

## ADVANCED HIGH STRENGTH THIN SHEET GRADES: IMPROVEMENT OF PROPERTIES BY MICROALLOYING ASSISTED MICROSTRUCTURE CONTROL

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### Abstract

The mechanical properties of materials are generally controlled by their microstructure. Therefore, a thorough knowledge of the impact of alloying elements and process parameters on the resulting microstructure is essential. For mild and conventional high strength thin sheet grades microalloying additions such as Nb are the basis to control the microstructure and therefore, the mechanical properties. However, for advanced high strength steel (AHSS) grades such as dual phase, partial martensitic and TRIP grades, the microstructure is mainly determined by alloying additions controlling the phase transformations during cooling. For this purpose Mn, Cr, Mo, Si, and Al are the most important alloying elements. However, the addition of microalloying elements results in a remarkable refinement of the microstructure of AHSS grades and a further improvement seems possible. In this contribution, the decisive impact of Nb on the microstructure and mechanical properties of mild and conventional high strength steel grades is shown. Then, the most important alloying and thermal treatment concepts for processing AHSS steel grades are demonstrated. In the final part, the very promising impact of microstructure control based on microalloying additions is shown for AHSS steel grades. This contribution also highlights the necessity for further research in this topic.

### Introduction

The availability of advanced materials is one decisive item for the future development of modern industrial nations. One of the most challenging applications of new materials is the automotive industry. More fuel-efficient engines, an improved design, and the reduction of mass are essential factors in order to achieve the goal of reducing fuel consumption of automobiles. Furthermore, improved stiffness and crash safety of the enclosure are of fundamental interest. A most important point to achieve these goals is, in addition to layout and design, the application of appropriate materials. Since the properties of engineering materials are within different characteristic ranges, the selection of the most suitable material for different parts is an extremely challenging task. The work of Ashby [1] on materials properties provides some fundamental guidelines. For the general guideline of lightweight construction and depending on the loading type and the design criteria for a specific part, materials with an optimized ratio of

stiffness (E or G) or yield strength ( $\sigma_y$ ) to density ( $\rho$ ) are required for the body-in-white as depicted below:

$$E^n/\rho, G^n/\rho \text{ or } \sigma_y^n/\rho$$

The exponent  $n$  depends on the loading type and the design criteria and is in the range between 0.33 and 1.00. Hence, elastic properties, density and yield strength of the material in the final part are decisive properties. The elastic properties and the density of metallic materials are hardly changed in contrast to the excellently adjustable strength level. A comparison of different materials, in particular metallic materials, in such a chart [1] shows that steel grades generally occupy an excellent position.

Considering the shear or Young's modulus, yield strength and density alone is insufficient, since an appropriate design is of considerable importance in order to improve the strength and the stiffness of components. Therefore, excellent formability is of high interest to allow for complex shaped parts. Furthermore, parts must be joined and thus good weldability of the material is of great importance for the automotive industry, even though an increasing importance of adhesive bonding and mechanical joining, or a combination of both, is expected. Additional crucial points are surface appearance, corrosion resistance, recyclability and material and processing costs. Due to the well-balanced properties of steel sheet materials, steels have maintained their importance for the body-in-white.

Due to their excellent balanced properties, mild steel grades have gained a remarkable share in the automotive industry and therefore, a further optimization of these steel grades is still desirable. Various high-strength steel grades have been developed by the steel industry to satisfy these demands. Owing to their excellent features, bake-hardening (BH) and high-strength IF grades are the most widely used high-strength thin sheet grades [2-6]. As a rule of thumb, the upper limits for the yield strength and the tensile strength of BH grades based on solid solution hardening and high-strength IF grades are about 320 and 450 MPa, respectively. Higher strength levels can be achieved by taking advantage of precipitation hardening in micro-alloyed steels.

Another step towards high-strength steel grades with excellent formability is advanced high strength steel grades (AHSS). This class of steel grades includes dual-phase (DP), partial martensitic (PM) and TRIP grades. DP grades consisting of a ferritic matrix with mainly hard martensite inclusions are characterized by a low yield ratio and high strain hardening [7-8]. Based on the fraction of hard components grades, these grades possess tensile strength levels of 450, 500 and 600 MPa. Using higher fractions of the hard components, DP grades with tensile strength levels of 800 and 1000 MPa were developed and very recently, a strong demand for these grades is observed. DP grades are generally recommended for deep drawing applications. In contrast, PM grades, characterized by a more complex microstructure consisting of ferrite, bainite, martensite and tempered martensite are suggested for parts in which a high localization of strains can occur, for example in bending operations. For these steel grades strength levels of 800, 1000, 1200 and 1400 MPa are now under discussion. A drawback of these grades is their lower  $n$  value and lower uniform elongations as compared to DP grades. An outstanding balance between strength and formability is obtained for low alloyed thin sheet TRIP steels [9-11] (TRIP = Transformation Induced Plasticity). The processing of TRIP steels is a very challenging task and a sophisticated adjustment of the alloy design to the actual processing parameters based upon the characteristics of available production lines is a prerequisite. At present, grades with tensile strength levels of 600, 700 and 800 MPa are available and attracting strong interest from the automotive industry.

The improvement of the properties of steel grades through the control and optimization of the microstructure is based on an adjustment of the chemical composition to the processing parameters. For mild and conventional high strength steel grades, the control of the microstructure based on microalloying additions such as Nb and Ti is a key point and results of extensive investigations are reported in the literature. In contrast, for advanced high strength grades such as DP, PM and TRIP steels, alloying additions controlling the austenite transformation behavior (Mn, Si, Cr, Mo, Al) are most decisive. These elements control in combination with the thermal treatment mainly the resulting phases and the mechanical properties of the AHSS grades. However, for a further improvement of the properties, a strict control of the grain size and the distribution of the different phases are essential. As a matter of fact, this could be done efficiently by additions of microalloying elements such as Nb. Hence, a main topic in further research and development of AHSS grades will focus on the impact of different microalloying additions.

In this contribution, the decisive role of Nb on the microstructure and the mechanical properties of mild and conventional high strength steel grades are highlighted. Then, the most important alloying and thermal treatment concepts for processing AHSS steel grades are demonstrated. In the final part of the paper This very promising approach to microstructure control of AHSS grades based on microalloying additions is described and the necessity for further research in this topic is pointed out.

## **Mild and Conventional High Strength Steel Grades**

### Mild IF grades

Mild IF grades still have a significant marked share and they are applied for the most complex shaped structural parts. For the processing of IF grades, the entire precipitation of C and N with the addition of Ti and/or Nb is essential. Most of the mild IF grades are stabilized with Ti. Based on the work of different authors [12 - 16], in the past years the important role of sulfur and the resulting  $Ti_4C_2S_2$  and TiS precipitates was shown. Hence, the contents of C, N, S and Ti are the most important parameters with regard to chemical composition. The precipitation of  $Ti_4C_2S_2$  particles at high temperatures during reheating and roughening is of particular interest as these large precipitates are favorable for low strength levels and excellent elongation,  $r$ - and  $n$ - values in contrast to the small and carbon-rich TiC particles precipitated during finishing and coiling. As a result, research work was necessary to establish a thermodynamic and kinetic understanding of the TiS and  $Ti_4C_2S_2$  formation. The impact of the processing parameters was investigated in detail [17 - 19] and can be summarized as follows: Low reheating temperature, high coiling temperature, high cold reduction and high annealing temperature result in improved formability. The influence of the reheating temperature is a consequence of the precipitation behavior of  $Ti_4C_2S_2$ . High coiling and high annealing temperatures produce coarser TiC particles and hence a lower strength level. Cold reduction generally improves the texture. Based on optimized processing parameters for Ti stabilized IF grades, outstanding mechanical properties are obtained (Figure 1). The material distinguishes itself by its low strength level and high elongation,  $n$ - and  $r$ -values. This low strength level is in agreement with the observed low density of small particles. However, a disadvantage of the pure Ti IF grade is a slightly reduced  $r$ -value in the diagonal direction (Figure 2).

Another possibility for stabilization is the application of Nb or a combination of Ti and Nb [17 - 19]. In contrast to the Ti-IF material, Nb-IF grades show higher strength levels due to the precipitation of small C-rich NbC precipitates during coiling of the hot strip. This effect again points to a strong impact of the coiling temperature on the mechanical properties. Additionally,

in contrast to the Ti stabilized material, Nb alloyed material shows a considerably higher influence of the carbon content on the mechanical properties. Advantages of the Nb stabilized grade are very small  $\Delta r$  values and, moreover, high mean  $r$ -values. This is due to a decrease of the  $r$ -value in longitudinal and an increase in diagonal direction (Figure 2). Therefore, the material shows almost no earing during drawing of cylindrical parts. An excellent compromise can be obtained by applying Nb and Ti. Based on such a concept, materials with almost the same low strength level as Ti IF grades and the same favorable non-earring behavior as Nb stabilized grades can be obtained. The addition of Nb and Ti is also advantageous for the production of galvanized material, particularly for the improvement of the flaking and powdering behavior [20].

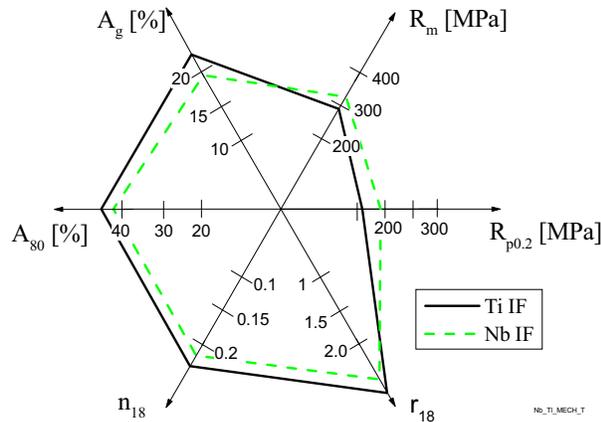


Figure 1. Comparison of the mechanical properties in transversal direction of a standard Ti-IF grade and a Nb-IF grade.

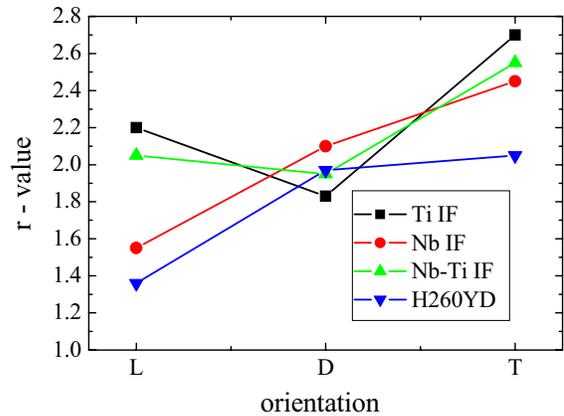


Figure 2.  $r$ -value in the longitudinal (L), diagonal (D) and transversal (T) direction for a soft Ti-IF, a soft Nb-IF, a soft Nb + Ti-IF and a high strength Nb + Ti-IF-grade with a minimum yield strength of 260 MPa (H260YD).

