Effect of Chromium on microstructure and the hot ductility of Nb Microalloyed Steel

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Abstract
The effects of chromium on \(\gamma/\alpha\) phase transformation and high temperature mechanical properties of Nb Microalloyed steel was discussed in detail. The results indicated that the starting temperature of the \(\gamma\rightarrow\alpha\) phase transformation decreases with increasing the Cr content. The hot ductility of Nb microalloyed steel is improved by adding 0.12wt% Cr. Chromium atoms inhibit the diffusion of carbon atoms, which leads to the reduction of grain boundary ferrite thickness. The number fractions of high angle grain boundaries is increased by adding chromium. In particular, the proportion is up to 48.7% when the Cr content is 0.12wt%. The high angle grain boundaries hinder the crack propagation and improve the ductility of Nb microalloyed steel.

Keywords: \(\gamma\rightarrow\alpha\) phase transformation; hot ductility; chromium; high angle grain boundaries; grain boundary ferrite

1. Introduction
Microalloying elements act an important part in improving the mechanical properties of steel. The essential reasons for the addition of strength by micro-alloying are the grain refinement and precipitation strengthening [1-5]. However, Nb-microalloyed steel exhibits a very low hot ductility in the range of 700–900°C, which can cause surface cracks during continuous casting [6]. This is mainly because during the phase transformation of austenite to ferrite, ferrite is preferentially formed at the austenite grain boundaries. As ferrite is the softer of the two phases, all the strain concentrates in ferrite. At the same time, Nb (C, N) precipitates are more easily precipitated at the grain boundary. Maehara et al.[7] showed that the synergistic effect of precipitates on the grain boundaries and austenite \(\rightarrow\) ferrite phase transformation increases the formation of cracks. Nakata [8] also suggested that the voids are easily formed near Nb precipitates or grain boundaries ferrite due to the stress concentration, which are connected to result in the cracking of slabs.

Recently, the methods for focusing on improving the hot ductility of niobium microalloyed steel have been studied which are mostly by adding the alloying elements such as Ti, B and Y [9]. Comineli [10] found that the coarse titanium-rich particles act as nucleation sites for NbC at high temperature when the titanium exists. Thus, there is little niobium being precipitated in finely detrimental forms at lower temperatures. Kim [11], Lce [12] and Faramarz [13] suggested that Fe\(_{23}\)(B,C)\(_6\) play the role of the preferential sites for the intragranular nucleation of ferrite and BN preferentially precipitates at the grain boundary [14-16]. It decreases the amount of grain boundary ferrites and improves the ductility of steel. Another possible alloying element is Cr. The addition of Cr to steel can enhance the corrosion resistance [17-19], improve the abrasion resistance [20]and increase the high temperature strength of steel [21]. Song [22] studied effect of alloying elements on work hardening behavior in cold drawn hyper-eutectoid steel wires, the results showed that the addition of Cr can increase the tensile strength by refining the interlamellar spacing and increasing the Hall-Petch parameter. Kim [23] suggested that the Cr contained in TRIP-aided cold rolled steels.
has high strength and ductility as well as a good recyclability. Rumana [24] found that the stability of retained austenite in steel can be improved by adding an appropriate amount of chromium. Several researches [25-28] have reported that the retained austenite improves the toughness and elongation of martensite by absorbing the energy from impacts and attenuation [29]. The above research mainly changes the volume fraction of retained austenite by adding Cr element, which affects the transformation of austenite to martensite and the distribution of microstructure. However, the influence of Cr addition on the phase transformation process of austenite to ferrite and the distribution of ferrite is limited. Siwecki [1] believes that Cr can promote the formation of bainite and martensite and inhibit the formation of pro-eutectoid ferrite. Then, the hardenability of steel is improved. The difference in microstructure distribution will directly affect the mechanical properties of steel. The confocal scanning laser microscope (CSLM) experiments are necessary to better explain the influence of Cr elements on the \( \gamma \rightarrow \alpha \) phase transformation. In recent years, there are studies focusing on the observation of the phase transformation process by the CSLM. Yin et al [30] detected that ferrite was easily nucleated at the austenite grain boundary by using the in-situ observation. Liu [31], Phelan and Dippenaar [32], and Haj [33] have summarized the development process of CSLM technology. Chen [34] observed the \( \gamma \)-austenite \( \rightarrow \alpha \)-ferrite interface migration by LSCM and found that \( \gamma/\alpha \) interface migrate in a retraceable way.

