

THE USE OF MOLYBDENUM AND NIOBIUM IN ULTRA-HIGH STRENGTH MULTIPHASE STEELS

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Abstract

Multiphase steels such as DP (Dual Phase), TRIP (Transformation Induced Plasticity) and CP (Complex Phase) can be produced either directly from the as rolled heat or via an additional heat treatment, usually after cold rolling. The latter has become the dominating route in automotive steel production. The primary effect of Mo alloying is to modify the phase fields in the CCT diagram in such a way that a sufficiently large processing window enables stable production with little property scatter in the final product. Niobium microalloying can improve the strength of multiphase steels in various ways. It is also particularly beneficial with regard to the phase morphology and homogeneity leading to a significant improvement of the mechanical properties. This paper will show processing strategies involving Mo and Nb and explain their metallurgical effects.

Challenges to Modern Vehicle Construction

No other industrial sector has pursued weight reduction as vigorously as the automotive industry. This has been motivated by the need to reduce fuel consumption and emissions as well as the requirement to improve crash safety, and these continue to be major technical targets. The total vehicle weight has an important impact in this respect as indicated in Figure 1. Indisputably, the fuel consumption and thus the CO₂ emissions decrease with reducing vehicle weight. Several studies have indicated that a weight reduction of 100 kg can lead to savings in fuel consumption of 0.15 to 0.5 liters per 100 km [1]. This corresponds to a reduction in CO₂ emissions of between 4 and 12 g/km. The intensive use of lighter materials is effectively offering a significant weight reduction potential. Another possibility for reducing emissions is to use hybrid engine technology, however in this case vehicles tend to become heavier due to a weight increase of the power train. Very efficient in terms of emission reduction is engine downsizing which simultaneously leads to a weight reduction of the power train. Lighter vehicles not only reduce fuel consumption but also feature faster acceleration, shorter braking distances and overall better handling.

The body-in-white (BIW), i.e. the body structure, including all hang-on parts such as fenders, doors and lids, constitutes the largest contribution to the total vehicle weight. Furthermore, the BIW is also primarily responsible for the weight increase from one vehicle generation to the next as bodies usually become bigger and crash requirements are increased. The weight of the BIW ranges roughly from 300 to 500 kg depending on vehicle size [2]. Consequently, many efforts have been made by the industry to lighten the BIW [3]. Bodies using an advanced steel design

usually account for 28 to 35% of the total vehicle weight. In some sports cars and larger sized luxury vehicles, bodies are manufactured from aluminum, reducing the BIW weight contribution to between 16 and 20%. Many of today’s mid-size vehicles apply a mixed materials concept for the BIW where the body structure is made with an advanced steel concept and hang-on parts are made from aluminum or plastics. This appears to be a good compromise between weight reduction, manufacturing complexity and cost.

The advanced steel BIW is the most cost-efficient way of reducing the vehicle weight. Weight reductions of 20 to 25% compared to a conventional steel body can be achieved at a simultaneously reduced cost [4]. Alternatively, when applying low-density materials such as aluminum, magnesium or plastics, weight reduction leads to a significantly increased cost of the BIW. Therefore steel remains the preferred material for vehicle construction. Additionally, established manufacturing technology such as press stamping, roll profiling and welding can still be used. In terms of steel development, the requirements of modern steels for vehicle construction are defined as being strong, formable, weldable and cost attractive.

Most of the components used for BIW, suspension, chassis or frame are produced from flat steel that comes either as hot rolled strip (for heavier gauges) or cold rolled strip (typically for gauges below 3 mm). The BIW of modern passenger cars contains up to 80% high strength steel of which the majority is covered by traditional (ferritic, ferritic-pearlitic or bainitic) HSLA steel. Multiphase steels, Figure 2, offering a good compromise of high strength and adequate elongation, have been gaining a significant share since the late 1990s. More recently, press-hardening steel (PHS) with a typical strength of above 1200 MPa has been introduced for applications requiring an extreme resistance against crash impact.

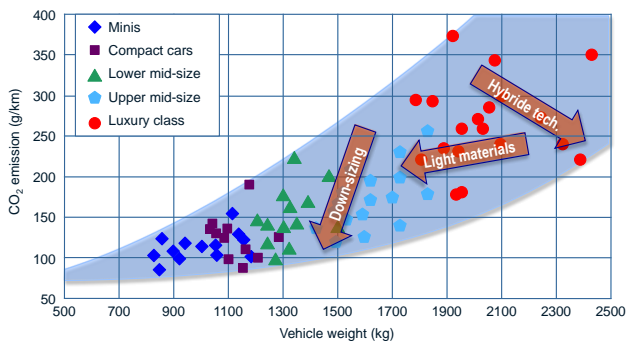


Figure 1. Influence of vehicle (curb) weight on CO₂ emission and concepts for reducing weight and emissions.

Molybdenum and niobium alloying is applicable to both hot rolled and cold rolled high strength steels. Niobium can be considered as an essential microalloying element in almost all high strength automotive flat steels. Besides its effect of grain refinement, niobium is also used for scavenging carbon (applicable to IF and BH steels), precipitation hardening and transformation

control. Mo alloying brings about valuable metallurgical advantages, especially when producing automotive steels with strengths exceeding 500 MPa. Mo suppresses the formation of ferrite and pearlite allowing the formation of bainite or martensite which are essential ingredients of multiphase steels.

Multiphase steels such as DP (Dual Phase), TRIP (Transformation Induced Plasticity) and CP (Complex Phase) steel can be produced either directly from the as rolled heat or via an additional heat treatment, usually after cold rolling. The latter has become the dominating route in automotive steel production.

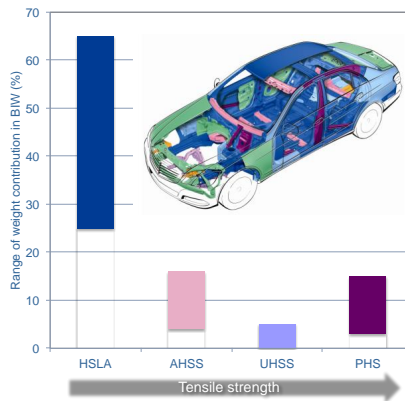


Figure 2. Contribution (min-max) of high strength steel classes to the total body-in-white (BIW) weight in the vehicle generation 2009-2010.

