Solution and Precipitation Behavior of Nb and Its Role in Medium Carbon Long Product Steels

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Abstract: Controlling of the solution and precipitation for microalloying additions of Nb, V, Ti and their combination is the basic building block of microalloyed steels. Among three microalloying elements, Nb has been regarded the most effective microalloying ingredient used for low carbon flat products due to marked strengthening effect of grain refinement and relatively weak precipitation strengthening effect by matching proper thermomechanical processing (TMP). However, Nb was not viewed as attractive as V for medium carbon long products in the past because of limited solubility during reheating process. What is more, hot working is usually carried out at high temperatures in the recrystallization regime, so it is difficult to exert conventional controlled rolling to obtain pancaked austenite, which has further affected the research and application of Nb in medium carbon long products. Because of these factors, studies of Nb in medium carbon long products were incomplete, and even some recognitions and conclusions are subjected to debate. In order to clarify the strengthening effects of Nb in medium carbon long products, the reinforcing bars have been chosen as experimental steels to clarify the role of Nb on microstructural changes along the whole hot working, cooling processes. In addition, qualitative and quantitative analyses of Nb’s state and distribution in reheating, rolling and cooling had been carried out to illustrate some singularities.

Key words: Nb microalloying, solution and precipitation, transformation strengthening, hardenability.

1. Introduction

Hot rolling of steels involves not only geometrical and final shape requirements, but also mechanical properties can be adjusted by microstructure conditioning resulted from hot working and subsequent transformation during and after cooling [1, 2]. During this process, grain refinement was proved the most effective strengthening approach to improve strength level and toughness simultaneously. Among three microalloying elements of Nb, V and Ti, Nb has been regarded the most effective to achieve grain refinement by matching thermomechanical processing (TMP) [3-5]. With years’ development and accumulation, Nb microalloying in low carbon flat products has been widely studied, and the role of Nb in hot rolled flat products had been understood well. However, there is less technical information regarding the role of Nb in medium carbon long products, like rebars. Hot rolling of rebars presents some particularities that affect the role of Nb, such as solubility product of Nb during reheating step, bainitic structure formation and continuous yielding [9], as well as the effect on tensile-to-yield ratio. In this paper, physical metallurgy of Nb in steels was reviewed firstly, and then the role of Nb in rebars was presented based on thermal simulation tests.

2. Metallurgical Considerations of Nb in Steels

For the low carbon flat products, the most prominent role of Nb in steels is achieved during austenite conditioning, where added Nb contents are dissolved
partly or completely in the upper austenite region and then get reprecipitated again during subsequent rolling and cooling process [6]. By controlling the solution and reprecipitation of added Nb, fine and uniform austenite grains can be obtained by inhibiting recrystallization and grain coarsening through solute drag effect and pinning effect by Nb(C,N) particles, both undissolved and strain-induced. In addition, Nb in solution after rolling should precipitate during transformation and subsequent cooling process, which can contribute to the increase of strength levels. For flat products, the most successful application case of Nb microalloying is the x80 steels with high strength and excellent low temperature toughness. In spite of a single application field, based on that, almost all significant body of knowledge on design and processing of microalloyed steels had been accumulated.

Figs. 1 and 2 show the production processing and corresponding microstructural changes of hot rolled plate and hot rolled rebar respectively. It is observed that the fundamental metallurgical principles of microstructural evolution governing the whole production process are no big difference [7]. However, the magnitude and the role of Nb in the solid solution matrix and in the precipitated Nb(CN) are of difference, which are strongly influenced by chemical compositions and production processing. Normally, the carbon contents of long products are higher than those of flat products, so it is difficult to put high Nb contents in solid solution considering relatively low reheating ability of billet furnace. Another big difference is rolling temperature change, the rolling temperatures of flat products decrease step by step, so low temperature and heavy reduction, namely TMP, can be performed easily. For the rebars, there is no Tnr due to the deformation features like high pass strain levels, high strain rates and short interpass times during rolling process. What is more, the final rolling temperature is even higher than rolling start temperature for small size rebars due to high rolling speed, which can affect the state of Nb in steels. In addition, grain refinement effect of Nb in rebars is not as strong as that of flat products due to high rolling temperatures.

