

Principal effects of Mo in HSLA steels and cross effects with microalloying elements
for

International Seminar in Applications of Mo in Steels

Beijing, China

June 28, 2010

by

Prof. Dr. Hardy Mohrbacher

Managing Director

NiobelCon bvba

Schilde, Belgium

Molybdenum is typically alloyed to high strength low alloy (HSLA) steels when mechanical properties of the highest level are demanded. Such steel grades find increasing application in the oil & gas, automotive and construction industry as more performance with less steel is targeted. Most prominently, molybdenum promotes the formation of bainitic or martensitic microstructures depending on the processing conditions. Yet, molybdenum can also precipitate as fine carbides and provide thus secondary precipitation hardening. Besides of its direct metallurgical effects, molybdenum has interesting cross effects and synergies with microalloying elements such as niobium. The combination of these elements can reinforce molybdenum's principal effects on the one hand side but also optimize the effect of the microalloying elements on the other side. The paper will describe such effects and demonstrates how these can be utilized to obtain intriguingly improved properties in HSLA steels.

1. More performance with less steel

Increasing attention is being paid to the economic advantages that high-strength low-alloy steels have to offer. These advantages include lower cost structural components, increased resistance to brittle failure, economies during construction and transportation as a result of lower cost in handling lighter sections, fewer man-hours of welding and lower electrode consumption as a result of lighter sections (Fig. 1). The advantages listed are of primary interest to the transportation and materials handling industry where the ratio of payload to dead weight load is of paramount importance. Fringe benefits resulting from this are greater speeds, less fuel consumption per load and smaller sized propulsion units. In addition to strength properties, structural steel selection is concerned with ease of forming, welding and other fabrication procedures. Service conditions require that the steel exhibits good toughness at the temperature of service, thus the candidate steel should possess adequate impact resistance at the lowest temperatures anticipated in service.

Traditional high strength structural steel is produced based on a carbon-manganese alloy concept having a ferritic-pearlitic microstructure and obtained by either normalizing or thermomechanical rolling. Such steel covers a yield strength range of up to around 460 MPa. To make the desired strength, different strengthening mechanisms are employed (Fig. 2). The base strength originates from the carbon content ranging up to 0.2%.

However increasing the carbon content severely deteriorates the steel's toughness. Solid solution strengthening is mainly obtained by manganese and silicon bulk alloying. The most important contribution to increasing the strength is grain refinement and the most effective way to achieve this is by microalloying in combination with thermomechanical rolling. Grain refinement is the only strengthening mechanism that also improves toughness. Niobium is in that respect by far the most effective element followed by titanium. The dispersion of fine precipitates, typically carbides or nitrides of the microalloying elements further increases the strength.

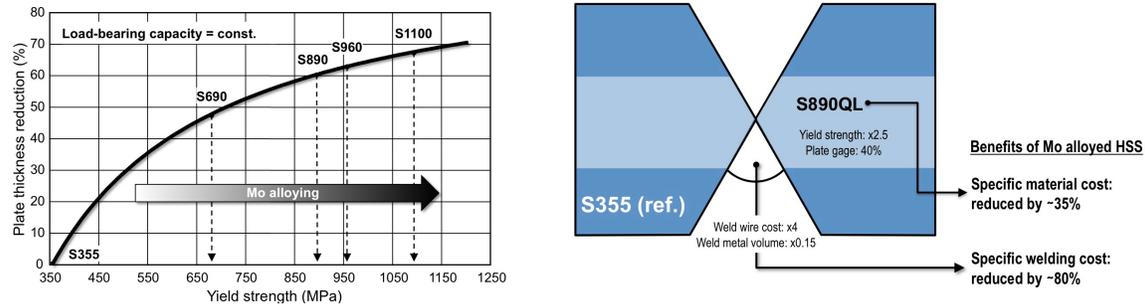


Figure 1: Benefits of using high strength steel with regard to steel consumption and processing efforts.

In modern high strength structural steels with strength levels above 460 MPa, it is necessary to modify the nature of the ferrite matrix and to avoid pearlite formation. One method is to force the austenite-to-ferrite transformation to occur at temperatures below 700°C and thereby increase the dislocation density and refine the subgrain size. The resulting microstructure is bainite or degenerated ferrite. The two alloying elements that prominently assist this transformation strengthening are molybdenum and boron. To a lesser extent chromium and niobium are also effective in that respect. With such alloy concepts a yield strength level of up to around 800 MPa can be achieved.

The highest strength is yet obtained with a martensitic microstructure. This microstructure is the result of quenching from the austenite, which can be done by a separate heat treatment or directly after finish rolling (Fig. 3). In order to obtain a fully martensitic structure, the cooling speed must be sufficiently high. Alloying of molybdenum and/or boron effectively help to reduce the critical cooling speed for martensite formation. The amount of alloys depends finally on the gage to be produced as well as on the cooling capacity of the production line. The strength of quenched martensite is controlled by the carbon content. With applicable carbon contents in the range of 0.1 to 0.2 %, the tensile strength ranges from 1200 to 1600 MPa. However, the toughness of fully quenched martensite is quite low, so that this type of material is only use for thinner sheet applications for instance in car bodies. For heavier gauged structural applications quenching and tempering is necessary in order to produce steels with minimum yield strength from 690 to 1100 MPa with simultaneous high toughness and good processing behavior. Quenched and tempered steels can be alloyed with chromium, molybdenum, nickel, niobium, boron and vanadium at carbon contents up to 0.2%. During heat treatment this leads to a fine bainitic-martensitic microstructure with optimum strength and toughness properties.

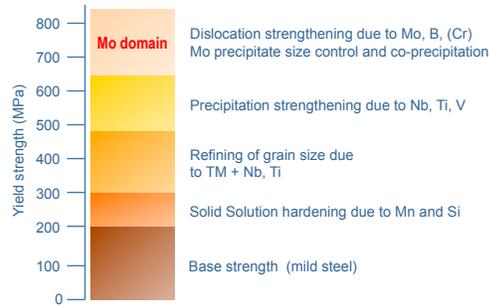


Figure 2: Strengthening effects in HSLA steel.

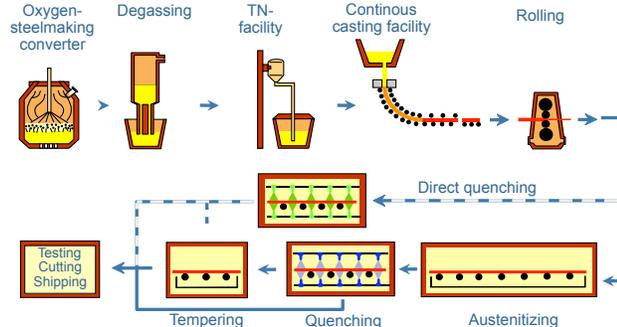


Figure 3: Processing routes for quenched & tempered steel.

2. Effects of molybdenum during hot rolling

2.1. Recrystallization

Adding molybdenum to (microalloyed) steel has important effects during all stages of the hot rolling process as is schematically shown in Figure 4. Thereby Mo acts directly as a solute atom and indirectly by influencing the behavior of microalloying elements such as Nb, Ti and V.

