Effect of cooling rate on the microstructure and mechanical properties of a high copper high nickel low carbon steel

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Abstract: A new composition steel was designed by adding 1wt.% Cu and 2wt.% Ni elements on the basis of low-carbon Ti-bearing microalloyed steel. The continuous cooling transition curve (CCT) is obtained by the phase transition curves, microstructure and hardness in the Gleeble3800 thermal simulation test machine. In order to further study the law of transformation and meet the needs of industrialized production, different cooling tests were carried out through industrialized trial production, and the corresponding organization and mechanical properties were analyzed. The results show that when the cooling rate increases, the microstructure transformation appears as granular bainite (GB) → granular bainite + lath bainite (GB+LB) → lath bainite (LB) → lath martensite (M). The mechanical properties increase with the increase of cooling rate, and the yield strength increases in a positive correlation trend. The results show that the steel can obtain good and stable comprehensive mechanical properties in a large cooling rate range without heat treatment. The best mechanical properties with a good combination of yield strength and impact performance are obtained under ultra-fast cooling conditions.

1. Introduction
In order to meet the requirements of energy saving and emission reduction, the development of high-strength steel has attracted much attention in recent years, and Q&P steel and DP steel have become popular research now[1-3]. However, the heat treatment process in the production process is a long cycle process, and the tempering process not only requires several or even dozens of hours but also consumes a lot of energy[4]. For a good product, good welding performance is essential. At present, the common high-strength steels are basically medium-carbon or even high-carbon steels, which is detrimental to the welding performance. The brittle martensite structure is easily formed during the cooling process of the molten pool after welding, and the impact toughness is drastically reduced, which seriously affects engineering safety. In recent years, low-carbon bainite steel has attracted the attention of many researchers due to its unique microstructure and superior comprehensive mechanical properties[5-7]. Bainite is a medium-temperature phase transformation product with a formation temperature below ferrite and above martensite which has a wide range of applications in engineering due to its remarkable strength and excellent plastic combination. H. K. D. H. Bhadeshia et al. have carried out a lot of research work in advanced bainite steel, and prepared the ultra-high strength bainite structure characterized by nano-scale bainite laths and thin film-like retained austenite between laths. The excellent performance
of strength 2.5GPa and fracture toughness 40 MPa•m$^{1/2}$ was obtained[8]. The bainite transformation is a phase transformation controlled by the diffusion mechanism and the shear mechanism. In general, the bainite structure needs to be isothermal at a certain temperature. Although the bainite obtained by the isothermal process has excellent comprehensive mechanical properties, the long production cycle largely limits the application of bainite. How to reduce the bainite transformation time and increase the driving force for bainite nucleation has become the key to breaking through this bottleneck. Adding alloying elements and reducing carbon content is one of the effective ways to accelerate the transformation of bainite[9]. There are two methods currently used to produce high-strength steel[10]. One method is the aforementioned series of heat treatments on raw steel, which is a very effective method that can obtain different properties for different scenarios as needed. Another method is to use TMCP technology to control the mechanical deformation and cooling rate of the raw material to obtain products with excellent performance, such as Ti-bearing microalloyed steel, which is produced in this way. That is to say, without subsequent heat treatment steps, which greatly reduces the production cycle and production costs, which has great advantages for enterprises. Pickering et al. developed the Mo series air-cooled low-carbon bainite steel by using the combined influence of molybdenum and boron on the continuous cooling transformation (CCT) curve[11]. FENG et al. prepared Mn air-cooled bainitic steel with excellent properties through the control of alloying elements[12].

Present study is based on the industrial Ti-bearing low-carbon low-alloy steel produced by the TMCP process, adding a certain amount of Cu and Ni elements, and using solid solution strengthening, phase transformation strengthening and precipitation strengthening to make up for the strength loss caused by low carbon content. Cu can produce solid solution strengthening in steel, and precipitation strengthening can be achieved by precipitating Cu-rich particles under certain conditions to further improve the strength of steel. At the same time, Cu can increase the stacking fault energy in steel, significantly reduce the bainite transformation point, increase the driving force for bainite transformation, and promote the transformation of bainite.