Therefore, this article is mainly to study the effect of Cr addition on the microstructure, precipitates and mechanical properties of niobium microalloy H-shaped steel. This article may provide a guideline for designing the composition to obtain high performance Nb microalloyed steels.

2 Experimental Procedures

The \( \gamma \rightarrow \alpha \) phase transformation were observed by CLSM. The temperature history was set in the computer program and the test was started. Fig.1 shows the heating and cooling process of the sample. The samples were heated from room temperature to 200°C and from 200°C to 1350°C at 50°C/min and 300°C/min, respectively. They were held for 600 s at 1350°C. Then, they were cooled to 830°C and 600°C at 180°C/min and 30°C/min, respectively. In order to better predict the effect of increasing the casting speed on the structure of the continuous casting of the beam blanks, the experimental cooling rate is equivalent to 3°C/s. When the sample was cooled to 830°C, the cooling rate was reduced to 0.5°C/s in order to better observe the effect of Cr on grain boundary ferrite growth. Finally, they were rapidly cooled to 25°C. The results of the phase transformations were recorded. The CSLM technology has been described in detail by previous researchers [35]. Three different chemical compositions of test steels (1# 2# and 3#) were selected as shown in Table 1.

Table 1. Chemical compositions of test steel (wt.%)

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Nb</th>
<th>Cr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.14</td>
<td>0.13</td>
<td>1.41</td>
<td>0.012</td>
<td>0.029</td>
<td>0</td>
<td>0.002</td>
</tr>
<tr>
<td>2#</td>
<td>0.14</td>
<td>0.14</td>
<td>1.45</td>
<td>0.012</td>
<td>0.030</td>
<td>0.12</td>
<td>0.003</td>
</tr>
<tr>
<td>3#</td>
<td>0.13</td>
<td>0.13</td>
<td>1.43</td>
<td>0.013</td>
<td>0.030</td>
<td>0.45</td>
<td>0.002</td>
</tr>
</tbody>
</table>
The steels (1#, 2#, 3#) were tensile tested by Gleeble-1500 thermo-mechanical. Specimens were 120 mm in length and 10 mm in diameter which were heated under a high-purity Ar (+99.9999). The Gleeble tensile specimen is heated to a high temperature 1350℃ at 10°C/S and held for 600 s to dissolve all the microalloying precipitates and produce a coarse grain size reminiscent of the as-cast grain size [15]. Then, they were cooled to the testing temperature (650℃, 700℃, 750℃, 800℃, 850℃, 900℃, and 950℃) at 3°C/s and held for 1 min to make the temperature uniform. The strain rate is 1.0×10⁻³ s⁻¹. Finally, they were quenched in water for the further analysis of microstructure and precipitates [36]. Fig.2 shows the analysis positions of electron backscatter detection (EBSD) and transmission electron microscope (TEM) near the fracture.

Fig.2. Fracture of hot ductility sample. (a) Fracture; (b) and (c) The analysis locations of EBSD and TEM.

3 Experimental Results and Discussion

3.1 γ→α Phase Transformation

As shown in Figs. 3-6, the evolutions of α phase at different Cr contents were described and compared. For the 1# microalloyed steel (0wt%Cr), the transformation occurred preferentially at triple points (a and e) and grew along the grain boundaries. In order to better observed the growth kinetics of grain boundaries ferrite, the magnification was further increased to 550×. As shown in
Fig. 3 (d-f), the curved $\gamma/\alpha$ phase boundary moved rapidly to 46 $\mu$m to the left. However, the faceted phase boundary migrated very slowly only 12 $\mu$m to the right. The migration rates of $\gamma/\alpha$ phase boundary is different. The main reason is the curved on the left is incoherent with high mobility and the faceted $\gamma/\alpha$ phase boundary on the right is semi-coherent with low mobility [30].