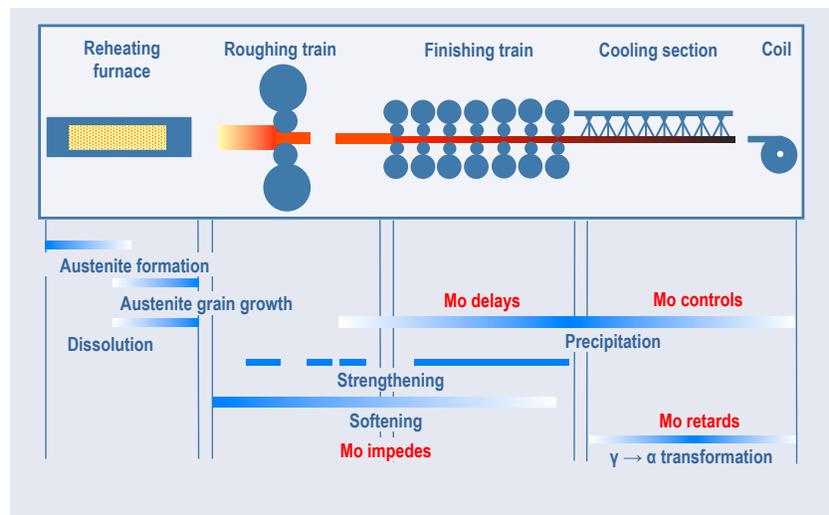


Figure 4: Principal effects of Mo alloying during the hot-rolling stage.

The addition of Nb to low carbon steel significantly retards the rate of static recrystallization (SRX). For instance, by microalloying of 0.04%Nb the time for 95% recrystallization (t_{95}) at 1060°C is around 20 seconds, whereas it takes over 50 seconds to complete the SRX if the Nb content of the steel is increased to 0.095%. Also an increase in the Mo content from 0.1% to 0.6% leads to a significant retardation of the SRX kinetics (Fig. 5). Since it is the aim of roughing rolling to obtain a homogeneous, fully recrystallized austenite microstructure this effect of Nb and Mo has to be taken into account when designing the rolling schedule. Taking the maximum interpass time in the roughing mill being 20 seconds, full recrystallization must occur within that period, i.e., t_{95} must be less than the interpass time. This demand determines the temperature level of roughing rolling. On the other hand, the slab discharge temperature has to be considered

that has typically maximum values of 1150°C and 1250°C or plate mills and strip mills, respectively. Thus the processing window, where fully recrystallizing roughing rolling passes can take place, is 80-180°C for the 0.1%Mo-0.04%Nb alloy, whereas it is reduced to 30-130°C for the 0.6%Mo-0.04%Nb alloy.

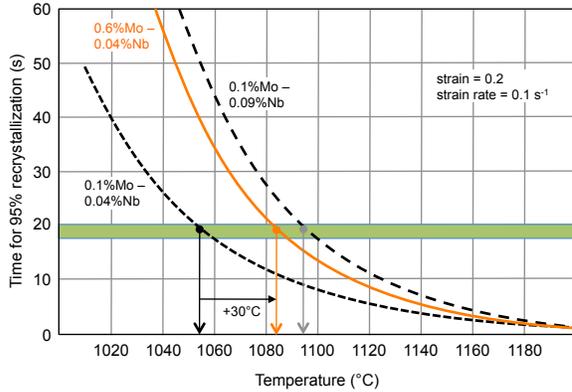


Figure 5: Influence of Mo-Nb alloy combinations on static recrystallization at high temperature.

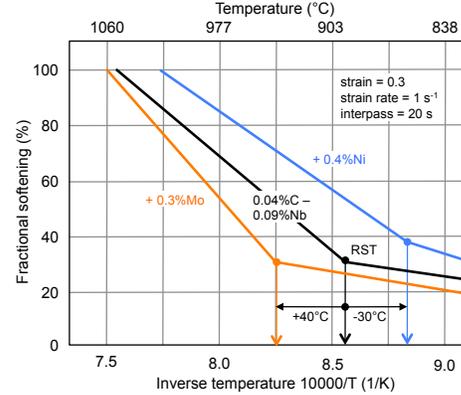


Figure 6: Effects of Mo and Ni addition to a low-C high-Nb base alloy on fractional softening behavior.

From stress-strain curves obtained in multi-pass tests, the interpass fractional softening (FS) was determined following a procedure described by Liu and Akben [1]. From the plot of fractional softening vs. the inverse temperature (Fig. 6) two characteristic temperatures with respect to recrystallization can be derived. The recrystallization limit temperature (RLT) indicating the temperature below which softening is less than 100%, and the recrystallization stop temperature (RST) indicating the temperature below which no softening is observed between deformation passes. Figure 6 shows the behavior for 0.04%C-0.09%Nb steel as a reference having a RST of around 900°C. Adding 0.3% Mo to such a steel has little influence on the RLT but further raises the RST by about 40°C to around 940°C. The influence of Mo can be understood as retarding recrystallization by solute drag. On the contrary adding 0.4% Ni reduces the RLT as well as the RST significantly. Since the recrystallization retarding effect of Nb saturates above 0.06%Nb [2] addition of Mo can effectively help to further raise the RST with respect to non-recrystallizing finish rolling without negative impact on the RLT with respect to recrystallizing roughing rolling.

2.2. Strain induced precipitation

Earlier experiments performed by Akben et al. [3] revealed the effect of Mo additions on the dynamic recrystallization (DRX) of microalloyed steels based on hot compression tests. When microalloyed steels are deformed above the solution temperature of their respective carbonitrides, the addition of Mo leads to a distinct retardation in the initiation of dynamic recrystallization. The solute retarding effect of Mo alone is intermediate between that of Nb, which has the greatest and that of V, which has the least effect on an equal atom fraction basis. The relative influence of these elements in solution is consistent with the relative magnitudes of their atomic size and electronic differences with respect to γ -iron. When such steels are deformed below the solution temperatures of their respective carbonitrides, in-situ precipitation of small particles results in a further component of retarding recrystallization. In this case the addition of Mo involves two

opposing effects. One is an increased retardation of recrystallization due to its effect as a solute. The other is a decrease in the amount of precipitation due to a reduced activity of C and N by Mo. It was observed that the onset of precipitation of Nb in a 0.05%C-0.04%Nb steel takes twice as long once 0.3% Mo is added as shown in Figure 7. It is evident that especially during hot strip rolling with short interpass time a large portion of Nb can be retained in solid solution. Microalloying elements prevailing in solid solution after finish rolling have the capability of reducing the austenite-to-ferrite transformation temperature (Fig. 8). This effect is most pronounced for solute Nb followed by that of solute Ti while solute V has only a weak influence. The effect becomes more significant when accelerated cooling is applied. Such a delay of transformation effectively results in a further grain refinement due to enhanced ferrite nucleation and reduced grain growth.

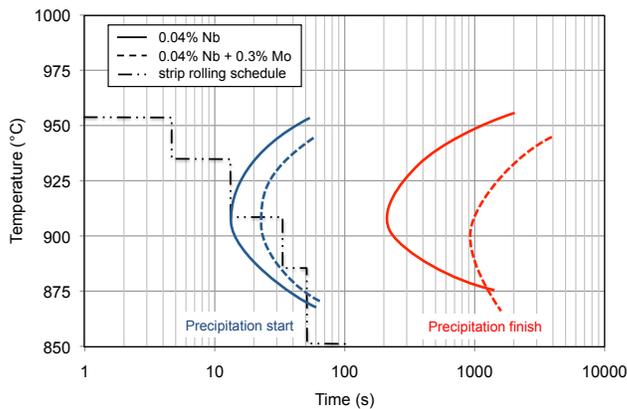


Figure 7: Influence of Mo addition on the dynamic precipitation behavior of Nb (schematic hot strip rolling schedule).

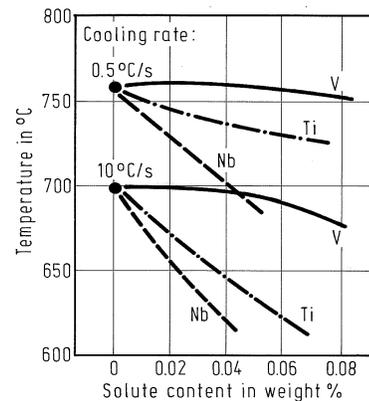


Figure 8: Effect of solute microalloying elements on γ - α transformation temperature.