### HS IF grades

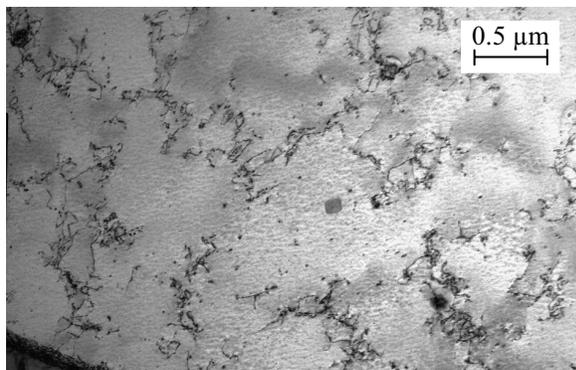
High-strength IF grades are based on solid solution hardened mild IF grades. Therefore, also for these grades the alloying with Nb and Ti are fundamental for controlling the microstructure and the mechanical properties. For the adjustment of the strength level, P, Mn and Si are used for solid solution hardening, with P being the most effective element and Mn providing the lowest hardening contribution [17, 19, 21]. To avoid a dramatic increase in the tendency to secondary cold work embrittlement (SCWE) caused by P, it is absolutely necessary to add B [22]. In such alloys, B has the same effect as C. Both elements segregate to the grain boundaries and increase grain boundary cohesion, since P also segregates to grain boundaries and decreases their strength [23]. The predominant effect of B, either for an increase of the grain boundary strength or the reduction of the P segregation due to site competition, is still in discussion. Nevertheless, an alloy design which guarantees B in solid solution is absolutely necessary for the production of high-strength IF grades.

Similar to the soft IF grades, high-strength IF grades can be based on stabilization with Ti or Ti and Nb. Advantages of the application of Ti stabilization are the well-known concept for the mild grades. In comparison to Nb and Ti stabilized grades, the following disadvantages can be stated. The application of Nb and Ti generally results in a higher strength level. Therefore, lower

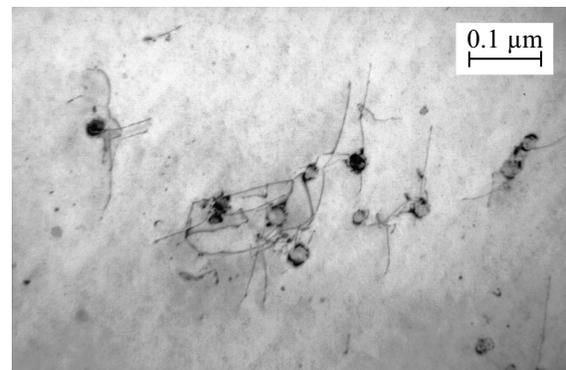
contents of solid solution hardening elements are necessary. Moreover, the Nb and Ti alloys lead to generally lower  $\Delta r$  values [24]. High Ti and P contents in solid solution can result in FeTiP precipitation in the coil [21]. These FeTiP precipitates deteriorate the mechanical properties in cold-rolled and annealed condition. The critical temperature range for the precipitation of FeTiP was determined in extensive investigations and this results for the Ti stabilized HSIF grades in restricted ranges for the coiling temperature.

With respect to the processing parameters, the highest impact on the microstructure and the mechanical properties results from the coiling temperature, the cold reduction and the annealing temperature. Lower coiling temperatures results in smaller precipitates, and this yields a smaller ferrite grain size. As a consequence, the strength level increases and at the same time, the elongation,  $n$ - and  $r$ -values decrease. Higher cold reduction improves the  $r$ -value. Additionally, the grain size is reduced and the strength level is slightly increased. Because of the tendency of P segregation during annealing in the temperature range of 500 – 600°C, batch annealing is not advisable for P alloyed high-strength IF grades [24, 25]. Moreover, the cooling rate should be as high as possible for continuous annealing in this temperature range, and high overaging temperatures are unfavorable. Concerning the annealing for high-strength IF grades, soaking temperatures in the range of 800 – 850°C are necessary. Higher annealing temperatures result in better mechanical properties.

As can be seen in Figure 3, the predominant precipitates for Ti and Nb stabilized high strength IF grades are large TiN and MnS precipitates. TiS and  $Ti_4C_2S_2$  particles are not observable. The small precipitates in Figure 3 are C and Nb rich (Nb,Ti)(C,N). FeTiP particles were not found. This precipitation sequence is in agreement with the predictions from the thermodynamic calculations. In comparison to the soft grades, a smaller grain size is measured in the cold-rolled and annealed condition.



Overview



Small C and Nb rich (Ti,Nb)(C,N) particles

Figure 3. Microstructure of a Ti and Nb stabilized high-strength steel grade IF in cold rolled and annealed condition.

Figure 4 shows typical mechanical properties of high-strength IF grades produced via a HDG line. The minimum yield strength values are 220, 260 and 300 MPa. Low yield strength, high tensile strength and excellent elongation,  $n$ - and  $r$ -values are observed for these grades. A further outstanding feature of these high-strength IF grades is their nearly vanishing  $\Delta r$  value (Figure 2).

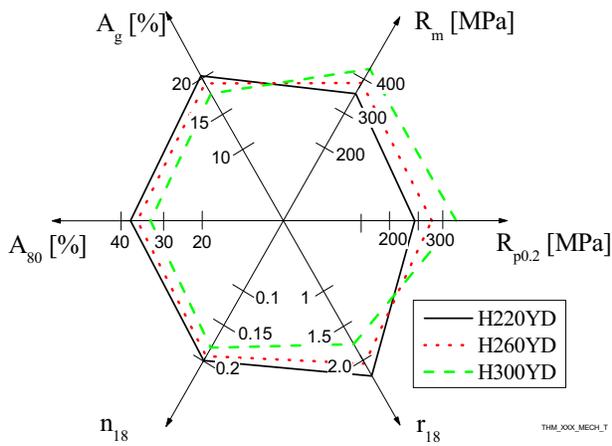


Figure 4. Mechanical properties in the transversal direction for HDG high-strength IF grades with minimum yield strengths of 220 (THM 220 IF), 260 (THM 260 IF) and 300 MPa (THM 300 IF).

### Partially stabilized ULC BH grades

The most important step during processing of BH grades is the precise adjustment of the carbon content in solid solution, which controls the BH value. In continuous annealing lines, an LC based alloy is used almost exclusively, and the necessary carbon content in solid solution is obtained by proper adjustment of the cooling and overaging conditions to the chemical composition. In contrast, HDG lines usually have only very short overaging zones (equalizing zone). Additionally, the overaging temperature of HDG lines is limited to the range of 460°C due to the fixed galvanizing temperature. Therefore, the advantage of an advanced cooling section for the acceleration of the carbon precipitation cannot be exploited. Consequently, the precise adjustment of the carbon content in solid solution is quite difficult on HDG lines.

A completely different approach has to be taken when producing HDG BH grades from partially stabilized ULC grades. The ULC BH grades are partially stabilized with Nb, Ti and V or a combination of these alloying elements. Research and development activities on such BH grades were launched based on the early work of Irie on Nb alloyed material. Two completely different approaches can be distinguished with regard to the alloy design. In the case of Nb [26, 27], Ti [28, 29] or Ti and Nb [19] alloyed grades the alloy design is always sub-stoichiometric. In contrast the atomic ratio of V to C is significantly larger than 1 in Ti and V alloyed grades [30]. These alloys use the high solubility of VC in ferrite. Additionally, also unstabilized ULC grades are used for producing BH material. The overall strength level of BH grades is adjusted by solid solution hardening with P, Mn and Si.

At present, Nb additions are often used and for such a material the most important parameter is the mutual adjustment of the total carbon and Nb contents (Figure 5). The dominant precipitation reaction takes place in the ferritic range due to the very low alloying content of this partially stabilized ULC material [31, 32]. Particularly the precipitation of carbides, which controls the remaining carbon content in solid solution and hence the BH level, takes place in the ferritic range. Contrary to the soft IF grades in which the most important precipitation takes place in the austenite, only a few examinations have been carried out for the ferritic range. In addition to the Nb and C relation, a fine-tuning of the carbon content in solid solution and, therefore, of the BH value is possible by adjusting the annealing temperature; higher annealing temperatures generally result in higher BH values. Cooling rates and overaging do not have a significant

impact on the BH behavior. However, plastic straining during cooling from annealing reduces drastically the carbon content in solid solution.

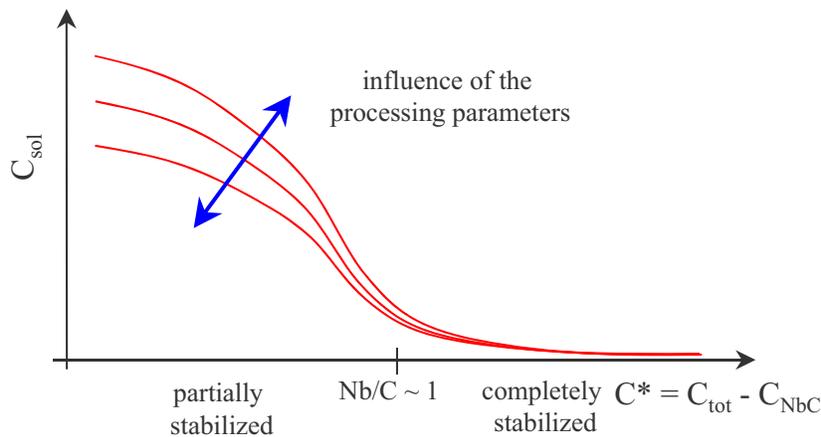


Figure 5. Impact of the carbon and Nb content on the carbon content in solid solution.

The mechanical properties of different ULC grades partially stabilized with Nb are shown in Figure 6. The three different grades with minimum yield strengths of 180, 220 and 260 MPa were produced on a commercial HDG line. The strength levels were adjusted with Mn and P. All grades possess an excellent balance between the strength level and the parameters describing formability. Moreover, all grades show satisfying BH values. A further advantage of partially stabilized BH ULC grades produced via a HDG is shown in Figure 7. In comparison to more common LC BH grades generally higher  $r$ -values are obtained for the ULC grades. Additionally, significantly lower  $\Delta r$  values are observed for grades partially stabilized with Nb. However, as mentioned before, the mechanical properties are mainly adjusted by the chemical composition, and therefore, an excellently working steel plant is necessary.

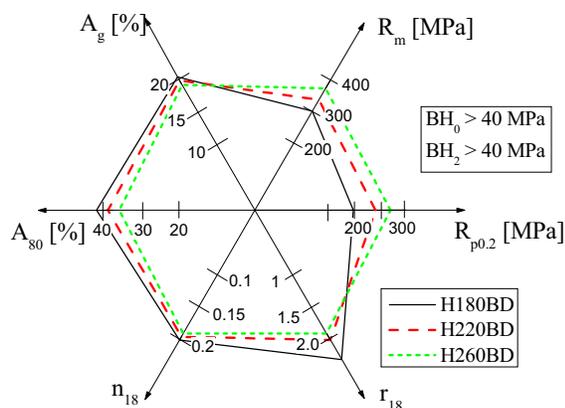


Figure 6. Mechanical properties in the transversal direction of partially stabilized Nb ULC grades produced via HDG (the BH values are measured in transversal direction, too).

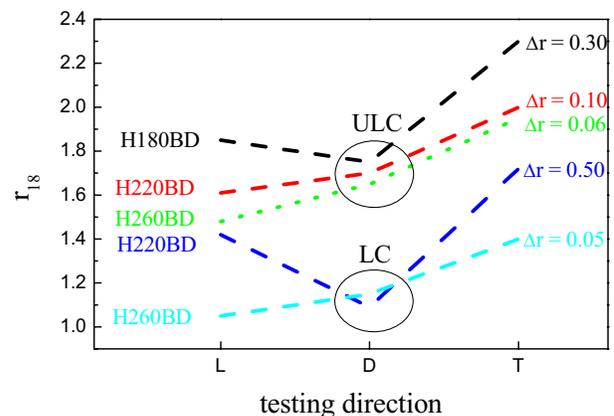


Figure 7.  $r$ -value in the longitudinal (L), diagonal (D) and transversal (T) direction of partially with Nb stabilized ULC BH grades and LC BH grades produced via HDG.