Similarly, the $\gamma\rightarrow\alpha$ transformation process of 2# (0.12wt%Cr) and 3# (0.45wt%Cr) were shown in Figs. 4 and 5, respectively. In Figs. 4 (a-c), during the cooling from 755°C to 695°C, a piece of Widmanstätten ferrite (WF) plates was emanated from the $\gamma/\gamma$ GBs and grew into the $\gamma$-austenite matrix at a rate of 1.3 $\mu$m/s. After 21 s, the growth direction of Widmanstätten ferrite plate changed by 28°. The Widmanstätten ferrite plate stop growing when it encounter grain boundaries or other ferrite structures as shown in Fig. 4 (e). However, some researchers suggested that the Widmanstätten plates had a small change of 0-15° in the growth direction before it grew fast [37-39]. This is because the grain boundary ferrite adjacent to the Widmanstätten hinders the growth direction of the Widmanstätten plates as shown in Fig. 4 (f). In Figs. 5 (a-c), the thickness of 3# grain boundary ferrite was obviously thinner than that of 1# and 2# during the cooling process. When the temperature dropped from 744°C to 722°C, there were some side-plates emanating from ferrite allotriomorph at the $\alpha/\gamma$ GBs (Figs. 5 (d-f)). Aaronson [40] described this as a sympathetic nucleation of ferrite. Many researchers suggested that the Widmanstätten plates have multiple growth stages [41-42].
Fig. 4. Evolution of the $\alpha$ phase of 2# microalloyed steel with decreasing temperature; (a), (b) and (c) 550×; (d), (e) and (f) 750×.

Fig. 5. Evolution of the $\alpha$ phase of 3# microalloyed steel with decreasing temperature; (a), (b) and (c) 275×; (d), (e) and (f) 550×.

However, there are still some differences between 1#, 2#, and 3# transformation process. In Fig. 6 (a), the starting temperature of the $\gamma \rightarrow \alpha$ transformation decreased with increasing the Cr content. It is consistent with the result of Thermo-Calc calculation (Fig. 6 (b)). The total times for the $\gamma \rightarrow \alpha$ transformation of the sample 1#, 2#, and 3# were about 227 s, 206 s, and 210 s, respectively. This result shows that the element of Cr increases the stability of supercooled austenite and reduces the $\gamma \rightarrow \alpha$ transformation onset temperature and the precipitation time of grain boundary ferrite.
3.2 Hot ductility

In Fig. 7, it was shown that there was a trough of hot ductility at 750°C. Previous studies showed that the transverse cracks can be avoided when the area reduction (RA) values were greater than or equal to 40% [15,43-44]. The range of the low temperature brittle zone of the 2# steels was narrower than that of Cr free steel (1#). The area of reduction of 2# steel was narrower than that of 3# steel in the whole test temperature range. The results show that appropriate amount of Cr can improve the hot ductility of Nb microalloyed steel.

![Fig. 6](image)

**Fig. 6.** Starting precipitation and fishing temperatures of α ferrite. (a) Experimental result (b) Thermo-Calc result

![Fig. 7](image)

**Fig. 7.** Hot ductility curves of (a), (b) and (c) 1#, 2# and 3# steel, respectively

**Figs. 8 (a-c)** show the Force-Stroke curves of Nb microalloy steels from the hot tensile test. The elongation increased and the ultimate force gradually decreased with increasing the deformation temperature increases. This softening phenomenon is mainly caused by the dynamic
At a higher temperature of 950°C, the stroke was the longest due to the activation of dynamic recrystallization. Fig. 8 (d) shows the force-stroke curves of the tested steels at 750°C. The peak force of 2# steel was a little higher than that of steel 1#. However, the peak force of 3# steel is the lowest which indicates that the appropriate amount of Cr is beneficial to increase the peak force of Nb microalloyed steel.

Fig. 8. Force-Stroke curves of the Nb microalloyed steel (a) 1# steel, (b) 2# steel, (c) 3# steel, and (d) 1#, 2#, and 3# at 750°C.

