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SYNERGIES OF NIOBIUM AND BORON MICROALLOYING IN MOLYBDENUM BASED BAINITIC AND MARTENSITIC STEELS

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Abstract

Bainitic and martensitic steels have a great potential for structural as well as automotive applications due to the lean alloying concept and the favorable combination of strength and ductility. These steels are being considered as the material of choice for many advanced applications where yield strengths above 500 MPa are required to reduce component weight. Traditionally Mo has been a key alloying element in producing such steels. In order to expand the envelope of such steels it is interesting to combine Mo alloying with the microalloying element Nb and in some cases B. Cross effects between these elements bear synergies that cannot be achieved by single alloying. This paper demonstrates how these synergies can be beneficially used in combination with appropriate processing.

Introduction

Increasing attention is being paid to the economic advantages that high-strength low-alloy steels have to offer. These advantages include lower structural weight, Figure 1, 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, Figure 2. 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.

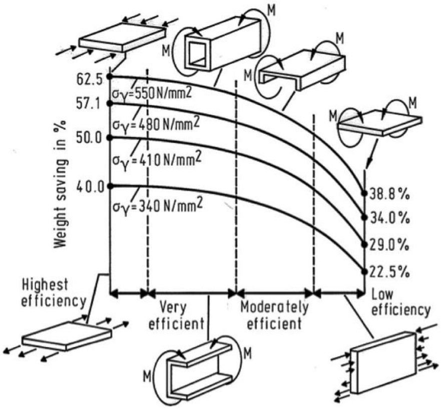


Figure 1. Weight saving potential by substituting 200 N/mm^2 steel with high strength steels for various loading conditions.

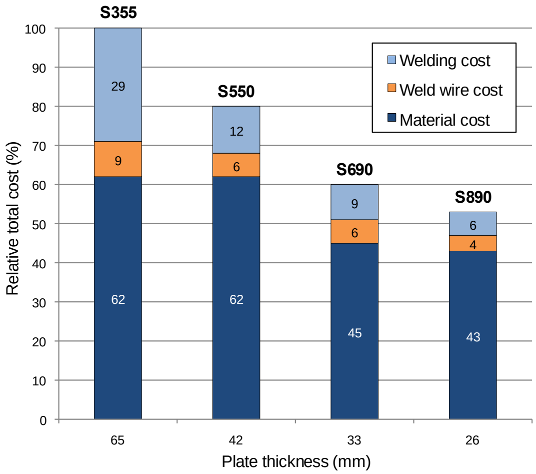


Figure 2. Material and welding cost of higher strength steels relative to S355.

Traditional high strength structural steel is produced based on a carbon-manganese alloy concept having a ferritic-pearlitic microstructure obtained by either normalizing or thermomechanical rolling. Such steels cover a yield strength range of up to around 460 MPa. To make the desired strength, different strengthening mechanisms are employed, Figure 3. 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 Nb 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. The dispersion of fine precipitates, typically carbides or nitrides of the microalloying elements, further increases the strength.

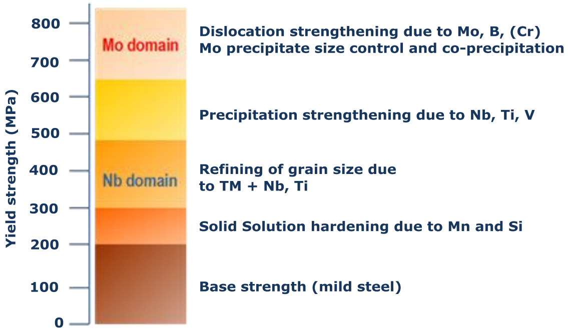


Figure 3. Strengthening effects in HSLA steel.

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 temperatures below 700 °C and thereby increase the dislocation density and refine the subgrain size. The resulting microstructure is bainite or degenerate 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 this respect. With such alloy concepts a yield strength level of up to around 800 MPa can be achieved.

The highest strength is still obtained by martensitic microstructures. This microstructure is the result of quenching from austenite, which can be done by a separate heat treatment or directly after finish rolling, Figure 4. In order to obtain a fully martensitic structure, the cooling speed must be sufficiently high across the entire plate cross-section. Alloying of molybdenum and/or boron effectively help to reduce the critical cooling speed for martensite formation. The amount of alloys required depends finally on the gauge 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. Tempering is necessary in order to produce steels with minimum yield strengths 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.

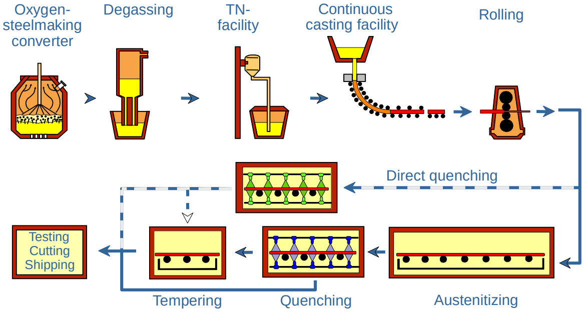


Figure 4. Processing routes for quenched and tempered steel.

Grain Size Control

Recrystallization

The addition of Nb to low carbon steel significantly retards the rate of static recrystallization (SRX). For instance, by microalloying with 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, Figure 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 to be 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 range of roughing rolling. On the other hand, the slab discharge temperature has to be considered and this typically has maximum values of 1150 °C and 1250 °C on plate mills and strip mills, respectively. Thus, the processing window, where fully recrystallizing roughing rolling passes can take place, is approximately 80-180 °C for the 0.1%Mo-0.04%Nb alloy, whereas it is reduced to approximately 30-l30 °C for the 0.6%Mo-0.04%Nb alloy.

