# The Development of High Performance Low Carbon Bainitic Steel

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### **Abstract**

The yield strength 550MPa-960MPa grade low carbon bainitic steels have been developing in China. By newly developed relaxation- precipitation-phase transformation control (RPC) process, the packet size of bainite can be refined to 3 microns in width and 6 microns in length. As the cost consideration, high Nb content (0.1%) concept (Mn-Nb-B) has been applied to develop 550MPa-960MPa grade plate steel too. The optimized thermo-mechanical control process (TMCP) and tempering process have been revealed, the role of solute and precipitate Nb has be discussed. These years, more than 100,000 tons/annul of low carbon bainitic plate steel have been produced by advanced gain refinement technology and lower cost microalloying approach.

### Introduction

Low carbon bainitic steel is a kind of high performance structural steel with high strength and good weldability. In 1998, the Chinese government proposed the fundamental research project on "New Generation Iron and Steel Materials" [1], the principle and technology to achieve ultra-fine high strength bainitic steel has been developing.

The strengthening mechanism of low carbon bainitic steel includes intermediate phase transformation control, high dislocation density inheritance, precipitation of microalloys and refinement of effective grain size. Meanwhile, controlling the multi-intermediate transformation phases is also very important to modify the high performance [2].

Refinement the grain size by TMCP had been studied broadly for more than 30 years [3,4]. Rough rolling, finish rolling, accelerated cooling are the main procedures for high performance steel. However, by the deeply understanding the physical metallurgy phenomenon during TMCP, it is found that during relaxing period of deformed austenite, the dislocation will evolve to form cell structure, and the stain induced precipitates will precipitate on the dislocation wall. Therefore, the dislocation

cells pinned by precipitation can act as sub-grain boundary to limit the growth of bainite during phase transformation. Therefore, refining the transformation phase by formation of enhanced dislocation cell structure (act as sub-grain boundary) during relaxation period after finish rolling could be a new process to refine the transformation phase. The physical metallurgy principle and effect on strengthening of low carbon bainitic steel have been studied [5-7], and the technology has been applied to developing high performance steel in Chinese steel company.

Nb is always used as a microalloying element for grain refinement and increase the non-recrystallization temperature [8]. These years, high Nb content (0.07-0.11%Nb) microalloying approach has been developed [9]. It shows that the high Nb content concept can be applied in Steckel mill for prohibited recrystallization during the prolonging interpass time and /or applied in severe mill to produce high performance steel. Besides, the theoretical simulation work also shows the mechanism of solute and precipitate of higher Nb content steel on the recrystallization of deformed austenite [10,11]. However, the recrystallization window for rough rolling and the non-recrystallization window for finish rolling should be determined more reliably and the role of Nb (solute and precipitate) should be understood more comprehensively for developing high performance steel. In this paper, there parts will review the influence of relaxation of deformed austenite on the grain refinement, control of multi-phase transformation and the physical metallurgy phenomenon of high Nb content steel during TMCP, respectively.

# Refinement the packet size of bainite & refinement principle

The refinement of grain size is one of the basic methods to improve the mechanical performance of steel. Therefore, refinement of the intermediate transformation microstructure, particularly the bainite/martensite packet size could improve the mechanical properties obviously.

In the deformed austenite, the heavily tangled dislocations will recover and/or polygonize, so that the dislocation cells will form during the relaxation of austenite. At the same time, the strain induced precipitates will precipitate on the dislocation walls during the relaxation period. The precipitates can reinforce the dislocation walls. While the austenite is cooling down, the deformation bands, precipitates and sub-boundary act as the nucleation site of acicular ferrite. Therefore, the previously transformed acicular ferrite will separate the prior-austenite grain; the reinforced cell (pinned by precipitates) would act as a sub-boundary to interrupt the growth of intermediate transformation phase.

The technology developed by the above model is called relaxation-precipitation-phase transformation control (RPC) process. The technology includes microalloying design, controlled rolling, and relaxation for several seconds after finish rolling and then accelerated cooling/direct quenching. The schematic diagram of the technology is

shown in Figure 1, it can be seen that the rolling and cooling process is as same as the TMCP, except the relaxation process employed after the finish rolling.

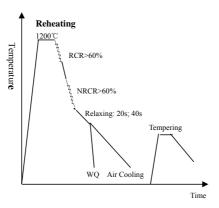


Figure 1. Scheme of RPC process

# Effect of relaxation on the refinement of bainitic packet size

The influence of processing parameters of RPC technology, such as finish rolling temperature, reduction ratio and relaxing time on the microstructure was studied by thermo-simulation for low carbon Mn-Mo-Nb-B micro-alloyed steel [5]. Figure 2 shows the microstructures after following simulation: deformed by 30% at 850°C and then relaxing for (a) 0s, (b) 30s, (c) 200s, respectively. In Figure 2 (a) to (c), it can be seen that, for the sample that did not relax after deformation (Figure 2(a)), the packet sizes are very large; the laths almost penetrate through the prior-austenite grain. When the sample was relaxed for 30s to 200s, the packet sizes decrease obviously (as shown in Fig.2 (b) and (c)). In Figure 2 (b), relaxed for 30s, the packet sizes are not homogeneous, but some fine packets appeared. When relaxed for 200s (Figure 2(c)), the packet sizes are the much fine and much more homogeneous compared with other conditions.

