Effects of trace Ce addition on critical cooling rate and Ti (CN) precipitation of ultra high strength steel plate

Zhiguo Gao¹,²,* and Liujie Xu¹

¹ College of Mechanical and Electrical Engineering, Wuyi University, Wuyishan 354300, People’s Republic of China
² Technology Center, Baotou Iron and Steel Group Co. Ltd, Baotou 014010, People’s Republic of China

* Author to whom any correspondence should be addressed.
E-mail: gzgghy2005@163.com

Keywords: cerium, ultra-high strength steel, hardenability, precipitation, critical cooling rate

Abstract
It is well-known that issues always occur for local non-hardenability of 1.5 GPa ultra-high strength steel plates during conventional hot forming processes, once the thickness of the plates is more than 2.5 mm. To resolve the issues, our recent research suggests that adding cerium during metallurgical processes is a prospective approach. This paper adopted a novel process to prepare 1.5 GPa ultra-high strength steel plates using a 25 kg smelting furnace. The research team investigated the effects of trace cerium addition on critical cooling rates characterizing the hardenability for the examined steel plates through measuring experimented continuous cooling transformation curves. The results showed the critical cooling rate of the investigated steel plate was about 10 °Cs⁻¹ only, which was at least 60% lower than that of traditional 1.5 GPa ultra-high strength steel plate. Cerium addition suppressed the diffusion of Ti atoms in the Fe matrix and improved Ti (CN) precipitation on the matrix of bcc Fe.

This paper revealed that cerium addition substantially reduced critical cooling rates of 1.5 GPa ultra-high strength steel plate and significantly improved the hardenability of the processed steel plates.

1. Introduction

1.5 GPa ultra-high strength steel plates are mainly used in automobile, engineering machinery, wear-resistant parts and other fields. These plates have high strengths, coating characteristics and others. In order to ensure the comprehensive properties such as strength, the hardenability of materials must be guaranteed first. Traditional 1.5 GPa ultra-high strength steel plate mainly refers to 22MnB5 hot-formed steel [1–3]. In process of hot forming and quenching, phenomena of local unhardened and many residual stresses in samples are discovered due to the large fluctuation of composition and other defects. Special performances of hot-quenched components are influenced by the microstructure, the interfacial heat transfer coefficient (IHTC) [4, 5], and geometrical defects imposed by the manufacturing process [6]. In the preparation of traditional 1.5 GPa ultra-high strength (UHS) steel plate, the stability of the content of boron is considered as an important factor to ensure the hardenability of researched steel grades. However, excessive boron will lead to the deterioration of toughness of steel plates.

At present, the most common ways to improve the hardenability of steel are to increase quenching heating temperatures, improve the cooling medium and utilize secondary quenching method. The high heating temperature makes the equipment consume more energy and shorten the furnace life. A large investment in equipment was involved in secondary quenching, the residual stress of the workpiece after quenching is difficult to eliminate. In this paper, cerium addition is considered as a promising way to improve hardenability of UHS steel plate due to its activity.

The hardenability of steel materials is characterized by hardness results from end quenching test [7]. It can also be characterized by critical cooling rate from continuous cooling transformation curve [8]. The latter is more effective in characterizing the hardenability of steel materials than the former. A cooling rate higher than
about 25 °C s⁻¹ resulted in a completely martensitic structure in 22MnB5 steel sheet as demonstrated [1]. For avoiding bainitic transformation and achieving a full martensitic microstructure for hot stamped parts of Usibor1500P steel, a cooling rate of above 27 °C s⁻¹ was introduced in the literatures [9, 10]. The slowest cooling rate was recognized to be 30 °C s⁻¹ for avoiding the bainitic transformation in 22MnB5 steel sheet [11–13]. Similar examples [14, 15] consistently showed that the critical cooling rate must be maintained 25 °C s⁻¹ or even higher for ensuring enough hardenability of UHS steel plate. However, the local part of the specimen cannot always achieve this condition. Of course, the demand for the lower cooling rate can reduce the cost of stamping mold [2]. Related research revealed the effects of lanthanum-cerium mischmetal on the kinetics and the microstructure of the super-cooled austenite continuous cooling transformation in 20MnCrNi2Mo wear-resistant cast steel [16]. Results showed that CCT curves were moved to the bottom right, the hardenability was improved. The twin substructure in lath martensite was increased due to the effect of the rare earth. A trace amount of solid-solution rare earth can exist in grain boundary, dislocation and other crystal defects. Rare earth addition reduced the grain boundary energy, blocked the diffusion channels, and then deferred the nucleation and growth of the new phase. Effects of cerium on CCT diagrams, phase transformation points and hardenability of UHS steel plate have been rarely reported in recent years. In this manuscript, rare earth cerium was introduced as an alloying element in order to improve the hardenability of UHS steel plates by decreasing critical cooling rates.