## Basic Alloy Design for AHSS Grades and the Resulting Properties

### Dual Phase Steels

#### Introduction

Dual-phase grades are a “composite material” which is characterized by a soft matrix with hard inclusions. The soft matrix is ferrite and the hard inclusions are mainly martensite (Figure 8). This two-phase microstructure results in exceptional mechanical properties such as low yield strength, high work hardening, high tensile strength and excellent uniform and total elongations. The reason for this behavior can be explained as follows [33]. During plastic deformation, the martensite is plastically deformed very little and the surrounding ferrite is additionally deformed to ensure geometrical compatibility. This results in an increased extent of work hardening which again is the reason for the high tensile strength and the excellent uniform elongation. A similar explanation of the high work hardening of DP steels is based on the concept of geometrically necessary dislocations as proposed by Ashby [34]. Then, additional dislocations are generated to ensure compatibility in the surroundings of the martensite, which results in an additional work hardening contribution. The yield ratio of industrially produced DP grades, including temper rolling for an appropriate surface roughness, is usually in the range of 0.55 – 0.65. The low yield strength of DP grades is generally determined by the strength of the soft ferrite, however, more detailed considerations also highlight the impact of the fraction of martensite based on some additional work hardening of the ferrite during transformation of austenite into martensite [35].

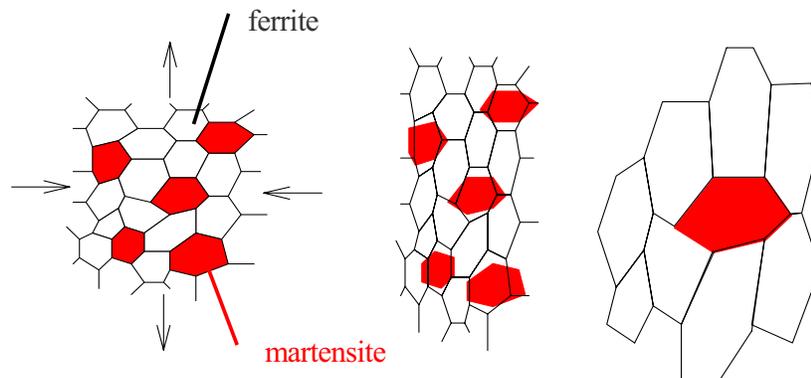


Figure 8. Schematic microstructure of a DP grade.

The development of cold-rolled DP grades started about 35 years ago [36, 37]. However, poorly equipped lines for processing this material and an almost missing pressure from the market resulted in a very delayed application. Only very recently, in the past 3 – 5 years, a remarkably increasing demand has been observed. At present, the R&D efforts concentrate on the improvement of existing grades and the processing of grades with a higher strength level.

#### Processing and resulting properties

The most important steps for the processing of DP steels are the formation of austenite during intercritical annealing and the transformation of this austenite into ferrite and martensite upon cooling. The material is annealed in the intercritical range with ferrite / austenite in the two-phase region (Figure 9) to allow recrystallization, cementite dissolution and austenite formation. During cooling, control of the ferrite formation and the transformation of the remaining austenite is essential. The formation of bainite or even pearlite must be suppressed or restricted to small amounts by either appropriate alloy additions or high cooling rates. As a consequence, processing of DP steels is only possible on CA or HDG lines. The heat treatment schedules of the two lines differ by the cooling due to the almost fixed temperature of the zinc pot at about

460°C. After intercritical annealing, ferrite formation and adjustment of the fraction of austenite is achieved by slow cooling in well equipped CA lines. High cooling rates in modern lines prevent the formation of pearlite and bainite. With a low overaging temperature, the amount of transformed bainite or tempered martensite can be adjusted to a low level. In contrast, in HDG lines, cooling is interrupted due to the zinc pot and a short equalizing zone at the critical temperature of bainite formation. Therefore, HDG-DP grades need slightly higher alloy contents.

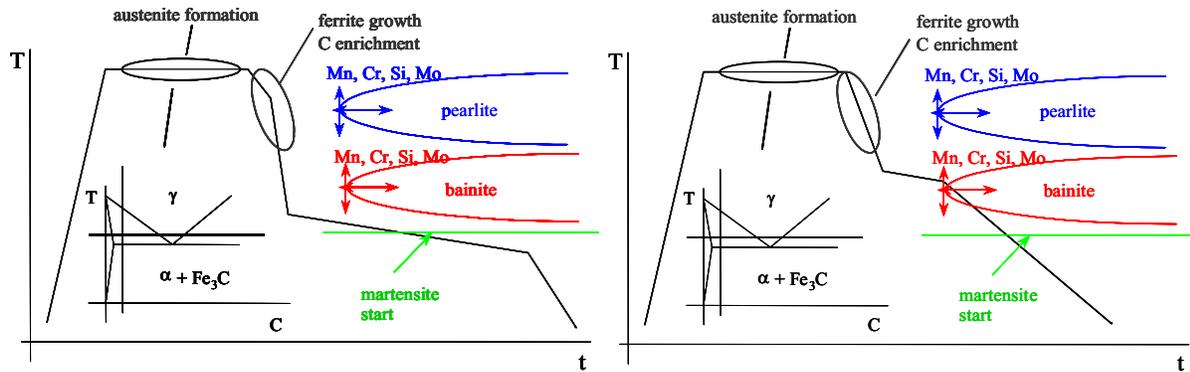


Figure 9. Schematic representation of the phase transformations of DP steel grades during heat treatment.

A typical DP microstructure is shown in Figure 10. The material consists of a blue-colored ferritic matrix, white and light brown-colored martensitic inclusions, and small fractions of brown-colored bainite or tempered martensite. Generally, also a small fraction of retained austenite is present transforming into martensite at low plastic strain levels. In Figure 11 the mechanical properties of a CA HT600X and a HDG HT600XD are compared to the properties of a micro-alloyed grade having the same yield strength. There is no significant difference between the DP materials produced via CA and HDG. However, in comparison to the micro-alloyed grade remarkable differences are evident. At the same yield strength, DP grades show remarkably higher tensile strength, *n*-value and uniform elongation.

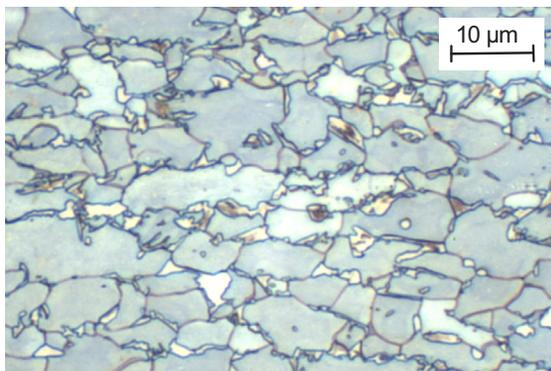


Figure 10. Typical microstructure of a DP grade.

The mechanical properties of DP grades with minimum tensile strength levels of 600, 800 and 1000 MPa are shown in Figure 12. Grades with higher strength levels show slightly reduced values describing the formability (uniform and total elongation and *n*-value). Hence, forming of not too complex parts should be possible. DP grades with even higher strength levels are available or are being developed. As the strength level of such high-strength grades is adjusted

by the fraction of hard martensite, a ferritic matrix is no longer possible. This in turn results in an increasing yield ratio and the steel grades are also termed partially martensitic.

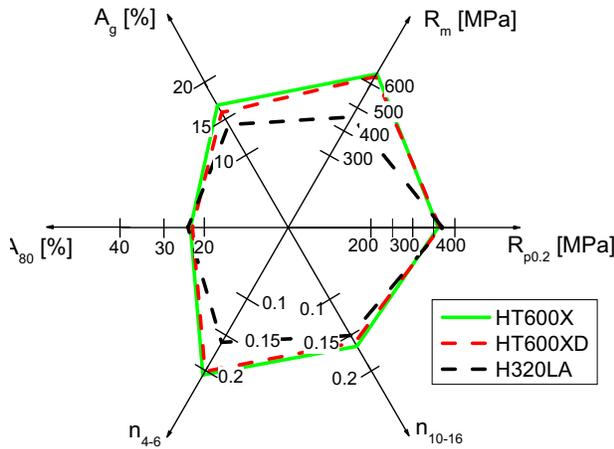


Figure 11. Comparison between the mechanical properties of the DP grades HT600X, HT600XD and the micro-alloyed grade H320LA.

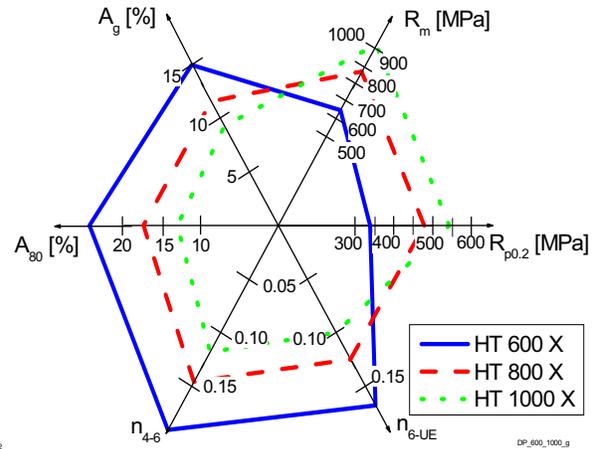


Figure 12. Typical mechanical properties of the DP grades HT600X, HT800X and HT1000X.

## Partially Martensitic Grades

### Introduction

Partially martensitic (PM) grades are composite materials with a multi-phase micro-structure consisting of ferrite, bainite, martensite and tempered martensite (Figure 13). In contrast to DP grades with a ferritic matrix, transformation hardened phases such as bainite, martensite and tempered martensite are predominant in PM grades. A clear differentiation between matrix and inclusion is difficult. Additionally, microalloying and therefore precipitation hardening and an increase of the strength due to the refinement of the different phases are often applied. This also has a favorable impact on formability.

In comparison to DP grades with similar tensile strength, PM grades have a considerably higher yield strength and therefore, also a higher yield ratio. Due to a significantly lower hardness difference between the microstructure constituents, fewer geometrical dislocations are necessary to achieve compatibility, and therefore, the work hardening of PM grades is lower than that of DP grades (Figure 14). This in turn results in a reduced uniform elongation because the start of necking is determined by the balance between work hardening and reduction of cross section. A homogenous hardness distribution in the microstructure reduces the localization of strain within the material remarkably and therefore, some advantages of this PM steels are expected for parts which require high localized external strains.

There exists almost no literature on PM grades. Investigations concerning materials with a decreased fraction of polygonal ferrite and an increased fraction of transformation hardened phases could be transferred to PM grades because the distinction between DP and PM grades is blurred. Nevertheless, research work highlighting the differences between these grades, or identifying an optimized microstructure for a formed part, is still missing and will be an important topic in the future.

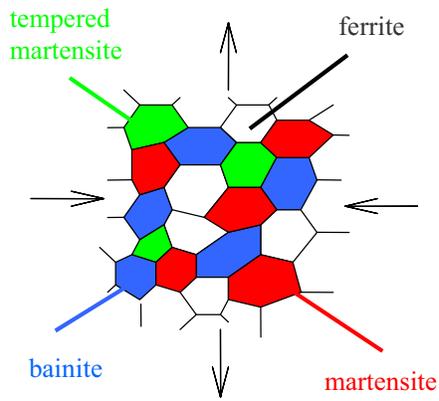


Figure 13. Schematic microstructure of a PM grade.

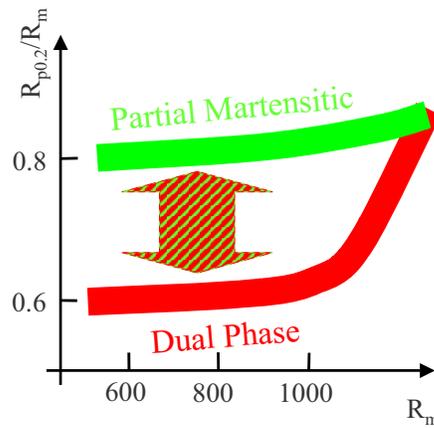


Figure 14. Yield ratio as a function of the tensile strength for DP and PM grades.