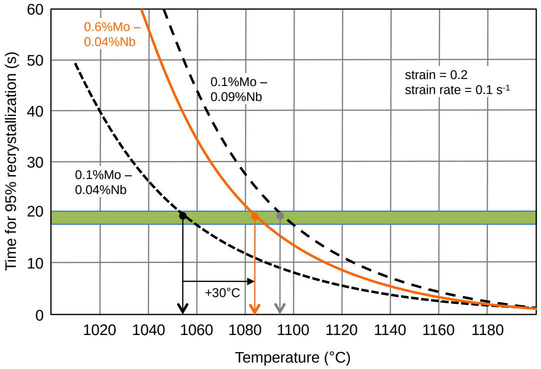


Figure 5. Influence of Mo-Nb alloy combinations on static recrystallization at high temperature.

It is well established that Nb is the most effective element in retarding the static recrystallization (SRX) of austenite at high temperature. This effect of Nb strongly increases up to an addition of 0.06% and then levels off [1]. Mo as a single alloying element does not remarkably retard SRX, however the combination of Mo and Nb leads to a synergetic increase in retardation of SRX. Earlier experiments performed by Akben et al. [2] revealed the effect of Mo additions on the dynamic recrystallization (DRX) of microalloyed steels. 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 addition of B alone can slightly retard SRX. However, when B is combined with Nb the effect is larger than the sum of the separate effects. According to He et al. [3], this has been attributed to the formation of Nb-B complexes exerting a strong dragging force on the grain boundary and hence reducing its mobility. Figure 6 exemplifies these effects for the addition of Mo and B to high-Nb ULCB steel. It is interesting to note that the addition of Ni has an adverse effect promoting SRX. Increasing the recrystallization stop temperature (RST) to values of 900 °C or above results in a particularly large processing window for finish rolling. It also allows reducing or even eliminating the holding period between roughing and finishing. This can significantly improve the productivity of a hot strip mill. Finishing at higher temperatures also reduces the mill loads resulting in less maintenance efforts. The increased recrystallization limit temperature (RLT) by B co-addition however can be a concern, as full recrystallization is desired during roughing. Especially for plate mills, the operating window is narrowed due to the relatively low slab discharge temperature.

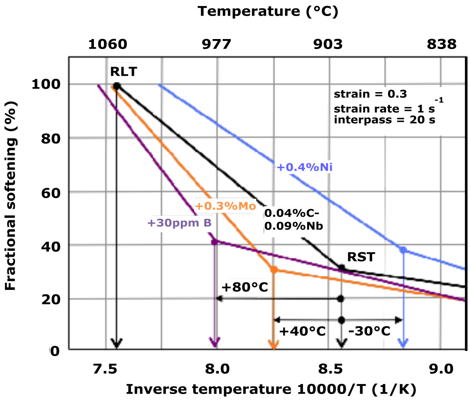


Figure 6. Effects of Mo, B and Ni addition to a low-C high-Nb base alloy on fractional softening behavior.

Strain Induced Precipitation

When Nb microalloyed steel is ausformed below the solution temperature of its carbide or carbonitride, 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, Figure 7. It was observed that the onset of precipitation of Nb in a 0.05%C-0.04%Nb steel takes twice as long when 0.3%Mo is added [2]. More recent results by Cao [4] confirmed this effect and indicated that the precipitation start in a 0.02%C-0.08%Nb steel is delayed by one order of magnitude after adding 0.15%Mo. It is evident that an increased portion of Nb can be retained in solid solution. Nb prevailing in solid solution after finish rolling has a significant capability to reduce the transformation temperature. Solute Mo and Nb strongly reduce the diffusivity of carbon in austenite as indicated by Figure 8 [5]. This effect is stronger for Nb than for Mo. However, Nb's solubility is limited and decreases with temperature whereas Mo remains fully soluble. Since Mo retards the Nb precipitation, as explained above, their individual effects on reducing the carbon activity are additive in dual alloyed steel. Hara et al. [6] have explained the effect of reduced carbon activity by Nb-C or Mo-C cluster formation. Microalloying elements available in solid solution after finish rolling have two important effects. Firstly, they delay the transformation from austenite to ferrite to a lower temperature. This effect increases with the cooling speed, Figure 9. 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. These precipitates can provide effective strengthening also known as secondary hardening.

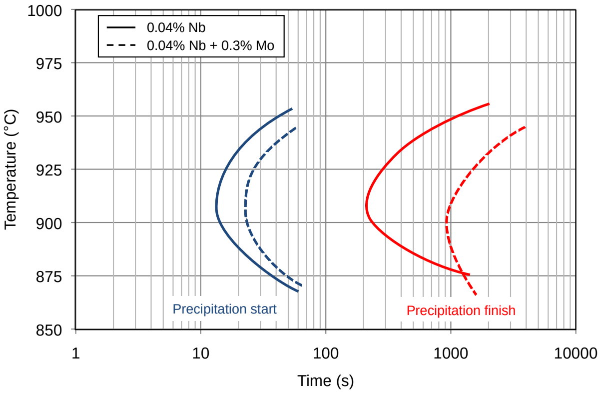


Figure 7. Influence of Mo addition on the strain induced precipitation behavior of Nb.