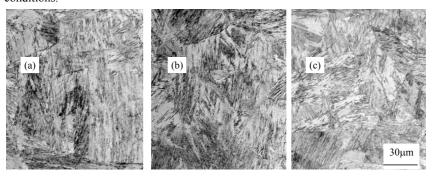


Figure 2. The microstructures of specimens that deformed at 850°C for 30% and relaxed for: (a) 0s, (b) 30s, (c) 200s.

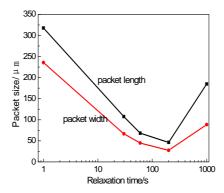


Figure 3. The statistic results of packet length vs. relaxing time for different process conditions.

Therefore, relaxation process can influence the refinement of intermediate transformation structure; the relaxation time is a very important parameter for obtaining fine packet structure. The length of a packet defined as the maxim length aligning the parallel laths direction and the width of a packet defined as the maxim length across the laths. The average length and width for each sample were measured. The curves of packet length and width as a function of relax time are shown in Figure 3. It can be seen that for a certain deformation temperature and reduction ratio, the packet size decreasing and reach a minim value with the relaxing time increase.

# Evolution of dislocation and precipitate during relaxation

Figure 4 demonstrates the evolution of dislocation configuration during the relaxation after deformed at 900°C of Fe-30%Ni (microalloyed with Nb, C, B) alloy [5]. The Fe-30%Ni alloy was used as a model alloy to demonstrate the evolution of dislocation structure and precipitate in the austenite at ambient temperature, as there is no phase transformation during cooling. Figure 4(a) shows that, for the no relaxing specimen, the dislocation density is very high, and they are tangled together. After relaxing for 60s it can be found from Figure 4 (b, c) that the dislocation cell formed evidently. Figure 4(c) shows that there are a few fine precipitates on the wall and dislocation. From Figure 4 (d) it can be found that when relaxed for 1000s the dislocation cells are perfect in shape and have uniform size, the precipitate size is a litter bit larger. It can be seen the dislocation cell structure can be formed during relaxation, the strain induced precipitate precipitated on the dislocation wall that would pin the dislocation cell and /or reinforced the cell structure. Although the dislocation density decreases during relaxation, the polygonized dislocation cell structure can play more important role for refining the intermediate transformation structure.

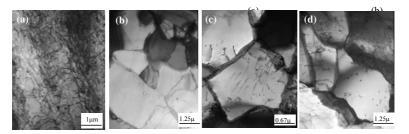


Figure 4. Dislocation configuration in the austenite during the relaxation for (a) 0s, (b) 60s, (c) 60s, (d) 1000s

The carbon extraction replicas in Figure 5 shows the precipitates in the specimens of Fe-30%Ni model alloy when relaxed for different time after deformed for 30% at 850 °C [12].

It can be seen that no strain induced precipitate can be observed in non-relaxation specimen (Figure 5(a)). Only few large inclusions can be detected in the tested specimen. Form Figure 5(b) and (c), we can see that very small precipitates with mean particle size about 4nm are occasionally observed after stress relaxation for 30s and 60s. They displayed chain-like or nearly straight-line distribution. The denser dislocation and deformed bands are the preferred nucleation sites for precipitating. As the relaxation time is prolonged to 200s, the distribution of precipitate becomes uniformly and the average particle size arrives to 10nm, as shown in Figure 5(d).

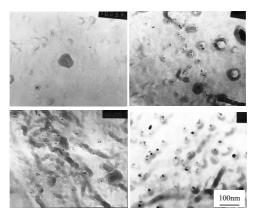


Figure 5. Precipitates in the specimens relaxed for (a) 0s (b) 30s (c) 60s (d) 200s after deformed for 30% at

The evidence of the evolution of dislocation configuration, the strain-induced precipitation during the relaxation period and the interaction of the precipitate with the dislocation cell reveal the mechanism of forming the reinforced dislocation cell structure. It has been also proved by EBSD mapping that, after relaxation, the fine

sub-grain will form in the austenite of Fe-30%Ni alloy [13]. The phenomenon of sub-grain boundary formation after relaxation for a certain time in the microalloyed steel was also revealed by PTA (particle trace autoradiograph) technique [14] in the other work too [7].

# Refinement microstructure and its mechanical property

The low carbon Mn-Mo-Nb-B bainitic steels were rolled in laboratory by RPC process. The influences of RPC process parameters on the microstructure and

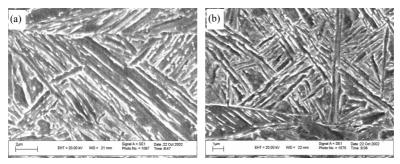


Figure 6. The morphologies of acicular ferrite and packet size in no relaxed (a) and relaxed for mechanical properties have been studied [15].