2. Experimental materials and methods

The composition of the alloy materials in this study is shown in Table 1. The experimental materials were smelted in a 60 kg medium-frequency vacuum induction furnace and poured into billets. The billets were then heated to austenitizing temperature and forged after holding for 2 hours to form a steel ingot with a cross-section of 40mm×40mm, in order to fully eliminate casting defects and refine grains. The billet forging starts at 1180℃ and ends at 980℃. The thermal simulation samples were sampled from the forging blank and the thermal simulation experiment is performed on the Gleeble3800 equipped with a thermal dilatometer. The process routine is shown in Fig.1. The sample is heated to 980℃ at a heating rate of 5℃/s for 5 minutes and then cooled to 900℃ at a cooling rate of 20℃/s, then 50% compression is performed at a strain rate of 1s⁻¹, and cooled to ambient temperature at different cooling rates. The temperature, time and expansion amount in the expansion curve were obtained at different cooling rates. The test sample was cut along the middle with a wire cutting machine and then mechanically polished and polished to observe the microstructure, and the hardness test was carried out. Combining the expansion curve, structure and hardness, a continuous cooling transition curve (CCT) is obtained. In order to further explore the transformation laws of different cooling speeds under industrial conditions, four different cooling speeds were selected for pilot experiments in the continuous cooling transition curve (CCT). The forging billet is heated to 1200~1250℃ and kept for 2h to ensure that the alloying elements are solid-dissolved in the austenite. Multi-pass rolling is carried out at 1000-1180℃ in the austenite recrystallization zone, the thickness after rolling is about 20mm, the total reduction is 20mm, and the total reduction is 50%. The samples were subjected to four different processes to investigate the evolution of different structures and the performance evolution of different cooling routes. The rolled steel plates are marked as air-cooling steel, fast-cooling steel, ultrafast-cooling steel, and water-cooling steel. For convenience, they are referred to here as AC, FC, UFC and WC respectively. The process of AC is to slowly cool to ambient temperature in the air surround after controlled rolling. The process of FC steel is to use a rapid cooling device to quickly cool (10-20℃/s) to ambient temperature after
controlled rolling. The process of UFC steel is to use ultra-fast after controlled rolling which cooling rate is a range of 40-60℃/s. The process of WC is quenching into water.

Table 1. Chemical composition of the experimental steel (wt.%).

| C  | Si  | Mn  | P   | S   | Cu  | Ni  | Cr  | Ti  | Fe  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.05 | 0.40 | 1.5 | 0.015≥ | 0.005≥ | 1.00 | 2.00 | 0.51 | 0.11 | Bal. |

3. Results and discussion

3.1 Continuous cooling transition curve (CCT)

The expansion curve of the test steel at different cooling speeds is obtained through Gleeble3800 equipped with a dilatometer, the expansion curve at different cooling speeds is obtained, and the phase transition point at different cooling speeds is determined. Combining the hardness and thermal simulation expansion curves, the continuous cooling transition curve (CCT) is drawn as shown in Fig.2, and the hardness value at each cooling rate is tested separately. It can be seen that as the cooling rate increases, the structure shows the evolution law of granular bainite (GB) → granular bainite + lath bainite (GB+LB) → lath bainite (LB). As the cooling rate further increased, a martensitic structure appeared. In the present study, 1wt.% Cu is added to the alloy composition. As an austenite stabilizing element, Cu can reduce the austenite transformation temperature and inhibit the formation of high-temperature transformation products, which has an impact on the transformation and refinement of the structure. Previous study has shown that for every one percent increase in Cu, Ac₁ drops by about 27℃, and Ac₃ drops by about 19℃, so a bainite-based structure can be obtained at different cooling rates[13].
It can be seen from the hardness distribution that the hardness shows a positive correlation trend with the increase of cooling rate. The hardness change is mainly related to the structure and grain size. As the cooling rate increases, the high-temperature phase transformation is suppressed, and the diffusion of carbon is also hindered, so that the structure of bainite changes from granular to lath. The reason for the refinement of subunits is related to the increase in cooling rate and the decrease in phase transition point of Cu. When the γ→α transition occurs, the free energy of the system will spontaneously change from a higher state to a lower state. The addition of Cu reduces the transformation point, resulting in a larger difference between the austenite free energy $G_\gamma$ and the ferrite free energy $G_\alpha$, and the driving force for phase transformation increases\cite{13}.