3.3 Microstructure near fracture

The microstructure of 1# (0 wt% Cr), 2# (0.12wt%Cr), and 3# (0.45wt%Cr) steel are compared as show in Fig. 9. It can be seen that the thin films of ferrite decorated the austenite boundaries at 750°C (Fig. 9 (a – c)). The thickness of grain boundaries ferrite decreased with increasing the Cr content. According to the statistics of the microstructure photos, the average thickness of the 1#, 2#, and 3# steel were 49 μm, 12.9 μm, and 8.7 μm, respectively, as shown in Fig. 10. It is indicated that the addition of Cr inhibits the formation of grain boundary ferrite in steels. Figs 9 (d-f) show that the cracks were easy to generate at the grain boundaries ferrite where the stress concentration was larger and the thickness of ferrite film was bigger [15]. This is mainly because austenite is harder than ferrite. During the deformation process, the amount of deformation of ferrite and austenite are different. It is easy to form voids in these locations with the increase of the stress. The voids are connected together, causing the intergranular failure with low ductility. There were many cracks in 1# steel, especially at the three point grain boundaries. The main reason is that the grain boundary ferrite films thickness is larger and unevenly distributed. In addition, the cracks were longer in the 3# steel than in the 1# steel. It may be because the average size of austenite grains in 3# steel is 346 μm which is larger than in 1# steel (207 μm). Many previous studies have considered that the hot ductility of steel is mostly controlled by austenite size [45-46].
Fig. 9. Microstructures near fracture surface at 750°C. (a) and (d) 1#, (b) and (e) 2#, (c) and (f) 3#).

Fig. 10. Frequency of thickness of grain boundaries in test steel. (a) 1#, (b) 2# and, (c) 3#

Fig. 11 shows the inverse pole figure (IPF) maps of the microstructures as shown in Figs. 11 (a-c). In 1# steel, the grain orientation is dispersion distribution state. However, with increasing Cr content, the grain has a relatively concentrated orientation distribution most of the area of Fig. 11 (c) is blue and close to [111]. It is also clear that the proportion of ferrite (white) distributed at the grain boundary is also reduced. The high temperature fracture process of microalloyed steel includes 3
stages [47-48]. Firstly, the nucleation of a microcrack in grain boundaries or precipitate. Secondly, microcracks become longer and wider under stress. Finally, the progression of the microcrack through the matrix. The crack is formed on the LAGB because the LAGB cannot effectively prevent the nucleation and extension of the crack. Once the crack has overcome the two first stages, the crack growth can only be stopped at high-angle grain boundaries (HAGB) [49]. However, it is obvious that the proportion of HAGB of 2# steel is the highest and that of 1# steel is the lowest. The number fractions of misorientation angle boundaries of the three steel are 40.9%, 48.7%, and 47.5%, respectively, as shown in Figs. 11 (d-g). The HAGB above 15 deg can hinder the crack propagation and change the propagation direction of the crack, which can effectively improve the ductility of the steel [50].

Fig. 11. EBSD analysis of Nb microalloyed steel. (a), (b), and (c) The IPF maps of 1#, 2#, and 3#, respectively; (d), (e), and (f) The HAGB of 1#, 2#, and 3#, respectively; (g) Proportion of LAGB and HAGB

3.4 Growth kinetics of grain boundary ferrite

Fig. 12 shows that the changes in grain boundary ferrite length with time. The maximum migration speed of $\gamma/\alpha$ phase boundary was obtained by the slope theorem at the beginning of $\gamma \rightarrow \alpha$ phase transformation. They were 1.7, 1.0, and 0.23 $\mu$m/s at the Cr content of 0, 0.12, and 0.45 wt.%, respectively. The results show that the migration speed of $\gamma/\alpha$ phase boundary decreases with increasing the Cr element content during the $\gamma \rightarrow \alpha$ phase transformation. This is mainly because
the $\gamma \rightarrow \alpha$ phase transformation is controlled by the diffusion elements. Yin et al. [30] suggested that the critical wavelength $\lambda_C$ to stabilize planar interface is described by Equation (1).

$$\lambda_C \propto \left( \frac{\sigma_{IB}}{G_C} \right)^{1/2}$$ (1)

Where $\sigma_{IB}$ is the free energy of the interphase boundary, and $G_C$ is the concentration gradient at the interface. The binding force of Cr and C atom is strong. The Cr element hinders the diffusion of C atoms from the $\gamma/\alpha$ phase boundary to the austenite. The carbon concentration at the front of the austenitic interface in 3# steel is smaller than that in 1# steel. Furthermore, as the Cr content increases, the $\gamma/\alpha$ interface energy increase. A high interface energy is beneficial to improve the stability of the $\gamma/\alpha$ phase boundary. Therefore, the interfacial perturbation will decay and the interface becomes stable. The starting temperature of $\gamma \rightarrow \alpha$ phase transformation decreases. The diffusion of carbon atoms is inhibited so that the proportion of grain boundary ferrite is reduced.

