Effect of ultra-trace rare earth elements on continuous cooling transformation curve of low carbon steel

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Abstract
Two groups of low carbon steel with ultra-micro amount (less than 20 ppm) rare earth lanthanum and without rare earth element were taken as experimental objects. Continuous cooling transformation curves of two kinds of low carbon steels were drawn by Formaster-F II automatic phase transformation instrument, alloy phase method and hardness method. According to the measured CCT curve, the microstructure and hardness of low carbon steel under different cooling rates were studied and analysed. The results show that the addition of ultra-trace rare earth elements can increase the Ac₁ and Ac₃ points of low carbon steel by about 20 °C; the starting temperature of martensite transformation MS point decreased by 19 °C, and the end temperature Mf point decreased by 6 °C; at low cooling rate, the transformation range of ferrite is increased and that of pearlite is decreased; the starting temperature of bainite Bs point increased by 20 °C, and the end temperature of bainite Bf increased by 13 °C; at low cooling rate, the ferrite transformation range becomes larger, while at high cooling rate, the ferrite transformation range becomes smaller.

There have been many achievements in the application of rare earth elements in steel [1–7]. Most of the early scholars [8–19] studied rare earth elements based on laboratory research. The content of rare earth added in previous studies is generally high (40 ~ 1200 ppm). In recent years, many enterprises and research institutes have focused on the production and mechanism of rare earth micro alloyed steel under continuous casting conditions [20–25]. The results show that the large particle inclusions produced by adding more than 30 ppm rare earth elements in the steel can easily lead to the phenomenon of ‘clogging’ in the submerged nozzle of tundish in the continuous casting process, resulting in production accidents such as broken casting and affecting the production efficiency. Therefore, in order to continuously cast rare earth micro alloyed steel under continuous casting conditions, the content of rare earth in steel should not exceed 30 ppm. Researchers need to study whether such a trace amount of rare earth elements have favourable effects on inclusions, microstructure, strength, plasticity, corrosion resistance and so on. In this paper, the effect of ultra-trace rare earth elements on continuous cooling transformation curve of low carbon steel is studied, which provides a theoretical basis for the production of rare earth micro alloyed low carbon steel by continuous casting process.

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1. Test materials and methods

Two groups of low carbon test steels produced by a steel plant were used as test materials. One group was added with ultra-micro amount (less than 20 ppm) rare earth element lanthanum, and the other group was blank test steel. The main chemical composition of test steel is shown in table 1.

According to Yb/T 5128-2018 standard, two groups of test steels were processed into samples with diameter of 3 × 10 mm. Through the process as shown in figure 1, heated from room temperature to 500 °C at a heating rate of 10 °C s⁻¹ and then heated to 1000 °C at a heating rate of 0.05 °C s⁻¹ for 3 min, and then cooled to room temperature at a cooling rate of 10 °C s⁻¹. The Ac1 and Ac3 point temperatures of the two test steels were measured; Through the process as shown in figure 2, the two groups of test steels were heated to 950 °C at the speed of 10 °C s⁻¹, after holding for 5 min, it is fully austenitized, and then cooled to room temperature at 1, 2, 5, 10, 20, 30, 40, 50, 60, 70 °C s⁻¹ respectively. The microstructure of the test steel at different cooling rates was observed by Axiovert 25 Zeiss microscope, the metallographic photos were taken by Olympus inverted system metallographic microscope, and the microhardness of the test steel at different cooling rates were tested by HVS-30Z/LCD Vickers hardness tester. Combined with metallography and hardness, the original data were drawn into CCT curve by Origin software.

| Sample number | C   | Si   | Mn   | P   | S   | La (wt.%) |
|---------------|-----|------|------|-----|-----|-----------|
| A             | 0.16| 0.32 | 1.37 | 0.012 | 0.001 | 10.2 ppm  |
| B             | 0.17| 0.29 | 1.33 | 0.011 | 0.001 | —         |

Figure 1. Experimental process chart for determination of Ac₁ and Ac₃.

Figure 2. Experimental process chart for determination of static CCT curve.
2. Results and discussion

2.1. Effect of trace rare earth elements on critical point

By measuring the expansion curve and tangent method, the $\text{Ac}_1$ point temperature and $\text{Ac}_3$ point temperature of test steel A which containing trace lanthanum are $689^\circ\text{C}$ and $790^\circ\text{C}$, respectively; the $\text{Ac}_1$ point temperature and $\text{Ac}_3$ point temperature of test steel B which without rare earth elements are $670^\circ\text{C}$ and $772^\circ\text{C}$, respectively. The addition of lanthanum increases the $\text{Ac}_1$ point of the test steel by $19^\circ\text{C}$ and the $\text{Ac}_3$ point of the test steel by $18^\circ\text{C}$. The $\text{Ac}_3$ temperature of steel A has risen by $18^\circ\text{C}$, it means that the austenite grains of steel B nucleate earlier than those of steel A during quenching and heating up. Consequently, the original austenite grain size of steel A should be smaller than that of test steel B without rare earth elements. To prove this deduction, the original austenite grains of both steel A and B were observed. The samples were polished, and the grain boundaries were corroded with picric acid solution ($30 \text{ ml distilled water} + 2 \text{ g picric acid} + 1.5 \text{ g Haiou brand shampoo} + 6 \text{ drops of hydrogen peroxide}$). Figure 3 shows the original austenite metallographic photos of two kinds of test steels after quenching and tempering. According to the requirements of GB/T 6394-2017, the average grain size of A is $11.30 \mu\text{m}$ and that of B is $13.99 \mu\text{m}$. The results show that the original austenite grains of steel A are refined, the grain boundaries of them are increased, the grain distribution is more uniform, and the number of large-sized grains is significantly reduced. The addition of ultra-trace rare earth elements in low carbon steel can increase the transformation point and refine the original austenite grain.