![Continuous cooling transition curve (CCT)](image)

Fig. 2. Continuous cooling transition curve (CCT).

3.2. Evolution of microstructure
The optical micrographs and scanning electron micrographs of the hot-rolled plates obtained under different cooling routes are shown in Fig.3 and Fig.4. It can be seen that with the increase of the cooling rate, the transformation of the structure from granular to lath-like can be clearly seen, and with the decrease of the grain size, which has a high consistency compare to the continuous cooling transition curve (CCT) obtained from the thermal simulation. Fig.4 shows the scanning electron micrographs of the samples prepared under different cooling routes which dynamically show the changes in the structure as the cooling rate increases. It can be seen from the SEM images of AC (Fig.4e) and FC (Fig.4f) that the structure changes from granular to lath as the cooling rate increases. When the cooling rate is in the middle position, granular and lath exist at the same time, and the M/A island can also be clearly seen. When the cooling rate is further increased, the UFC structure appears as shown in Fig.4g, which is basically composed of lath bainite. Under extreme cooling conditions (AC), a smooth lath martensite as shown in Fig.4h is obtained. During the cooling process of AC, the cooling rate is about 3°C/s. Excessive residence time in the high temperature zone leads to high thermal activation energy of carbon atoms at high temperatures, which is conducive to the carbon atoms in the parent phase austenite expelling carbon to the surroundings through the diffusion mechanism, forming many carbon-rich regions\cite{14} which increases the mechanical stability of austenite. As the cooling rate increases, the granular bainite transformation occurs, which wraps the carbon-rich retained austenite in the middle,
and finally forms part of the retained austenite transforms into martensite, forming a coarse M/A structure, shown in red in Fig.4e. In the ferrite matrix, there are only a few M/A islands in the middle part, and the lath bainite structure is not observed. Compared with AC steel, the microstructure of FC is composed of granular bainite structure with a small amount of lath bainite, and there are small grains formed by oriented acicular ferrite structure. The precipitation of carbide particles between the ferrite laths was observed. The acceleration of the cooling rate strongly inhibits the diffusion of carbon elements and reduces the carbon-rich areas, which ultimately leads to a decrease in the number and size of M/A on the quasi-polygonal ferrite. The grain distribution can be clearly observed through the different orientations of the ferrite laths. The structure of UFC is an obvious lath structure, and different lath bundles are parallel to each other, showing different orientations, indicating that nucleation and growth are carried out in different crystal grains. Different with high temperature, the diffusion of carbon atoms at the interface between austenite and ferrite is easier, so that subsequent sheets can nucleate at the interface. At low temperatures, the alloying elements basically do not diffuse, and the diffusion of
carbon atoms is also hindered. Carbon atoms are concentrated at the interface between austenite and ferrite, while the carbon content at the tip of lath bainite ferrite is usually lower than that at the side, so it is more inclined to diffuse atoms along the non-coherent interface at the tip. The lath bainite ferrite formed later is also easier to nucleate at the tip, maintaining the same spatial orientation relationship with the previous lath bainite ferrite[15-17]. The driving force for the transformation from austenite to bainite is controlled by Gibbs free energy. As the cooling rate increases, the driving force for phase transformation increases. Bainite nucleates at the grain boundaries of the austenite grains because defects at the grain boundaries provide a large number of nucleation sites. The fluctuations in composition and energy provide the driving force for the growth of bainite, which then grows from the grain boundary to the grain in parallel laths. Previous studies have pointed out that the bainite growth mechanism is divided into the carbon diffusion mechanism and the replacement mechanism[18].