### Processing and resulting properties

As a ferritic matrix is unfavorable for a high yield strength, ferrite formation during annealing and cooling must be suppressed, utilizing high cooling rates or appropriate alloying concepts (Figure 15). Therefore, most PM grades are annealed in the austenitic range to increase the fraction of austenite transforming during cooling into transformation hardened phases by making necessary an additional nucleation step for ferrite. To avoid or reduce the formation of polygonal ferrite, high cooling rates or increased alloying contents are necessary. Processing such grades via HDG lines, which are often not equipped for high cooling rates, necessitate increased Mn, Si, Cr or Mo contents.

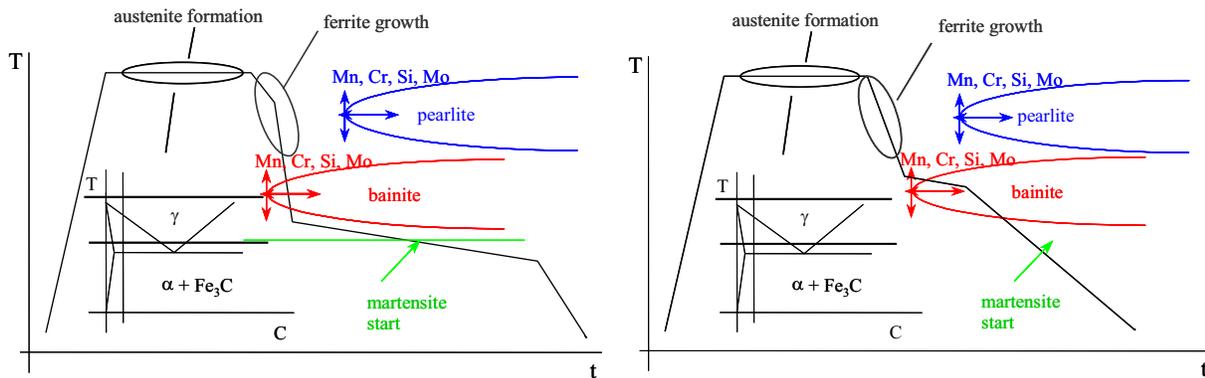


Figure 15. Schematic representation of the phase transformations of PM steel grades during heat-treatment.

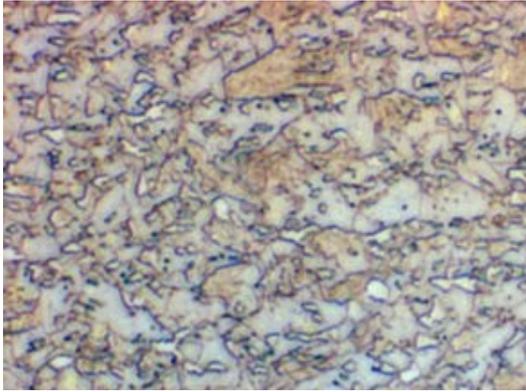


Figure 16. Typical microstructure of a PM thin sheet steel grade (HT800C).

The microstructure of the PM-grade HT800C is shown in Figure 16. The material consists of a white substructured bainite and light-brown martensite or tempered martensite. Polygonal ferrite is hardly detectable. Typical mechanical properties of continuously annealed PM grades and comparable DP grades are shown in Figs. 17 and 18. The PM material has a remarkably higher yield strength, however, as far as uniform and total elongation and  $n$ -values are concerned, the DP material is superior. At *Voestalpine*, the development of PM grades is still in progress. First industrial trials for continuously annealed HT800C and HT1000C were successful. However, optimization is still necessary and in progress. Concerning hot-dip galvanized material, first promising industrial trial was done on a line with a rapid cooling facility.

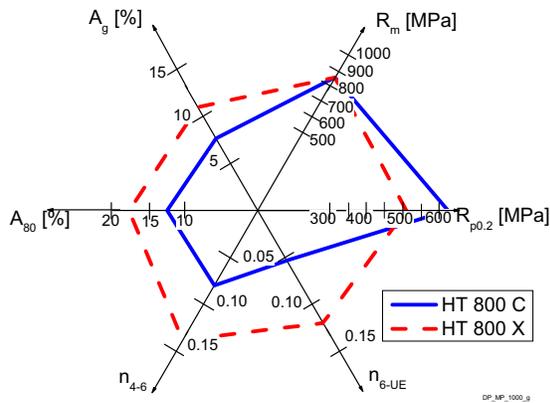


Figure 17. Comparison of the mechanical properties of the DP grade HT800X and the PM grade HT800C.

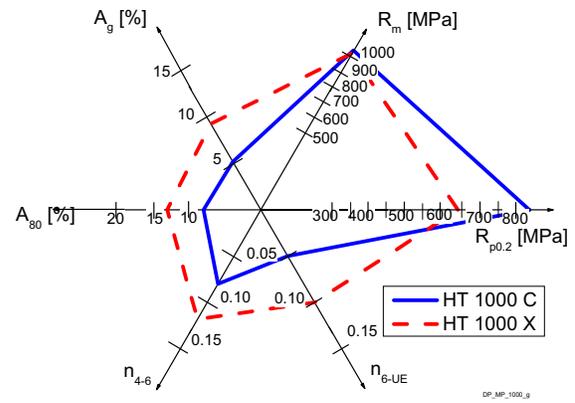


Figure 18. Comparison of the mechanical properties of the DP grade HT1000X and the PM grade HT1000C.

## TRIP Grades

### Introduction

A further step towards grades with a high strength level and excellent formability was the development of low-alloyed thin sheet TRIP steels [8, 9] (TRIP = TRansformation Induced Plasticity). TRIP steel grades are characterized by a ferritic matrix with bainite and retained austenite inclusions (Figure 19). 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 phenomenon of transformation induced plasticity has been well known for high-alloyed steels since Zackay's paper [11] was published, but for thin sheet applications austenite-stabilizing alloying elements such as Ni are too expensive. In low-alloyed TRIP grades, retained austenite is therefore mainly stabilized by C, and to some extent also by Mn. The excellent mechanical properties of TRIP steels can be explained similarly to that of DP grades. The transformation of austenite into martensite is accompanied by an increase of the volume of

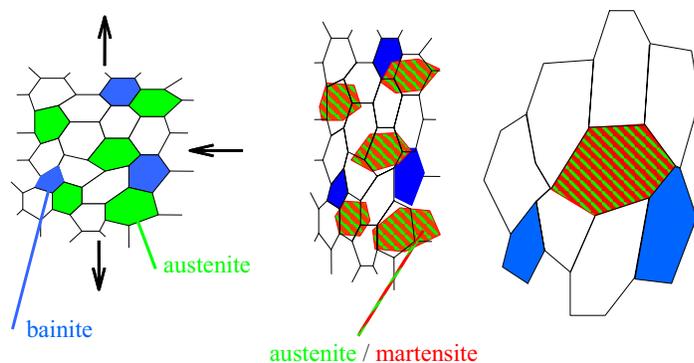


Figure 19. Schematic microstructure of a TRIP grade.

the transformed region and a strong shear deformation in the surround microstructure. To meet the requirements of compatibility, geometrically necessary dislocations in the surrounding ferrite result in a high work hardening rate and therefore a high  $n$ -value. Controlling the stability of retained austenite, the work hardening rate or the  $n$ -value as a function of the strain can be adjusted. Through optimized processing, almost constant or even increasing  $n$ -values as a function of strain can be achieved. These high  $n$ -values in turn result in outstanding elongation values and excellent formability.

### Processing and resulting properties

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 [56, 57]. In contrast to dual-phase grades [58], the annealing temperature is, however, 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 therefore 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 Fe<sub>3</sub>C. According to [16], 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.

Numerous investigations were conducted on alloys with 0.15 - 0.40 % C, 1 - 2 % Mn and 1 - 2 % Si with respect to the influence of the production parameters and, in particular, the annealing treatment of the cold-rolled material on the mechanical properties [39 - 47]. Moreover, remarkable efforts were made to characterize the microstructure and different kinds of retained austenite [42, 44]. However, almost all of the investigations focused on materials with 1.5 mass % or even higher silicon contents. Only few investigations [48 - 55] were conducted with regard to the impact of P, Al or combinations with Si, although very promising results have been achieved for these alternative alloy concepts.

The microstructure of the TRIP-grade HT700TD is shown in Figure 20. The blue or brown-colored matrix phase is the ferrite, the white phase is retained austenite and the brown-colored phase linked with retained austenite is bainite. Typical mechanical properties of grades HT700T and HT700TD are shown in Figure 21. Due to the shorter overaging zone available in the HDG line, the retained austenite is less stabilized which results in a lower yield strength and slightly higher *n*-values at low strain and decreasing *n*-values. The outstanding mechanical properties of TRIP grades are shown in Figure 22. In contrast to DP grades with similar tensile strength, TRIP grades have a higher yield strength and significantly better elongation and *n*-values. A comparison of TRIP grades with different strength levels is shown in Figure 23. Even though an increasing strength level results in decreasing elongation and *n*-values a uniform elongation of about 20 % is outstanding for a material with a minimum tensile strength of 800 MPa.

At present, TRIP grades with minimum tensile strength levels of 600, 700 and 800 MPa are common. The present research and development concentrates on the optimization of these existing grades and additional efforts on a grade with 1000 MPa are in progress.

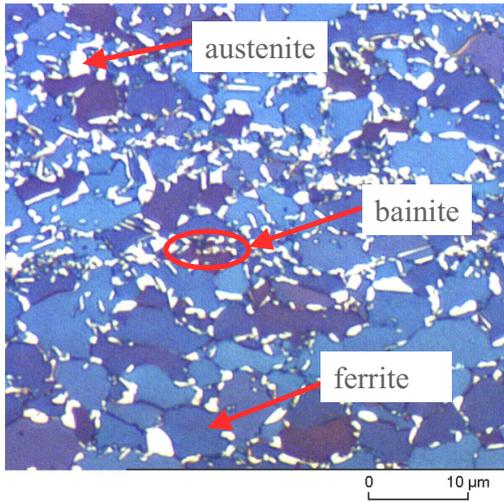


Figure 20. Microstructure of a TRIP thin sheet steel grade (HT700TD).

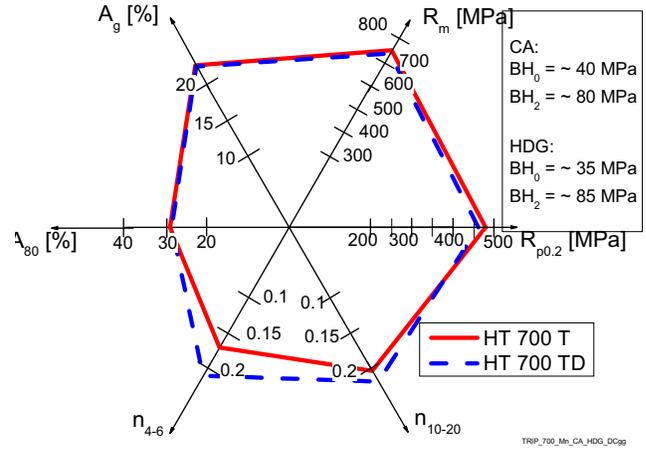


Figure 21. Mechanical properties of a continuously annealed (HT700T) and a hot-dip galvanized (HT700TD) TRIP grade.