2. Materials and methods

The chemical composition of the new UHS steel plate meets the following expected design scope (wt %): C: 0.22%–0.24%, Si: ≤0.9%, Mn: 1.40%–2.00%, Ti: 0.02%–0.05%, B: 0.0010%–0.0025%, Ce: 0.009%, Al: 0.027%, S ≤0.01%, P ≤0.015%, and Fe. Raw materials used in this experiment include pure cerium, ultra-low sulphur steel scrap, pure iron (99.99%), S < 0.005%, P < 0.020%) and ferroalloy elements. The content of alloy additions must be considered because of the feasibility of continuous casting in industrial production. Two ingots were smelted in 25 kg vacuum furnace, one of which was added with rare earth cerium block by 0.009%. Hot rolling was carried out on a hot rolling experimental mill with a roll width of 550 mm. Heating temperature for the ingots was held 1250 °C for more than 2 h, and finishing rolling temperature was held 860 °C for a 15%–40% rolling reduction.

Continuous cooling transformation (CCT) curves of supercooled austenite were measured by Formastor dilatometer. Φ 3 mm × 10 mm samples for CCT study were cut from the hot rolled steel plate. The samples were austenitized at the same heating rate. Furthermore, the beginning and end points of transformation under different cooling speeds were determined by Formastor dilatometer. HV-10B hardness tester was used to measure Vickers hardness of samples corresponding to different cooling rates. The loading time of hardness test was 15 s and the load was 10 kg. Axio observer A1M optical microscopy (OM) was used to observe effects of cooling rates on morphological details of produced multiphase microstructures. Three corresponding cooled samples of each cooling plate were selected as representative samples for OM observation. Zeiss LEO 5.0 HV scanning electron microscope (SEM) was used to observe the microstructural evolution of matrix and precipitates. Tecnai G2 F20 field emission transmission electron microscopy (TEM) was used to observe the surface microstructure of cerium-bearing nanoparticles in samples. The disk specimens for TEM investigation were cut out from rolled plates. The disks were subsequently ground down to about 0.05 mm in thickness, electropolished in 10% perchloric acid alcohol solution cooled to about −20 °C in twin-jet electropolishing unit at a voltage of 30 V. The element analysis was carried out by energy dispersive spectrometer (EDS) from EDAX company. Average area fraction and average equivalent diameter of holes and precipitates were analyzed by Image J software.

3. Results

3.1. Critical cooling rate in CCT diagrams

CCT diagrams of UHS steel plates were shown in figure 1. The specific cooling time in CCT diagrams (from left to right in turn) was transformed to a cooling rate. Austenite, ferrite, pearlite, bainite and martensite were simplified to A, F, P, B and M respectively. For example, 88 s was transformed to a cooling rate as 10 °C s⁻¹ according to the equation cooling rate was equal to (900–20)/cooling time. The converted cooling rates were listed in the following table 1. In order to meet the needs of CCT curve drawing, 10 cooling rates of investigated steel plates were selected as important variables.

It showed the critical cooling time of the two investigated steel plates were 26 s and 88 s, respectively. As shown in table 1, these data were converted to critical cooling rates of 33, 10 °C s⁻¹, respectively. It was decreased due to cerium addition. In other words, a low cooling rate can make the sample quenched to achieve or exceed
the expected comprehensive properties. It was obvious that trace cerium significantly improved the hardenability of the sample. It should be noted that further research and confirmation was necessary.

3.1.1. Hardness
The hardness results of specimens cooled at different rates were showed in figure 2. Specimens experienced an obvious change in hardness accompanied by a significant increase in cooling rate. The measured hardness increased from 273 to 539 HV corresponding to cooling rates of 2–66 °Cs⁻¹. The hardness of UHS steel plate is generally considered to be an indicator of microstructural evolution due to the change in volume fraction of martensite or bainite. Furthermore, the hardness of cooled specimens is useful to estimate the strength of UHS steel plate. The hardness curve of cerium-bearing UHS steel plate is different from that of cerium-free UHS steel plate. The hardness results of cerium-bearing specimens cooled at less than 20 °Cs⁻¹ were higher than that of cerium-free specimens. It increased rapidly from 265 to 526 HV corresponding to cooling rates of 2–20 °Cs⁻¹. However, a hardness peak was captured as 526 HV corresponding to the cooling rate of 20 °Cs⁻¹ although 10 °Cs⁻¹ was confirmed as the inflection point of hardness curve. In particular, the hardness corresponding to the