Figure 6 shows the microstructures of steels that processed by different relaxation time. It shows that, when the relaxation time is short, the acicular ferrite would not grow up larger and the number is less (as shown in Figure 6 (a)); but when the relaxation time is prolonged, the needles grow up and form many cross-like patterns. The prior-austenite is separated by these acicular ferrites, the randomly orientated packets within the section which surrounded by the acicular ferrites are much fine, as shown in Figure 6(b), the packet size is about 3 microns in width and 6 microns in length.

Table 1 shows the yield strength of steels processed by RPC and reheat and quenching (RT-Q) processes, respectively.

property	Rel	Rm	A
process	N/mm <sup>2</sup>	N/mm <sup>2</sup>	%
RT-Q, T @630℃,1h	619	655	19
RPC,T @ 630°C, 2h	816	851	18

Table 1 Mechanical property of RPC and RT-Q steel

After tempered at 630°C for 1h, it can be seen that the 800MPa grade yield strength

can be achieved easily following RPC process, the yield strength of RPC processed steel is about 200MPa higher than comparing with RT-Q processed steel.

## Control the phase transformation

### Intermediate phase transformation

In the intermediate temperature ranges, it is often leads to the many kind of transformation phases. For Mn-Mo-Nb-B low carbon bainitic steel, synthetic microstructures of bainitic ferrite and acicular ferrite will be more strong, tough and ductile [16].

The isothermal tests have been carried out [17]. When the austenization specimens were isothermally held at  $580^{\circ}\text{C}$ ,  $530^{\circ}\text{C}$  and  $480^{\circ}\text{C}$  for 900s, respectively, three kinds of intermediate transformation phases could be formed. It can be seen that when the specimen is held at  $580^{\circ}\text{C}$  (As shown in Fig.7 (a)), the transformation phase is allotriomorphic ferrite during isothermal treatment. The acicular ferrite was transformed while isothermally treated at  $530^{\circ}\text{C}$ , the acicular ferrites were distributed randomly in the prior-austenite grain, the width is about  $2\mu\text{m}$  and the length is about  $10\sim20\mu\text{m}$ . This kind of acicular ferrite grew up independently with each other (as shown in Figure 7 (b)). When the specimen isothermally held at  $480^{\circ}\text{C}$  (as shown in Figure 7 (c)) the transformed phase was lath-like bainitic ferrite.

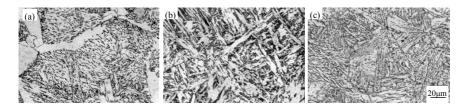


Figure 7. Optical micrographs of Mn-Mo-NB-B low carbon bainitic steel show the isothermal transformation microstructures after isothermally holding at various temperatures for 900s: a small amount of allotriomorphic ferrite at  $580^{\circ}\text{C}(a)$ , acicular-like ferrite at  $530^{\circ}\text{C}(b)$ , bainitic ferrite at  $480^{\circ}\text{C}(c)$ 

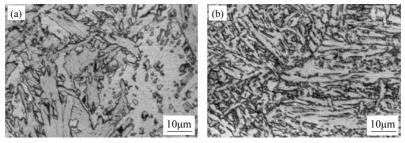


Figure 8. Optical micrographs of the specimens that deformed at 850 for 30% and continuously cooled at (a) 1 /s, (b) 5 /s to room temperature

The CCT diagram of the Mn-Mo-Nb-B steel shows that continuously cooled at rate from  $0.5^{\circ}$ C/s to  $30^{\circ}$ C/s, the transformation mainly took place between  $600^{\circ}$ C and  $450^{\circ}$ C [17]. According to CCT diagram, the overcooling austenite can transform into quasi-polygonal ferrite, acicular ferrite, granular bainite and lath-like bainite depending on the cooling rate [16]. Figure 8 shows the microstructures of Mn-Mo-Nb-B steel obtained from the continuously cooled specimens. At cooling rate of  $1^{\circ}$ C/s, the predominant microstructure is acicular ferrite and granular bainite, and no clear prior-austenite grain boundary can be observed in the matrix (as shown in Figure 8 (a)). Cooled at  $5^{\circ}$ C/s, the microstructure is main lath like bainite (as shown in Figure 8(b)).

#### Formation and control of acicular ferrite

From Figure 8, it can be seen that in addition to main phases of granular ferrite (Figure 8(a)) and bainitic ferrite (Figure 8(b)), there are acicular ferrites in both matrixes. From isothermal treatment result of Figure 7, it shows that, the acicular ferrite is transformed before bainite transformation [17]. On the other hand, the granular ferrite only forms during continuously cooling at relatively slow cooling rate, the isothermal treatment cannot obtain the granular ferrite (as shown in Figure 7). Therefore, it supposes that the granular ferrite is evolved from the acicular ferrite.

Figure 9 shows the microstructures of specimens that cooled continuously to  $600^{\circ}$ C,  $500^{\circ}$ C and  $450^{\circ}$ C at  $1^{\circ}$ C/s, respectively, and then quenched. There are two kinds of phases, one is acicular ferrite (transformed during slowly cooling) and the other is lathlike bainitic ferrite or martensite (transformed during quenching). The acicular ferrite nucleates on the grain boundary and intragranularly (at the deformation band or other sun-boundary).