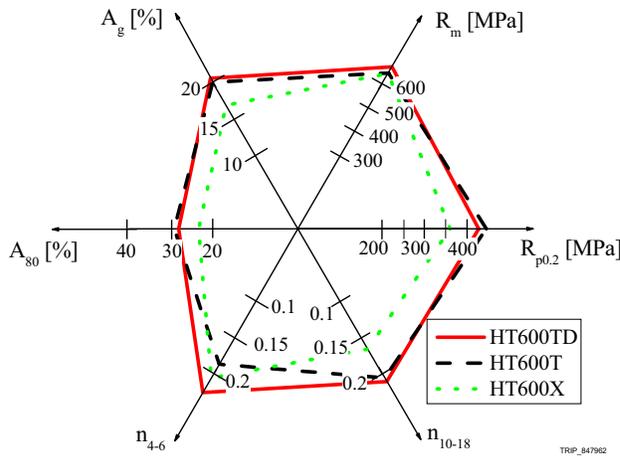


Figure 22. Comparison between the mechanical properties of the DP grade HT600X and the TRIP grades HT600T and HT600TD.

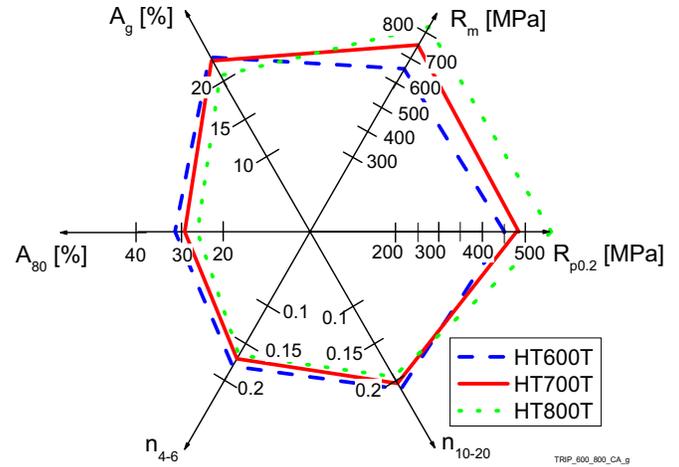


Figure 23. Mechanical properties of TRIP grades with minimum tensile strength of 600 MPa (HT600T), 700 MPa (HT700T) and 800 MPa (HT800T).

## Microstructure Control in AHSS Grades by Microalloying

### DP grades

#### Introduction

The mechanical properties, particularly the strength level, of DP grades are mainly determined by the fraction and strength of ferrite and martensite. The strength level of ferrite can be adjusted by solid solution hardening, precipitation hardening and the grain size. As the addition of the most efficient solid solution hardening elements Si and P is restricted due to surface defects and weldability aspects, respectively, the application of microalloying elements such as Nb resulting in precipitation hardening and grain refinement is favorable for controlling the ferrite strength. In the present work first results concerning the addition of Nb to typical alloy designs for hot dip galvanized DP 600 and 800 grades are presented. After an overview of the impact of Nb on the phase transformation kinetics, the resulting microstructure and the mechanical properties are shown and compared to results from grades without Nb. Finally, further work still in progress and future investigations are detailed.

#### Phase transformation and microstructure

During heating and soaking in a continuous annealing or HDG line, the recrystallization dissolution of cementite and formation of austenite are the most important steps. Investigations reveal negligible impacts of Nb additions on cementite dissolution and austenite formation, however, recrystallization is slightly delayed. The most important phase transformations which must be controlled during cooling are ferrite growth, the avoidance of pearlite, the control of the bainite fraction and the martensite transformation. Therefore, these transformations were investigated in detail with dilatometric experiments and annealing trials in combination with

intensive microstructure investigations. Additionally the hardness and mechanical properties were used as an indicator for phase transformations.

In Figure 24, the length change as a function of the temperature is shown for DP 600 alloys without and with Nb. For the higher cooling rate, a significantly increased transformation rate at high temperatures, which is attributable to ferrite formation, is observed for the material with Nb. However, also for the lower cooling rate of 60 K/s an enhanced transformation kinetics for ferrite is evident for the Nb alloyed material. Microstructures obtained after cooling with 80 K/s are shown in Figure 25 for the alloys with and without Nb. The Nb containing material exhibits a remarkably finer microstructure. A quantitative characterization of the microstructure indicates also a higher fraction of ferrite for the Nb alloyed material.

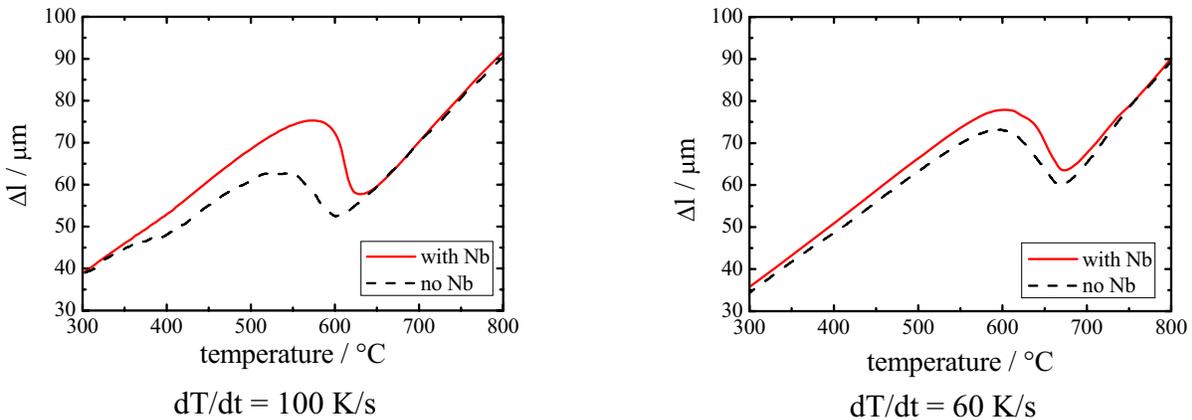


Figure 24. Measured length change as a function of the temperature for DP 600 alloys without and with Nb.

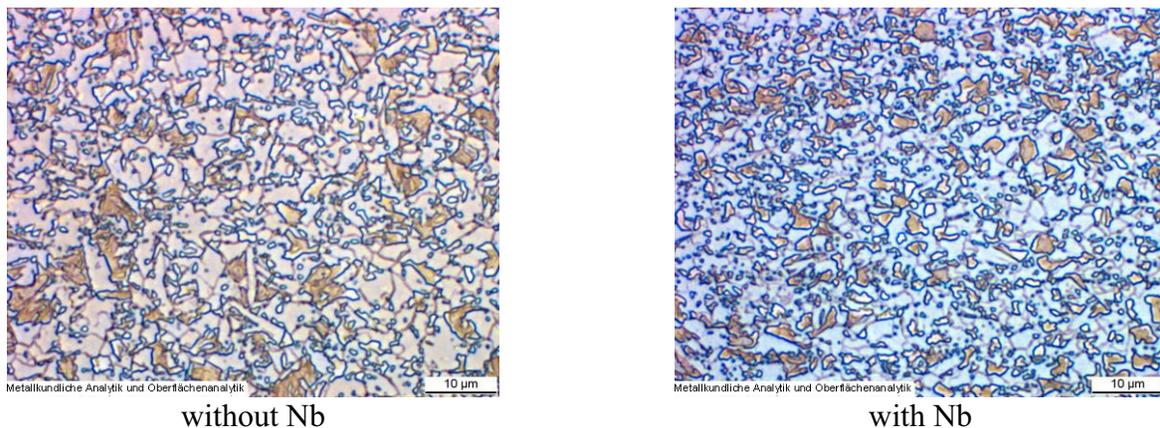


Figure 25. Microstructure of DP 600 alloys without and with Nb after annealing at 850 °C / 60 s and cooling with 80 K/s.

In Figure 26, the microhardness of the samples annealed in the dilatometer is shown as a function of the cooling rate. At high cooling rates, the alloy without Nb has a higher hardness. At lower cooling rates, the material with Nb is harder. Due to the grain refinement and precipitation hardening, higher hardness would be expected for the material with Nb. Nevertheless, the increased ferrite formation kinetics results especially at high cooling rates in significant higher amounts of ferrite and therefore reduced amounts of martensite in the Nb alloyed material. Therefore, the strength and hardness of the Nb material is lower due to the lower content of hard martensite despite the hardening contribution from grain refinement and precipitation hardening.

At low cooling rates, sufficient ferrite formation can take place resulting in similar amounts of ferrite and martensite for both materials. Therefore, the contribution of Nb to grain refinement and precipitation hardening results in higher hardness values.

The effect of Nb can be summarized as follows. Nb results in a remarkable refinement of the microstructure. This grain refinement results in a marked increase of the ferrite formation

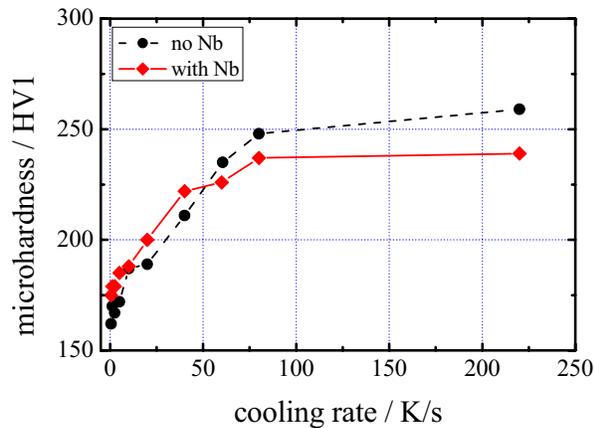


Figure 26. Microhardness as a function of the cooling rate for DP 600 alloys with and without Nb after annealing at 850 °C / 60 s.

kinetics. Concerning the formation of bainite and martensite, the increased carbon content in the austenite reduces the bainite formation kinetics and decreases the martensite start temperature when applying high cooling rates [60].

Quite similar results were obtained for a DP 800 material. Due to the increased alloying additions of C, Mn, Cr and Mo, the effect of the grain refinement on the ferrite formation kinetics resulting from the Nb additions are even more pronounced. As demonstrated in Figure 27 for a DP 800 alloy without Nb even cooling rates as low as 40 K/s result in an almost fully martensitic microstructure. In a similar alloy with Nb, a significant amount of ferrite is formed.

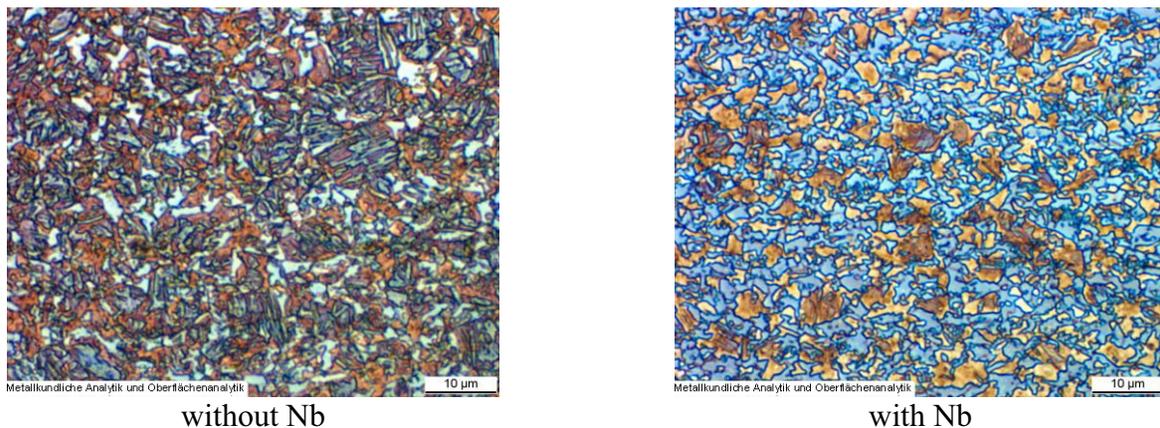


Figure 27. Microstructure of DP 800 alloys without and with Nb after annealing at 850 °C / 60 s and cooling with 40 K/s.