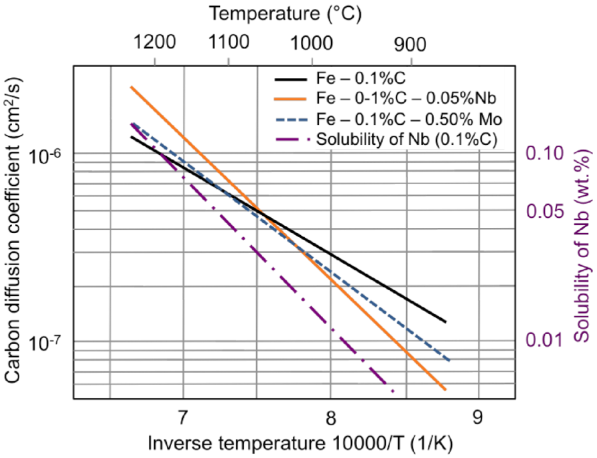


Figure 8. Solubility of Nb in 0.1%C steel and influence of solute Mo and Nb on the diffusivity of C.

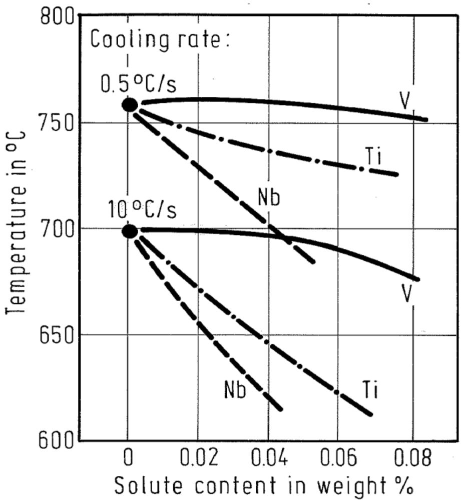


Figure 9. Effect of solute microalloying elements on the γ–α transformation temperature.

Hardenability

Molybdenum's effect of reducing the carbon activity was also found to be 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 in providing hardenability is based on its segregation to the austenite grain boundaries 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×wt%N) to protect B, however, B can still be lost by forming a complex $Fe_{23}(C,B)_6$ precipitate. This happens at the austenite grain boundary, particularly when increased amounts of B and C are present due to segregation. Asahi [7] and Hara et al. [6] have identified this phenomenon for steels with ultra-low as well as hyper-peritectic carbon contents. In both cases the addition of Mo and/or Nb to the alloy improved the effectiveness of B. Nb in contrast to Mo has a limited solubility, which depends on the carbon content.

Besides rendering a better effectiveness of boron in preventing grain boundary ferrite formation, molybdenum acts as a hardenability element by itself. This effect of Mo additionally enhances the B effect as becomes evident from Figure 10 [6]. Compared to the Nb-B steel where only B acts as a hardenability agent, the Mo-B steel shows a lower transformation temperature as well as a 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 [8]. 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 greatly 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 result 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.

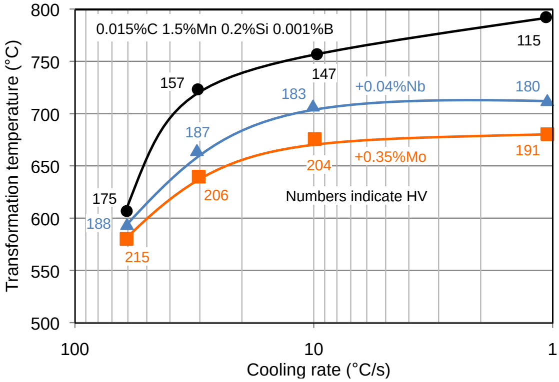
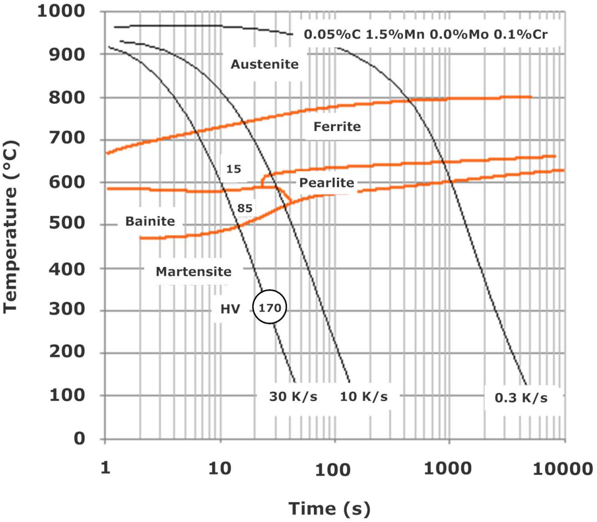
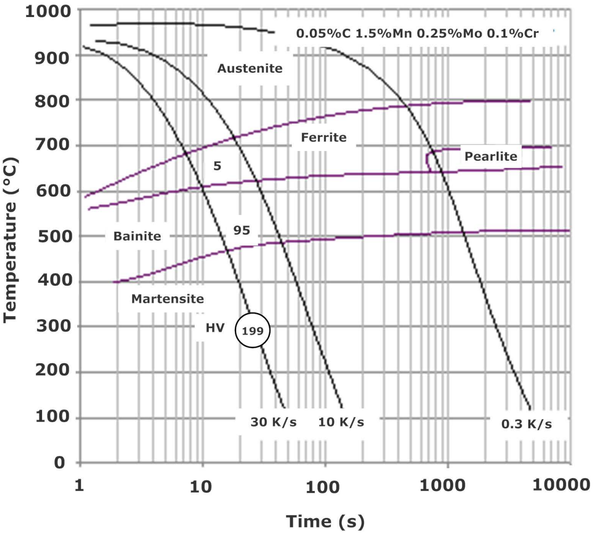


Figure 10. Effect of cooling rate on transformation temperature and hardness in ULCB steel with B, Nb-B and Mo-B alloying.