Hara et al. [4] have explained the effect of reduced carbon activity by adding Mo as being a consequence of Mo-C cluster formation. Earlier Tanaka et al. [5] reported already the diffusion of C in austenite to be slowed down by Mo addition. This effect of Mo makes carbon less available for forming carbides with Nb or Ti. In other words, the amount of microalloying atoms being preserved in solid solution during austenitic rolling is increased. Microalloying elements that are in solid solution after finish rolling have two important effects. They delay the transformation from austenite to ferrite to a lower temperature. This delay increases with the cooling speed (Fig. 8). Secondly, solute microalloying elements have the potential to precipitate during or after the phase transformation to a much finer particle size than that of precipitates formed in austenite. The finer the particle size the higher is the strengthening effect as will be discussed later in detail.

2.3. Hardenability

The molybdenum effect of reducing the carbon activity was also found beneficial with respect to boron-alloyed steels. Boron is a very powerful hardenability element that is added to steel in minute amounts, usually not more than 50 ppm. As such it is used in (ultra-) low carbon bainitic steels as well as in quench-hardening steels. The effectiveness of boron to provide hardenability lies in its segregation to the austenite grain boundary where it obstructs the formation of grain boundary ferrite at transformation temperature.

This mechanism is however only possible if B is in solid solution. Since B is a strong nitride former, Ti is usually added at around stoichiometric ratio ($Ti = 3.4 \times wt.\%N$) to protect B. However, B can still be lost by forming a complex $Fe_{23}(C,B)_6$ precipitate. This happens in the austenite grain boundary particularly when increased amounts of B and C are present due to segregation. Asahi [6] and Hara et al. [4] have identified this phenomenon for steels with ultra-low as well as over-peritectic carbon contents. In both cases the addition of Mo to the alloy improved the effectiveness of B since intragranular Mo-C cluster forming reduces the carbon diffusion into the austenite grain boundary (Fig. 9). Niobium microalloying was found to have a similar effect of avoiding $Fe_{23}(C,B)_6$ precipitation, which however is rather related to NbC precipitation removing solute carbon.

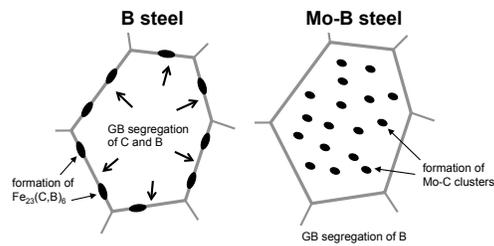


Figure 9: Schematic of boron grain boundary (GB) segregation and precipitation in B and Mo-B steel.

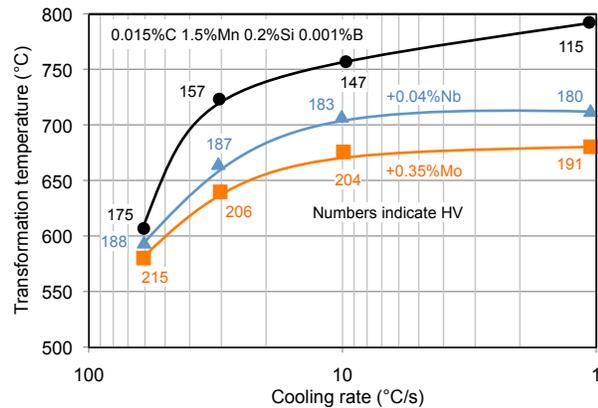


Figure 10: Effect of cooling rate on transformation temperature and hardness in ULCB steel with B, Nb-B and Mo-B alloying.

Besides of rendering a better effectiveness of boron in preventing grain boundary ferrite formation, molybdenum acts as a hardenability element by itself. This Mo effect additionally enhances the B effect as becomes evident from Figure 10 [4]. Compared to the Nb-B steel where only B acts as hardenability agent the Mo-B steel shows lower transformation temperature as well as higher hardness at any cooling rate.

Figure 11 exemplifies the hardenability effect of molybdenum by adding different levels of Mo to a constant low carbon Mn-Cr base alloy [7]. Each alloy was heated to a temperature of 50°C above the Ac3 temperature and held for 10 minutes. Afterwards the alloy was cooled at various rates and the microstructure was evaluated. Adding 0.25% Mo to the base composition significantly delays pearlite formation and lowers the transformation temperature. Simultaneously, the bainite field is largely extended. As such, practically at all technically relevant cooling rates a ferritic-bainitic microstructure is obtained. Increasing the Mo content further to 0.5% leads to a delay of ferrite formation and a complete suppression of pearlite formation. At cooling rates of above 30 K/s a fully bainitic microstructure exists.

More detailed analysis of the bainitic phase revealed that the block size decreases with increasing Mo content whereas the misorientation angle between bainite laths as well as the dislocation density increases. These effects in an increased hardness (strength) of

bainite as the Mo content is raised. Increasing the cooling rate at a constant Mo content leads to the same effects. Simplified this means that raising the Mo content in such low carbon steel can substitute for lack of cooling rate. This is relevant to mills equipped with less powerful accelerated cooling devices. On the other hand, Mo helps to achieve bainitic transformation and sufficient strengthening for heavier gauged strip or plate material.

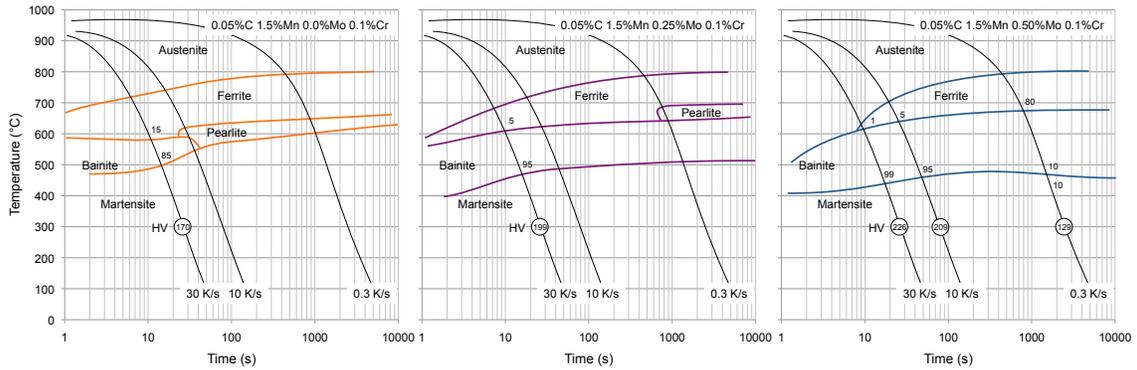


Figure 11: Effect of Mo alloying on the transformation behavior of a low-carbon base alloy (heating to $A_{c3}+50^{\circ}\text{C}$ – holding for 10 minutes without deformation – cooling at various rates).

Industrial alloys for HSLA steel applications are usually composed of different alloying elements to combine several effects as discussed before. A standard element in such steel is niobium, which in more recent alloy design is added in the order of 0.1%. Combining a low-carbon high-niobium alloy with Mo leads to a synergetic effect on the transformation behavior. For this alloy pearlite formation is suppressed and the onset of ferrite formation is significantly delayed (Fig. 12a). The critical cooling rate to obtain full bainite formation in the 0.04%C-1.4%Mn-0.1%Nb-0.3%Mo alloy is around 10 K/s. Modifying this alloying concept by increasing carbon and manganese levels, reducing the molybdenum content and adding chrome results in a further improved hardenability (Fig. 12b). The critical cooling rate for full bainite transformation in this alloy variant is in the order of only 4 K/s.