Hot Rolled Multiphase Steels

Hot rolled multiphase steel is used for heavier gauge applications such as used in chassis parts, anti-intrusion beams, reinforcements, and wheels. Hot-rolled dual phase and complex phase steel with tensile strengths of 600 and 800 MPa are the grades of most relevance.

Dual Phase Steel

Dual phase (DP) steels are characterized by a unique combination of strength and formability. Their soft ferritic matrix accounts for a low yield strength and good ductility whereas dispersed hard martensite islands ensure a high tensile strength. The resulting low yield-to-tensile strength ratio provides a high strain hardening capacity making these steels particularly suitable for uniaxial or biaxial stretching. With regard to crash deformation, this behavior also guarantees high energy absorption capability. Due to their high tensile strength, DP steels are also very suitable for applications subjected to cyclic loading.

During the production of dual phase steel directly from the rolling, the cooling strategy on the run-out table must allow sufficient formation of pro-eutectoid ferrite (matrix phase) without nucleation of pearlite. The carbon is partitioned to the remaining austenite phase, increasing its stability against transformation to ferrite. The boundary conditions are defined by the exit speed of the strip from the last finishing stand, the length of the run-out table, the configuration of the cooling headers and the coiling temperature. Accordingly, it becomes necessary to modify the CCT diagram by alloying in order to produce a ferritic-martensitic dual phase microstructure. The challenge is to avoid bainite or pearlite formation and to have the desired share of soft polygonal ferrite in the microstructure, typically 70-85% for the most common grades. The remaining carbon enriched austenite is transformed into martensite upon further cooling.

By way of reducing carbon diffusivity and exerting a strong drag force on moving grain (phase) boundaries, Mo delays ferrite formation and, to a much stronger extent, pearlite formation. Other bulk alloying elements like Mn and Ni also delay ferrite and pearlite formation. However the effectiveness of Mo is about 3 times stronger than that of Mn and 6 times stronger than that of Ni [5].

Two principal cooling strategies can be practiced depending on the capabilities of the run out table cooling arrangement, Figure 3. In single-step cooling the activation of accelerated cooling by water is delayed to allow sufficient formation of ferrite after finish rolling. Accelerated cooling is then applied to enable coiling below the martensite start temperature. The position of the ferrite nose in the CCT diagram has to be adapted to the required cooling path, by alloying. Using two-step cooling, fast cooling to a temperature of around 700 °C is applied right after finish rolling. Cooling is then interrupted and a stage of quasi-isothermal holding allows sufficient ferrite formation. Finally, the second cooling step aims for a coiling temperature of below 250 °C converting carbon-enriched austenite into martensite. It is apparent from Figure 3 that increasing the time gap between the initial bainite-martensite phase field and the pearlite phase field enhances the processing window regardless of the cooling strategy. Yet, the two-step cooling process is the preferable strategy. Molybdenum alloying can most efficiently influence the phase fields in the CCT diagram [6]. Figure 4 demonstrates the effect of Mo on the relevant times of ferrite start, pearlite start and 75% ferrite formation. It is evident that, for the given base alloy, the addition of 0.1% Mo sufficiently delays the pearlite start to allow the formation of 75% ferrite. Mo has a pronounced effect on the pearlite nose, shifting it by several orders of magnitude in time as the Mo content is raised from 0% to 0.50%. Its retarding effect on the polygonal ferrite reaction is much smaller; with the net result being that Mo increases the window of allowable cooling rates (CR_{max}/CR_{min}) very strongly. The effects of Cr and Si on the allowable cooling rates are much smaller than that of Mo, however, an inherent benefit of Si is the acceleration of polygonal ferrite formation. Si and Cr also contribute to the hardenability of austenite islands. Thus Mo additions in the range of 0.1-0.2% appears a reasonable compromise between processing conditions and alloy cost. More severe austenite conditioning, promoted by a microalloy addition of Nb and the consequent faster ferrite nucleation, can counteract the small delay in ferrite formation caused by Mo.

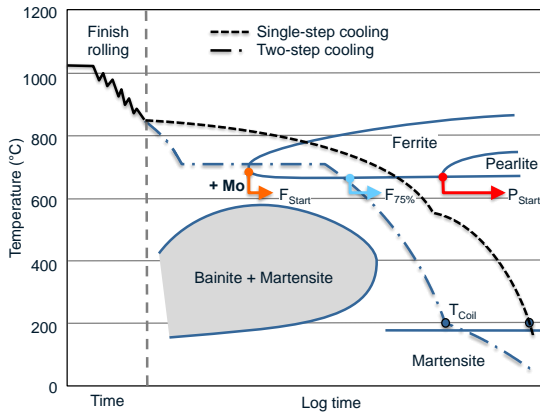


Figure 3. Finishing strategies for hot-rolled dual phase steel and the effect of Mo-alloying on the ferrite and pearlite phase fields.

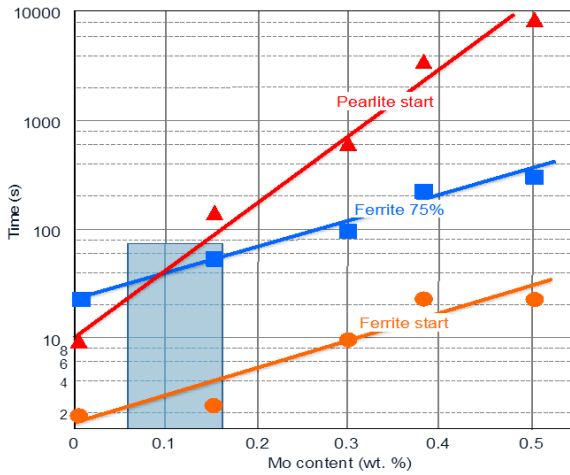


Figure 4. Effect of Mo-alloying on the ferrite and pearlite start time after finish rolling and typical alloy range for production of hot-rolled DP600.