1000
900
800
700
600
500
400
300
200
100
0
Temperature (°C)
1
10
100
1000
10000
Time (s)
0.05%C 1.5%Mn 0.0%Mo 0.1%Cr
Austenite
Ferrite
15
Pearlite
85
Bainite
Martensite
HV
170
30 K/s
10 K/s
0.3 K/s

(a)


1000
900
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400
300
200
100
0
Temperature (°C)
1
10
100
1000
10000
Time (s)
0.05%C 1.5%Mn 0.25%Mo 0.1%Cr
Austenite
Ferrite
Pearlite
5
95
Bainite
Martensite
HV
199
30 K/s
10 K/s
0.3 K/s

(b)

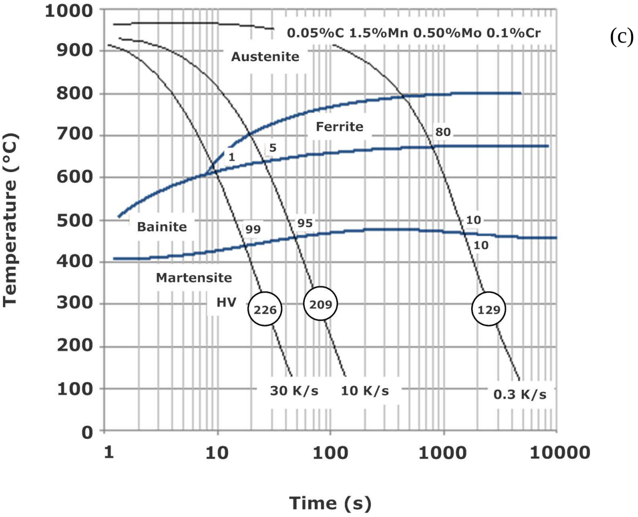
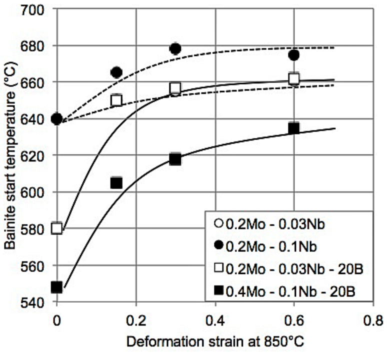


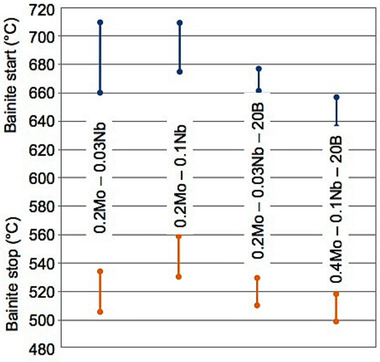
Figure 11. Effect of Mo alloying on the transformation behavior of a low-carbon base alloy (heating to A_{c3}+50 °C – holding for 10 minutes without deformation – cooling at various rates); (a) 0.05%C, 1.5%Mn, 0.0%Mo, 0.1%Cr, (b) 0.05%C, 1.5%Mn, 0.25%Mo, 0.1%Cr, (c) 0.05%C, 1.5%Mn, 0.50%Mo, 0.1%Cr.

Dissolved Nb and Mo substantially delay ferrite formation by reducing carbon diffusivity and exerting a strong drag force on moving grain (phase) boundaries. Other bulk alloying elements like Mn and Ni also delay ferrite formation, however the effectiveness of Mo is about 3x and 6x stronger than that of Mn and Ni respectively [9]. Besides alloying, two processing variables have a great influence on ferrite formation. Increasing the cooling rate (CRt) after finish rolling suppresses ferrite formation and reduces the transformation temperature. On the contrary, increasing the final deformation in the non-recrystallizing regime promotes ferrite nucleation and increases the transformation temperature. Figure 12 demonstrates the influence of process variables in combination with different alloy concepts. The bainite start (Bs) temperature increases with the accumulated deformation in austenite, Figure 12(a). Mo-Nb steels have a similarily low sensitivity of the Bs temperature to the degree of deformation. A higher Nb content in the Mo-alloyed HTP steel further raises the Bs temperature since in this steel recrystallization is very strongly suppressed and hence the driving force for transformation is particularly high. Adding boron to Mo-Nb steel results in a significant decrease of the Bs temperature in the undeformed austenite. Under this condition B can easily segregate to the austenite grain boundary. Deforming austenite in the non-recrystallizing regime enhances the austenite grain boundary area and generates deformation bands inside austenite grains that can act as nucleation sites.

The effectiveness of B is then reduced. Increasing the Mo content is the most efficient way of decreasing the Bs temperature in strain-accumulated austenite. This holds for all cooling rates, Figure 12(b). In Mo-Nb steels the Bs temperature is quite sensitive to the CRt. Adding B to the steel strongly reduces the CRt sensitivity. The Bs temperature has a direct influence on the strength of the steel, Figure 12(c). The present data indicate that the strength increases by approximately 17 MPa for every 10 °C reduction of the Bs temperature. This change is similar in magnitude for yield and tensile strength. In an earlier study, Wang et al. [9] found the influence to be around 15 MPa per 10 °C reduction of the Bs temperature. Bai et al. [10] investigated the influence of CRt and strain on the formation of transformation products in ultra low carbon steels. It can be concluded that Nb in combination with high deformation, under industrially feasible CRt, results in the partial formation of polygonal ferrite (PF) thereby reducing strength. The addition of B alone is not sufficient to prevent PF formation. However the further addition of Mo significantly facilitates the formation of bainitic microstructures under industrially achievable conditions.