Based on past production experiences of Nb microalloying in steels, in particular hot rolled flat products, the role of Nb along the whole hot working and cooling is briefly summarized as follows:

![Diagram](image)

**Fig. 1** Production process and corresponding austenite evolution of plate products.
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3. Experimental Steels and Simulation Tests

Hot rolled ribbed bars used for the reinforcement of concrete have been the largest single products in China, up to 200 million tons per year since 2013. In the past, V microalloying with high N contents has been firstly and widely used for production of 400 MPa and above grades, but huge market demand on V would lead to big fluctuation of price, affecting the promotion of high strength rebars. For this reason, more and more rebar producers have started to try Nb microalloying process for cost saving. Compared to the VN microalloying, some technical issues and singularities have affected the promotion and application of Nb microalloying for rebars, like high reheating temperature required to dissolve added Nb due to high carbon contents, formation of bainitic structure and resulted continuous yielding, as well as special effects of Nb on anti-seismic performance of tensile-to-yield ratio. Through trial and error, it was found that Nb microalloying can achieve equal strengthening effect on yield strength as that of V microalloying. In addition, some singularities about Nb microalloying were found by industrial mass production. Firstly, high reheating temperature required to put all added Nb in solution is not desired to yield strength. As shown in Fig. 3, optimum reheating temperature is far lower than calculated solution temperature according to popular Irvine’s equation. Secondly, given equal production processing conditions, the ferrite grain of Nb-bearing rebars is bigger than that of V-bearing rebars, as shown in Fig. 4 which is contrary with accepted strengthening effect of grain refinement of Nb. Finally, it was interestingly found that the tensile-to-yield value of small size Nb-bearing rebars is higher than those of V-bearing rebars, as shown in Fig. 5. For flat products, main strengthening effect of Nb is grain refinement, which can contribute more to yield strength than that of tensile strength. But for rebars, Nb microalloying can contribute more to tensile strength than that of yield strength. For these phenomena, thermal simulation tests by simulating reheating, rolling and cooling have been conducted for experimental steels, as shown in Table 1.
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Fig. 3  Effect of reheating temperatures on yield strength.

Fig. 4  Microstructures of HRB400E with Nb and V.

Table 1  Chemical compositions of experimental steels, wt%.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.23</td>
<td>1.32</td>
<td>0.42</td>
<td>0.028</td>
<td>0.0056</td>
</tr>
<tr>
<td>B</td>
<td>0.19</td>
<td>1.28</td>
<td>0.36</td>
<td>0.015</td>
<td>0.0052</td>
</tr>
<tr>
<td>C</td>
<td>0.24</td>
<td>1.25</td>
<td>0.50</td>
<td>0.030</td>
<td>0.0055</td>
</tr>
<tr>
<td>D</td>
<td>0.26</td>
<td>1.50</td>
<td>0.44</td>
<td>0.030</td>
<td>0.0058</td>
</tr>
</tbody>
</table>

3.1 Austenization Tests

According to the Irvine’s solubility product equation, Nb in solid solution is a function of temperature, C and N contents. For steel A, the required reheating temperature to put all Nb contents in solid solution is not less than 1,250 °C according to the calculation of Irvine’s equation, but it is very difficult for rebar production to keep so high reheating temperature for long time in mass production. Some rebars makers refuse to use Nb for the limitation of billet reheating furnace. Interestingly, it was found high reheating temperature up to 1,150 °C is not beneficial to yield strength. Apart from solution of added Nb, austenite grain size also plays one important role to final yield strength. Take steel A as
Fig. 5  Tensile-to-yield ratio for HRB400E with Nb and V.

Fig. 6  Schematic presentation of the experimental program for austenitizing.

The experimental steel, experimental program for austenitizing with different soaking temperatures is shown in Fig. 6. The experimental steels were reheated to 950 to 1,250 °C for holding 120 min, and then quenched to room temperature to observe austenite grain size and undissolved Nb(C,N) by chemical extraction technique.

Figs. 7 and 8 show the analysis results of Nb(C,N) and austenite grain sizes at different austenitizing temperatures respectively. As we can see from Fig. 7, with the increase of austenitizing temperature, Nb(C,N) particles will start to dissolve into the steel gradually, only about 0.0023% Nb particles exist in precipitation when reheating temperature was set at 1,250 °C. By comparison, it was validated that the analysis results are in good agreement with the calculated results of Irvine’s equation. On the other hand, austenite grains also start to grow, and even coarsen with the increase of reheating temperatures, and start to coarsen when reheating temperature is set at 1,200 °C and more.

As shown from Fig. 9, it is observed that there is a bimodal distribution at 1,200 °C, which also means grain coarsening. By validating with the test results of mass production, it was found that yield strength levels start to decrease when soaking temperature is higher than 1,150 °C. From the perspective of maximizing yield strength, complete dissolution of added Nb may be undesired for rebars due to disappearance of pinning effect of Nb(C,N) on austenite grain boundary.