However, if the quenching temperature decreases to  $500\text{-}450^{\circ}\text{C}$ , it can be seen from Figure 9(b) and (c) that the acicular ferrites are coarsened and connected with each other. Only a small amount of residual austenite is trapped between the coarsened ferrites (as shown in Figure 9(b)). The morphology of the transformation phase in Figure 9(c) is as same as the granular ferrite (as shown in Figure 8(a)).

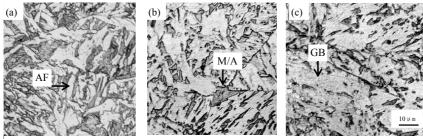


Figure 9 . Optical micrographs of specimens deformed at  $850^{\circ}$ C for 30% , cooled at  $1^{\circ}$ C/s and then quenched at  $600^{\circ}$ C(a),  $500^{\circ}$ C(b),  $450^{\circ}$ C(c), respectively

The shape of the acicular ferrite is short and coarse. It distributes randomly inside the grain. The SEM morphology (Fig. 10) shows that the acicular ferrite is flat and featureless. Moreover, the packet of lathlike bainitic ferrite is refined by homogenous distribution of the acicular ferrite.

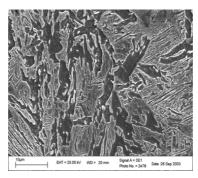


Figure 10. SEM image of specimen cooled at  $1^{\circ}\text{C/s}$  to  $600^{\circ}\text{C}$  and then quenched in water

The nanohardness of acicular ferrite and bainitic ferrite in low carbon microalloying steel shows that the granular ferrite which formed after continuously cooled at  $1^{\circ}$ C/s to ambient temperature is as same as the nanohardness of acicular ferrite as shown in Figure 11 [18,19]. Figure 11(a) and (b) are morphology of granular fe<sup>AF</sup>: which transformed during continuously cooling to ambient temperature at  $1^{\circ}$ C/s and the acicular ferrite which obtained by continuously cooling to  $580^{\circ}$ C at cooling rate of  $1^{\circ}$ C/s and then quenching, respectively. Figure 11(c) shows that the nanohardness of acicular ferrite and the bainite ferrite are almost same.

The EBSD result [19] of misorientation of the acicular ferrite within an austenite grain also shows that the nearby acicular ferrites nucleated on the one part of grain boundary are almost orientated in the same direction (small angles between the acicular ferrites as shown in Figure 12(a), but within one austenite, there are several parts of same orientation areas, as shown A and B areas in Figure 12(b), just like the granular ferrite formed within a prior-austenite grain. It can deduce that the acicular ferrites grow and/or coarsen during continuously cooling at 1°C/s, and consequently form the granular ferrite by the evidence of morphology, nanohardness and EBSD results.

The relationship of acicular ferrite and granular ferrite show that when continuous cooling to 600°C and then quenching, there are two types of transformation phase, acicular ferrite and lathlike bainitic ferrite. Control the formation of acicular ferrite during the continuous cooling not only benefits to introduce the relatively soft phase (comparing with the lathlike bainitic ferrite) in the matrix, but also profits to make "chaotic" structure to fine the packet size of aligned lathlike bainitic ferrite/ martensite.

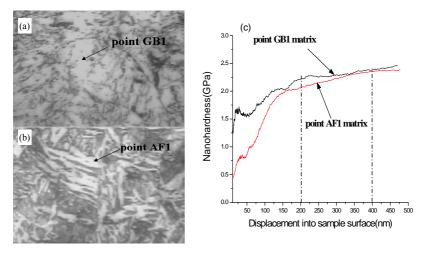


Fig.11 Optical images of the indentation positions of granular bainite(GB) (a) and acicular ferrite(AF) (b) and the typical nanohardness-displacement curves of AF and GB in the tested samples(c).

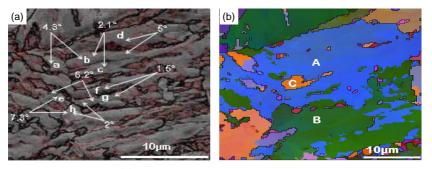


Fig.12 Pattern quality map (a) showing the misorientation angles between the nearby acciular ferrite and the orientation map (b) showing the effective grains (A,B,C) of granular ferrite

A multi-phase ultra-fine microstructure has been thermo-simulated [16]. The microstructure of simulated specimen is shown in Fig.13, it can be seen that the microstructure is composed of typical acicular ferrite and bainitic ferrite. The microstructure is much more "chaotic" than the unitary bainitic ferrite/ martensite.

The characteristic and principle of the evolution of acicular ferrite could be employed to control the ratio of acicular ferrite/bainitic ferrite in the low carbon microalloying steel. As there are both acicular ferrite and lathlike bainitic ferrite, this kind of multi-phase steel will be more strong, tough and ductile. By the control cooling process, acicular ferrite and bainitic ferrite multi-phase structure can be obtained.