(a)



(b)

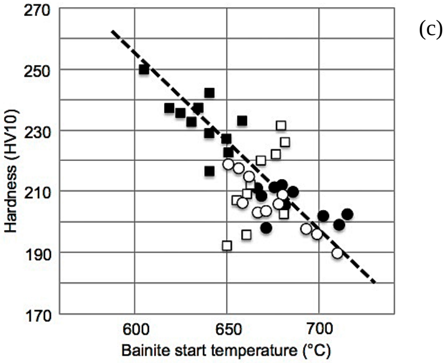


Figure 12. (a) Effect of Mo, Nb and B on bainite start temperature in 0.03%C steel at a cooling rate of 15 K/s, (b) bainite start and stop temperatures in 0.03%C steel; strain ε=0.6 at 850 °C; cooling rates: 1 – 15 K/s; Mo, Nb, B variable, other alloying elements constant, (c) hardness as a function of bainite start temperature (symbols correspond to (a)).
All compositions in wt% except B ppm.

Secondary Hardening

Nb has the lowest diffusivity and solubility in ferrite of the three carbide-forming microalloying elements (Nb, Ti, V). Both properties together promote the formation of very fine precipitates. NbC also has the largest lattice parameter of the three MC carbides consequently resulting in higher interfacial distortion for coherent precipitates, and thus in more effective strengthening. Obtaining the maximum precipitation strengthening effect depends furthermore on optimized selection of cooling pattern after finish rolling. Table I indicates the time – temperature dependence of precipitation strengthening in a 0.03%C steel alloyed with either Nb (0.02%) or Mo (0.15%) – Nb (0.10%) by isothermal holding at 600 °C and 650 °C after finish rolling at 930 °C and fast cooling at a rate of 30 °C/s. The isothermal holding time was varied between 5 and 60 minutes. From the results (Table I) it can be concluded that the Nb steel requires a lower holding temperature and shorter holding time to achieve optimum precipitation strengthening [11]. At longer holding times the Nb steel loses strength due to Ostwald ripening. The Mo-Nb steel has superior strength for any of the simulated isothermal conditions. It can be concluded that Mo delays the precipitation of NbC and obstructs Ostwald ripening [12,13]. The latter effect is well known and is being utilized for instance in fire-resistant steel [14].

Table I. Influence of Isothermal Holding Temperature and Time on Precipitation Strengthening in 0.03%C Steel with Nb and Mo-Nb Addition

	Isothermal holding for 1h		**Hardness change during isothermal holding time**	
	YS (MPa)	**TS (MPa)**	**5 → 30 min**	**30 → 60 min**
Nb/600 °C	458	602	+22	-53
Mo-Nb/600 °C	670	670	+16	+42
Nb/650 °C	429	575	-19	-17
Mo-Nb/650 °C	690	670	+11	+12

The combination of low carbon content, Mo alloying and fast cooling provides conditions for maintaining a substantial amount of Nb in solid solution after finish rolling. This Nb is available for nano-precipitation either by a secondary heat treatment (plate) or by appropriate coiling conditions (hot strip). Simulation of a DQ treatment with subsequent tempering at 600 °C for one hour, Figure 13(a), was used to estimate the strengthening potential at various C and Nb contents. It is obvious that with an enhanced amount of both elements the yield strength significantly increases. It is however not exactly clear how much C and Nb were effectively available to form fine precipitates and how much other carbide formers such as Mo and Cr were involved. Nevertheless, for the samples with a C content below 0.02% conditions were such that an interstitial free (IF) matrix can be obtained by carbide precipitation. In this case the DBTT (Ductile Brittle Transition Temperature) is further reduced to a level of below -100 °C, Figure 13(b). The higher C content leads to a more pronounced precipitation hardening. This also results in a loss of toughness, as expected. The increase in DBTT is moderate for the 0.05%Nb steels, yet quite significant in the 0.1%Nb steel. In the latter steel, Nb at full precipitation binds about 0.014%C. Since this steel also contains a relatively high amount of Mo it is possible that additionally Mo_2C precipitates have been formed. The needle-shaped morphology of Mo_2C precipitates can be harmful to impact properties [15]. Therefore a suitable balance between different carbide forming elements as well as appropriate tempering conditions has to be achieved in order to avoid precipitation of Mo_2C.

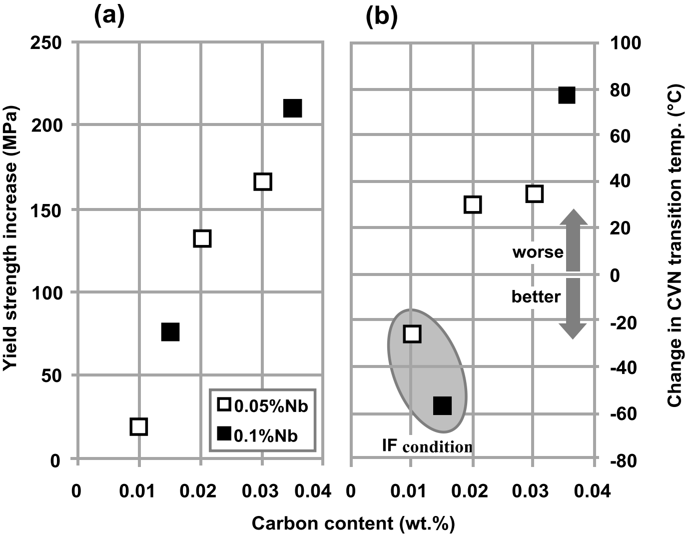


Figure 13. (a) Precipitation hardening effect after DQ cooling and subsequent tempering at 600 °C/1h in Mo-Nb ULCB steels, (b) corresponding change in the DBTT.