3.2 Torsion Tests for Austenite Conditioning

For bar and other long products, hot working is usually carried out at high temperatures in the recrystallization regime, and microalloying in these products is adopted to improve required strength level by precipitation strengthening rather than by grain refinement. For this reason, some thought Nb microalloying in long products is not as effective as those of flat products. In order to figure out the role of Nb in hot rolling process, multi-pass torsion tests simulating actually industrial conditions had been performed. The reheating temperatures of three sizes rebars were set at 1,100 °C for 120 min, and the
Fig. 7  Phase analysis results of Nb(C,N).

Fig. 8  Austenite microstructure at different soaking temperatures.

Fig. 9  Austenite grain sizes at different soaking temperatures.
strain-stress curves of three sizes are presented in Fig. 10. As we can see, softening happens for all three sizes after the 9th pass, which means dynamic recrystallizations have taken place due to high pass strain levels, strain rates and short interpass times. As shown in Fig. 11, all austenite microstructures are composed of equiaxed austenite, instead of pancaked austenite grains, which can explain why grain refinement effect is not as strong as that of flat products.

![Stress-strain curves of rebars](image)

**Fig. 10** Stress-strain curves of rebars.
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Fig. 11  Austenite microstructure of rebars.

Fig. 12  TEM (transmission electron microscope) analysis results of Nb(C,N) phase.

However, some precipitates of 10-30 nm size are observed by TEM, as shown in Fig. 12, which are typical of strain-induced Nb(C,N) particles. Due to high deformation temperatures and very short interpass times, precipitated Nb(C,N) particles cannot inhibit recrystallization, but can retard austenite grain coarsening. Based on the simulation results, following conclusions can be obtained:

• Special singularities of hot rolling schedule affect the behavior of Nb in rebars. Due to very short interpass times, Nb precipitation cannot avoid recrystallization.

• There is no strain accumulation because dynamic recrystallization occurs, so no pancaked austenite grain can be obtained, and grain refinement is relatively weak.

• Nb(C,N) particles of undissolved and strain-induced precipitated can avoid the coarsening of austenite.

• From the view of thermodynamics, more Nb contents are in solution before phase transformation.

3.3 CCT (Continuous Cooling Transformation) Diagram for Ferrite Phase Transformation

For low carbon flat products, in particular high strength pipeline steels with high Nb design, the low C bainitic structure (acicular ferrite) is desired for ideal balance of strength and low temperature toughness, but it is required ferrite plus pearlite for hot rolled rebars. For the Nb-bearing rebars, one of the main issues is continuous yielding resulted from bainitic structure. Through industrial trials, water cooling is used to control or totally eliminate bainitic structure. According to the newly revised standard of Gb1499.2-2018, the tempered martensite on the surface of rebars was strictly banned, so quenching and self-tempering process (QST) was not permitted to use for rebars. Based on the information, the principles to set up cooling strategy for rebars are as follows:

• to get a fine ferrite-pearlite microstructure;

• to avoid the formation of high fraction of acicular/bainitic phases;

• to avoid the formation of tempered martensite structure;

• to promote the occurrence of Nb(C,N) precipitation strengthening.

The schematic diagram of CCT for steel B, steel C and steel D is presented in Fig. 13. The experimental steels were reheating to 1,200 °C for holding 120 min to dissolve more Nb contents, and then quenched to room temperature, and finally reheated to 1,050 °C for holding 10 min.

Figs. 14 and 15 show the CCT curves of steel B and steel C with different austenite grain sizes of 6 μm and 20 μm. As we can see, there is no big difference between steel A and steel B when austenite grain sizes are 6 μm, but it is obvious that ferrite start temperature will move to low and right for steel B when austenite grain sizes are 20 μm.
Fig. 13  Dilatometry tests for three steels.

Fig. 14  CCT curves for steel A and steel B, 6 μm.

Fig. 15  CCT curves for steel A and steel B, 20 μm.
Fig. 16  CCT curves of steel B, 6 μm and 20 μm.

Fig. 17  CCT curves of steel B and steel C.

Fig. 16 shows the CCT curves of Steel B with different austenite grain sizes of 6 μm and 20 μm respectively. As we can see, the influence of austenite grain is more marked to increase hardenability, so the bainite structure can easily form when cooling rate is faster than 2 °C.

Fig. 17 shows the integrated effects of compositions and austenite grains resulted from the reheating temperatures. It was observed that adding of high Mn contents has a greater impact on the overall hardenability. Considering the integrated effect of big austenite grains from higher reheating temperature, the bainitic structure can form when cooling rate is 0.5 °C/s. Fig. 18 demonstrates the room temperature microstructures, as shown, there are large amounts of bainite structures.