Nb microalloying of hot rolled DP steel results in a significantly higher yield and tensile strength. The total elongation (A_{80}) for this much stronger Nb microalloyed variant is only slightly reduced at low cooling temperatures ($<250\text{ }^{\circ}\text{C}$). A small addition of 0.04% Nb to the base alloy (0.11% C, 0.1% Si, 1.2% Mn, 0.8% Cr) lifts the tensile strength by around 200 MPa at lower

coiling temperatures and by around 100 MPa at higher coiling temperatures, Figure 5. The Nb-alloyed variant would still meet the strength requirements of DP600 after coiling at 350 °C. However, the yield to tensile strength ratio also increases from around 0.6 to above 0.7 indicating that the typical dual phase character is being lost at increasing coiling temperatures. The total elongation is only slightly reduced for the Nb-alloyed variant at lower coiling temperatures. Thus, Nb microalloying of the DP600 base grade can achieve a DP780 strength level with comparably good elongation and low yield-to-tensile ratio.

The tensile strength of DP steel is basically controlled by the martensite content and increases linearly with the martensite fraction. The addition of 0.05%Nb to a 0.18%C-Mn-Si-Cr base alloy results in an increase of the tensile strength by 100-150 MPa, Figure 6, at any martensite level [7]. Consequently by Nb microalloying, a specified strength level can be achieved with a lower martensite content and hence a better elongation. Niobium microalloying in combination with a high cooling rate results in an extremely fine-grained microstructure, as demonstrated in Figure 6. The finish rolling temperature appears to have no significant influence on the grain size.

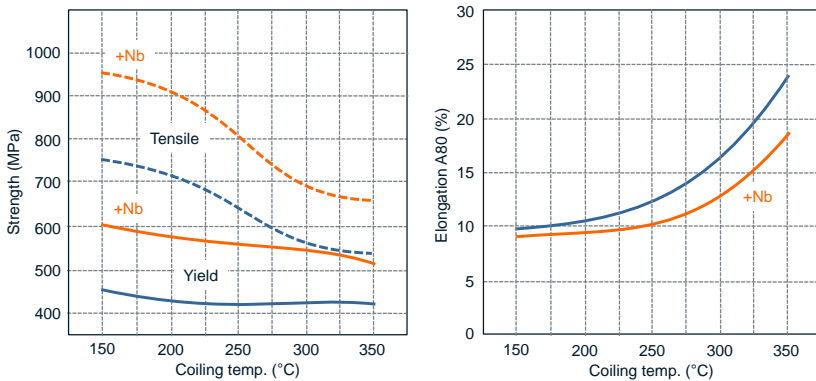


Figure 5. Effect of 0.04%Nb on strength and elongation of hot-rolled DP steel (0.11%C, 0.1%Si, 1.2%Mn, 0.8%Cr) as a function of coiling temperature.

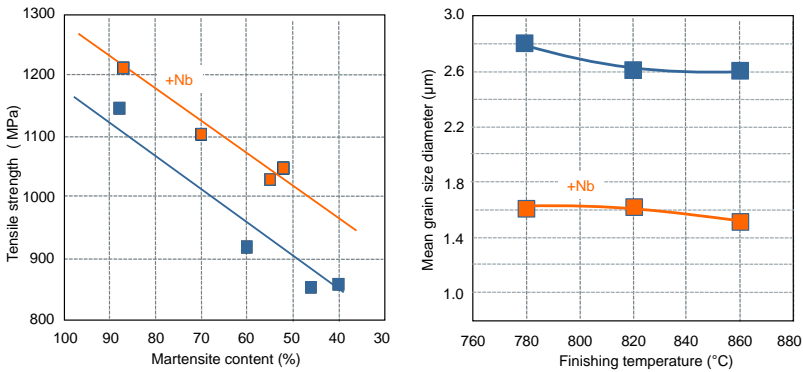


Figure 6. Effect of 0.05%Nb on tensile strength as a function of martensite fraction (cooling temperature 200 °C) and average grain size of hot-rolled DP steel (0.18%C-Mn-Si-Cr) as a function of finish rolling temperature.

Complex Phase Steel

Complex phase (CP) steels cover the very high tensile strength range of 800 to 1000 MPa and still offer reasonably good cold forming properties. Compared to DP steels of the same tensile strength, CP steel has a considerably higher yield strength but lower elongation. CP steel is very suitable for components that require high deformation resistance in the event of a crash, therefore most applications are found in the lateral crash reinforcement structure.

CP steels have a microstructure consisting of ferrite, bainite and martensite together with a small amount of retained austenite. The best compromise between high strength and good elongation essentially depends on the combination of microstructural constituents. The amount of martensite primarily determines the tensile strength. The yield strength is influenced by the grain size, the amount of bainite as well as by possible precipitation of microalloy carbides. Retained austenite ensures sufficient elongation. The excellent bendability and stretch-flangeability of these steels are due to the considerable amounts of bainite and/or tempered martensite, and suppression of the formation of polygonal ferrite, which results in a lower hardness difference between the microstructural constituents present. Also, the extremely fine-grained microstructure of CP steel (ASTM 14-15) is favorable with regard to strength and hole-expansion behavior. This grain refinement is mainly promoted by Nb microalloying in combination with intensive non-recrystallizing rolling and fast cooling after finish rolling.

The characteristic microstructure of CP steel is achieved when austenite transforms into several phases such as ferrite, martensite, bainite and retained austenite. The alloying concept and processing differ from that of a hot rolled DP steel. The cooling rate is adjusted so that only a relatively small amount of soft, polygonal ferrite is formed, and coiling occurs at a higher temperature in the bainite phase field. During bainite formation, carbon partitions to the remaining austenite phase, and the latter decomposes into martensite and retained austenite. In order to achieve sufficient carbon enrichment in the untransformed austenite it is important not to

lose carbon by carbide precipitation, i.e. formation of pearlite at higher temperatures, and cementite precipitation in bainite should be suppressed. When the coiling temperature is set to a low value, below 550 °C, the kinetics of microalloy carbide formation is very slow. Therefore, most of the microalloy content, which was not precipitated during austenite conditioning, will remain in solution. The optimum coiling temperature for a Mo-Nb alloyed CP steel, to achieve maximum precipitation hardening, was found to be in the range of 585-610 °C [8].

To bring all effects together, a stepped cooling schedule on the run-out table is necessary. Fast cooling after finish rolling into the ferrite phase field prevents recrystallization thus providing transformation from a pancaked austenite structure. Slow cooling in the ferrite phase field allows sufficient formation of ferrite phase which provides reasonable elongation in the final product. This is followed by a second fast cooling step to the coiling temperature.