![Fig. 12. Changes in the lengths of the grain boundary $\alpha$ phases.](image)

### 3.5 Precipitates in Nb microalloyed steel with various Cr contents

The influence of precipitate NbC or Nb(C,N) has a crucial effect on the austenite grains size. In Fig. 13, the average size of NbC or Nb(C,N) precipitated in 1# steel was least and that in 3# steel was biggest. The average size were 1.9 nm and 10.3 nm, respectively. The precipitates in 1# steel were relatively dispersed and the amount was small. In Figs. 13 (d-f), the amount of NbC or Nb(C,N) precipitates in 1#, 2#, and 3# steel were 68/µm², 223/µm², and 138/µm² at 750°C, respectively. The number of precipitates in 2# steel increased and the dumbbell-shaped precipitates appeared. The cluster-like precipitates appeared in 3# steel. The austenite grains were refined in 2# steel (Fig. 9(b)). However, the precipitates aggregated to form a large-sized precipitates when the Cr content was increased to 0.45%. In Fig. 13 (c), the size of the precipitate is bigger than 50 nm account for 6.5%. Therefore, the average size of austenite grains in 3# steel is a maximum of 346 µm. The size of the precipitate is smaller than 50nm, which has the most obvious pinning effect on the $\gamma/\gamma$ grain boundaries [51-53]. At the same time, due to the large austenite grain size and few grain boundaries, the resistance to cracks is small. As the grain sizes increase, the ductility trough (which is defined as the range in the RA value below 40%) is deepened [54-55]. Maki [56] suggested that the morphology of grain boundary ferrite is related to the austenite grain size. The coarser the austenite grains, the easier it is to form film-like ferrite at the $\gamma/\gamma$ grain boundaries. In contrast, the
spherical ferrite was formed around the small austenite grain which reduced the formation of cracks and improved the ductility of the slab. Furumai [57] also confirmed that the area reduction is seen to linearly decrease with decreasing the inverse \( \gamma \) grain size. The fine grains can be easily rotated to compensate for the deformation, reduce the stress concentration at grain boundary locations, and inhibit the crack nucleation and expansion [58].

![Graph](image1.png)

**Fig. 13.** Size and amount of precipitation at different steel. ((a), (d), and (g) 1# 0wt% Cr; (b), (e), and (h) 2# 0.12wt% Cr; (c), (f), and (i) 3# 0.45wt% Cr; (g - i) Analysis of NbC and Nb(C,N)).

### 4 Conclusions

1. The starting temperature of the \( \gamma \rightarrow \alpha \) transformation decreases with the increase of Cr content. At the start of the \( \gamma \rightarrow \alpha \) transformation, the maximum migration speed of IB are 1.7 \( \mu \text{m/s} \), 1.0 \( \mu \text{m/s} \) and 0.23 \( \mu \text{m/s} \) at the Cr content of 0, 0.12, and 0.45wt%, respectively. The element of Cr increases the stability of super-cooled austenite and reduces the \( \gamma \rightarrow \alpha \) transformation onset temperature and the precipitation time of grain boundary ferrite. The thickness of 3# grain boundary ferrite was thinner than that of 1# and 2# during the cooling process.

2. The addition of 0.12wt% Cr to Nb microalloyed steel is beneficial to the hot ductility and peak force. This is because the proportion of grain boundary ferrite is reduced with increasing the Cr content. The thickness of ferrite in 2# steel is thinner than that in 1# steel. The proportion of HAGB increases with increasing the Cr content. The HAGB hinders the crack propagation and changes the propagation direction of the crack, which can effectively improve the ductility of the steel.

3. The amount and size of NbC or Nb (C, N) precipitates increase with increasing the Cr content. The precipitate of 2# steel effectively refines the austenite grains and improves the ductility of the steel. However, the precipitates in the 3# steel aggregate together so that the size of the precipitate is greater than 50 nm account for 6.5%.
Disclosure statement

No potential conflict of interest was reported by the authors.

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