3.3. Effects of cooling rate on the mechanical properties

The tensile and impact mechanical properties of the experimental steel are shown in Table 2. It can be seen that there are obvious differences in mechanical properties under different cooling process conditions. Comparing the yield strength of AC, FC, UFC, and WC, it can be found that as the cooling rate increases, the yield strength gradually increases, showing the same increasing trend as the hardness in the thermal simulation test. Comparing the structure under four different cooling paths, as the content of lath structure increases, the content of block structure decreases, the yield strength gradually increases, and the elongation gradually decreases. The yield strength of the quenched sample increased from 572 MPa of UFC to 738 MPa, a significant increase of 166 MPa, which is very considerable. It is mainly due to the fact that alloying elements and carbon atoms do not have enough time to diffuse under extreme cooling conditions, and they are supersaturated in ferrite, resulting in severe lattice distortion and forming a martensite structure with extremely high dislocation density. At the same time, because of the fast cooling rate, the new crystal grains have no time to grow after nucleation, resulting in a small and dense structure. Both of these factors contribute to the substantial increase in yield strength. However, compared to other cooling routes, WC exhibits poor plasticity. The total elongation of UFC drops from 18.5% to 7%, which is unfavorable for industrial applications. In general, the ductility of structural metals and alloys decreases significantly as the length of the microstructure decreases, which can be reflected in WC steel. But for UFC, although the cooling rate is faster, the microstructure of the lath ferrite and the soft and tough phase film-like retained austenite layer alternately ensures a certain degree of plasticity[19]. Except for the WC yield ratio of 0.74, the other three cooling routes all get a yield ratio of about 0.6. The steel with low yield ratio has better forming ability, because of the high hardening index and high elongation, it shows higher safety performance.

| Sample | YS(MPa) | UTS(MPa) | TEL(%) | PSE(GPa,% | Ak(J) | YS/UTS |
|--------|---------|----------|--------|------------|-------|--------|
| AC     | 490     | 802      | 25     | 20.1       | 201   | 0.61   |
| FC     | 535     | 796      | 21     | 16.7       | 179   | 0.67   |
| UFC    | 572     | 942      | 18.5   | 17.4       | 200   | 0.6    |
| WC     | 738     | 1000     | 7      | 7.0        | 94.5  | 0.74   |

It has better low temperature toughness in a larger cooling speed range. The granular bainite structure of AC and the lath bainite structure of UFC can reach 200J at -20°C, indicating that both granular bainite and lath bainite have good low-temperature toughness. The impact toughness of FC where granular bainite and lath bainite coexist is lower, due to the large number of M/A islands in FC steel. Although it improves the strength of granular bainite as a strengthening phase, the presence of M/A islands destroys the continuity of the ferrite matrix, causing lattice distortion in the matrix, which is likely to occur cracks at the junction of the M/A island and the matrix to affect the toughness of the material[10]. In addition, the grain boundary has a significant effect on the toughness, and the large-angle grain boundary is
beneficial to the toughness. In the quenched water samples, due to the rapid cooling rate, the selection of austenite variants is enhanced, and small-angle grain boundaries are formed, which negatively affects the toughness. The bainite-ferrite lath bundles in UFC steel are interlocked, and the orientation difference is large, which can absorb energy during the impact process and effectively hinder the propagation of cracks. Taken together, UFC has the best combination of mechanical properties. The results show that the steel grade of this composition system can obtain better performance and higher stability in a larger cooling rate range.

4. Conclusions

Four groups of sample AC, FC, UFC, and WC were prepared subjected to different cooling process routes. Their microstructure, mechanical properties were analyzed.

(1) The continuous cooling transition curve (CCT) is drawn by thermal simulation experiment on Gleeble3800 to obtain the phase transition point and hardness. The result shows that as the cooling rate increases, the Vickers hardness increases. The structure changes to granular bainite (GB) → granular bainite + lath bainite (GB+LB) → lath bainite (LB) → lath martensite (M).

(2) The analysis of mechanical properties shows that with the increase of cooling rate, due to phase transformation strengthening and grain refinement, the yield strength shows an increasing trend. The tensile strength reaches a peak value of 998 MPa during water quenching, but the impact energy and elongation rate decrease significantly. The yield ratios under different cooling processes are all around 0.6, which has good formability and safety. From the comprehensive point of view of strength, plasticity and toughness, this steel grade can obtain relatively stable performance without heat treatment. UFC has the best comprehensive mechanical properties.

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