Effect of La-Ce on Microstructure and Properties of 30MnCrNiMo Alloy Steel

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Abstract. The 30MnCrNiMo alloy steel was modified by La-Ce mixed rare earth. The experiment used metallographic microscope, scanning electron microscope and energy spectrum to analyze the improvement behavior of rare earth on the as-cast structure of the alloy steel, the structure after heat treatment, and the morphology of inclusions; a thermal dilatometer was used to analyze the phase transition point, and a reasonable heat treatment process was developed; the effect of rare earth on the mechanical properties of alloy steel at room temperature, low temperature impact and tensile was analyzed. The results show that the 30MnCrNiMo alloy steel modified by rare earth has better refinement of the as-cast grains and the grains after heat treatment, and the size, morphology and distribution of inclusions have been improved. The addition of rare earths improves the impact toughness, especially the low-temperature impact. Compared with alloy steel without rare earth, the toughness can be increased by up to 38%, and the alloy strength has been improved to a certain extent.

1. Introduction
In recent years, with the widespread application of lightweight wheeled armored vehicles, armored protective materials have continued to develop in the direction of lightweight while meeting basic protective performance [1]. As the most basic and most important structure and protective material of armored vehicles, bulletproof steel plates must not only have high comprehensive mechanical properties to meet the protective performance indicators, but also adapt to the development trend of lightweight and thin plate [2-4]. In addition, in the civilian field, such as bullet-proof cash transport vehicles, anti-terrorism and anti-riot vehicles, armed escort vehicles, thin bullet-proof steel plates are also needed to meet the needs of vehicle structure and protection. Due to the special military use, our national defense bullet-proof steel plates are very widely used in the civilian field. Few, most of them need to be imported [5]. It can be seen that there is a wide range of demands for thin bullet-proof steel plates no matter in the military or civilian fields.

30MnCrNiMo steel is a low-alloy ultra-high-strength steel, which can be used as a thin bulletproof steel plate in military and civilian fields, but its heat treatment process and comprehensive mechanical properties still have many shortcomings [6]. Rare earth elements are known as "vitamins" in steel, and their main roles in steel are mainly focused on improving the morphology of inclusions, refining grains, strong microalloying and purification, etc. When extremely small amounts of rare earth elements are
added to steel, the structure and properties of steel materials can be significantly improved. In bulletproof steel plates, the application of rare earths mostly focuses on thick plates (≥45mm), and there is almost no application in thin plates [7,8]. Based on the special role of rare earths, adding rare earth elements to the thin plate 30MnGrNiMo steel to achieve the improvement of its heat treatment process and comprehensive mechanical properties is a better technical path.

The research on the application of bulletproof steel at home and abroad mainly focuses on the anti-elasticity and related heat treatment process, but there is very little research on the application of rare earth in the bulletproof steel. Although my country's research on the application of rare earths in steel has been carried out relatively early, and the application in some typical steels has achieved relatively obvious results, there has been no report on the application of mixed rare earths in steel. In this paper, 30MnCrNiMo bulletproof steel is taken as the research object. Different amount of mixed rare earth La-Ce is added on the basis of its original composition. Through composition analysis, microstructure observation and property testing, the action mechanism of rare earth in steel is deeply studied, and at the same time, the structure and comprehensive mechanical properties of steel are improved, so as to enhance its elastic resistance.

2. Test materials and methods
The test uses a 50Kg vacuum melting furnace for test steel smelting. The test steel is divided into 1#, 2# and 3# according to different rare earth contents. The specific rare earth design amount is: 1#RE: 0ppm; 2#RE: 40ppm; 3#RE: 80ppm. Use chemical analysis method, metallographic microscope and other methods to analyze the chemical composition and as-cast crystal grain of the as-cast sample; use the forging and rolling process to prepare the rare earth steel plate, and use the thermal dilatometer to test the phase transition point, and make reasonable The heat treatment process, the structure and grain size observation of the treated steel plate, the mechanical performance test, and the analysis of the effect of rare earth on it.