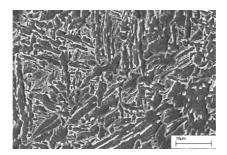


Figure 13. SEM micrograph of the specimen processed by two stages cooling process

# The High Nb Content Microalloying Approach

# The Softening Behavior of Higher Nb Content Steel

Refinement of prior-austenite grain size and accumulative the defect density would be the physical metallurgy criteria for manufacture the high performance steel. Conventionally, TMCP can achieve both grain-refinement and stain accumulation by severely rough rolling and finish rolling processes. However, for the higher Nb content microalloying approach steel, the softening behavior, controlled by static and dynamic recrystallization process, has to be understood clearly because of the solute and precipitate characteristics higher Nb content. The softening behavior which influenced by recrystallization and precipitation will determined the control rolling parameters such as rough rolling window and finish rolling window, respectively.

The stress relaxation curve can always characterize the softening of deformed austenite [20].

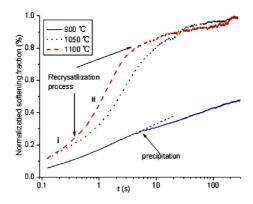


Figure 14. Normalization softening curves in recrystallization region and precipitation region Normalizing the data from the relaxation curve, the normalization softening fraction can be obtained for the higher temperature (1050°C, 1010°C) procedure and lower

temperature (900°C) procedure, as shown in Figure 14. It can be seen that for the high Nb content t(0.1%Nb) steel [20], at higher temperature (1100°C and 1050°C) the softening process only influenced by recrystallization, and the softening rate increase rapidly in the initial stage of the curve. But at lower temperature (900°C), the soften rate become slower, the recrystallization would be deeply retarded, since the nucleation rate of recrystallization grain and mobility of grain boundary declined by precipitation at lower temperature [10].

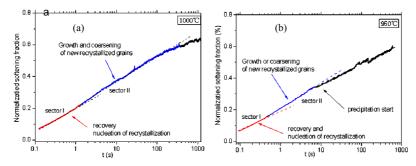


Figure 15. Normalization softening curves at (a) 1000 °C and (b) 960 °C

However, there are some complex phenomena at  $1000^{\circ}$ C and  $960^{\circ}$ C, as shown in Figure 15. The slope change of the curve at  $1000^{\circ}$ C, as shown in Figure 15(a), is not very sharp, and it looks like the softening behavior is a simple recovery process, but in fact, the curve contains the information of recrystallization, which the slope of the sector II is greater than of the sector I. This change can show the softening result from static recrystallization.

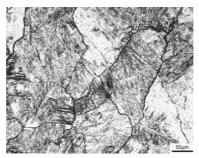


Figure 16. The morphology of austenite grains after deformed at 1070°C for 30%

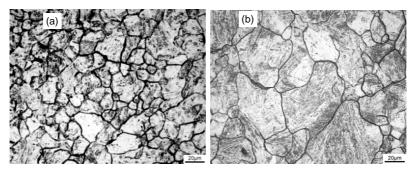


Figure 17. The morphology of austenite grains after 30% deforming at  $1000^{\circ}$ C and holding time for 10s (a) and 240s (b)

The morphology of prior-austenite grains were characterized by picric etching. It obviously shows in Figure 16 that compete recrystallization (deformed at 1070°C for 30%) austenite grain size is about 70-100 microns in diameter. But after deformed at 1000°C (as shown in Figure 17), nearly all static recrystallized austenite grains have been nucleated after holding for 10s, the grain size is less than 20 microns. After holding for 240s at this temperature the nucleated grains growth to

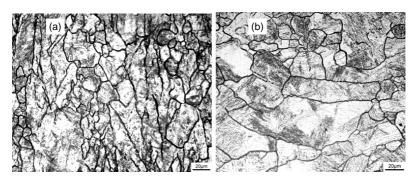


Figure 18. The morphology of austenite grains after 30% deforming at 960℃ and holding for 10s(a) and 120s(b)

about 50microns in diameter, it shows that growth rate of recrystallized grains at  $1000^{\circ}$ C was relatively very much slow comparing with at  $1070^{\circ}$ C. That is saying, after compression at  $1000^{\circ}$ C, the nucleation of recrystallized grain took place but grow was retarded for the higher Nb content steel.

The slowly growing of static recrystallized grain and /or very fine grain size are the main reasons to the delay of softening. Therefore, the softening at 1000°C should be only influenced by static recrystallization. Moreover, the mobility of grain boundary is lower because of intense drag effect of solute in higher Nb-bearing steel [11], so the static recrystallization grain size does not grow so fast comparing with conventional Nb-bearing (<0.05%Nb) steel.

The slope change of the softening curve at 950°C (Figure 15(b)) shows that the softening is accelerated by the partial static recrystallization (sector I in Figure 15(b)), After delaying for several seconds, the softening was suppressed (sector II in Figure 15(b)) and the hardening was taken place. The softening at 950°C is influenced by two kinds of mechanism, partial recrystallization softening and precipitation hardening. According to the morphology of austenite grains that deformed at 960°C for 30% (Figure 18), the partial recrystallization occurs, which results in the mixing grains size. The pinning effect of precipitation halt the growth of grain greatly, so the occurrence of precipitation is the main reason which may result in partial recrystallization.