![Figure 1. CCT diagrams of UHS steel plate, (a) cerium-free and (b) 0.009% cerium addition.](image)

| Specimen          | Cooling rate (°Cs⁻¹) |
|-------------------|---------------------|
| Cerium-free       | 66  33  25  20  15  10  5  3  2  1 |
| Cerium-bearing    | 68  34  20  15  10  8  5  3  2.5  2 |
critical cooling rate was not the peak value due to the increase in the number of martensites. With the further increase of cooling rate, the hardness of cerium-bearing samples decreased slightly, but that of cerium-free samples tended to be stable.

### 3.1.2. OM observation

The CCT diagrams revealed the relationship between continuous cooling transformation temperature and cooling time. The hardness results only showed the relationship between hardness and cooling rate. However, these results were not enough to visually characterize effects of cerium addition on the hardenability of specimens. Further research on effects of cooling rate on metallographic structure was necessary. Three representative specimens were selected for the research. OM microstructures determined by three cooling rates below the critical value in the CCT diagram were presented in Figure 3. For the cooling rate of 2 °C s⁻¹, the microstructure was composed of ferrite/pearlite. For 5 °C s⁻¹, bainites besides ferrite/pearlite were formed. By applying a cooling rate of 33 °C s⁻¹, the specimen of the researched steel presented only the martensite phase. Thus, 33 °C s⁻¹ was considered as the critical cooling rate of cerium-free UHS steel plate.

For the effects of trace cerium on microstructures of UHS steel plates, OM microstructures of specimens cooled by three cooling rates below the critical rate were presented in Figure 4. Generally, the lower the critical cooling rate, the easier to obtain martensite [17]. For the cooling rate of 2 °C s⁻¹, the microstructure was composed of bainite, ferrite and pearlite. For 5 °C s⁻¹, the bainite was presented. With the increase of cooling rates, original ferrite and pearlite gradually disappeared although a very small amount of bainite was observed. For a cooling rate of 10 °C s⁻¹, the specimen of the modified steel presented the martensite phase. 10 °C s⁻¹ was undoubtedly identified as the critical cooling rate of cerium-bearing UHS steel plate. However, once the cooling rate reached a critical level, no matter how much cerium was added, the martensite phase inevitably occupied the whole structure. These results were in good agreement with the hardness test results. The transformation of supercooled austenite can be controlled by adjusting cooling rates. Issues of local non-hardenability of UHS steel plates were resolved, although the thickness of the plates is more than 2.5 mm. The addition of 0.009% cerium shifted CCT curve of UHS steel plates to the right. The results showed that trace cerium addition effectively reduced the critical cooling rate of UHS steel plate, improved the hardenability.

### 3.2. Mechanism on precipitation of Ti(CN) due to trace cerium addition

SEM observation on the microstructure of UTS steel plate as-received and EDS analysis on precipitates was shown in figure 5. Table 2 showed statistical results of average area fraction and average equivalent diameter of holes and precipitates. Pearlite and ferrite in cerium-free specimens were observed in figures 5(a) and (b). Holes were enriched on the grain boundary due to vacancy defects. Average area fraction and average equivalent diameter of holes were 0.065% and 0.8 μm, respectively. The results of Ti(CN) precipitates were 0.10% and 1.6 μm, respectively. However, the microstructures were modified by cerium addition. In figures 5(c) and (d), the holes on the grain boundary were disappeared besides accelerated Ti(CN) precipitation in the grains. It’s probably occupied by cerium sulfide once cerium atoms were introduced. Due to the interference of metal atoms such as Fe and Mn, except for a few cubic-shaped TiN, Ti(CN) precipitates were spherical or irregular.

![Figure 2. Hardness of specimens of UHS steel plates as a function of cooling rates.](image)
Average area fraction and average equivalent diameter of Ti (CN) precipitates were 0.14% and 0.5 μm, respectively. The area fraction of Ti (CN) precipitates was increased although the reduced equivalent diameter. In other words, the nucleation of Ti (CN) precipitates was obviously accelerated. The number of detected Ti (CN) precipitates in the same visual range increased from 18 to 238. Furthermore, the enriched carbide area on grain boundaries was significantly decreased due to cerium atom making up for the vacancy. Further STEM observation and EDS analysis on cerium sulfide were shown in figure 6. Although Mn or other metal atoms segregation, cerium sulfides were detected in the holes as the nuclei. In fact, the shape of cerium sulfide was not identical due to vacancy concentration gradient.
4. Discussion