Molybdenum alloying can contribute to the production of CP steel in different ways. During finish rolling it helps prevent partial dynamic recrystallization caused by high strain accumulation. This effect supports the transformation into a very fine-grained and homogeneous final microstructure. Molybdenum also retards the strain-induced precipitation of microalloying elements making them available for strengthening in the final product. As in DP steel, Mo prevents the formation of pearlite, which would result in a loss of solute carbon (stabilizing austenite) and deteriorate the final properties. The decomposition of undercooled austenite preferably occurs into carbide-free bainite, promoted by Si or Al alloying. Thus the remaining austenite is further enriched with carbon and the martensite-start temperature drops, and hence the chance of stabilizing retained austenite in the final product increases. Solute microalloying elements, typically Nb and Ti, together with Mo, provide excellent tempering resistance. This is important when the hot rolled strip is to be coated on a hot dip galvanizing line. By using an appropriate time-temperature cycle, the solute microalloying elements mainly co-precipitate with Mo thus increasing the yield and tensile strength [9].

Figure 7 summarizes the characteristic features of hot rolled high strength steels. Single-phase steels with bainitic or ferritic microstructures are the best performers with regard to hole expansion ratio. These steels also have a high yield to tensile ratio (YR) indicating limited work hardening. Multi phase steels perform well with regard to elongation. They have a low yield-to-tensile ratio thus featuring pronounced work hardening capability.

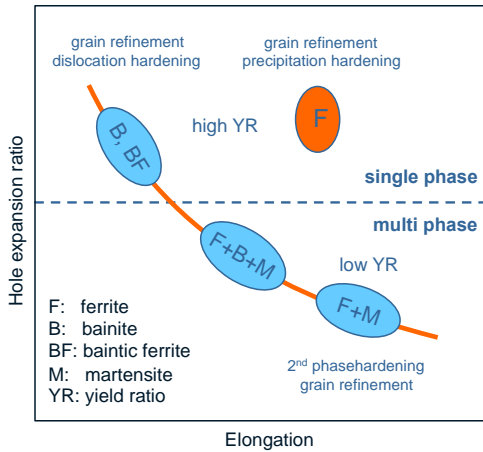


Figure 7. Relationship between elongation and hole-expansion ratio in single and multiphase steels.

Cold Rolled Annealed Multiphase Steels

The majority of flat steels used for light vehicle body construction are cold rolled and annealed materials covering the gauge range from 0.5 to 2.5 mm. The hot strip is mainly conditioned to have a ferritic or ferritic-pearlitic microstructure prior to cold rolling in order to keep the rolling loads low. For conventional steels, the annealing temperature after cold rolling is below A_{r1} . In this case, recrystallization of the heavily deformed cold rolled microstructure occurs but the phase composition of the hot rolled precursor strip is retained. When producing multiphase steels, the annealing temperature is raised into the intercritical region between A_{C1} and A_{C3} . In this case, some part of the cold deformed material recrystallizes whereas the rest transforms into austenite and existing cementite is dissolved. The actual annealing temperature determines the share of austenite generated. The cooling strategy after annealing controls the decomposition of austenite into phases like martensite, bainite or retained austenite. A continuous annealing line or a hot dip galvanizing line is necessary for such processing of multiphase steels. The grain size in the cold rolled annealed strip is always somewhat larger than that of the hot rolled mother strip due to grain growth during annealing.

Cold rolled multiphase steels can be divided into three groups: DP steels, TRIP (Transformation Induced Plasticity) steels, and partially martensitic steels (PM). The superior strength-ductility balance of multiphase steels is due to the tailored combination of soft and hard phases and, additionally, in the case of TRIP steels, the presence of metastable austenite. The tensile strength of these steels ranges between 450 and 1000 MPa and minimum total elongation (A_{80}) values lie between 7 and 27%.

In cold rolled strip, the amount of ferrite in the multiphase microstructure is adjusted by intercritical annealing between the A_{C1} and A_{C3} temperatures, Figure 8. The newly formed austenite fraction enriches in carbon and transforms into ferrite, bainite, martensite or stays as retained austenite, depending on the cooling program. The production of such steels requires a continuous annealing line (CAL) or a continuous galvanizing line (CGL).

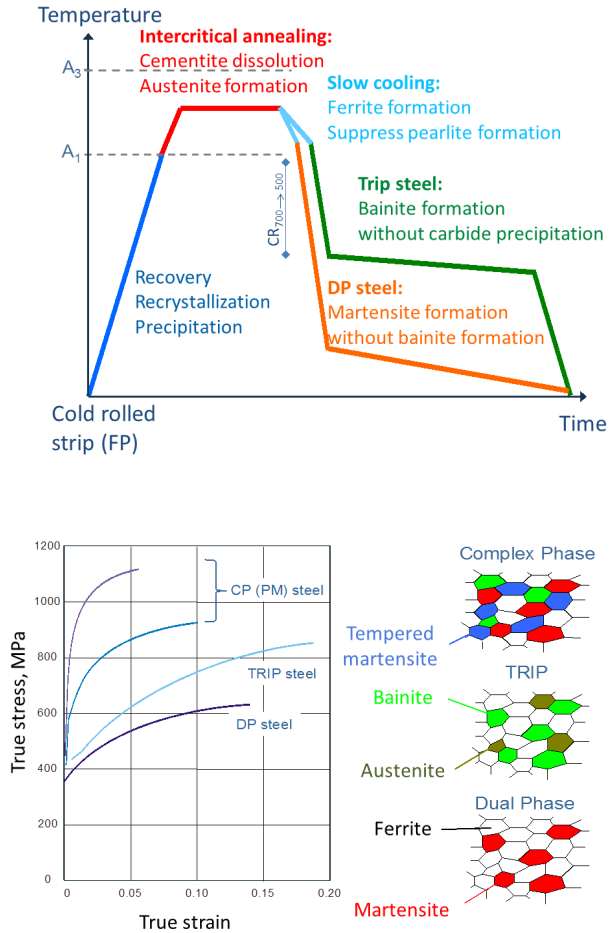


Figure 8. Schematic continuous annealing time-temperature curve for production of multiphase microstructures in low carbon steel and characteristics of multiphase steels.