In yet another alloy variant molybdenum was substituted by a combination of nickel and copper. Although this alloy also results in fully bainitic microstructure at cooling rates of above 4 K/s, several differences in the transformation behavior can be observed (Fig. 12c). The start temperature of bainite transformation is increased by around 50°C . At slower cooling rate (1 K/s) such as occurring by air-cooling, no bainite is formed anymore but a small fraction of pearlite appears, which is detrimental to toughness. At high cooling rates (95 K/s), as they can occur after welding, martensite formation is possible.

These three examples particularly underline the effect of molybdenum in promoting bainite and avoiding pearlite formation, respectively. With regard to mechanical properties, all three alloys reach a strength level of 650 MPa tensile and 550 MPa yield under suitable rolling conditions and fully bainitic microstructure.

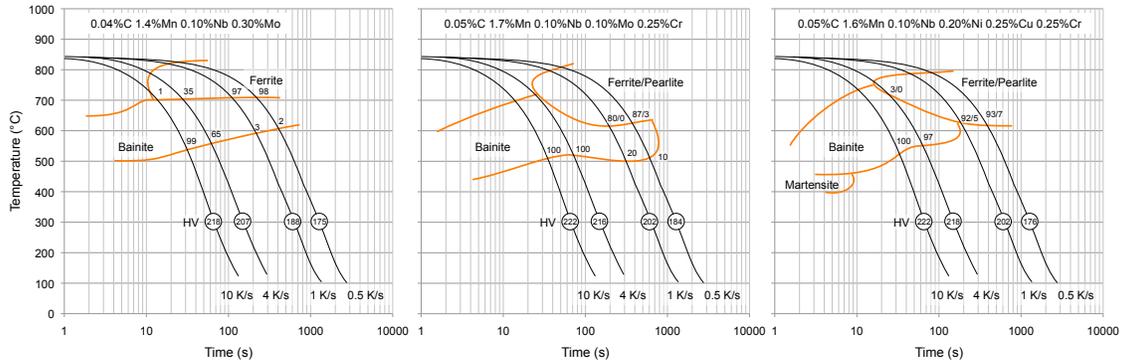


Figure 12: Transformation behavior of various low-carbon alloys of similar P_{cm} and strength level (holding at 1200°C for 10 minutes – deformation $\varphi = 0.6$ at 1050°C – deformation $\varphi = 0.6$ at 850°C – cooling at various rates).

For continuously cooled molybdenum-boron steels, the main effect of bulk alloying elements such as manganese or chrome is to lower the temperature at which the transformation to bainite begins. In carbon-manganese steels, the addition of molybdenum in combination with solute titanium or niobium reduces the critical cooling rate for producing bainite, i.e., suppresses transformation to polygonal ferrite.

2.4. Interphase precipitation

Any microalloying element being in solid solution after finish rolling has the potential of precipitating during or after the austenite-to-ferrite transformation. During austenite decomposition so-called interphase precipitation occurs by a mechanism of periodical particle nucleation at the moving austenite/ferrite interface during transformation [8]. The austenite side of the moving phase boundary enriches with carbon and microalloying elements due to their lower solubility in ferrite. At certain intervals supersaturation leads to precipitation manifesting itself by row arrangement of precipitates (Fig. 13). Since the entire process is diffusion controlled, interphase precipitation is most effective at a comparably slow cooling rate. Increasing the alloy content progressively lowers the temperature of transformation at a given cooling rate, reducing the diffusivity of the solute elements, which finally becomes insufficient for interphase precipitation. Hence, interphase precipitation is mostly feasible for ferritic microstructures, unless the bainite start temperature is pushed upwards by suitable alloy design. From a practical point of view, one would cool down the material after finish rolling to a temperature that is providing efficient precipitation and hold the material isothermally until the phase transformation is completed. This temperature should not be too high since particle ageing (Ostwald ripening) leads to coarsening and a corresponding loss of particle strengthening effect. Most suitable for precipitation hardening is the temperature range between 630 and 650°C.

For particular applications it is not favorable to have pearlite phase in the final microstructure. Therefore it is important to delay the pearlite formation to times longer than the isothermal holding period. Molybdenum alloying is efficient in achieving this delay as discussed above. Furthermore, in practice coiling in a hot strip mill naturally provides isothermal holding since the cooling rate in the coil is slow (around 30°C/h). In fact the coil is still at high temperature after precipitation is complete and this promotes particle coarsening by Ostwald ripening. In this respect molybdenum is found to inhibit

particle coarsening by segregating to the particle matrix interface and blocking the diffusion of carbide forming elements between particle and matrix. This mechanism results in a much-reduced loss of particle strengthening even for extended isothermal holding at 650°C (Fig. 14) [9]. In reality, the temperature continuously drops by natural coil cooling. At temperatures below 550°C diffusion is so limited that particle coarsening does not take place effectively. This situation would be reached in the example of Figure 14 after around 12,000 seconds. The molybdenum alloyed steel shows after that time almost no loss in hardness (strength). In absence of molybdenum, particle coarsening of TiC would lead to a hardness drop of approximately 30 HV (corresponding to 100 MPa strength).

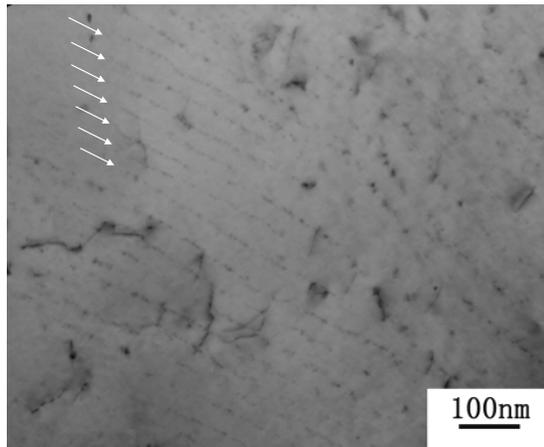


Figure 13: Example of row-like precipitate arrangement (arrows) in a 0.05%C Mo-Nb-Ti steel coiled at 630°C.

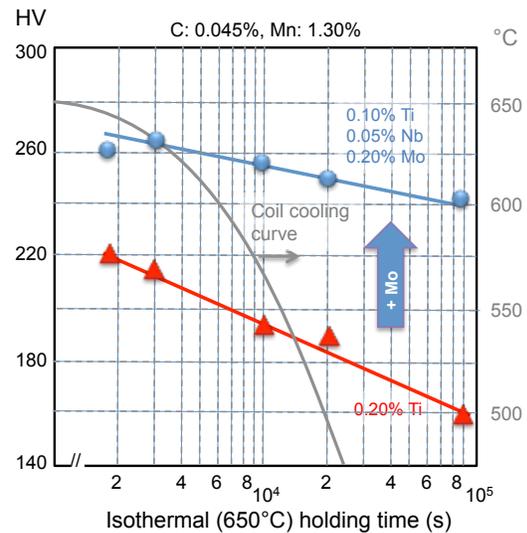


Figure 14: Influence of isothermal holding at 650°C on precipitation hardening (typical coil cooling curve is indicated).

If the coiling temperature is set below the range allowing efficient interphase precipitation and / or rapid cooling is applied, microalloying elements will remain in solution and can only precipitate during a secondary heat treatment.

Figure 15 summarizes the strengthening effects by transformation and / or precipitation hardening for the Mo-Nb and Mo-V alloy system respectively [10]. The precipitation strengthening, having a maximum in the range of 630 to 650°C, adds to the strengthening effect in the matrix. The latter one increases with decreasing coiling temperature. For the Mo-Nb system this strength increase continues below 600°C whereas it levels off at that temperature for the Mo-V system. This is because the synergetic effect of Mo and Nb effectively promote the forming of a bainitic microstructure providing transformation hardening. It appears that the gain in transformation hardening nearly equals the loss of precipitation hardening at lower coiling temperature. Hence the total strength being the sum of the two strengthening components remains nearly constant. This constitutes a considerable advantage as in a hot strip mill one can encounter considerable drifts of the actual coiling temperature along the strip. In the Mo-V system such a temperature drift would necessarily reflect in substantial scattering of the final yield strength.