## Mechanical properties

The impact of an addition of 0.025 % Nb on the mechanical properties of a DP 600 grade as a function of the quenching temperature is shown in Figure 28 for a simulation of the continuous annealing line of *Voestalpine*. For this line configuration strength levels higher by 30 – 50 MPa can be obtained depending on the quenching temperature. Concerning the uniform and total elongation and  $n$ -values, a significant impact of the Nb addition cannot be observed. Therefore, Nb is advantageous for a fine-tuning of the strength level. Preliminary investigations of the bendability and hole expansion measurements indicate an improvement caused by Nb. This is also supported by first press trials of the material. The advantage of an Nb addition seems to be more relevant for DP grades with higher strength levels.

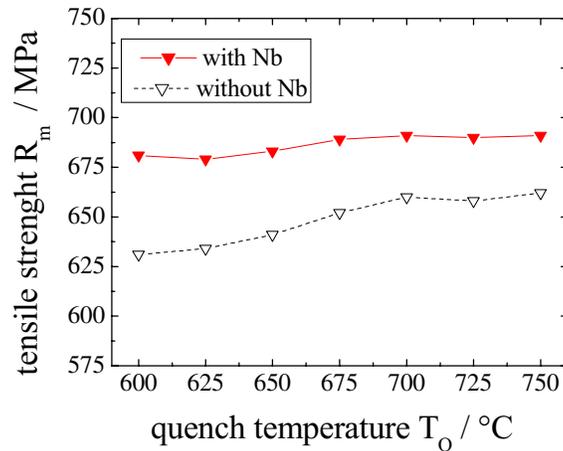


Figure 28. Mechanical properties as a function of the quenching temperature  $T_Q$  for DP 600 with and without Nb after simulating an annealing cycle according to the continuous annealing line of *voestalpine*

## Future Development

As the first investigations were quite successful further investigations will be necessary in the future. Generally the role of the size of the different phases on the mechanical properties and in particular the overall formability will be a challenging task for future research. Based on such a work more knowledge-based improvement of DP grades will be possible. Additionally, substantial work investigating the precipitation of Nb in such grades and the impact on grain refinement will also be of high interest. Therefore, research and development efforts on microalloyed DP grades will be of fundamental interest in the future.

## TRIP grades

### Introduction

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 to 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. One approach to be followed is the addition of microalloying elements as Nb.

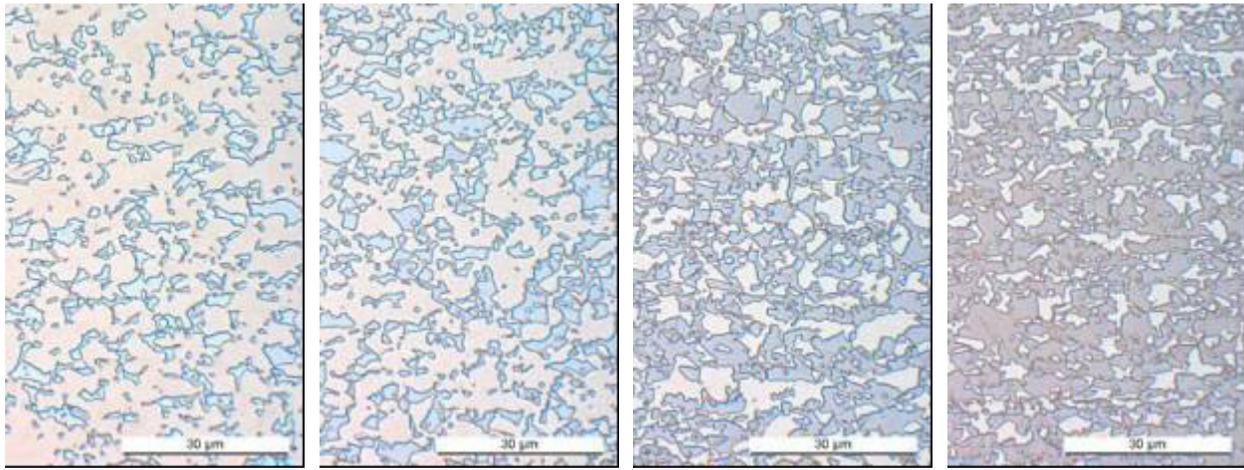
Microalloying elements such as, Nb, strengthen the ferritic matrix by means of grain refinement and precipitation hardening [9-13]. An increase of the yield and the tensile strength by approximately 15 MPa per 0.01 % of Nb is reported and this can be of particular interest for Al-based TRIP steel grades. According to [12-13], 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 is supposed to stay partly in solid solution or assist in 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 re-finishing 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 [12]. 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 [12]. Small amounts of Nb staying in solid solution are reported to retard the bainite formation kinetics [11].

In the following, a short overview of the impact of Nb on the overall behavior of TRIP steel grades is given. After reporting the influence of Nb on the phase transformations the resulting mechanical properties are discussed and necessary future work is described.

### Phase transformation and microstructure

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. [59]. For these investigations, dilatometric experiments and interrupted annealing trials together with detailed microstructure investigation and determination of the resulting mechanical properties as an indicator for phase transformations were conducted. 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. For the investigation of the ferrite formation kinetics samples were intercritically annealed at 800°C, cooled to quenching temperatures between 800 and 620°C with 10°K/s and then quenched in water. Figs. 29 and 30 show that the addition of Nb results in an increase of the ferrite formation kinetics during cooling.



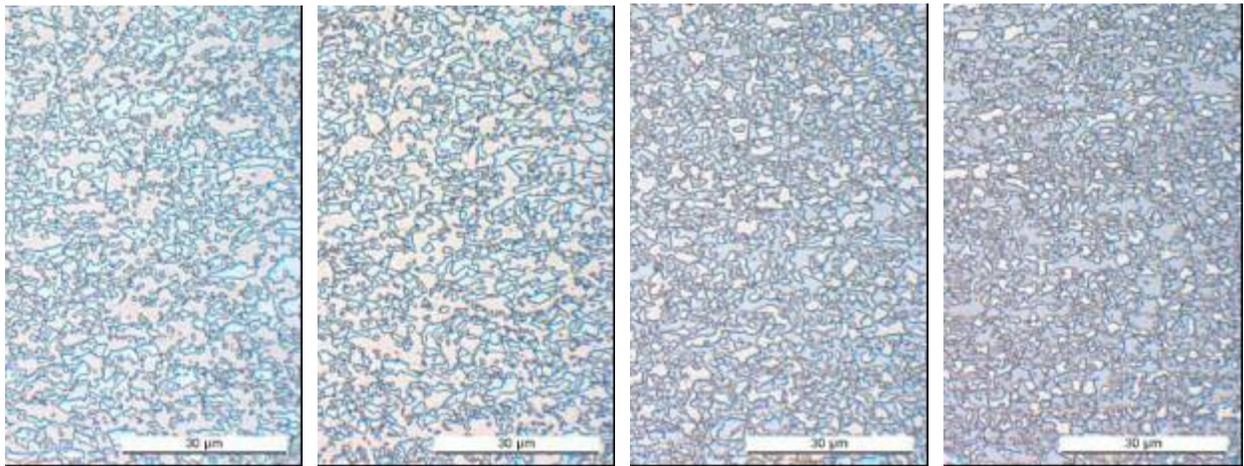
$T_Q = 800^\circ\text{C}$

$T_Q = 760^\circ\text{C}$

$T_Q = 660^\circ\text{C}$

$T_Q = 620^\circ\text{C}$

Figure 29. Influence of the quenching temperature on the microstructure of alloy containing Si (alloy A,  $T_{IC}=800^\circ\text{C}$ ,  $dT/dt=10^\circ\text{K/s}$ ); etched with LePera's etchant.



$T_Q = 800^\circ\text{C}$

$T_Q = 760^\circ\text{C}$

$T_Q = 660^\circ\text{C}$

$T_Q = 620^\circ\text{C}$

Figure 30. Influence of the quenching temperature on the microstructure of alloy containing Si and Nb (alloy B,  $T_{IC} = 800^\circ\text{C}$ ,  $dT/dt = 10^\circ\text{K/s}$ ); etched with LePera's etchant.

The measured mechanical properties show a more continuous and smooth decrease of the strength for the Nb alloyed material (Figure 31). For the material without Nb (alloy A) only a minor decrease of the strength is observed until quenching temperatures of  $700^\circ\text{C}$ . 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.

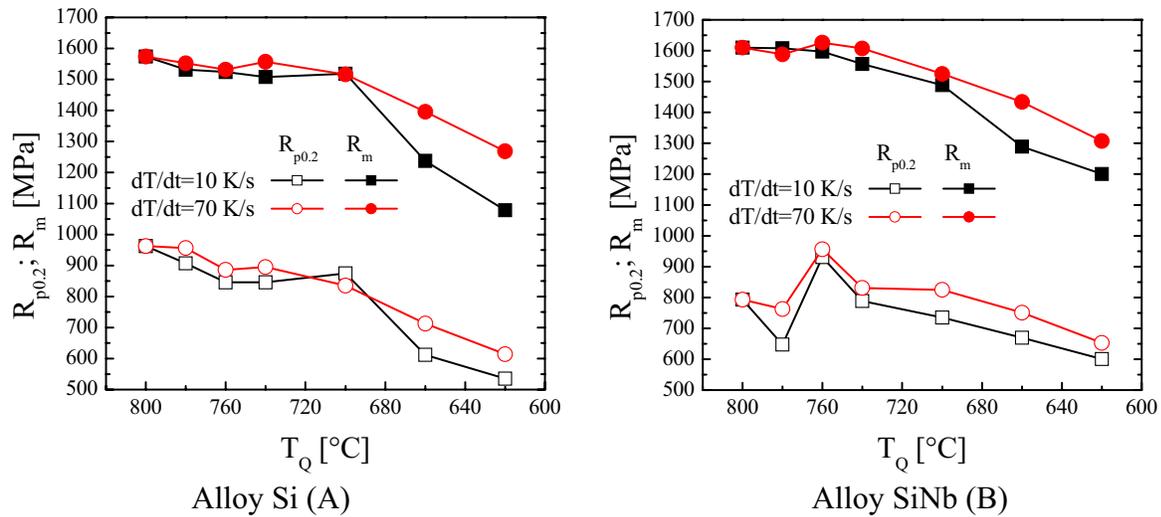


Figure 31. Yield and tensile strength of alloys A and B as a function of the quenching temperature ( $T_{IC} = 800^\circ\text{C}$ , cooling rate from intercritical annealing to the quenching temperature  $dT/dt = 10^\circ\text{K/s}$ ).

Dilatometric experiments were conducted to study also the transformation of the austenite during isothermal holding in the bainitic range [59] (Figure 32). The transformation behavior of the austenite is nearly the same for these two alloys. 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 [59].

