreases and the transformation kinetics is accelerated when increasing the holding temperature. Applying a holding temperature of 475 °C the transformation of the austenite occurs in two steps for the first time. Compared to the Si-
alloyed grade the overall amount of austenite transforming decreases and the kinetics of the transformation is delayed for the SiNb-alloyed grade. Al-alloyed grades show a similar transformation behavior in the bainitic range with respect to the enhanced transformation kinetics and the decreasing amount of austenite transforming when increasing the holding temperature.

The reduced fraction of bainite formed in the Nb alloyed material during the isothermal holding is in agreement with the enhanced formation of ferrite during cooling and, therefore, the reduced amount of available austenite for bainite formation. Moreover, the increased ferrite formation in the Nb material results also in an increased carbon content in the austenite and, therefore, the observed reduced bainite formation kinetics. The determination of the amount of retained austenite and the carbon content in the as-annealed material does not indicate any impact of a Nb addition [16].

The mechanical properties of Al and Si alloyed TRIP-steels with and without Nb are shown in Figure 6. Generally, the Si based TRIP material results in higher strength levels. For the Al based material, a remarkably increased effect of the isothermal holding time is observed indicating a faster bainite reaction. The increased ferrite formation kinetics and the resulting higher carbon content in the austenite in the Nb alloyed material is responsible especially for the Al TRIP grade for a remarkable high yield strength and low tensile strength even without overaging indicating a high stability of the retained austenite after cooling.

A Nb addition of 0.045 mass % yields an increase of the tensile strength of about 50 MPa. Compared to microalloyed grades, the influence of Nb on the strength level is rather weak for cold rolled TRIP-grades. The strength level is mainly governed by the ferrite hardness and the amount and morphology of bainite and retained austenite. Additions of Nb alter the contributions of the individual phases. While the ferrite hardness is increased due to grain refinement and precipitation hardening, the fraction of bainite is reduced in Nb-alloyed grades. Figure 7 shows the influence of Nb on the microstructure of industrial produced TRIP steel. For this Al + Si based HDG TRIP material, Nb markedly reduces both ferrite and austenite grain size. By overall adjusted alloy design and processing parameters very similar
strength levels can be obtained. Concerning the uniform and total elongation measured in tensile tests, a significant difference was not seen. However, first practical press trials indicate improved behavior for the material with the finer microstructure.

![Graph showing R_p0.2 and R_m as a function of t_b for Al based TRIP and Si based TRIP](image)

**Figure 6.** Impact of a Nb addition to Si and Al based TRIP material as a function of the overaging treatment at 400 °C [59] (T_an = 780 °C, T_Q = 700 °C and CR = 70 K/s) [17].

![Micrographs of TRIP 700 with Nb and TRIP 700 without Nb](image)

**Figure 7.** Impact of Nb addition on an industrially produced HDG TRIP 700 material.

**Conclusions**

Microalloying additions of Nb to TRIP steel grades besides a fine tuning of the strength level, allow to the control and refinement of the overall microstructure. Since Nb additions enhance the strength of a TRIP steel, the carbon content can be reduced by about 0.03% while the original formability is still maintained. A reduction of carbon on the other hand improves the weldability of the steel. Especially for thicker material with a reduced degree of cold reduction the refinement of the microstructure by Nb additions is a key point for the further improvement of TRIP steel grades. It helps avoiding the formation of a martensite band structure in the center which can lead to unexpected failure during bending operations in the forming process. Due to the refined and thus more homogeneous microstructure of Nb
microalloyed TRIP steel, the bending radius can also be reduced. This has to be seen as a further advantage regarding the avoidance of spring-back in press stamping parts.

References

11. O. Matsumura, Y. Sakuma, and H. Takechi, “TRIP and its Kinetic Aspects in Austempered 0.4C-1.5Si-0.8Mn Steel”, Scripta Met. 21 (1987) pp. 1301.