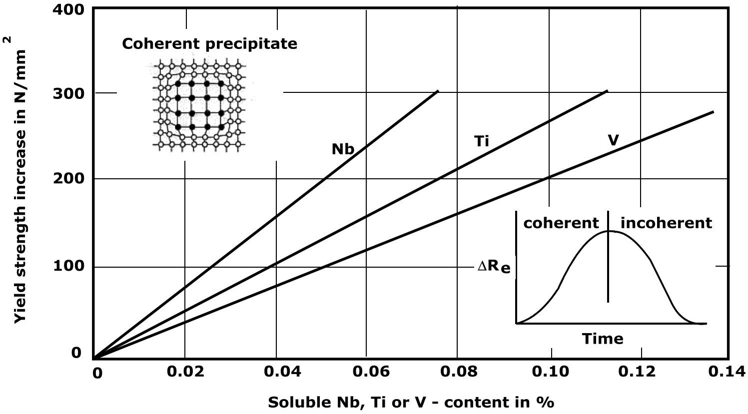


Figure 14. Strength increasing potential of microalloying elements by coherent precipitation.

The strengthening potential of nano-sized coherent precipitates of microalloying elements is in the order of 300 MPa, Figure 14. The actual strength increase by precipitation hardening depends on the amount (i.e. soluble microalloy content) and distribution of such particles. Furthermore, the lattice distortion and thus the resulting stress field at the particle-matrix interface is controlled by the lattice constant of the carbide species. The larger lattice constant of NbC as compared to that of TiC or VC consequently results in a higher strengthening potential of NbC for the same amount and size distribution of particles.

Advanced Processing Concepts

Direct Quenching of Plate

When producing steels of the highest strength level, quenching & tempering is an often-used treatment. The rolled material after cooling down from rolling is re-austenitized and then quenched, Figure 4. This results in a very strong but often brittle material. Subsequent tempering provides a much better toughness and ductility at the expense of strength. Molybdenum effectively enhances the so-called tempering resistance, which counteracts the loss of strength as described by Krauss [16].

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 [17]:

- ACC (Accelerated cooling) results in cooling with ideal cooling rate, i.e. the difference of cooling rate between surface and center is kept low.
- HACC (Heavy ACC) is a special variant of the classical ACC but with a 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 have the decisive difference that the steel only goes once through the α–γ phase transformation (instead of 3 times in conventional Q&T). Accordingly, 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 grain 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 [18]:

- 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 the 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 [7] with 0.15%C-Mn-B steels, the critical cooling rate to obtain 90% of the full martensite hardness is thus higher in the Mo-free steel, especially when the B-content is below 20 ppm, Figure 15.

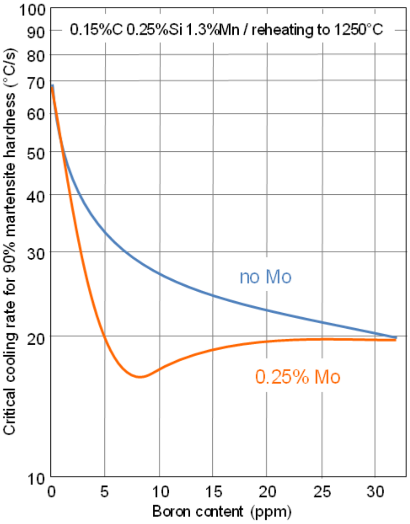


Figure 15. Influence of Mo on the effectiveness of B alloying with regard to the critical cooling rate to obtain 90% martensite hardness.

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, Figure 16 [19]. 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 the obstruction of crack propagation by the elongated austenite grain structure.

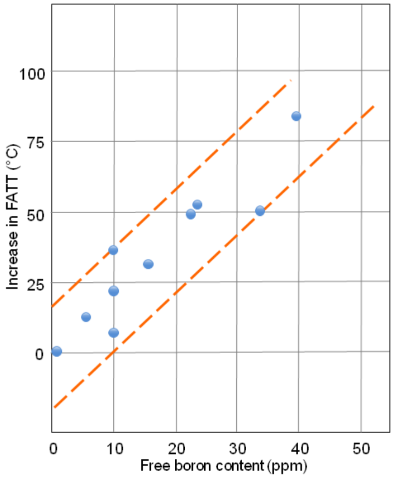


Figure 16. Influence of the free B content (not fixed as BN) on the fracture appearance transition temperature (FATT) in 0.10-0.12%C steels.

An alternative alloy design for good quench hardenabilty 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 [20]. Due to molybdenum’s effect of retarding pearlite formation, only martensite-austenite (MA) or bainite are expected to appear as second phases. Figure 17 shows the yield-tensile behavior 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 from the HACC route. Considering the yield ratio, the DQ route results in a particularly low value, as 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 the addition of Nb changes the microstructure of the second phase 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.