3. Results and discussion

3.1. Chemical composition detection
The design principle of chemical composition is based on the chemical composition of 30MnCrNiMo steel, adding different content of rare earth La-Ce. The specific composition design is shown in Table 1.

| No. | C   | Si  | Mn  | P   | S   | Cr   | Ni   | Mo  | Ce+La |
|-----|-----|-----|-----|-----|-----|------|------|-----|-------|
| 1#  | 0.26-0.31 | 0.20-0.40 | 0.75-1.10 | ≤0.015 | ≤0.010 | 0.75-1.10 | 1.05-1.30 | 0.25-0.45 | - |
| 2#  | 0.26-0.31 | 0.20-0.40 | 0.75-1.10 | ≤0.015 | ≤0.010 | 0.75-1.10 | 1.05-1.30 | 0.25-0.45 | 0.0040 |
| 3#  | 0.26-0.31 | 0.20-0.40 | 0.75-1.10 | ≤0.015 | ≤0.010 | 0.75-1.10 | 1.05-1.30 | 0.25-0.45 | 0.0080 |

The addition of rare earth adopts the method of adding rare earth metal coated with iron sheet. The yield of rare earth is calculated at 25%. The chemical composition is determined by the method of chemical detection, and the chemical composition of the test steel measured is shown in Table 2.

| No. | C    | Si  | Mn  | P   | Cr  | Ni  | Mo  | O   | S      | RE    |
|-----|------|-----|-----|-----|-----|-----|-----|-----|-------|-------|
| 1#  | 0.30  | 0.33 | 1.01 | 0.009 | 1.04 | 1.30 | 0.43 | 40  | 39    | 0     |
| 2#  | 0.31  | 0.33 | 0.97 | 0.010 | 1.08 | 1.29 | 0.44 | 30  | 31    | 0.0038 |
| 3#  | 0.31  | 0.31 | 0.99 | 0.009 | 1.05 | 1.29 | 0.44 | 22  | 21    | 0.0082 |
Comparing Table 2 with Table 1, it can be seen that the composition of the test steels smelted in the three groups meets the design range. The solid solution content of Re in the two sets of test steels with rare earth addition basically meets the design requirements, and the deviation of the solid solution amount between the rare earth La and Ce is small. The design mixed rare earth solid solution content of the 2# test steel is 0.004%, and the solid solution content of rare earth is 0.004%. The total volume is 38ppm, which is 0.0038%; the additive amount of mixed rare earth of 3# test steel is 0.0080%, and the total solid volume of rare earth is 82ppm, which is 0.0082%.

Analyzing the deoxidation and desulfurization of rare earths, it can be seen from Table 3 that the oxygen and sulfur content of the 1# test steel without rare earth addition is at a relatively low level, 40 ppm and 39 ppm, respectively. Compared with the 1# test steel, the oxygen content of 2# test steel is reduced from 40ppm to 30ppm, and the deoxidation rate is 25%; the sulfur content is reduced from 39ppm to 31ppm, and the desulfurization rate is 20.5%. Compared with the 1# test steel, the oxygen content of 3# test steel is reduced from 40ppm to 20ppm, the deoxidation rate is 45%, the sulfur content is reduced from 39ppm to 21ppm, and the desulfurization rate is 46.1%, which further plays the role of deoxidation and desulfurization. This shows that with the increase of the solid solution of mixed rare earths, the deoxidation and desulfurization effects of rare earths will be further enhanced, thus playing a role in purifying molten steel.

3.2. Effect of rare earth on as-cast grain size

ObserverA1m metallurgical microscope was used to observe the as-cast structure of the rare earth test steel, as shown in Figure 1.

![Figure 1](image1)

Figure 1 The effect of different rare earth additions on as-cast grains
(a) 1# steel ingot without rare earth, (b) 2# RE residual 0.0038%, (c) 3# RE residual 0.0082%

Figure 1 shows the effect of different rare earth additions on as-cast grains under the same initial conditions. It can be clearly seen from Figure 1 that the grain size of steel ingots without rare earths is larger than that with rare earths. Further statistical analysis by metallographic software shows that the average size of grains in as-cast steel ingots without rare earths is about 54 μm, however, the average size of grains in as-cast steel ingots with rare earths is about 27 μm, which shows that Rare earth can significantly refine the as-cast grains. However, as the amount of rare earth added increases, the as-cast grain refinement is not obvious. This result may be due to the fact that after the addition of rare earths, the purity of molten steel increases sharply, and there are few impurity particles that can be used as the substrate for heterogeneous nucleation.