Intercritical Annealed Dual Phase Steel

In the DP production route the carbon-enriched austenite is rapidly cooled below the martensite start temperature without forming any other phases. Obviously, for the DP steel route it is important to apply a high cooling rate to avoid bainite formation. This becomes particularly relevant for low-carbon DP alloys, which are preferred by carmakers due to their better weldability. Figure 9 indicates the critical cooling rate for a 0.05% C-Mn steel [12]. Increasing the Mn content indeed reduces the critical cooling rate, however, a too high Mn content can cause significant casting problems and centerline segregation. Therefore it is common to add other hardenability elements such as Cr or Mo or a combination of both. Molybdenum is approximately 3 times more effective than Cr in reducing the critical cooling rate. It allows the production of DP steel even on less powerful galvanizing lines that are not specifically equipped with a high speed cooling section. Furthermore, a small addition of Mo tremendously widens the process window, making production more robust against line speed and cooling rate variations. These can occur when a wider spectrum of sheet gauges has to be processed. Table I demonstrates several DP steel concepts currently in industrial production. Many of these concepts (B, D, F) use Mo in combination with Cr. Only galvanizing lines equipped with fast cooling sections specifically designed for multiphase steel production use Cr-only alloy concepts (A, E, G). The more exotic alloy concept, C, combines high Al with Mo alloying and appears to be a derivative of a TRIP steel concept. The production of DP780 (H, I, J) often involves an increase of the Mn content in combination with Cr and Mo alloying. Nb microalloying is more common in these grades as compared to DP600.

Nb microalloying has multiple effects with regard to the metallurgical mechanisms occurring during the intercritical annealing cycle. Nb precipitates usually exist in the hot rolled strip when coiling at conventional temperatures in the range of 600-650 °C. Any Nb remaining in solid solution has the potential to precipitate in-situ during the annealing cycle. The precipitation potential is enhanced when the coiling temperature is lowered to 500-550 °C as more Nb is retained in solid solution. This coiling condition also results in a very fine bainitic microstructure. Figure 10 shows the evolution of Nb precipitation during a CGL cycle. It is obvious that Nb precipitation is practically complete after reaching the intercritical soaking phase. For the bainitic coiling condition, most of the Nb is retained in solid solution, which then precipitates during the heating cycle as very fine particles giving a significant contribution to strengthening. The existing precipitates, produced in larger amounts after conventional coiling, are subjected to some degree of coarsening during the heating phase of the annealing cycle and hence have less effect on strength.

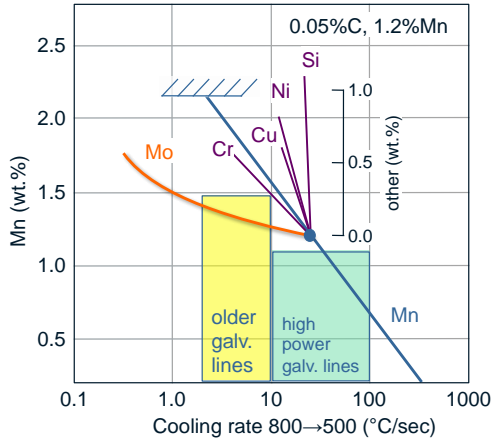


Figure 9. Relationship between critical cooling rate and alloying elements to produce ferritic-martensitic dual phase microstructure.

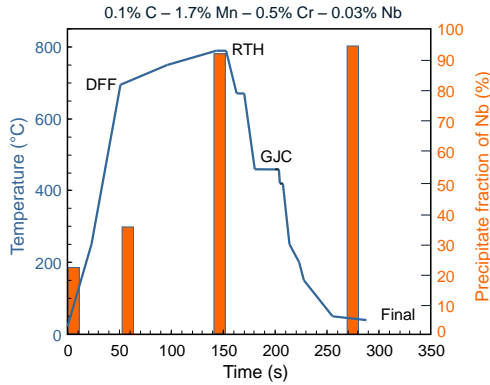


Figure 10. Progress of NbC precipitation (hot strip CT: 525 °C) during the intercritical annealing cycle.

Table I. Industrial Alloying Concepts for Dual Phase (DP) Steel Grades with 600 and 780 MPa Minimum Tensile Strength (wt%)

Grade		C	Si	Mn	Al	Cr	Mo	Ti	Nb
DP600	A	0.09	0.13	1.5	0.05	0.75	-	-	-
	B	0.12	0.30	1.4	0.03	0.25	0.08	0.01	-
	C	0.10	0.07	1.2	0.91	-	0.19	-	-
	D	0.10	0.18	1.4	0.04	0.15	0.20	-	-
	E	0.11	0.21	1.5	0.03	0.45	-	0.03	-
	F	0.07	0.15	1.9	0.05	0.21	0.18	-	-
	G	0.09	0.25	1.8	0.04	0.40	-	-	0.03
DP780	H	0.16	0.17	1.7	0.03	0.32	0.16	-	-
	I	0.15	0.18	2.1	0.04	0.26	-	-	0.03
	J	0.08	0.05	1.9	0.03	0.50	0.15	-	0.02

Nb delays the recrystallization of cold deformed ferrite either by precipitation or by the solute drag effect of Nb on the grain boundaries. Experience with Nb alloyed DP steel indicated that the recrystallization temperature is typically raised by around 20 °C as compared to the same base composition without a Nb addition. The retarded recrystallization also preserves dislocation networks that act as nucleation sites for austenite. Hence, austenite formation should be accelerated in Nb alloyed DP steels. On the other hand, the grain-refined microstructure of Nb microalloyed strip additionally provides an increased grain boundary area which increases nucleation sites for austenite when annealing in the intercritical temperature range. Measurements have indeed confirmed that at a given intercritical annealing temperature the amount of austenite in the Nb alloy is higher compared to the Nb-free base alloy [13]. During the soaking phase, carbon partitioning is accelerated and more homogeneous in the finer grained microstructure of the Nb alloyed strip due to the shorter diffusion distances in the smaller grains. By slow cooling to the quenching temperature, a defined amount of new ferrite is nucleated from the existing austenite. Again, the refined microstructure of the Nb microalloyed steel exhibits quicker kinetics of this ferrite formation. A consequence of the enhanced amount of ferrite is that the remaining austenite phase is further enriched in carbon. This means that the hardenability of the carbon enriched and smaller austenite grains is increased. With regard to mechanical properties, Nb microalloyed DP steel should have less but stronger martensite as a second phase when subjected to a given annealing cycle as compared to the Nb-free base alloy. The systematic variation of annealing and quenching temperatures reveals that the Nb microalloyed DP steel always has the higher tensile strength, Figure 11, however its yield strength decreases with increasing annealing temperature due to delayed recrystallization at lower annealing temperature. In combination, this leads to better formability expressed by a lower yield-to-tensile ratio and higher total elongation. The variation of quenching temperature shows a significantly smaller impact on the properties of the Nb microalloyed variant since the transformation kinetics in the finer grained material is faster. The work hardening rate is directly proportional to the square root of the martensite share and inversely proportional to the square root of the martensite island size [14,15]. Hence, it is particularly interesting to reduce the martensite island size with regard to improving the stretch forming behavior, as was demonstrated by experimentally based data in forming limit diagrams (FLD) [16].