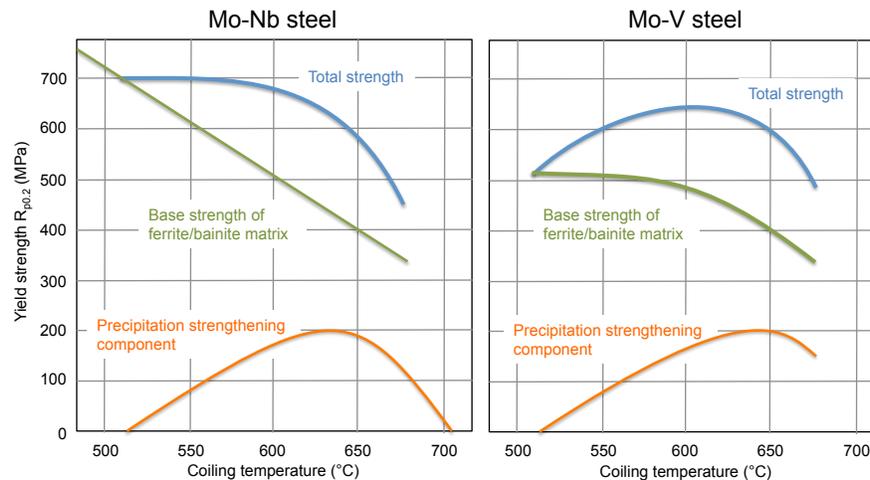


Figure 15: Effect of coiling temperature on yield strength in low-carbon Mo-Nb and Mo-V steel.

3. Effects of molybdenum in advanced processing concepts

3.1. Direct quenching of plate

When producing steels of the highest strength level quenching & tempering is the traditional treatment. The rolled material after down cooling from the rolling heat is re-austenitized and then quenched (Fig. 3). This results in a very strong but often brittle material. Subsequent tempering provides a much better toughness and ductility on the expense of strength. Molybdenum effectively enhances the so-called tempering resistance, which counteracts the loss of strength as described by Krauss [11].

In more recent processing concepts, the rolled material is fast cooled immediately after finish rolling. Depending on the cooling severity and the cooling stop temperature, the following cooling variants can be distinguished for plate mills [12]:

- ACC (Accelerated cooling) results in cooling with ideal cooling rate, i.e. difference of cooling rate between surface and center is kept low.
- HACC (Heavy ACC) is a special variant of the classical ACC but with lower final cooling temperature and somewhat higher cooling rate.
- DQ (Direct Quenching) with fastest possible cooling of the surface, similar to conventional quenching. The center of the plate is also cooled to below the martensite-start temperature by means of continuation of cooling.
- DQST (DQ + Self Tempering) means that the center heat still present is exploited after an extremely short cooling time and self-tempering is achieved.

Compared to the traditional Q&T procedure, DQ or DQST has the decisive difference that the steel only goes once through the α - γ phase transformation (instead of 3 times in Q&T). That means the microstructure of the finish-rolled austenite has an influence on the properties of the quenched material, as it will not be normalized. The microstructure before direct quenching depends on the hot-rolling schedule. If the finishing temperature is above the recrystallizing stop temperature (HR = hot rolling), the austenite shape will be equiaxed and relatively coarse. On the contrary, if finish rolling is done below the

recrystallization stop temperature (CR = controlled rolling), the austenite grain is elongated in the rolling direction and flattened in the normal direction.

Applying either of the rolling schedules to a 0.15%C-Mn-B steel without and with 0.25% Mo leads to the following results [13]:

- Strength and toughness are better for the HR/DQ than for the CR/DQ route in the Mo-free steel. The strength of the CR/DQ material is particularly low since ferrite has formed along the boundaries of the former austenite grains.
- The strength of the Mo-added material is nearly equal for the HR/DQ and CR/DQ material and in both cases significantly better than for the Mo-free steel.
- When comparing the toughness of HR/DQ treated steels, the Mo-free material performs better.
- The toughness of the Mo-added steel considerably improves when applying the CR/DQ route.

These differences can be explained by the cross effects between Mo and B as indicated before in Figure 9. In the Mo-free steel part of the boron precipitates as $Fe_{23}(C,B)_6$ and is not available for hardenability. In absence of free B at the austenite grain boundary, ferrite nucleation is facilitated particularly when the finish rolling temperature is coming close to the A_{c3} temperature. Based on experiments by Asahi [6] with 0.15%-Mn-B steels the critical cooling rate to obtain 90% of the full martensite hardness is thus higher in Mo-free steel especially when the B-content is below 20 ppm (Fig. 16).

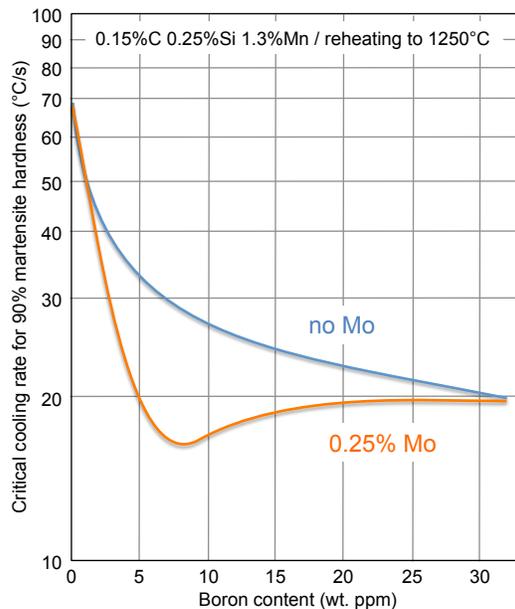


Figure 16: Influence of Mo on the effectiveness of B alloying with regard to the critical cooling rate to obtain 90% martensite hardness.

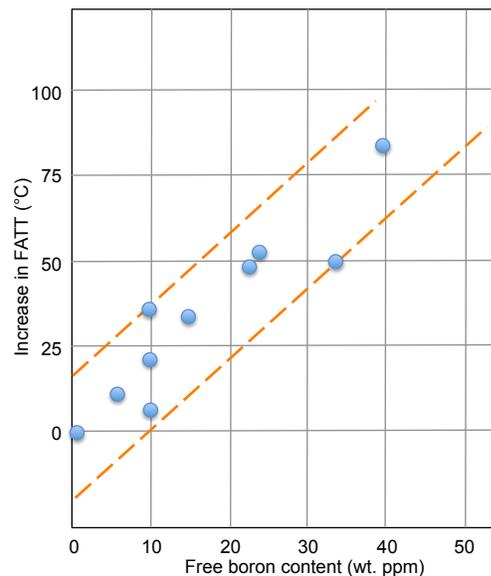


Figure 17: Influence of the free B content (not fixed as BN) on the fracture appearance transition temperature (FATT) in 0.10-0.12%C steels.

On the other hand, solute boron at grain boundaries, reduces the cohesive forces that hold neighboring grains together, and thereby reduces impact toughness through grain boundary decohesion. This is seen as an increase in the fracture appearance transition temperature (FATT) with increasing free boron content in the steel (Fig. 17) [10].

Consequently, grain boundary precipitation of boron carbide and boride particles improves toughness by essentially removing boron from (segregated) solid solution in the vicinity of the grain boundary, which explains the better HR/DQ toughness of the Mo-free steel. The toughness improvement in the Mo-added CR/DQ steel is related to obstructing crack propagation by the elongated austenite grain structure.