The experimental data show that the addition of trace rare earth elements can reduce the martensitic transformation start temperature $\text{Ms}$ from $390^\circ\text{C}$ to $371^\circ\text{C}$ and the martensitic transformation termination temperature $\text{Mf}$ from $263^\circ\text{C}$ to $257^\circ\text{C}$. Due to the strong adsorption capacity of rare earth to carbon, the activity of carbon in austenite is reduced and the chemical driving force of martensitic transformation is increased. According to the thermodynamic principle of martensitic transformation, the addition of rare earth elements reduces the $\text{Ms}$ point [8]. On the other hand, as the martensite transformation is a shear process, when the temperature drops to $\text{Ms}$ point, the germ in high temperature austenite is activated and grows rapidly at the most favourable position for nucleation. Rare earth elements are enriched in these positions, which reduces the interfacial energy, weakens the thermal activation conditions for martensite nucleation, improves the shear strength of austenite, hinders martensitic transformation and reduces $\text{Ms}$ point [9]. With the addition of trace rare earth elements, the starting temperature of bainite transformation $\text{Bs}$ increased from $556^\circ\text{C}$ to $576^\circ\text{C}$ and the end temperature of bainite transformation $\text{Bf}$ increased from $403^\circ\text{C}$ to $416^\circ\text{C}$. Because of the addition of trace rare earth elements, the original austenite grain size of test steel A is refined, the grain boundary area is increased, the probability of forming ferrite core is increased, the diffusion distance of carbon is shortened, the incubation period of bainite transformation is shortened, the transformation speed is accelerated, and the starting temperature $\text{Bs}$ of bainite transformation is increased.

![Figure 3. Metallographic photos and grain size distribution of original austenite of test steels (a) steel A bearing 10.2 ppmRE (b) steel B without RE.](https://example.com/figure3.jpg)
2.2. Effect of trace rare earth elements on microstructure and hardness

Figures 4 and 5 show the microstructure of the two test steels at different cooling rates. It can be seen from the metallographic diagram that when the cooling rate is 1 °C s⁻¹, the microstructure of the two test steels are ferrite and a small amount of pearlite, of which the white is polygonal ferrite and a small amount of pure black is
pearlite. The ferrite content of test steel A added with ultra-trace rare earth elements is obviously more than that of blank test steel B. When the cooling rate is 2 °C s⁻¹, the structure of test steel A is 26%B + 7%P + F, and that of test steel B is 23%B + 10%P + F. The bainite in the two test steels is needle like, and the bainite structure in test steel A is more than that in blank test steel B, because bainite transformation can only occur when austenite is undercooled below Bs point, and test steel A with higher Bs temperature has bainite transformation first and contains more bainite. When the cooling rate is 5 °C s⁻¹, the microstructure of test steel A is 39%B + M and that of test steel B is 27%B + M. The addition of ultra-trace rare earth element lanthanum not only increases the acicular lower bainite of test steel A, but also refines the bainite structure, because the addition of rare earth makes the original austenite grain refinement, and the bainite structure is also refined. When the cooling rate is 10 °C s⁻¹, the microstructure of test steel A is 63%B + M and that of test steel B is 59%B + M. The white polygon is ferrite and the gray part is bainite. However, the bainite in test steel A is obviously more than that in test steel B. Because the addition of trace rare earth elements can refine the original austenite grains, increase the grain boundary area, increase the nucleation position of proeutectoid ferrite and bainite, and promote the production of transformation products [26]. When the cooling rate is 20 °C–30 °C s⁻¹, the microstructure of A and B steel is bainite and martensite. In Metallography, the bright structure with obvious boundary is bainite, and the other parts are martensite. When the cooling rate is 20 °C s⁻¹, the content of martensite in test steel A and blank test steel B is 72% and 64%, respectively. Because the addition of trace rare earth elements reduces the activity coefficient of carbon in austenite and increases the chemical driving force required for martensitic transformation; at the same time, rare earth refines austenite grains, makes austenite strengthen, and increases the non-chemical driving force required for martensitic transformation [27]. With the increase of cooling rate, bainite decreases and martensite increases. When the cooling rate is 70 °C s⁻¹, the content of martensite in the metallographic structure of the two test steels is more than 90%.