According to literature, due to the drag effect of solute Nb on grain boundary, the boundary moving is suppressed intensely in high Nb-bearing steel [11], so it was supposed that static recrystallization stop temperature of higher Nb bearing steel is higher than of the lower Nb content steel. However, from the softening curve in Fig. 15(a) and prior-austenite grain morphology in Fig.17, it can be seen that, the static recrystallization grain nucleated homogeneously in the temperature range around  $1000^{\circ}$ C. But in the temperature range around  $960^{\circ}$ C, the partial recrystallization occurs. It is to say that the non-recrystallization temperature ( $T_{n95}$ ) range should be lower than  $950^{\circ}$ C.

To refining the prior-austenite grain size and preventing the mixing grain size, the stop temperature of rough rolling for the plate mill should be controlled around  $1000^{\circ}$ C, and the finishing rolling start temperature should be below 950°C for higher dislocation density accumulation.

# Development of 690 MPa and 960Mpa grade high Nb content steel

The high Nb content microalloying approach has been applied for Steckel mill or severe mill to produce X grade pipeline and HSLA steel. The research and practice also show that with the increase the Nb content to 0.08-0.10%, Molybdenum free approach steel can reach X70 and /or X80 grade level [21]. The low carbon, higher Mn and higher Nb alloy approach is new route for developing high performance steel with lower alloying cost.

By the following experiment, the adequate rolling process had been revealed, and optimized TMCP had been promoted to developing 550-690MPa high Nb content microalloying steel. The main composition of 550-690MPa grade lower cost low carbon bainite steel is 0.03%-0.055 C,1.7-1.9% Mn and 0.08%-0.11%Nb, 5-15 ppm boron is added to increase the hardenability insuring to obtain the bainite, the other alloying approach is just like HTP concept [9].

The rolling schedule of experimental steels was as following: reheated at 1200°C, the rough rolling temperature window is above 1070°C, the finish rolling start temperature (Tfs) is 1030°C to 900°C, respectively. The finish temperature is corresponding to the start temperature of finish rolling stage. The thickness of the

plate is 16mm. After control rolling the plates accelerated cooling to  $500^{\circ}$ C. The as rolled plates were also tempered at temperature range from  $550^{\circ}$ C to  $700^{\circ}$ C. The mechanical properties of as rolled plate following high finish rolling start temperature ( $1030^{\circ}$ C) and lower starting temperature ( $950^{\circ}$ C) were shown in Table 2. It can be seen that, decreasing the finish rolling start temperature from  $1030^{\circ}$ C to  $950^{\circ}$ C can increase the yield strength more than 100MPa. The yield strength of the as rolled plate can reach 690MPa grade for the lower temperature rolling steel. Moreover, if the plates were tempered at  $600^{\circ}$ C for 1 h, the yield strength of lower or higher temperature processes can both reach 690MPa grade, the elongation of both steels have been improved obviously too.

It can be seen that if high temperature process (finish rolling start at 1030°C) was accept to produce 690MPa grade steel for Mn-Nb<sup>+</sup>-B steel, as the finish rolling window is relatively very wide, it can be applied for severe mill and achieve higher productivity in condition of tempering, and the elongation and toughness can be improved by the tempering process. Elsewhere, if the facilities are not a problem for the advanced mill, lower the finish rolling window can achieve high strength just by TMCP without tempering.

The industry trail of Mn-Nb<sup>+</sup>-B 690MPa plate steel was carried out in An-steel. Table 3 is the properties of the industry trail plate. It can be seen that the yield strength of as-rolled plates that thicker than 20mm are higher than 690MPa, and with excellent elongation, yield ratio and toughness. But, the yield strength of thin plate (16mm) cannot reach 690MPa, only about 600MPa. The reason is that for the thicker plate the start rolling temperature during the second stage rolling can be relatively lower because the temperature decline is not much faster than the thin plate. As illustrated by softening behaviors of higher Nb content steel, the deformed austenite at low temperature will not softening too quickly.

Table 2 Mechanical properties of as rolled and tempered plate with different rolling process.

Tfs ℃	As rolled				tempered at 600°C for 1 h			
	R <sub>el</sub> N/mm2	R <sub>m</sub> N/mm2	A %	$R_{el}/R_{m}$	R <sub>el</sub> N/mm2	R <sub>m</sub> N/mm2	A %	$R_{el}/R_{m}$
1030	590	820	14	0.72	735	870	16.5	0.84
950	715	925	12.5	0.77	750	850	15.5	0.88

Table 3. Mechanical properties of as rolled industry trail plate

number	Thickness mm	R <sub>el</sub> N/mm2	R <sub>m</sub> N/mm2	A %	R <sub>el</sub> /R <sub>m</sub>	Impact energy $A_{kv}$ ,-20°C, J		
1	16	605	775	18.5	0.78	126	168	160
2	20	710	825	18.0	0.86	175	161	203
3	25	730	825	18.5	0.87	222	201	222
4	30	765	835	18.0	0.92	210	182	111

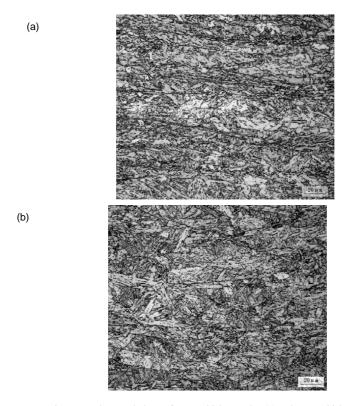


Figure 19. The morphology of 16mm thickness plate(a) and 30mm thickness plate(b)