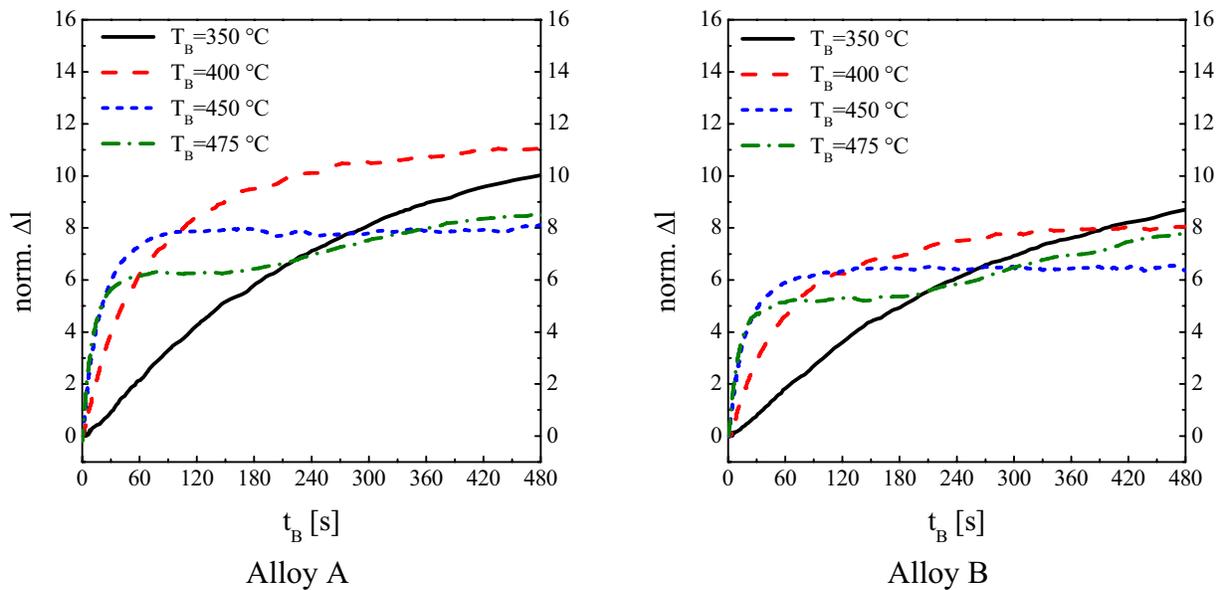
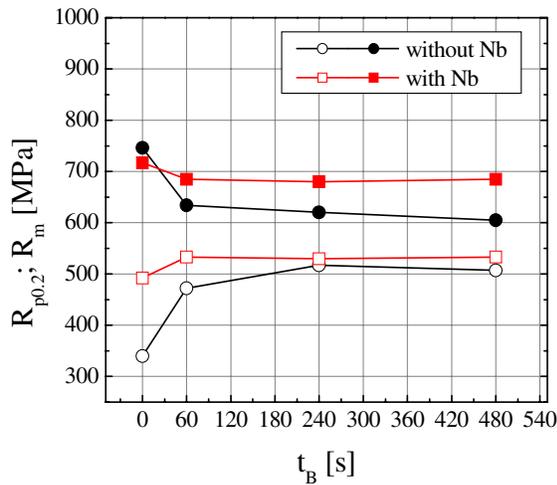


Figure 32. Influence of the isothermal holding temperature on the transformation behavior of the austenite in the bainitic range for alloys A and B ( $T_{IC} = 800^{\circ}\text{C}$ ,  $t_{IC} = 60\text{s}$ ,  $dT/dt = 70^{\circ}\text{K/s}$ ).

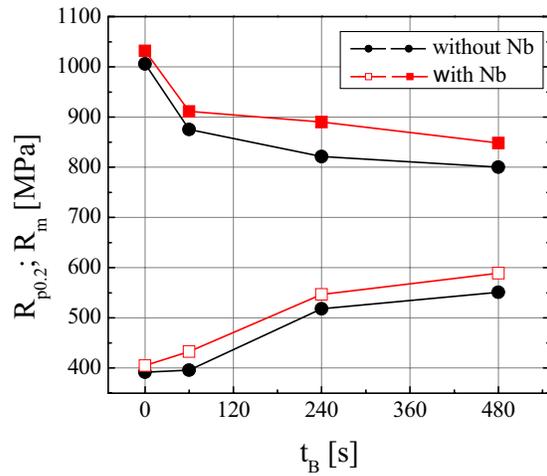
### Mechanical properties

The mechanical properties of Al and Si alloyed TRIP-steels with and without Nb are shown in Figure 33. 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 TRIP-grades. The strength level is governed mainly 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 34 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. Much further work is necessary to confirm these first results.

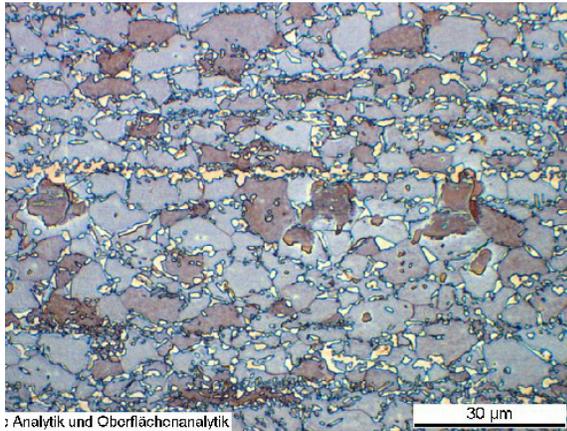


Al based TRIP

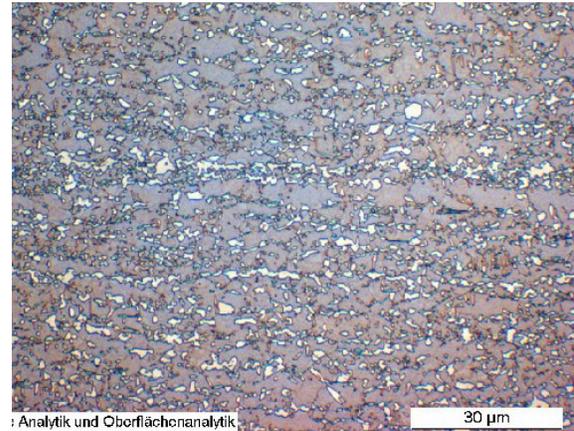


Si based TRIP

Figure 33. 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).



TRIP 700 without Nb



TRIP 700 with Nb

Figure 34. Impact of Nb addition on an industrially produced HDG TRIP 700 material.

### Future development

Basic investigations shed light on the benefit of microalloying additions such as Nb for TRIP steel grades. Besides a fine tuning of the strength level, the overall microstructure can be controlled and refined by the addition of Nb. Starting from first promising practical results, the future role of Nb in TRIP steels will be investigated in more detail. Especially for thicker material with reduced cold reduction where the refinement of the microstructure by microalloying additions may be a key point for the further improvement of TRIP steel grades.

## Summary

The mechanical properties of materials are controlled to a large extent by their microstructure. Therefore, a fundamental knowledge of the impact of alloying elements and process parameters on the resulting microstructure is essential. For mild and conventional high strength thin sheet grades, microalloying additions such as Nb control the microstructure and therefore, the mechanical properties. For mild IF grades, high strength IF grades and partially stabilized ULC grades, the impact of the microalloying additions, in particular Nb, is summarized in this work.

For advanced high strength steels (AHSS) like DP, PM and TRIP grades, the microstructure is mainly determined by alloying additions controlling the phase transformations during cooling. In this context, Mn, Cr, Mo, Si and Al are the most important alloy additions. Through well adjusted alloy designs and processing parameters, materials with appropriate microstructures and mechanical properties can be produced.

By the addition of microalloying elements, a remarkable refinement of the microstructure of AHSS grades is possible. The reduced grain sizes along with the precipitation hardening result in an increase of the strength level. Nevertheless, the increase is often only in the range of about 50 MPa and can, therefore, be used only for a fine tuning of necessary strength levels. Recent investigations indicate, however, that the overall refinement of the microstructure results in an improved formability in the press shop. Frequently, this can be explained by the improved bendability and better hole expansion behavior.

These first results being indicative for the benefits of microalloying additions to AHSS grades are promising. For a future improvement and optimization of these AHSS grades, however, extensive research work is still necessary. Such work should shed light on the quantitative relations between the microstructure and the mechanical behavior. Also, a more fundamental understanding of the precipitation sequence in these AHSS grades and its impact on grain refinement is essential for applying a knowledge based optimization of properties.

## References

1. M. Ashby, "Materials Selection in Mechanical Design", Pergamon Press, Oxford, 1992.
2. P. Stiaszny, A. Pichler, E. Tragl, M. Kaiser, W. Schwarz, M. Pimminger, K. Kösters, and K. Spiradek, "Influence of Annealing Technology on the Material Properties of LC and ULC Steel Grades", International Symposium: Modern LC and ULC Sheet Steels for Cold Forming, Department of Ferrous Metallurgy RWTH Aachen University of Technology, 1998, pp. 225.
3. N. Ohashi, T. Irie, S. Satoh, O. Hashimoto, and I. Takahashi, "Development of Cold-Rolled High Strength Steel Sheet with Excellent Deep Drawability", SAE Technical Paper Series (810027), Warrendale, 1981.
4. A. Pichler, M. Mayr, G. Hribernik, H. Presslinger, and P. Stiaszny, "High Strength IF Steels: Production, Parameters and Properties", International Forum for Physical Metallurgy of IF Steels IF.IFS-94, The Iron and Steel Institute of Japan, 1994, pp. 249.
5. L. Meyer, W. Bleck, and W. Müschenborn, 'Product-Oriented IF Steel Design', International Forum for Physical Metallurgy of IF Steels IF.IFS-94, The Iron and Steel Institute of Japan, 1994, pp. 203.

6. M. Blaimschein, K. M. Radlmayr, A. Pichler, E. Till, and P. Stiaszny, "Bake Hardening Effects in Components", *Advanced Sheet Metal Forming, Proceedings of the 19th Biennial IDDRG Congress, The University of Miskolce, Miskolce, 1996*, pp. 445.
7. T. Davenport, "Formable HSLA and Dual Phase Steels", *The Metallurgical Society of AIME, Warrendale, 1979*.
8. R. A. Kot and J. W. Morris, "Structure and Properties of Dual Phase Steels", *The Metallurgical Society of AIME, Warrendale, 1979*.
9. 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.
10. O. Matsumura, Y. Sakuma, and H. Takechi, "Enhancement of Elongation by Retained Austenite in Intercritical Annealed 0.4C-1.5Si-0.8Mn Steel", *Transaction ISIJ* 27 (1987) pp. 570.
11. V. F. Zackay, E. R. Parker, D. Fahr, and R. Busch, "The Enhancement of Ductility in High-Strength Steels", *ASM Trans. Quart.* 60 (1967) pp. 252.
12. S. V. Subramanian, M. Prikryl, A. Ulabhaje, and K. Balasubramanian, 'Thermo-Kinetic Analysis of Precipitation Behavior of Ti-Stabilized Interstitial-Free Steel', *Interstitial Free Steel Sheet: Processing, Fabrication and Properties*, eds. L. E. Collins and D. L. Baragar, Canadian Institute of Mining, Metallurgy and Petroleum, Ottawa, 1991, p. 15.
13. N. Yoshinaga, K. Ushioda, S. Akamatsu, O. Akisue, 'Precipitation Behavior of Sulfides in Ti-Added Ultra-Low-Carbon Steels in Austenite' *ISIJ* 34 (1994) 24.
14. X. Yang, D. Vanderschueren, J. Dilewijns, C. Standaert, Y. Houbaert, 'Solubility Products of Titanium Sulfide and Carbosulfide in Ultra-Low Carbon Steels', *ISIJ* 36 (1996) 1286
15. M. Hua, C.I. Garcia and A.J. DeArdo, 'Precipitation Behavior in Ultra-Low-Carbon Steels Containing Titanium and Niobium', *Metall. and mat. Trans.* 28A (1997) 1769.
16. G. Dupuis, R. A. Hubert, and R. Taillard, 'A Detailed Study of Sulphide Precipitation in Ti-IF Steels', *40<sup>th</sup> MWSP Conf. Proc.*, ISS, Warrendale, 1998, p. 117.
17. I. Gupta and D. Bhattacharya, 'Metallurgy of Formable Vacuum-Degassed Interstitial-Free Steels', *Metallurgy of Vacuum-Degassed Steel Products*, ed. R. Pradhan, The Minerals, Metals & Materials Society, Warrendale, 1990, p. 43.
18. H. Takechi, 'Metallurgical Aspects of IF Sheet Steel from Industrial Viewpoints', *Physical Metallurgy of IF Steels IF-IFS-94*, The Iron and Steel Institute of Japan, Tokyo, 1994, p. 1.
19. K. Ushioda, N. Yoshinaga, K. Koyama, and O. Akisue, 'Application of Ultra-Low-Carbon Steels to the Development of Superformable Sheet Steels, Solution-Hardened High-Strength Sheet Steels and Bake-Hardenable Sheet Steels', *Physical Metallurgy of IF Steels IF-IFS-94*, The Iron and Steel Institute of Japan, Tokyo, 1994, p. 227.
20. J. Inagaki, M. Sakurai, and M. Yamashita, 'Metallurgical Viewpoints of Producing IF Base Galvannealed Steel Sheets with Good Press Formability', *Modern LC and ULC Sheet Steels for Cold Forming: Processing and Properties*, ed. W. Bleck, Verlag Mainz, Aachen, 1998, p. 237.
21. O. Hamart, T. Jung, and S. Lanteri, 'Study of Mechanical Properties and Precipitation in High-Strength IF Steels', *40th MWSP Conf. Proc.*, ISS, 1998, Warrendale, p. 189.
22. M. Beatens, J. Dilewijns, and D. Vanderschueren, 'The Effect of Boron on the Mechanical Properties of Hot and Cold-Rolled High Strength IF Steels', *Modern LC and ULC Sheet Steels for Cold Forming: Processing and Properties*, ed. W. Bleck, Verlag Mainz, Aachen, 1998, p. 579.