Based on CCT simulation results, it is confirmed that both high Mn contents and big austenite grain size contribute to formation of bainitic structure. As for the effect of Nb, it depended on state of Nb, namely Nb remaining in steel or Nb(C,N) in precipitation. For hot rolled flat products, more Nb contents exist in Nb(C,N)
due to low temperature and heavy reduction schedule, and strain-induced precipitates can inhibit recrystallization for obtaining pancaked austenite, which can increase ferrite phase transformation temperature. But for rebars, the rolling temperature will increase with the decrease of rebar sizes in diameter, so both big austenite grains and more Nb in solution can promote the formation of low temperature phase transformation products, bainite or/and pearlite. For the rebar with high volume fraction of bainite, working rate is high due to high dislocation density. Likewise, high pearlite volume fractions also contribute to high tensile strength level. According to the CCT simulation results, the cooling strategy of rebars is shown in Fig. 19. Firstly, water cooling after rolling is used for avoiding austenite coarsening. Secondly, the cooling stop temperature is higher than ferrite phase transformation start temperature of $A_\text{f}$.

### 3.4 Precipitation Strengthening

Fig. 20 shows the analysis results of rebar samples with 0.022% and 0.030% Nb respectively. It is observed that the precipitates of rebar with 0.030% Nb are more than that of rebar with 0.022% Nb. In addition, almost all precipitates are carbides of Nb, instead of carbonitrides or nitrides of Nb. Interestingly, more fine precipitates of Nb distribute on pearlite, which can further prove that dispersion precipitation takes place in relatively low temperature zone.

All three microalloying elements such as Nb, Ti and V may precipitate either in austenite or ferrite, but precipitation in austenite is sluggish compared to that in ferrite because of higher solubility and slower diffusion rate. For Nb-bearing flat products, low temperature and heavy reduction can promote precipitation of Nb(C,N) in austenite, so less Nb additions are left for subsequent precipitation in ferrite.
However, the final rolling temperature for long products is far higher than that of flat products, solution and reprecipitation is governed by thermodynamics, and it is one dynamic process. For small rebars, the final rolling temperature is even higher than that of reheating temperature, so more Nb additions are left for subsequent precipitation in ferrite, which pave the way for subsequent precipitation strengthening.

In order to maximize the precipitation strengthening of Nb in ferrite, water cooling after rolling is very significant to suppress the precipitation in relatively high austenite temperature zone after rolling and before ferrite transformation. Compared to the flat
products, precipitation strengthening of Nb in rebars is more prominent than that of grain refinement. Compared with V microalloying process, Nb microalloying is more flexible and versatile to meet the requirements of mechanical properties.

4. Strengthening Role of Nb in Rebars

Although given chemical compositions and production processing can obtain confirmed microstructure and mechanical properties, the role of Nb during the whole process is difficult to distinguish specific strengthening effects. Firstly, instantaneous state of Nb is changing with the processing temperature and pass deformation. Take the reheating temperature as example, maybe only 0.015% Nb is in solution when reheating temperature is set at 1,050 °C, but more Nb will be in solution if final rolling temperature is up to 1,150 °C, which will affect subsequent transformation and precipitation strengthening. So instantaneous composition is the key to understand the role of Nb in rebars systematically. For the flat product, more attentions were paid to austenite conditioning for grain refinement, less Nb contents are left for transformation and precipitation strengthening [8]. However, due to high final rolling temperature, more Nb contents are in solution before transformation, and then precipitation during and after ferrite transformation. Take Nb-free 20MnSi as comparison, total strengthening role of Nb with 0.03% to yield strength is about 60 MPa, of which precipitation strengthening, grain refinement and transformation strengthening are 36 MPa, 16 MPa and 8 MPa, as shown in Fig. 21.

5. Conclusions

Up to now, about 150 million tons Nb-bearing HRB400E bars had been produced; all meet the requirements of newly revised standard of GB1499.2-2018, including both microstructure and mechanical properties. In the meanwhile, some new recognitions on strengthening effects of Nb had been developed based on industrial trials and lab research.

(1) Nb(C,N) particles undissolved at reheating step are beneficial to avoid austenite grain coarsening during all austenite range.

(2) High reheating temperature will coarsen austenite grain sizes and leave more Nb in solution, both of which promote the formation of bainite structure, so high reheating temperature is not desired.

(3) Dynamic recrystallizations occur during rolling process, so no pancaked austenite grains can be obtained.
(4) For Nb-bearing rebars, properly setting of cooling strategy is very significant to obtain fine ferrite-pearlite structure. Fast cooling after rolling can keep fine austenite grains, which can counter the effect of Nb remaining in solution for increase of hardenability. In addition, quick cooling rates can keep more Nb in solution for subsequent precipitation in cooling bed, so dispersed precipitates can be achieved.

(5) Through qualitative and quantitative analysis, it is confirmed that Nb in rebars can present precipitation strengthening, grain refinement and transformation strengthening.

References