An alternative alloy design for good quench hardenability is Mo-Ni steel. When subjecting such an alloy concept to HACC or DQ cooling the obtained base microstructure is granular bainite being a mixture of irregular ferrite with second phases (MA, bainite, or pearlite) distributed between the irregular ferrite grains [14]. Due to molybdenum's effect of retarding pearlite formation, actually only martensite-austenite (MA) or bainite are expected to appear as second phase. Figure 18 shows the yield-tensile behaviour for the two cooling concepts. It is obvious that the DQ route leads to the highest tensile strength, yet the yield strength is lower than in the HACC route. Considering the yield ratio the DQ route results in a particularly low value, as it is typical for ferritic-martensitic dual phase steel. Therefore it is reasonable to assume that the second phase is MA in the DQ route. In the HACC route the yield ratio is much higher indicating that bainite is the second phase. Adding Nb at different levels to this Mo-Ni alloy the strength significantly increases for both routes. In the HACC route the yield ratio stays nearly constant whereas in the DQ route it increases. This indicates that by adding Nb the microstructure of the second phase is changing towards bainite. Toughness is lowest for the Mo-Ni steel without Nb produced via the DQ route and significantly increases with the addition of Nb. In the HACC route toughness is on a high level for all alloys.

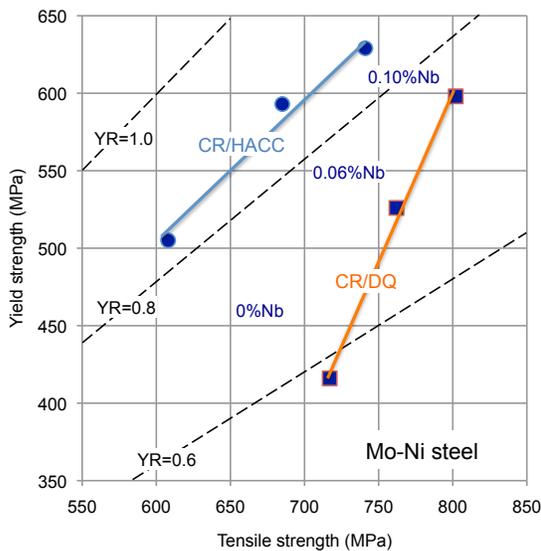


Figure 18: Influence of the cooling route on the yield-tensile strength of 0.07%C-0.2%Mo-0.3%Ni steel and cross effects of Nb alloying.

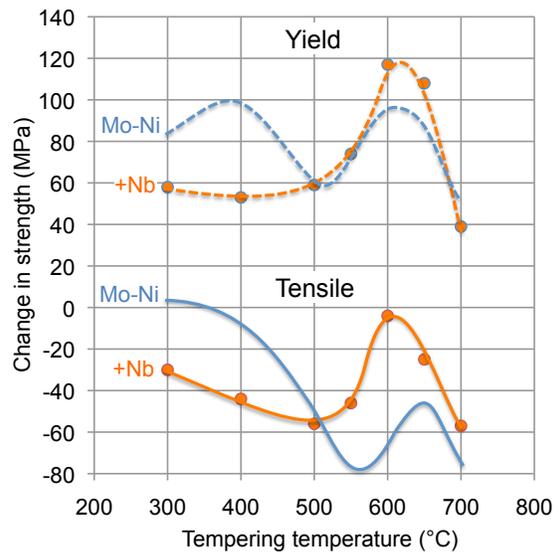


Figure 19: Influence of tempering temperature (30 minutes) on the yield-tensile strength of 0.07%C-0.2%Mo-0.3%Ni steel and cross effects of Nb alloying.

When applying a tempering treatment to the DQ route produced material, competing mechanisms such as the Cottrell effect, recovery and secondary precipitation are leading to a modified strength as shown in Figure 19. The tensile strength is decreasing for

tempering temperatures up to around 550°C, which is mainly due to a reduction of strength of the second phase. The regain of strength in the tempering range of 550 to 650°C is due to secondary precipitation, which is more pronounced in a Mo-Ni+Nb steel. The yield strength however shows a significant increase at low tempering temperature due to pinning of mobile dislocations by carbon diffusion (Cottrell effect). This effect is most pronounced in the low yield ratio (Mo-Ni) steel. Secondary precipitation hardening is stronger in the Nb-added steel, indicating that a substantial amount of Nb is in solid solution. It is widely known that solute Mo and Nb have effects of retarding the climb motion and recovery of dislocations as well as grain boundary migration. In low-carbon HSLA steel these solute elements retard dislocation recovery at temperatures of up to 550°C [15]. This can explain the moderate loss of strength of the Nb-added steel when tempering in the range of 400-500°C. The retention of dislocation networks has also a beneficial effect secondary precipitation since such defects act as a nucleation site during tempering [16].

3.2. Dual phase hot rolled strip

Compared to a multi-purpose cooling device in a plate mill the cooling profile in a strip mill is much less flexible. The limits are set by the exit speed of the strip at the finishing stand, the length of the run-out table, the configuration of the cooling headers as well as the coiling temperature. Therefore, it becomes necessary to modify the CCT diagram in an appropriate manner by alloying to obtain a particular microstructural mix. To produce a dual phase (F-M) steel the challenge is to avoid any bainite or pearlite formation and to have the right share of ferrite in the microstructure (typically 75-85%). The remainder must be pure martensite. Two principal cooling strategies can be practiced depending on the capabilities on the run-out table (Fig. 20). Single-step cooling aims for a coiling temperature between 600 and 500°C. It is here important not cooling too sharp in order to avoid bainite formation. On the other hand, cooling too slowly may result in pearlite formation. In two-step cooling fast cooling to a temperature of around 700°C is applied right after finish rolling. Then cooling is interrupted and a phase of quasi-isothermal holding allows sufficient ferrite formation. Finally the second cooling step aims for a coiling temperature of around 200°C. It is apparent from Figure 20 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 open the gap between the phase fields [17]. Figure 21 indicates the effect of Mo on the relevant times of ferrite start, pearlite start and 75% ferrite formation. It is clear that for the given base alloy the addition of only 0.1% Mo sufficiently delays the pearlite start to beyond 75% ferrite formation. Thus Mo addition increases the window of allowable cooling rates very significantly. The small delay in ferrite start by Mo can be counteracted by more severe austenite pancaking, for instance by a small amount of adding Nb to the alloy.

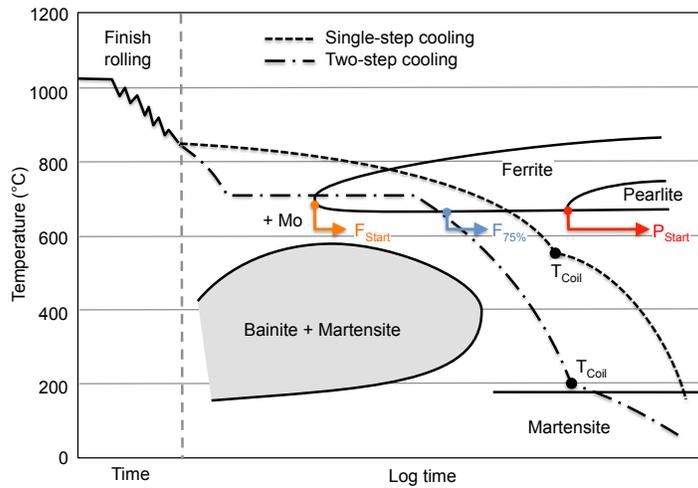


Figure 20: Cooling strategies for producing dual phase steel out of the rolling heat and schematical influence of Mo in modifying the CCT diagram.