3.3. The effect of rare earth on inclusions in steel

Figure 2 shows the overall morphology of inclusions in steel with different amounts of rare earth added. It can be seen from the figure that the size of inclusions in the steel ingot without rare earth is slightly larger, and they are occasionally gathered together and distributed in the matrix (Figure 2a). The morphology of such inclusions is extremely irregular, and some are angular, which can be noticeable. Decrease the performance of steel. In the steel ingot with a rare earth residual content of 0.0038% (Figure 2b), it can be clearly seen that the size of the inclusions has become smaller and uniformly dispersed, and most of them are round or elliptical rare earth inclusions, indicating that rare earths are very good. Improved the morphology of inclusions in the steel. In the steel ingot with a rare earth residual content of 0.0082% (Figure 2c), it can be found that with
the increase in the amount of rare earth addition, the size of the inclusions increases, and they occasionally aggregate and distribute in the matrix, which indicates that the addition amount of rare earth should not be too much, too much will contaminate the molten steel, causing the inclusions in the steel to gather and grow, and have the opposite effect.

Figure 2 The effect of different rare earth additions on inclusions in steel
(a) 1# steel ingot without rare earth, (b) 2# RE residual 0.0038%, (c) 3# RE residual 0.0082%

Figure 3 Energy spectrum diagram without rare earth and rare earth inclusions
(a) without adding rare earth steel ingot, (b) adding rare earth steel ingot

Figure 3 shows the typical energy spectrum of inclusions without rare earth and after adding rare earth. It can be seen from the figure that the types of inclusions in steel ingots without rare earths are mainly Al2O3 and MnS; after rare earths are added, the inclusions mainly contain rare earths, oxygen and sulfur. It can be seen that after adding rare earths to steel, oxides or sulfides interact with rare earths to form rare earth oxysulfide inclusions, which change the morphology, size and distribution of the inclusions, which is a good countermeasure for the inclusions. The role of material modification and size control.

Table 3 shows the statistical analysis results of the inclusion sizes with different rare earth additions. It can be seen from the table that the proportion of inclusions smaller than 2 μm in the steel ingot with a rare earth residual content of 0.0038% is about 90%; with the increase of the residual rare earth content, the proportion of small-sized inclusions decreases significantly. In addition, compared with steel ingots without rare earth, when the residual rare earth content is 0.0038%, the percentage of small-sized inclusions in the steel increases from 7% to 90%, which is very useful for improving the performance of the material. Important meaning, because the size of inclusions has a very important impact on material properties.

Table 3  Percent statistical results of the addition of different rare earths on the size distribution of inclusions in steel (%)

| Steel ingot | 0-1μm | 1-2μm | 2-5μm | 5-10μm | >10μm |
|-------------|-------|-------|-------|--------|-------|
| 1#          | 0     | 7     | 22    | 69     | 2     |
| 2#          | 19    | 71    | 8     | 2      | 0     |
| 3#          | 5     | 40    | 45    | 8      | 2     |
3.4. The effect of rare earth on the phase transformation point of test steel

Figure 4(a), Figure 4(b) and Figure 4(c) show the thermal simulation test expansion curves of the three groups of test steels. When steel is continuously cooled, austenite will undergo a solid phase transformation, which will cause intermittent changes in the volume of the steel. This change appears on the expansion curve as an inflection point at the corresponding temperature, and the inflection point of the expansion curve corresponds to the corresponding Phase transition point.