As previously reported [18], the solid solubility of rare earth atoms in Fe matrix is very low, even at high temperatures. The mechanism of microalloying of rare earth in steel is that the microstructure is affected by the segregation of rare earth atoms, so that special properties of the steel material are tailored. The diffusion coefficients of titanium at the certain temperature can be usually obtained via the slope of the MSD curve versus time [19]. And the temperature dependence of the obtained diffusion coefficient does obey the Arrhenius...
equation:

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]

where \( D \) is the diffusion coefficient at the temperature \( T \), \( D_0 \) denotes the pre-factor, \( Q \) denotes the activation energy, and \( R \) is the universal gas constant. \( D_0(\text{Cerium}) \) and \( D_0(\text{Titanium}) \) in the bcc Fe matrix were reported as 7.76 \( \times \) 10\(^{-6}\) m\(^2\) s\(^{-1}\) and 4.04 \( \times \) 10\(^{-7}\) m\(^2\) s\(^{-1}\) in references [20, 21], respectively. \( Q_{\text{Cerium}} \) and \( Q_{\text{Titanium}} \) were also reported as 275.8 kJ mol\(^{-1}\) and 251 kJ mol\(^{-1}\) in references [20, 22], respectively. Assuming in bcc Fe matrix, according to Arrhenius equation, \( D_{\text{Cerium}} \) is assessed as 0.58 times as \( D_{\text{Titanium}} \) at 850 K. Therefore, trace cerium addition suppresses the diffusion of titanium atoms in the Fe matrix. According to the reference [22], the growth of Ti(CN) precipitates is controlled by the diffusion of Ti. Cerium addition leads to a decrease in the growth rate of Ti(CN) precipitates. However, in addition to being a heterogeneous nucleus, cerium addition increases lattice distortion and dislocation density of the matrix [16]. The increase in dislocation density is beneficial to Ti(CN) nucleation [23]. These are the main reasons for the accelerated nucleation of Ti(CN) precipitates. All of these deductions are in accordance with the analysis results in figure 5. Based on the above deductions, the results of the microstructural evolution of matrix and precipitates due to cerium addition are summarized in figure 7.

In this study, the segregation of cerium atoms on austenite grain boundaries results in blocking Ti diffusion. The movement of the austenite grain boundary is restrained. The cerium addition improves the stability of undercooled austenite. Bainite or pearlite phases are not nucleated on austenite grain boundaries for a cooling rate of more than 10 °C s\(^{-1}\) as a critical cooling rate. However, since the martensite transformation is a non-diffusion type transformation, the appearance of new martensite does not require more carbon atom migration except for enough degree of supercooling. It is for these reasons that the critical cooling rate of ultra-high
Figure 6. STEM microstructural observation on detected cerium sulfide, (a) grown as the nuclei in the holes, (b) energy spectrum of detected cerium sulfide, (c) cerium map and (d) sulfur map.

Figure 7. Schematics showing microstructural evolution of matrix and precipitates due to cerium addition.
strength steel plate is significantly reduced. It is inevitable to improve the hardenability of ultra-high strength steel plate.

5. Conclusions

(1) For local non-hardenability of UHS steel plates more than 2.5 mm in thickness during conventional hot forming processes, our recent research confirmed that cerium addition is a prospective solution to such issues. A novel process to prepare UHS steel plates was adopted.

(2) The critical cooling rate of UHS steel plates was decreased from 33 °C s⁻¹ to 10 °C s⁻¹ by 0.009% cerium addition, which was at least 60% lower than that of the traditional UHS steel plate in addition to causing CCT curve to move right. The hardenability of traditional UHS steel plate was significantly improved.

(3) Microstructure evolution during processing assured a critical role in tailoring hardenability of UHS steel plate. The enriched carbide area on grain boundaries was significantly decreased due to cerium atom making up for the vacancy. The holes on the grain boundary were occupied by cerium sulfide, and Ti (CN) precipitation was also accelerated in the grains. The area fraction of Ti (CN) precipitates was increased from 0.10% to 0.14% although the reduced equivalent diameter.

(4) For the general law of effects of rare earth on hardenability of UHS steel plates, the addition of other rare earth elements is worth further studying.

Acknowledgments

The authors are grateful for the technical support from the national laboratory of Baotou Iron and Steel Group Co. Ltd. Thanks to Y. S. Zhao for participating in part of the research work.