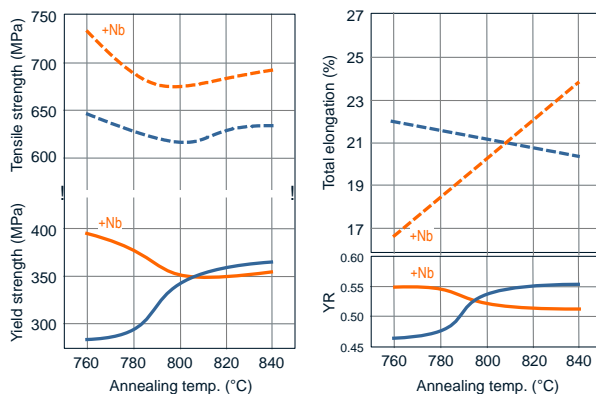


Figure 11. Effect of annealing temperature (QT = 750 °C) on the mechanical properties of cold rolled DP steel.

A recent trend in DP steel production is to further increase the tensile strength from the mainstream level of 590 MPa to 780 and 980 MPa. Simultaneously, steelmakers try to reduce the carbon level from around 0.15% to below 0.1% for better weldability. The strength increase demands a higher martensite fraction in the microstructure. Consequently, the average carbon content in the intercritical austenite is markedly reduced and the tendency of forming bainite at the expense of martensite is enhanced. This requires adapting the alloy concept as well as the annealing and cooling strategy.

When large fractions of austenite have to be transformed into martensite, the critical cooling rate is very much greater for low-carbon austenite than for high carbon austenite. The critical cooling rates required for the transformation of 90% and 50% of the intercritical austenite to martensite are plotted, as a function of carbon content of the austenite, in Figure 12 [17]. The data indicate that the hardenability of the austenite decreases slowly with decreasing carbon content at austenite carbon contents above 0.2%, but very rapidly at lower carbon contents. Furthermore, the cooling rate for converting 50% of the existing austenite into martensite is much lower than that for converting 90% austenite into martensite. These observations have a clear influence on the methodology of producing dual phase steels. Over the range of austenite carbon content within which martensitic hardenability varies slowly, i.e. above 0.2%C, it is beneficial to increase the intercritical annealing temperature in order to obtain a desired volume fraction of martensite at a lower cooling rate. This strategy would apply for dual phase steels containing up to about 20% martensite, covering the grades DP600 or lower. For the production of DP780 however, 40% martensite is needed in the microstructure. It is then more favorable to work with a lower intercritical annealing temperature. To enhance the stability of retained austenite with low carbon concentration during the galvanizing step it is necessary to delay bainite transformation by a suitable alloy concept. From research on TRIP steels it appeared that Mo makes the bainite transformation very sluggish [18]. The grain refinement induced by Nb

microalloying is also beneficial in this respect since the carbon distribution in the smaller austenite islands is more homogeneous due to the shorter diffusion path.

Figure 13 demonstrates the capabilities of different alloying concepts with respect to producing different strength levels. The low-C, high-Mn base alloy with Cr is capable of achieving strength levels up to 700 MPa. Adding a small amount of Nb raises the strength level to around 780 MPa, but the process window of applicable intercritical annealing temperatures is very narrow. The combined addition of Mo and Nb provides a strength level of around 900 MPa over a much wider range of intercritical annealing temperatures. Industrial low-C alloy concepts for hot dip galvanized DP980 apply Mo, Cr and Nb alloying in combination with an increased Mn addition.

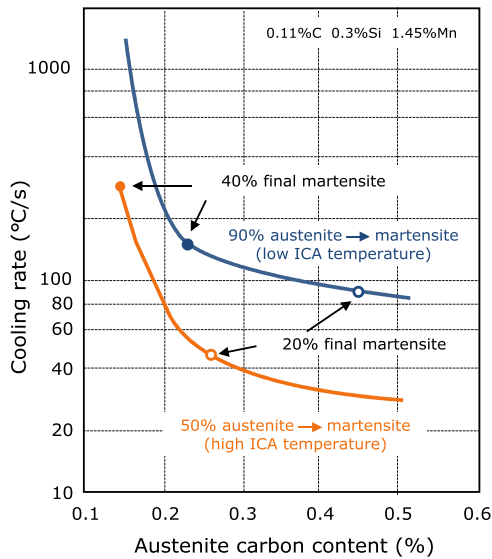


Figure 12. Annealing strategy with respect to carbon content and cooling rate.

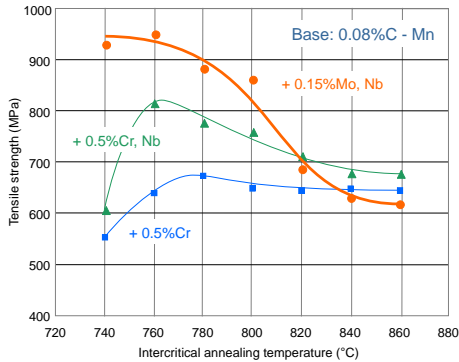


Figure 13. Effect of intercritical annealing temperature and various alloying concepts on achievable strength of dual phase steel with sub-peritectic carbon content [13].

Intercritical Annealed TRIP Steel

When producing TRIP steel, the annealed strip is quenched to an intermediate temperature to form carbide-free bainite. Increased additions of Si or alternatively Al help suppress carbide precipitation. During holding in this temperature range the progressing formation of carbide-free bainite leads to enrichment of carbon in the remaining austenite phase. A sufficiently high level of carbon concentration stabilizes this share of austenite down to room temperature. Depending on the average carbon content in the steel the amount of retained austenite in the final microstructure can be in the range of 10 to 20%.