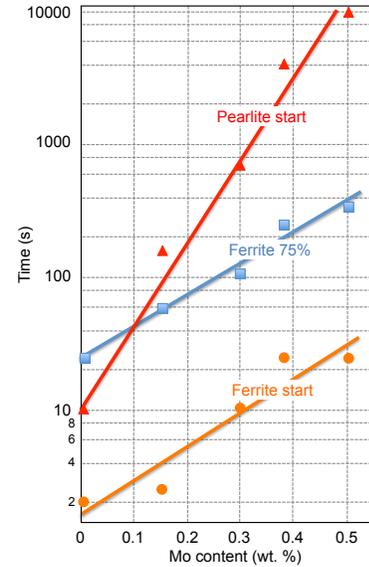


Figure 21: Effect of Mo on the phase formation times in a 0.05%C-1.2%Si-0.9%Mn-0.5%Cr alloy.

3.3. Cold rolled multiphase steels

High strength - cold formable automotive steels often rely on achieving a combination of relatively low yield strength and high tensile strength. This behavior typically requires a multiphase microstructure consisting of soft ferrite and hard martensite (DP steel) or optionally containing additional phases such as bainite and retained austenite (TRIP steel). Therefore the hot rolled strip is adjusted to a ferritic pearlitic microstructure that is easy to cold roll. The cold rolled strip is subjected to an intercritical annealing cycle according to Figure 22, be it in a continuous annealing line (CAL) or a hot-dip galvanizing line (CGL). During the intercritical annealing phase a determined amount of austenite is adjusted, while the remaining ferrite is recrystallized and the pearlite is being dissolved. During a slow cooling phase to the so-called quenching temperature new ferrite is formed and the amount of intercritical austenite is correspondingly decreased but further enriched with carbon.

In the DP production route the carbon-enriched austenite is then rapidly cooled below 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 the better weldability. Figure 23 indicates the critical cooling rate for 0.05%C-Mn steel [18]. Increasing the Mn content indeed reduces the critical cooling rate. However, a too high Mn content can cause significant centerline segregation, which is detrimental to some forming properties. 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 at a constant Mn level of 1.2%. It allows producing DP steel even on older galvanizing lines that are not particularly equipped with high power cooling devices. Furthermore, a small addition of Mo tremendously widens the process window making the process more robust against line speed and cooling rate variations.

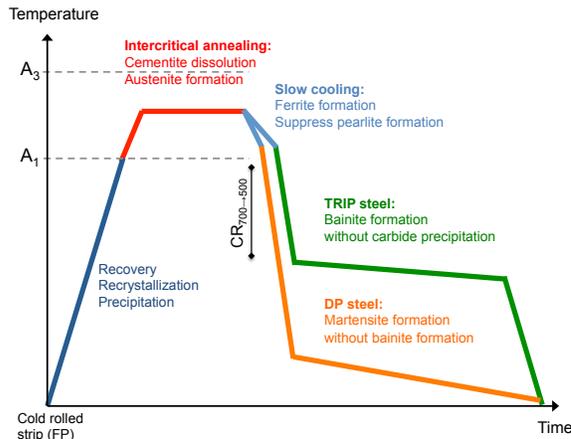


Figure 22: Principal intercritical annealing cycles for DP and TRIP steel processing.

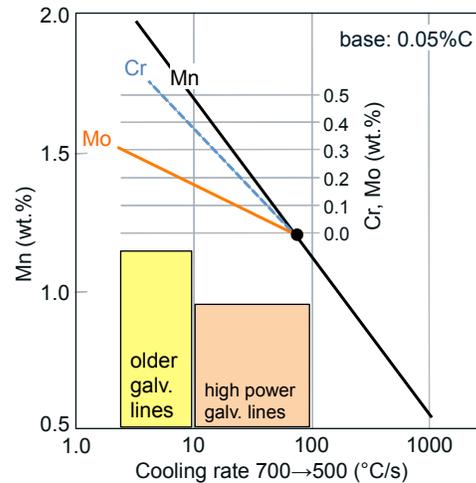


Figure 23: Influence of Mn, Mo and Cr on the critical cooling rate of a low-carbon DP590 steel grade.

Another trend in automotive steel production is to further increase the tensile strength of low-carbon DP steel from the mainstream level of 590 MPa towards 980 MPa. This can only be achieved by increasing the martensite share in the microstructure and requires thus a higher intercritical annealing temperature to produce the correspondingly increased amount of austenite precursor phase. However, the average carbon content in the austenite will be reduced and the tendency of forming bainite on the expense of martensite is enhanced. Figure 24 demonstrates the capabilities of different alloying concepts in that respect. The base alloy added with Cr is capable of achieving a strength level of around 650 MPa only. Adding Nb in a small amount lifts the strength level to around 780 MPa, yet over a narrow range of intercritical annealing temperatures. The combined addition of Mo and Nb provides a strength level of around 900 MPa over a much wider range of intercritical annealing temperatures. Several synergetic effects, amongst them grain refinement and delayed bainite formation contribute to this improvement [19].

In TRIP steel processing rapid cooling to a temperature of around 500°C is followed by isothermal holding allowing bainite formation (Fig. 22). During bainite formation the remaining austenite further enriches with carbon content so that it can finally exist as metastable austenite at room temperature. Thereby it is important not losing carbon by cementite precipitation. If the bainitic holding time is too short the material tends to show mechanical characteristics resembling rather those of DP steel. A long bainitic holding time bears the risk of pearlite formation. Aluminum as a standard alloying element in TRIP steel suitable for galvanizing lines has the effect of delaying pearlite formation. Yet, at somewhat increased holding temperature as is necessary when producing galvanized coatings the amount of retained austenite drops drastically for a mere Al-based alloying concept (Fig. 25) [20]. On the contrary, the Al-Mo-Nb concept demonstrates a much higher amount of retained austenite after annealing at increased holding temperature. Thereby, Mo further delays pearlite formation and Nb prevents carbide precipitation in the bainite phase [21]. The interaction Mo with carbon at the α - γ

interface affects the activity of carbon at the interface making the bainite transformation extremely sluggish.

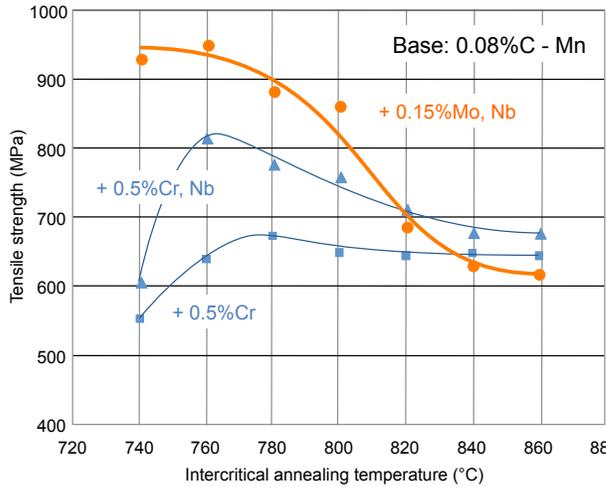


Figure 24: Influence of intercritical annealing temperature on the tensile strength of DP steel for Cr, Nb and Mo alloying.

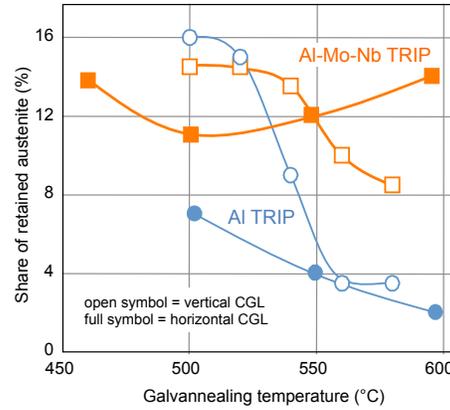


Figure 25: Influence of galvannealing (bainitic holding) temperature on the amount of retained austenite in TRIP steel for Al and Al-Mo-Nb alloys.