Figure 6 shows the microhardness of the two groups of test steels at different cooling rates. It can be seen from the figure that the microhardness of the two groups of test steels increases with the increase of cooling rate. When the cooling rate is less than 5 °C s⁻¹, the microhardness difference of test steel A and B is less than 10 HV5; when the cooling rate is 10 °C s⁻¹, the microhardness value of test steel A containing trace rare earth elements is 28 HV5 higher than that of blank test steel B; when the cooling rate is 20 °C s⁻¹–70 °C s⁻¹, the difference of microhardness between the two steels is less than 20 HV5; The appearance of martensite leads to a large slope of cooling curve from 10 °C s⁻¹ to 20 °C s⁻¹. Martensite has a body centered cubic structure, and there is no dense slip surface, so dislocation is not easy to slip; There are a lot of supersaturated carbon atoms in martensite, and the hardness is improved by solution strengthening. When the cooling rate is 20 ~ 60 °C s⁻¹, the microstructure is bainite and martensite. With the increase of cooling rate, the martensite increases gradually, and the hardness gradually increases and tends to be flat. When the cooling rate is 70 °C s⁻¹, the microstructure is all martensite, and the hardness reaches the maximum value. It can be seen from figure 6 that the microhardness values of test steel A added with ultra-trace rare earth elements are higher than that of test steel B at different cooling rates. At low cooling rate, because of the addition of ultra-trace rare earth elements, the original austenite grains are refined, the grain boundaries are increased, and the strength is improved. At the same time, the increase of grain boundary area also provides a place for the nucleation of bainite and martensite.
promotes the growth of proeutectoid ferrite and bainite, and increases the hardness. At high cooling rate, the addition of rare earth elements reduces the width of martensite lath and increases the microhardness of test steel [28].

2.3. The effect of ultra-trace rare earth elements on CCT curve
According to the established process, the expansion curves of the two groups of test steels at different cooling rates were measured, figure 7 shows the continuous cooling transformation curve of the two groups of test steels determined by metallographic structure and microhardness at different cooling rates, It can be seen from the figure 7 that the curves of the two groups of test steels are basically the same. Compared with blank test steel B, the martensitic transformation curve of test steel A with ultra-trace rare earth elements decreases as a whole, the starting temperature Ms of martensitic transformation decreases from 405 °C to 373 °C, and the ending temperature Mf of martensite transformation decreases from 263 °C to 257 °C. The addition of rare earth elements improves the chemical driving force required for martensitic transformation, because rare earth elements have good adsorption of carbon, which reduces the activity of carbon in austenite, and increases the non-chemical driving force required for martensitic transformation by refining the austenite grain size [28]. According to the thermodynamics of martensitic transformation, the greater the chemical driving force, the greater the resistance, and the lower the Ms point [29]. When the cooling rate is 70 °Cs⁻¹, IPP software can be used to calculate that the microstructure of test steel A with trace rare earth elements is 3% bainite and martensite, and that of blank test steel B is 5% bainite and martensite. It is basically considered that the critical quenching cooling rate of the two groups of test steels is 70 °Cs⁻¹, and the hardenability is related to the austenite grain size of the test steel. Rare earth elements (less than 20 ppm) have little effect on the hardenability of the test steel, and the change of the C curve is also small.

3. Conclusion
(1) The addition of lanthanum increases the Ac1 point of the test steel by 19 °C and the Ac3 point of the test steel by 18 °C, at the same quenching temperature, the austenitizing time and grain growth time of the test steel with higher transformation point are shorter. The analysis by IPP software shows that the addition of ultra-trace rare earth elements can refine the original austenite structure of the test steel, make the distribution more uniform, and reduce the number of large-size grains. The microhardness of low carbon steel at different cooling rates was increased.

(2) Compared with the blank steel, the temperature of Ms point and Mf point of the test steel added with ultra-trace rare earth elements decreased, and the chemical driving force and non-chemical driving force of martensitic transformation increased; when the cooling rate was 1 °Cs⁻¹–30 °Cs⁻¹, the start line and end line of bainite transformation moved up, and when the cooling rate was 40 °Cs⁻¹–70 °Cs⁻¹, bainite transformation began line and the termination line move down as a whole; When the cooling rate is 1 °Cs⁻¹–5 °Cs⁻¹, the ferrite transformation start line of the test steel moves up and the end line moves down, which expands the transformation range; when the cooling rate is 5 °Cs⁻¹–20 °Cs⁻¹, the ferrite
transformation start line decreases and the ferrite transformation end line rises. The test steel which added with ultra-trace rare earth, the Ps point (Fs point) rises, and the Pf point (Bs point) rises.

(3) The results show that the microstructure and content of the two groups are basically the same at different cooling rates. When the cooling rate is 1 °C s⁻¹–5 °C s⁻¹, they are ferrite, bainite and pearlite. The addition of lanthanum makes the bainite and ferrite increase; The results show that when the cooling rate is 5 °C s⁻¹–20 °C s⁻¹, the bainite in the test steel containing rare earth elements is significantly more than that in the blank test steel; when the cooling rate is 20 °C s⁻¹–60 °C s⁻¹, the microstructure is bainite and martensite, and the martensite in the test steel with lanthanum is more than that in the blank test steel, and when the cooling rate is 70 °C s⁻¹, the two test steels have martensite structure.

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