Figure 14 exemplifies the development of different phase fractions as a function of the bainitic holding time. Short holding times result in the efficient formation of martensite, rendering only a small share of retained austenite which produces steel with DP characteristics. Very long holding times lead to carbide precipitation which also lowers the amount of austenite with sufficient carbon enrichment. The amount of retained austenite obtained for intermediate holding times depends on the absolute carbon content, the intercritical annealing temperature as well as the formation kinetics of pro-eutectoid ferrite and carbide-free bainite. The mechanical properties of an exemplary TRIP steel are displayed in Figure 15 as a function of the bainitic holding time at a temperature of 410 °C [19]. It is evident that at short holding times the DP character is pronounced whereas the TRIP character is established at longer bainitic holding times. It also becomes clear that a conventional galvanizing line (CGL) is not the best option to produce TRIP steel as it allows only a relatively short holding period. Better suited is a galvanizing line with an overageing (OA) section. The best conditions concerning the time temperature schedule are offered by continuous annealing lines (CAL), which would however require ad hoc galvanizing on an electro galvanizing line.

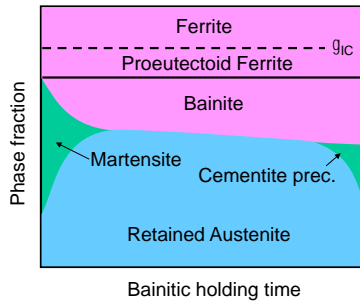


Figure 14. Development of phase fractions during bainitic holding after intercritical annealing of TRIP steel.

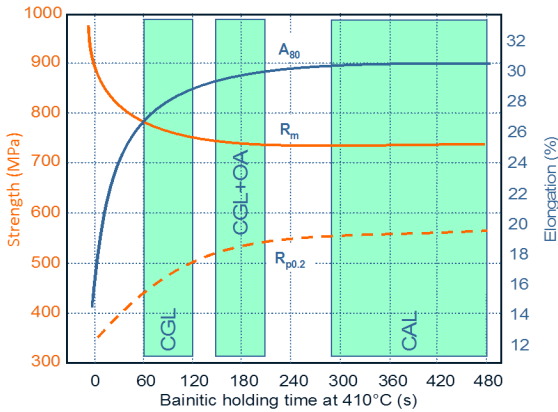


Figure 15. Development of strength and elongation in TRIP steel as a function of bainitic holding time.

As mentioned before, Mo makes the bainite transformation sluggish [18] leading to a higher amount of austenite with lower carbon enrichment at a given bainitic holding time and temperature. The martensite transformation-start temperature increases with reduced carbon enrichment. Consequently, Mo alloying promotes the formation of martensite and hence increases the tensile strength, especially for short bainitic holding times. Simultaneously, the amount of retained austenite and thus elongation is reduced. According to the findings shown in Figure 10, Nb is nearly completely precipitated after intercritical annealing and thus it is metallurgically inactive during bainitic holding. However, the grain refinement provided by Nb microalloying has a clear effect on the phase transformation kinetics through the intercritical annealing cycle as was already experienced for DP steels. During down cooling from the intercritical annealing temperature, the formation kinetics of pro-eutectoid ferrite is accelerated

due to the enhanced amount of nucleation sites offered by the refined microstructure. Thus the average carbon content in the remaining smaller austenite fraction is correspondingly higher. Similar to molybdenum, niobium is also known to delay bainite formation but this effect is only apparent at a rather low bainitic holding temperature [20]. At temperatures typically applied in galvanizing lines, the kinetics of bainite formation is hardly affected by niobium. Based on these effects, one can expect that Mo alloying of TRIP steels provides higher strength and lower elongation due to a higher martensite fraction. Nb microalloying has an opposite effect as it increases the share of ferrite and retained austenite leading to higher elongation and lower strength.

Accordingly, dual alloying with Mo and Nb has the potential of combining higher strength with good elongation. Figure 16 demonstrates that for an Al-Mo-Nb alloy concept, the processing robustness is considerably improved as compared to the Al-TRIP concept. The amount of retained austenite is less sensitive to the bainitic holding temperature, which is particularly advantageous when galvanized grades have to be produced. Also, processing in a horizontal CGL configuration yields sufficient retained austenite with the Al-Mo-Nb TRIP concept. Figure 17 indicates the possibilities of the Al-Mo-Nb alloy concept by varying the bainitic holding time. With shorter holding times, so-called TRIP aided DP steel can be obtained by producing a fair amount of retained austenite within a primarily ferritic-martensitic microstructure. For longer holding times the TRIP character is more pronounced as the share of retained austenite is increased whereas the tensile strength is reduced. In a continuous annealing line, the duration of bainitic holding can be adjusted over a wide range, Figure 15. The bainitic holding period in a continuous galvanizing line depends on the specific design of the equipment. Lines with a horizontal furnace allow only a short holding period and thus promote the DP character [21]. Longer bainitic holding can be achieved by operating with reduced line speed, however, this reduces the productivity of the line thus increasing production cost.

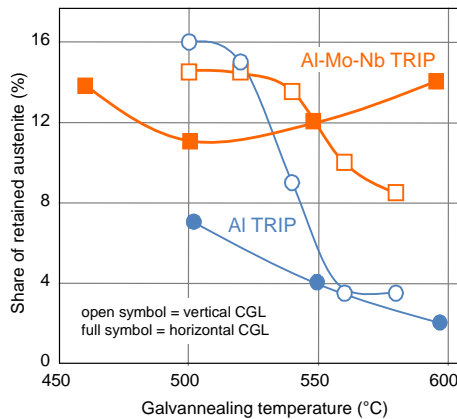


Figure 16. Influence of galvannealing temperature on the retained austenite share in Al and Al-Mo-Nb TRIP steel for different CGL configurations.