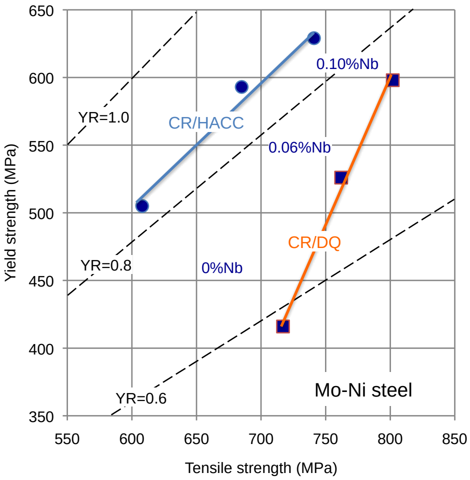


Figure 17. Influence of the cooling route on the strength of 0.07%C-0.2%Mo-0.3%Ni steel and effects of Nb alloying.

When applying a tempering treatment to the DQ route produced material, competing mechanisms such as the Cottrell effect, recovery and secondary precipitation influence the strength as shown in Figure 18. 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 regaining 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 temperatures 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 the effect 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 up to 550 °C [21]. This can explain the moderate loss of strength in the Nb-added steel when tempering in the range of 400-500 °C. The retention of dislocation networks also has a beneficial secondary precipitation effect since such defects act as nucleation sites during tempering [22].

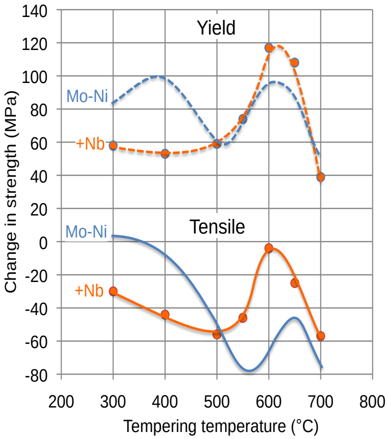


Figure 18. Influence of tempering temperature (30 min.) on the yield and tensile strength of 0.07%C-0.2%Mo-0.3%Ni steel and cross effects of Nb alloying.

Wear Resistant Plate

Machines and equipment for industry, mining, agriculture and other constructions often require heavy plates, which have to guarantee good wear resistance. The most typical application is for machines to excavate raw materials such as coal, ores, stone, etc. These steels comprise as characteristic alloying elements manganese, chromium, molybdenum and nickel and are based on carbon levels up to 0.40%. Consequently they attain high hardness values of 400 to 600 HB (Brinell Hardness), Table II. Typical plate thicknesses range up to 100 mm. The characteristic wear type in most applications is ploughing leading to abrasive wear. Thereby, usually the plate surface gets scratched when exposed to an abrasive and hard material such as sand or other minerals. High hardness of the material is one important feature for good wear resistance. Furthermore, a higher toughness of the material improves the wear resistance and thus reduces material loss.

The necessary high hardness is achieved by quenching the plate into a martensitic microstructure. The hardness of the as-quenched martensite directly correlates with the amount of carbon. For sufficient through-hardenability, especially of heavier plate gauge, the addition of alloying elements such as Mo, Ni, Cr, and Mn are used. Their hardening capabilities are demonstrated in Figure 19 for a 0.4%C steel (600 HB class). It is evident that Mo is particularly powerful in raising the hardening depth. To limit the Mo content to a maximum of 0.5% a micro-addition of boron (typically 20 ppm) can be used as a hardness booster. In this case, boron has to be protected from combining with nitrogen by microalloy additions of Ti or Nb plus Al. The Nb+Al combination was shown to be successful in reducing the free N to a level below which BN formation is suppressed. A substantially finer particle dispersion, which is beneficial for toughness, exists in the Nb microalloyed steel due to the lower formation temperatures of the AlN and Nb(C,N) particles compared to TiN [23].

Table II. Chemical Composition Boundaries for Abrasive Resistant Steel Plates

Target hardness (HB)	**Max. plate gauge (mm)**	**Base alloy composition (max. %)**						**Typ. CET* (%) at gauge**	
		C	**Si**	**Mn**	**Cr**	**Ni**	**Mo**	**8 mm**	**40 mm**
400	100	0.20	0.80	1.50	1.00		0.50	0.26	0.37
450	100	0.22	0.80	1.50	1.30		0.50	0.38	0.38
500	100	0.28	0.80	1.50	1.00	1.50	0.50	0.41	0.41
600	40	0.40	0.80	1.50	1.50	1.50	0.50	0.55	0.55

*CET = C + (Mn+Mo)/10 + (Cr+Cu)/20 + Ni/40

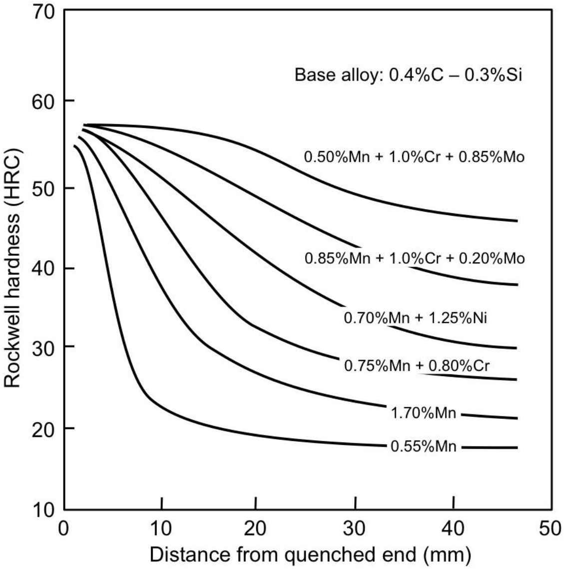


Figure 19. End quenching curves demonstrating the effect of various alloy combinations on through-hardenability.