ORCID iDs

Zhiguo Gao @ https://orcid.org/0000-0003-1389-7243

References

[1] Naderi M, Saeed-Akbari A and Bleck W 2008 The effects of non-isothermal deformation on martensitic transformation in 22MnB5 steel Mater. Sci. Eng. A 487 445–55
[2] Tian P, Liang W, Cui Z N, Zhu G M, Kang Y L, Li B S, Lin L and Liu R D 2019 Study on microstructure and properties of a new warm-stamped niobium-alloyed steel Metals. 9 765
[3] Kuhlmann M, Mitzsche N and Jüttrner S 2019 Determination of hydrogen transport behaviour in boron-manganese steels using different methods and boundary condition Metals. 9 1087
[4] Gorriño A, Angulo C, Muro M and Ieaga J 2016 Investigation of thermal and mechanical properties of quenchable high-strength steels in hot stamping Metall. Mater. Trans. B 47 1527–31
[5] Muro M, Artola G, Gorriño A and Angulo C 2018 Effect of the martensitic transformation on the stamping force and cycle time of hot stamping parts Metals. 8 385
[6] Barcellona A and Palmeri D 2009 Effect of plastic hot deformation on the hardness and continuous cooling transformations of 22MnB5 microalloyed boron steel Metall. Mater. Trans. A 40 1160–74
[7] ASTM A255–10 2018 Standard test Methods for Determining Hardenability of Steel (West Conshohocken, PA: ASTM International) 2018Available online www.astm.org (accessed on 1 Sept. 2018)
[8] Grajcar A, Zalecki W, Burian W and Kozłowska A 2016 Phase equilibrium and austenite decomposition in advanced high-strength medium-Mn bainitic steels Metals. 6 248
[9] Merklein M and Lechler J 2006 Investigation of the thermo-mechanical properties of hot stamping steels J. Mater. Process. Tech. 177 452–5
[10] Zhao D, Zhu Y G, Ying L, Hu P, Chang Y and Zhang W X 2014 Numerical simulation of deformation behavior of 22MnB5 boron steel at elevated temperatures and experimental verification Acta Mech. Solida Sin. 27 579–87
[11] Turetta A, Bruschi S and Ghioitti A 2006 Investigation of 22MnB5 formability in hot stamping operations J. Mater. Process. Tech. 177 396–400
[12] Min J Y, Lin J P, Min Y A and Li F F 2012 On the ferrite and bainite transformation in isothermally deformed 22MnB5 steels Mater. Sci. Eng. A 550 375–87
[13] Ximenes D A C, Moreira L P, Carvalho J E R, Leite D N F, Toledo R G and Silva Dias F M 2020 Phase transformation temperatures and Fe enrichment of a 22MnB5 Zn–Fe coated steel under hot stamping conditions J. Mater. Res. Technol. 9 629–35
[14] Naderi M, Durrenberger L, Molinari A and Bleck W 2008 Constitutive relationships for 22MnB5 boron steel deformed isothermally at high temperatures Mater. Sci. Eng. A 478 130–9
[15] Somani M C, Karjalainen L P, Eriksson M and Oldenburg M 2001 Dimensional changes and microstructural evolution in a B-bearing steel in the simulated forming and quenching process ISIJ Int. 41 361–7
[16] Ji Y, Ren H, Liu X, Hou J and Jin Z 2017 Effect of rare earth on super-cooled austenite transformation of 20MnCrNi2Mo wear-resistant cast steel and its mechanism Rare Metal. Mat. Eng. 46 997–1002
[17] Wei S Z and Xu L J 2020 Review on research progress of steel and iron wear-resistant material Acta Metall. Sin. 56 523–38
[18] Li L F and Xing Z S 1993 Solubilities of Ce, Nd and Y in α-Fe Acta Metall. Sin. 29 40–5
[19] Wang H, Yao Z, Gao X, Cui P and Ren H 2018 Molecular dynamics investigation of the effect of lanthanum on the diffusivity of niobium in austenite Mater. Trans. 59 706–11
[20] Gao X Y, Ren H P, Li C L, Wang H Y, Ji Y P and Tan H J 2016 First-principles calculations of rare earth (Y, La and Ce) diffusivities in bcc Fe J. Alloy Comp. 663 316–20
[21] Wang X, Yu X H, Rong J, Li X Y, Yi Z, Feng J and Zhan Z L 2018 The diffusion behavior of Ti atoms in pure nanocrystalline Fe by first principles calculations Mater. Res. Express 5 095810
[22] Liu W J and Jonas J J 1988 Ti(CN) precipitation in microalloyed austenite during stress relaxation Metall. Trans. A 19 1415–24
[23] Liu W J and Jonas J J 1989 Nucleation kinetics of Ti carbonitride in microalloyed austenite Metall. Trans. A 20 689–97