Figure 19 shows the morphology of 16mm thickness plate and 30mm thickness plate. We cannot see too much different between them, but the yield strength has about 100MPa difference. The solute Nb content was measured by electroanalysis method. Figure 20(a) shows the Nb content of the as rolled plate of thickness of 16mm, 25mm and 30mm, respectively. It can be seen that the solute and precipitate Nb of 25mm and 30mm are almost same and it is about 50% to 50% of soluble and precipitate. But for the 16mm thickness plate, it obviously shows that the precipitate Nb is less than the

soluble, it is about 30% to 70%. It can be concluded that the precipitation in the different thickness plate effect the strength markedly. As the finish rolling start temperature of thin plate is higher than the thick, the reduction under the precipitation nose temperature is less, so the lesser of precipitate can be precipitated during the rolling process.

The Nb soluble contents after tempering at various temperatures were also detected by electroanalysis method (as shown in Figure 20(b)). The results show that with the increase of tempering temperature higher than  $550^{\circ}$ C, the precipitate of Nb increase dramatically until  $650^{\circ}$ C, the precipitate Nb increase from 60% at  $550^{\circ}$ C to more that 90% at  $650^{\circ}$ C.

Therefore, for developing low cost Mn-Nb<sup>+</sup>-B steel, the appropriate rolling schedule and the tempering process would be key point to ensuring the yield strength. Although it is a HTP concept microalloying approach, the finish rolling temperature window should be lower for

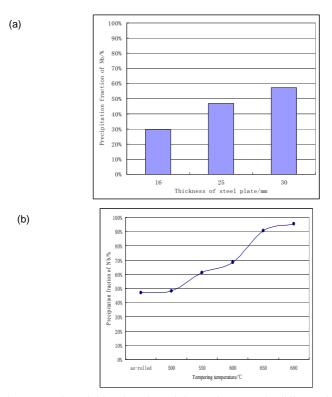


Figure 20. The soluble Nb and precipitate Nb content in different thickness as rolled plate (a), and after tempered at various temperatures by electroanalysis method.

Table 4. The mechanical property of 960MPa grade 6mm thickness plate steel

Heat	As rolled				Tempered at 600°C			
	R <sub>el</sub>	$R_{m}$	R <sub>el</sub> /R <sub>m</sub>	A	$R_{m}$	R <sub>el</sub>	A	
	N/mm2	N/mm2	Kel/Km	%	N/mm2	N/mm2	%	
	1	875	1190	0.74	9.5	1105	1085	12
	2	850	1190	0.71	12.0	1110	1095	12.5

ensuring enough precipitates to precipitate during deformation. Otherwise, the tempering process can also strengthen the strength obviously; tempering the high Nb-bearing steel is also an advisory process for strengthening the yield strength.

Not only 690MPa grade steel, the 960MPa grade plate steel was also developed by high Nb content concept. The chemical composition is low carbon Mn-Mo-Cu-Cr-Ni-Nb<sup>+</sup>-B. The steel was control rolled and direct quenched. The as rolled plate mechanical properties were shown in Table 4. The results show that the yield strength of as rolled plate is around 850MPa, the tensile strength is about 1190Mpa, but after tempered at 600°C, the yield strength can increase more than 130MPa. As the alloy approach contain 0.5%Cu and 0.1%Nb, the precipitation of Cu and Nb may play important roles to strengthening the matrix. By the simulation study of 0.01%C-1.5%Mn-1.6%Cu- 0.16%Nb steel[22], it shows that there are a lot of precipitates of Cu and Nb after tempering at 600°C, the TEM micrograph shows the particle size Nb precipitation is about 3-4nm. High Nb content can be used as precipitation element to strengthening the matrix for developing ultra high strength steel.

## Summary

The yield strength of 500MPa-960MPa grades low carbon bainitic steel has been developed in China. This kind of high strength steel has been developed by intermediate transformation products control and grain refinement. In addition to conventional physical metallurgical principles of TMCP, the relaxation effect of deformed austenite on the grain refinement of microalloyed steel has been used to obtain an ultra-fine bainitic structure. The study shows that the relaxation of deformed austenite can refine the intermediate transformed bainitic packet size. The evolution of dislocation cell structure and the precipitation of Nb(C,N) on the dislocation wall during the relaxation period will make the reinforced cell structure to act as sub-boundary in the austenite; it will benefit the transformation of the acicular ferrite and limited the growth of bainitic ferrite.

For high Nb content steel, the softening is controlled by static recrystallization in the temperature range even around  $1000^{\circ}$ C, the softening delayed just by slowly growth

of static nucleated grains. The partial recrystallization can only happened at temperature around 960 °C. Therefore, the rough rolling may stop at around 1000 °C to obtain ultra-fine prior-austenite grains, the start temperature of finishing rolling process should be below 950 °C to avoid mixing grain size and to accumulate dislocation density for refining and strengthening the transformation phases.