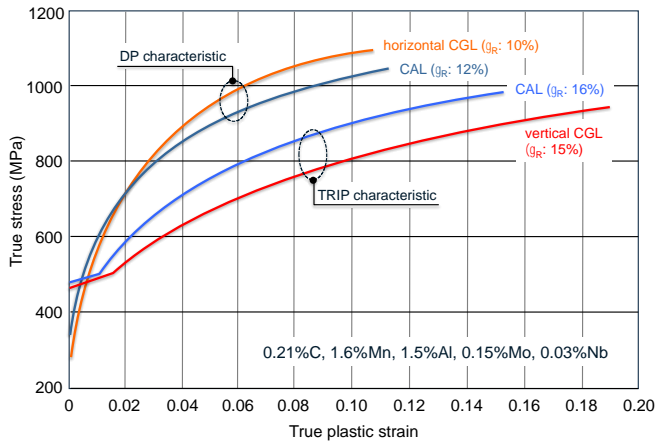


Figure 17. Influence of the annealing cycle and the amount of retained austenite (γ_R) on the stress-strain characteristics of multiphase steels.

Improvement of Microstructural Damage Resistance

Although multiphase steels have good elongation and formability, they are sensitive to microstructural damage when intensive localized straining is applied. In this situation all plastic flow is concentrated in a few grains of the softer phase. Dislocation pile-up against the hard undeformable phase may lead to microvoid formation as shown in Figure 18(a). The size of such microcracks is related to the grain size of the material and the mean free path length between hard and soft phases. Individual micro voids link up forming a microcrack, Figure 18(b), and it is evident that larger grains or inhomogeneously distributed phases accelerate the progress of microcracks and lead to faster macroscopic damage. Niobium microalloying considerably improves the microstructural resistance against the above mentioned damage initiation. As shown in Figure 19, the addition of Nb to DP steel results in a significant refinement of both ferrite and martensite phases. Furthermore, agglomeration of hard phase particles is reduced and the phase distribution is more homogeneous.

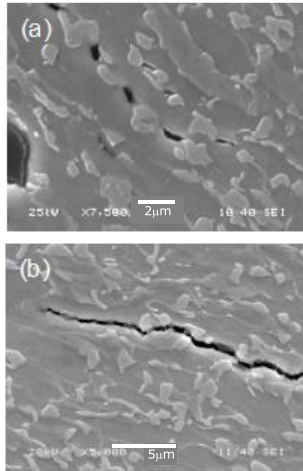


Figure 18. (a) Micro void formation in soft phase of DP600 and (b) macroscopic crack propagation in DP600 steel.

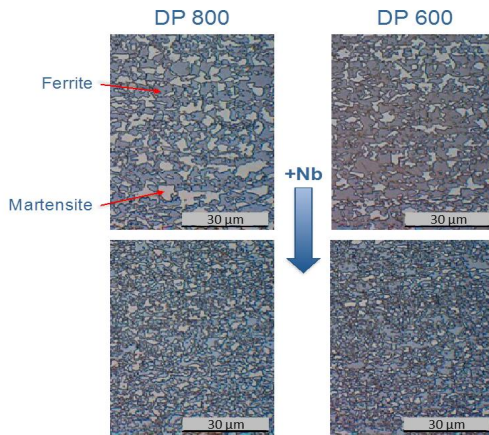


Figure 19. Grain refining effect of Nb microalloying in DP600 and DP800 steel.

The finer grained and more homogeneous microstructure leads to better results under forming conditions where highly localized straining predominates. These are sheared edge flanging, hole expansion and bending. Figure 20 shows the hole expansion ratio for a DP600 steel. The Nb microalloyed variant achieves an improvement of more than 50%. More critical is the situation in DP800 as the amount of martensite is much increased and clustering of the hard particles is more likely than in DP600. Here Nb microalloying results in an improvement of around 90% for the hole expansion ratio, Figure 21. Likewise the bending behavior is drastically improved which is particularly important for roll profiling operations. For this reason Nb microalloying is already well established in DP800 or higher strength grades. These positive effects of Nb microalloying have also been observed in TRIP steel [19].

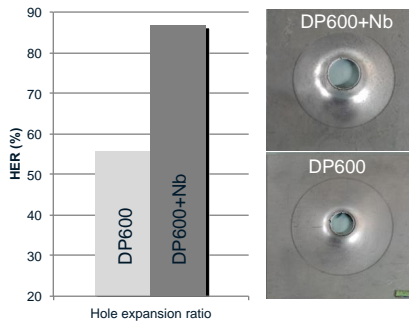


Figure 20. Influence of Nb microalloying on hole expansion behavior of DP600 (punched hole, sheet thickness 2.5 mm).

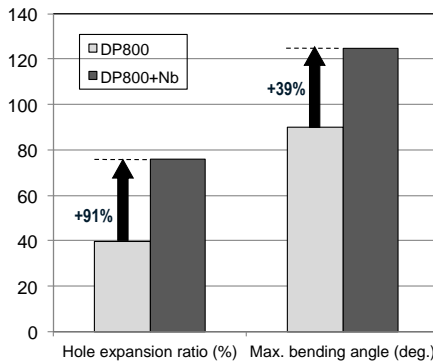


Figure 21. Influence of Nb microalloying on hole expansion and bending behavior of DP800 (punched hole, sheet thickness 1.5 mm).

Conclusions

Molybdenum and niobium alloying have distinct effects in the production of multiphase steels. Their effects are partly similar and in some respects complementary. Molybdenum exists in solid solution in multiphase steels and is as such metallurgically active in reducing the diffusivity of carbon. This effect retards ferrite formation and, to a much larger degree, pearlite formation from austenite. Molybdenum also efficiently retards the decay of metastable austenite into bainite. Therefore molybdenum is particularly useful in promoting dual phase microstructures even under critical processing conditions. Consequently, molybdenum is very beneficial for all multiphase steels aiming at very high strength levels. Niobium, like molybdenum, has the effect of reducing the carbon diffusivity when present in solid solution. However, niobium's solubility is much lower than that of molybdenum, thus it precipitates almost completely during hot rolling and intercritical annealing. The grain refining effect of niobium accelerates the kinetics of phase transformations and therefore ferrite formation is promoted after intercritical annealing. The resulting smaller amount of martensite has a higher and more equalized carbon content promoting a higher stability. During bainitic holding, the grain refined microstructure promotes the nucleation and growth of carbide-free bainite and thus supports the accumulation of retained austenite. When molybdenum and niobium are alloyed in combination they facilitate producing multiphase steels of the highest strength level. Depending on the processing conditions, such steels can be adjusted to have either a DP-like or a TRIP-like character. All grain-refined multiphase steels exhibit substantially improved hole expansion behavior and bendability.

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