23. J. S. Rege, G. I. Garcia, and A. J. DeArdo', 'The Segregation Behavior of Phosphorus and its Role in the Cold Work Embrittlement and Annealing Behavior of Ti-Stabilized Interstitial Free Steels', 39th MWSP Conf. Proc., ISS, Warrendale, 1998, p. 149.
24. A. Pichler, M. Mayr, G. Hribernig, H. Presslinger and P. Stiaszny, 'High-Strength IF-Steels: Production Parameters and Properties', Physical Metallurgy of IF Steels IF-IFS-94, The Iron and Steel Institute of Japan, Tokyo, 1994, p. 249.
25. K. P. Boyle, A. Perovic, J. D. Embury, J. G. Thomson, J. E. Hood, and D. D., Perovic, 'Some Observations on the Annealing Response and Post-Annealing Processing Effects for Fully Stabilized Steels', 39th MWSP Conf. Proc., ISS, Warrendale, 1998, p. 167.
26. K. Sakata, S. Satoh, T. Kato, and O. Hashimoto, 'Metallurgical Principles and their Applications of Producing Extra-Low Carbon IF steels with Deep Drawability and Bake Hardenability', Physical Metallurgy of IF Steels IF-IFS-94, The Iron and Steel Institute of Japan, Tokyo, 1994, p. 279.
27. A. Van Snick, D. Vanderschueren, S. Vandeputte, and J. Dilewijns, 'Influence of the Carbon Content and Coiling Temperature on Hot and Cold-Rolled Properties of Bake Hardenable Nb – ULC Steels', 39th MWSP Conf. Proc., ISS, Warrendale, 1998, p. 225.
28. W. Bleck, R. Bode, O. Maid, and L. Meyer, 'Metallurgical Design of High-Strength ULC Steels', High-Strength Sheet Steels for the Automotive Industry, ISS and AIME, Warrendale, 1994, p. 141.
29. N. Mizui, 'Precipitation Control and Related Mechanical Properties in Ultra Low Carbon Sheet Steels', Modern LC and ULC Sheet Steels for Cold Forming: Processing and Properties, ed. W. Bleck, Verlag Mainz, Aachen, 1998, p. 169.
30. K. A. Taylor and J. G. Speer, 'Development of Vanadium-Alloyed Bake-Hardenable Sheet Steels for Hot-Dip Coated Applications', 39th MWSP Conf. Proc., ISS, Warrendale, 1998, p. 49.
31. R.C. Sharma, V.K. Lakshmanan, J.S. Kirkaldy, 'Solubility of Niobium Carbide and Niobium Carbonitride in Alloyed Austenite and Ferrite', Met. Trans. 15A, 545 (1984).
32. D.C. Houghton, 'Equilibrium Solubility and Composition of Mixed Carbonitrides in Microalloyed Austenite', Acta Metall. et Mater. 41, 2993 (1993).
33. H. Fischmeister and B. Karlsson, 'Plastizitätseigenschaften grob-zweiphasiger Werkstoffe', Z. Metallkde. 68 (1977) 311.
34. M. F. Ashby, 'The deformation of plastically non-homogeneous materials', Phil. Mag. 21 (1969) 399 – 424.
35. U. Lidl, S. Traint, E. A. Werner, 'An unexpected feature of the stress/strain diagram of dual-phase steel', Comput. Mater. Sci.
36. A. Pichler, H. Spindler, K. Spiradek, and P. Stiaszny, 'ULC Steels, A Basis for the Production of Thin Sheet Grades with Excellent Formability', IF Steels 2000 Proceedings, ISS, Warrendale, 2000, p. 69.
37. T. Davenport, 'Formable HSLA and Dual Phase Steels', The Metallurgical Society of AIME, Warrendale, 1979.
38. P. Tsipouridis, C. Kremaszkey, E. Werner, E. Tragl, S. Traint, A. Pichler, 'Influence of grain refinement on the mechanical properties of dual phase steel, MST 2004 p. 735.
39. O. Matsumura, Y. Sakuma, and H. Takechi, 'Retained Austenite in 0.4C - Si - 1.2 Mn Steel Sheet Intercritically Heated and Austempered', ISIJ International 32 (1992) 1014.

40. 17. Y. Sakuma, O. Matsumura, and H. Takechi, 'Mechanical Properties and Retained Austenite in Intercritically Heat-treated Bainite-Transformed Steel and their Variation with Si and Mn Additions', *Met. Trans.* 22A (1991) 489.
41. Y. Sakuma, O. Matsumura, and O. Akisue, 'Influence and Annealing Temperature on Microstructure and Mechanical Properties of 400 °C Transformed Steel Containing Retained Austenite', *ISIJ International* 31 (1991) 1348.
42. K. Sugimoto, N. Ususi, M. Kobayashi, and S. Hashimoto, 'Effects of Volume Fraction and Stability of Retained Austenite on Ductility of TRIP-aided Dual-phase Steels', *ISIJ International* 32 (1992) 1311.
43. K. Sugimoto, M. Kobayashi, and S. Hashimoto, 'Ductility and Strain-Induced Transformation in a High-Strength Transformation-Induced Plasticity-Aided Dual-Phase Steel', *Met. Trans.* 23A (1992) 3085.
44. K. Sugimoto, M. Misu, M. Kobayashi, and H. Shirasawa, 'Effects of Second Phase Morphology on Retained Austenite Morphology and Tensile Properties in a TRIP-aided Dual-Phase Steel Sheet', *ISIJ International* 33 (1993) 775.
45. W. C. Jeong, D. K. Matlock, and G. Krauss, 'Observation of Deformation and Transformation Behavior of Retained Austenite in a 0.14C-1.2Si-1.5Mn Steel with Ferrite-Bainite-Austenite Structure', *Mat. Sci. and Eng.* A165 (1993) 1.
46. W. C. Jeong, D. K. Matlock, and G. Krauss, 'Effects of Tensile-Testing Temperature on Deformation and Transformation Behavior of Retained Austenite in a 0.14C-1.2Si-1.5Mn Steel with Ferrite-Bainite-Austenite Structure', *Mat. Science and Eng.* A165 (1993) 9.
47. Itami, M. Takahashi, and K. Ushioda, 'Plastic Stability of Retained Austenite in the Cold - Rolled 0.14 % C - 1.9 % Si - 1.7 % Mn Sheet Steel', *ISIJ International* 35 (1995) 1121.
48. H. C. Chen, H. Era, and M. Shimizu, 'Effect of Phosphorus on the Formation of Retained Austenite and Mechanical Properties in Si-Containing Low-Carbon Steel Sheet', *Met. Trans.* 20A (1989) 437.
49. Thyssen Stahl AG, DE Patent 196 10 675 C1, 'Mehrphasenstahl und Verfahren zu seiner Herstellung' March 19, 1996.
50. A. Pichler, P. Stiaszny, R. Potzinger, R. Tikal, and E. Werner, 'TRIP Steels with Reduced Si Content', 40th Mechanical Working and Steel Processing Conference Proceedings, ISS, Warrendale, 1998, p. 259.
51. M. De Meyer, D. Vanderschueren, and B. De Comman, 'The Influence of Al on the Properties of Cold Rolled C-Mn-Si TRIP Steels', 41st Mechanical Working and Steel Processing Conference Proceedings, ISS, Warrendale, 1999, p. 265.
52. M. De Meyer, D. Vanderschueren, K. De Blauwe, and B. De Comman, 'The Characterization of Retained Austenite in TRIP Steels by X-Ray Diffraction', 41st Mechanical Working and Steel Processing Conference Proceedings, ISS, Warrendale, 1999, p. 483.
53. S. Traint, A. Pichler, R. Tikal, P. Stiaszny, and E. A. Werner, 'Influence of Manganese, Silicon and Aluminum on the Transformation Behavior of Low Alloyed TRIP-Steels', 42nd Mechanical Working and Steel Processing Conference Proceedings, ISS, Warrendale, 2000, p. 549.
54. M. De Meyer, D. Vanderschueren, and B.C. De Cooman, 'The influence of the substitution of Si by Al on the properties of cold rolled C-Mn-Si TRIP steels', *ISIJ International* 39 (1999) 813.

55. P. Jacques, E. Girault, T. Catlin, N. Geerlofs, T. Kop, S. van der Zwaag, and F. Delanny, 'Bainite Transformation of Low Carbon Mn – Si TRIP-assisted Multiphase Steels: Influence of Silicon Content on Cementite Precipitation and Austenite Retention', *Mat. Science and Engineering A273 – 275* (1999) 475.
56. T. Akbay and C. Atkinson, 'The Influence of Diffusion of Carbon in Ferrite as Well as in Austenite on a Model of Reaustenitization from Ferrite/Cementite Mixtures in Fe - C Steels', *J. of Mat. Sci.* 31 (1996) 2221.
57. T. Minote, S. Torizuka, A. Ogawa, and M. Niiura, 'Modeling of Transformation Behavior and Compositional Partitioning in TRIP Steel', *ISIJ International* 36 (1996) 201.
58. A. Pichler, S. Traint, G. Arnoldner, E. Werner, R. Pippan, and P. Stiaszny, 'Phase Transformation during Annealing of a Cold-Rolled Dual Phase Steel Grade', 42nd Mechanical Working and Steel Processing Conference Proceedings, ISS, Warrendale, 2000, p. 573.
59. S. Traint, A. Pichler, K. Spiradek-Hahn, K. Hulka, E. Werner, "The influence of Nb on the phase transformations and mechanical properties in Al- and Si-alloyed TRIP-steels", *Proceedings of Symposium Austenite Formation and Decomposition*, Chicago, Illinois, Nov. 9-12, 2003, p. 577-594.
60. S. Traint, A. Pichler, K. Spiradek-Hahn, P. Stiaszny, C. Kremaszky, E. Werner, , Microstructure characterization of cold-rolled dual-phase steels, 2<sup>nd</sup> International Conference on Thermomechanical Processing of Steels '2004, *Stahl&Eisen*, p. 448.