Tempering the high Nb content steel can ensure the yield strength by adequate amount of fine precipitates in the matrix, the solute Nb in the as rolled matrix can be precipitated during tempering process for strengthening the matrix.

The Mn-Nb-B and Mn-Mo-Nb-B microalloying approach have been applied to developing yield strength 550MPa, 690MPa, 800MPa and even 960MPa grade high performance structural steel extensively in China. The mechanical properties and the production cost can be met the requirement of the domestic market.

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#### Reference

- [1] Y.Q. Weng, Ultra Fine Grain Steel, Metallurgy Industry Press, 2003. (in Chinese)
- [2] A.J. DeArdo, Muti-phase microstructures and their properties in high strength low carbon steels, ISIJ International, Vol. 35, 1995, p946-954.
- [3] A.J. DeArdo, The Physical Metallurgy of Thermomechanical Processing of Microalloyed Steels, Thermech'97, TMS, 1997, p13-29.
- [4] A.J. DeArdo, Fundamental Metallurgy of Niobium in Steel, Nb Science and Technology, TMS, 2001, p427-500.
- [5] X.M. Wang, X.L. He, S.W. Yang, C.J. Shang, H.B. Wu, Refining of Intermediate Transformation Microstructure by Relaxation Processing, ISIJ Int, 42(2002), p.1553.

- [6] C.J. Shang, X.M. Wang, X.L. He, S.W. Yang, Y. Yuan. A Special TMCP Used to Develop a 800 MPa Grade HSLA Steel, Journal of University of Science and Technology Beijing, Vol 8 (3), 2001, p224-228.
- [7] X.M Wang, C.J. Shang, S.W. Yang, X.L. He, X.Y. Liu, The Refinement Technology for Bainite and its Application. Materials Science and Engineering: A, 438-440, 2006, p162-165.
- [8] L. J. Cuddy, The Effect of Microalloy Concentration on the Recrystallization of Austenite During Hot Deformation of Metals, (Academic press, New York, 1975), p129-140.
- [9] K. Hulka, J.M. Gray, Nb Sicence and Technology, TMS, 2001, p587-612.
- [10] H.S. Zurob, C.R. Hutchinson, Y. Brechet, and G.R. Purdy, Rationalization of the softening and recrystallization behaviour of microalloyed austenite using mechanism maps, Materials Science and Engineering A, Vol382, 2004, p64-81.
- [11] H.S. Zurob, G. Zhu, S.V. Subramanian, G.R. Purdy, et al. Analysis of the Effect of Mn on the Recrystallization Kinetics of High Nb Steel: An Example of Physically-based Alloy Design. ISIJ International, Vol45, 2005, p713–722.
- [12] S. Q. Yuan, S. W. Yang, C. J. Shang, X. L. He, Strain Induced Precipitation in a Multi-microalloyed Steel Contain Nb and Ti During Processing, Materials Science Forum, Vol 426-432, 2003, p1302-1312.
- [13] X. M. Wang, C. J.Shang, X. L. He, et al. The Structure Variation of Deformed Austenite During the Relaxation and the Refinement of Bainite in Nb-B steel, Materials Science Forum, Vol 426-432,2003, p1307-1312.
- [14] X. L. He, Y J Chu. The Application of the 10B(n,α)7Li Fission Reaction to Study Boron Behaviour in Materials, J. Phys. D: Appl. Phys, Vol 16,1983, p1145-1158.
- [15] C. J. Shang, S. W. Yang, X. M. Wang, et al. Influence of relaxation process on the microstructure and properties of low carbon bainitic steel. Materials Science Forum, 426-432,2003, p1439-1444.
- [16] C. J. Shang, Y. T. Zhao, X. M. Wang et al. Formation and Control of the Acicular Ferrite in Low Carbon Microalloying Steel, Materials Science Forum, 475-479,2005, p85-88.
- [17] Y.T. Zhao, C.J. Shang, S.W. Yang, X.M. Wang and X.L. He. The Metastable Austenite Transformation in Mo–Nb–Cu–B Low Carbon Steel, Materials Science and Engineering: A, 433, 2006, p69-74.

- [18] C. J. Shang, X. Liang, X. M. Wang et al. The Nonohardness of Acicular Ferrite and Bainitic Ferrite in Low Carbon Microalloying Steel, Materials Science Forum, Vol. 561-565, 2007, 65-68.
- [19] C. J. Shang, X. M. Wang, Z. J. Zhou etal., Evolution of Intermediate Transformation Microstructures in Mn-Mo-Nb-B Low Carbon Microalloyed Steel, Acta Metallurgical SINICA, 44, 2008, p287-291.(in Chinese)
- [20] C.L. Miao, C.L. Shang, The Softening Behavior of Higher Nb Content X80 Pipeline Steel, ICAMP-5, Harbin, China, 2008.
- [21] K. Hulka, P. Bordignon, J. M. Gray, Experience with low carbon HSLA Steel Containing 0.06 to 0.10 percent Niobium, Niobium Technical Report. No1/04, August, 2004, CBMM.
- [22] H. Guo, Technical Report of CITIC&CBMM R&D Project, 2007.