Toughness is an important property for the application of wear plates and there are several ways of improving it. A common method is tempering of the as-quenched plate. This treatment leads to a trade-off of properties as hardness is reduced and toughness is increased. Sufficient additions of Mo and optional microalloying of Nb counteract the hardness loss under a given tempering condition by increasing the tempering resistance as shown in Figure 20. Toughness decreases with increasing hardness of untempered martensite according to Figure 21. However, there are metallurgical methods to still improve toughness at a given hardness level. It is beneficial to keep impurity levels of P, S and N as low as possible. P segregates to prior austenite grain boundaries reducing grain boundary cohesion. S can form MnS inclusions that are much softer than the martensitic matrix. Excessive N leads to the formation of coarse TiN particles, which can act as crack initiation sites. Adding Nb has the effect of refining the prior austenite grain structure. In martensitic steels intragranular fracture propagates primarily interfacially along martensite lath boundaries. Lath boundaries develop within the prior austenite grain. The propagating intragranular crack is forced to stop or to change direction at the prior austenite grain boundary. Intergranular fracture separates prior austenite grain boundaries during propagation. Hence, refining the prior austenite grain size requires more energy for the crack to propagate and is thus beneficial. Figure 22 demonstrates the toughness increasing effect of Nb microalloying in a 450 HB grade. Over the entire range of testing temperatures the impact resistance is substantially improved. Additionally, alloying of Mo can help prevent P segregation to the austenite grain boundaries and thus counteract the P-induced loss of grain boundary cohesion [24]. This is particularly helpful when the steel shop has difficulties achieving ultra-low P levels. Studies on abrasive wear properties showed that the better toughness in the niobium microalloyed steel also results in an improvement of the wear resistance due to a change in wear mechanism. Under a given test condition of abrasive wear by hard minerals on a 450 HB grade, the service life could be increased by around 20% using niobium microalloying [25].

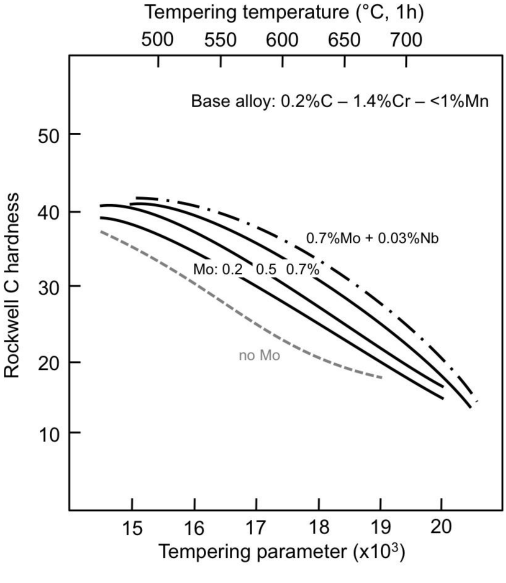


Figure 20. Effect of increasing Mo additions and Nb microalloying on the tempering resistance.

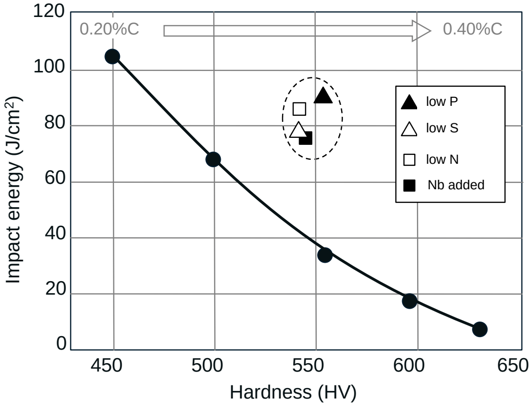


Figure 21. Dependence of impact toughness on hardness (C-content) of as-quenched martensite and metallurgical methods of increasing toughness.

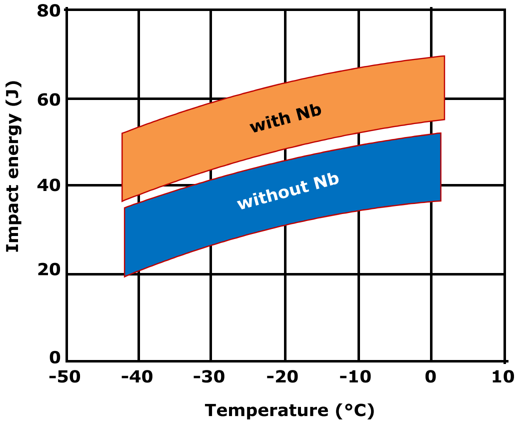


Figure 22. Toughness as a function of impact temperature for 450 HB abrasive resistant plate steels without and with Nb microalloying.

Conclusions

Additions of Mo and Nb to low carbon plate steel allow an increase in both yield and tensile strength. The two alloying elements have beneficial individual effects and reveal interesting synergies when alloyed in combination. Nb is particularly effective in retarding recrystallization. This is the basis for efficient grain refinement thus improving strength and toughness simultaneously. Secondly, Nb provides a high potential for precipitation hardening. Mo is a potent hardenability element as it retards ferrite formation and lowers the bainite transformation temperature. It also assists Nb in retarding recrystallization and optimizes the precipitation hardening effect of Nb. Both elements significantly enhance the tempering resistance. The simultaneous presence of solute Mo or Nb also increases the effectiveness of B microalloying. Solute B segregated to the austenite grain boundaries efficiently inhibits pro-eutectoid ferrite nucleation. On the other hand, B strongly enhances the recrystallization retarding effect of Nb. A well-considered coordination of these alloying elements with the plate processing conditions is required to exploit their metallurgical effects and thus obtain the optimum mechanical properties [22].

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