In a vertical CGL the highest amount of retained austenite is obtained. In addition the carbon content in retained austenite is at its highest level here. This is caused by the longer bainitic holding time compared to a horizontal CGL. In a horizontal CGL this alloying concept offers the possibility of producing strong TRIP-aided DP steels. With increasing intercritical annealing temperature the work-hardening characteristic is shifted from RA to DP behavior, noticed by the reduction of the yield strength ratio. Raising the intercritical annealing temperatures leads to higher amount of austenite, which, on the other hand, is less carbon-enriched and consequently the amount of retained austenite at room temperature is lowered.

According to the above statements about the influence of Mo on the bainite transformation, TRIP aided DP steel in the tensile strength level 900 MPa can be reached. Reducing the holding time in the bainitic region, typical for horizontal CGL leads to a DP 1000, caused by a higher amount of martensite. With 10.5 % retained austenite good forming behavior can be expected. In a vertical CGL a TRIP 800 is obtained with this alloying concept. With a modified CAL cycle using an increased bainitic holding temperature a TRIP steel of the same tensile strength class can be produced. The characteristic tensile curves of these variants are shown in Figure 26 [22].

It can be concluded that Mo additions can be used in order to achieve higher amounts of martensite and less retained austenite after processing. Hence the tensile strength level can be increased remarkably without deteriorating weldability in terms of carbon equivalent too much. Nb has been proven to stabilize retained austenite. Furthermore the grain refining effect of Nb precipitates is known to facilitate higher strength levels.

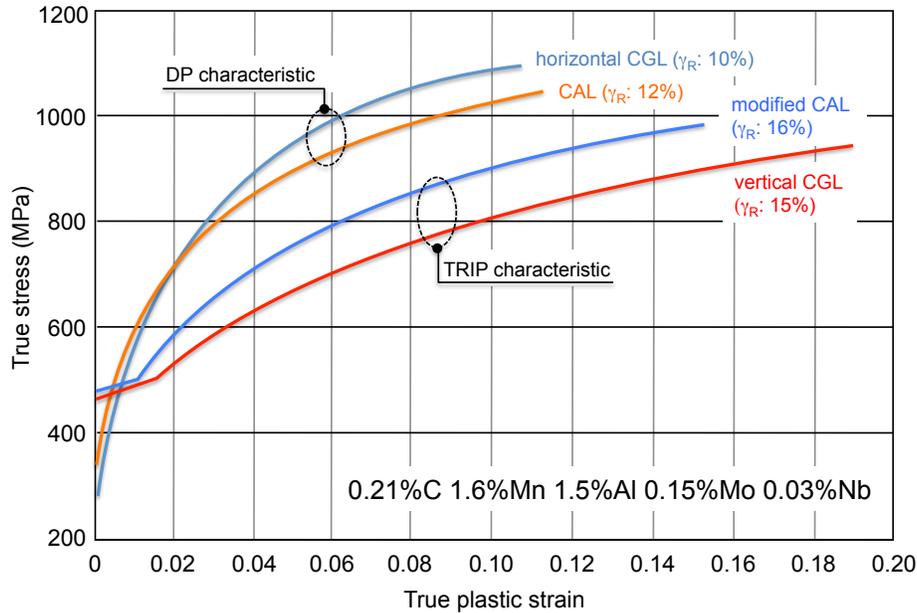


Figure 26: Tensile characteristics of a C-Mn-Al-Mo-Nb alloy processed by various intercritical annealing cycles (amount of retained austenite is indicated in parentheses).

4. Conclusions

Molybdenum as an alloying element in low-carbon steels has powerful effects with regard to the recrystallization behavior and hardenability. Its full potential, however, is developed when molybdenum interacts with other alloying elements leading to synergetic effects. In combination with Cr, Ni or B the hardenability is much increased. Interaction with the microalloying elements results in clearly improved precipitation strengthening. Particularly in combination with Nb, molybdenum shows a very interesting potential in producing some of the highest strength steels for structural, pipe and also automotive applications. A pre-requisite of utilizing these advantages is the design of suitable processing route, which necessitate a thorough understanding of molybdenum's metallurgical effects.

References

1. W. J. Liu and M. G. Akben, *Can Metall. Q.*, 26 (1987), p. 145.
2. L. J. Cuddy, "The Effect of Microalloy Concentration on the Recrystallization of Austenite During Hot Deformation," *Thermomechanical Processing of Microalloyed Austenite*, Warrendale, PA: TMS-AIME (1984), p. 129.
3. M.G. Akben, B. Bacroix and J. Jonas, *Acta Met.*, 29 (1981), p. 111.
4. T. Hara, H. Asahi, R. Uemori and H. Tamehiro, *ISIJ International*, Vol. 44 (2004), No. 8, p. 1431.
5. T. Tanaka and T. Enami, *Tetsu-to-Hagané*, 58 (1972), p. 1775.
6. H. Asahi, *ISIJ International*, Vol. 42 (2002), No. 10, p. 1150.
7. M. Masimov and N. Kwiaton, A study of Mo-induced bainitic transformation in continuously cooled steels by X-ray and electron diffraction, *Euromat 2009*, Glasgow.
8. R.W. Honeycombe, *Trans A.I.M.E.*, 7A (1976), p. 915.
9. Y. Funakawa and K. Seto, *Tetsu-to-Hagane*, 93 (2007), p. 49

10. A. P. Coldren, R. L. Cryderman and N.L. Semchysheh, Strength and Impact Properties of Low-Carbon Structural Steel Containing Molybdenum, Climax Molybdenum Company.
11. G. Krauss, Heat-Treated Low-Alloy Carbon Steels: The Benefits of Molybdenum, these proceedings.
12. H.J. Kirsch, P. Fluess, W. Schuetz and A. Streisselberger: New Property Combinations in Heavy Plate via the Accelerated Cooling Process, Stahl und Eisen 119 (1999) No. 3, p. 57.
13. C.S. Lee and W.Y. Choo, Proc. from Materials Solutions '97 on Accelerated Cooling/Direct Quenching Steels, ASM (1997), p. 51.
14. V. Schwinn, P. Fluess and D. Ormston, Proceedings of Recent Advances of Niobium Containing Materials in Europe, Verlag Stahl Eisen (2005), p. 43.
15. Mizutani et al., Nippon Steel Technical Report No. 90 (2004), p. 45.
16. C. Klinkenberg, K. Hulka and W. Bleck, steel research 75, No. 11 (2004), p. 744.
17. A.P. Coldren and G.T. Ellis, Journal of Metals, Vol. 32, No. 3 (1980), p. 41.
18. T. Irie, S. Satoh, K. Hashiguchi, I. Takahashi and O. Hashimoto, Kawasaki Steel Technical Report, No. 2 (1981), p. 14.
19. O.A. Girina, N.M. Fonstein and D. Bhattacharya, Proceedings of New Developments on Metallurgy and Applications of High Strength Steels, Buenos Aires (2008).
20. T. Heller, I. Heckelmann, T. Gerber and T.W. Schaumann, Proceedings of Recent Advances of Niobium Containing Materials in Europe, Verlag Stahl Eisen (2005), p. 21.
21. W. Bleck, A. Frehn and J. Ohlert, Niobium Science & Technology – Proceedings of the International Symposium Niobium 2001, TMS (2001), p. 727.
22. B. Ehrhardt, T. Gerber and T.W. Schaumann, Proceedings of the International Conference on Advanced High Strength Sheet Steels for Automotive Applications, Winter Park (2004), p. 39.