![Thermal expansion curve of test steel](image)

Figure 4 Thermal expansion curve of test steel
(a) Expansion curve of 1# test steel without rare earth; (b) Expansion curve of 2# test steel with 38ppm rare earth; (c) Expansion curve of 3# test steel containing 82ppm rare earth

The common methods of using the expansion curve to determine the phase transition point are the vertex method and the tangent method. The tangent method was used to analyze the expansion curves of the three groups of test steels in the heating and cooling process, and the critical points of phase transformation Ac1, Ac3, Bs and Bf of each group of test steels were obtained. The test results were the average of the three test data. The result as shown in Table 3.

| No. | Phase transition point | Ac1 | Ac3 | Bs  | Bf  |
|-----|------------------------|-----|-----|-----|-----|
| 1#  |                        | 645 | 808 | 588 | 343 |
| 2#  |                        | 655 | 809 | 550 | 330 |
| 3#  |                        | 660 | 814 | 558 | 315 |

According to Table 4 with the increase of rare earth content, Ac1 and Ac3 of the test steel increased, while Bs and Bf decreased.

3.5. Heat treatment of rare earth steel and its structure after treatment

The quenching heating temperature of hypoeutectoid steel is 30–50°C above Ac3. According to the critical point of phase transformation of the above-mentioned steel, a heat treatment process of 870°C×1h oil cooling + 190°C×1h water cooling is adopted. Observe the treated structure and grain size as shown in Figure 5.

![Metallographic structure of 1# and 3# samples after heat treatment](image)

Figure 5 Metallographic structure of 1# and 3# samples after heat treatment
(a) 1# metallographic organization; (b) 3# metallographic organization
Figure 6 1# and 3# sample grain size after heat treatment
(a) 1# grain size; (b) 3# grain size

Figure 5 and Figure 6 show the metallographic structure and grain size of 1# test steel (without Re) and 3# test steel (with 0.0082% Re) after tempering. It can be seen from Figures 5(a) and 5(b) that the metallographic structure of the 1# and 3# test steels is tempered martensite and a small amount of retained austenite, and the martensite morphology is mainly flaky and a small amount Needle-shaped, but the structure of 1# test steel is coarser than that of 3# test steel, indicating that rare earths have the effect of refining the steel structure.

Comparing the grain sizes of the two sets of test steels, as shown in Figures 6(a) and 6(a), it is not difficult to find that the grains of the 1# test steel are larger than those of the 3# test steel. For its grain size rating, the grain size of 1# test steel is 4.5~8.5, and the grain size of 3# test steel is 7~10, which shows that the mixed rare earth La and Ce in 30MnCrNiMo steel can be Plays the role of refining the grain, and then refines the structure of the steel.

3.6. Effect of Rare Earth on the Impact Toughness of Test Steel
Carry out room temperature impact and -40℃ low temperature impact tests on the heat-treated samples. Table 5 is the average value of impact energy absorbed by each group of samples.

| Sample                  | 1#  | 2#  | 3#  |
|-------------------------|-----|-----|-----|
| KU2/J at room temperature | 26  | 28  | 32  |
| KU2/J at low temperature of -40℃ | 22  | 25  | 27  |

From the data analysis in Table 5, it can be seen that the low temperature absorption impact energy of the test steel is lower than the normal temperature absorption impact energy. With the increase of the rare earth content, the normal temperature and low temperature absorption impact energy both increase. The improvement of impact toughness in steel mainly depends on the refinement of grains and the fine dispersion of inclusions. Because only by effectively refining the structure and making the inclusions smaller and evenly distributed in the matrix, can the stress concentration of the material during the impact be effectively relieved, thereby greatly improving the toughness of the material. This shows that adding mixed rare earth La and Ce to 30MnCrNiMo steel can effectively refine the structure and inclusions to improve the impact performance of the steel.

3.7. Effect of Rare Earth on the Tensile Properties of Test Steel
Table 6 is the average value of the tensile properties of the experimental steel at room temperature.
| Sample | $R_m$ (MPa) | $R_{p0.2}$ (MPa) | $A$ (%) | $Z$ (%) | $R_{p0.2}/R_m$ | $R_m*Z$ (MPa*%) |
|--------|-------------|-----------------|--------|--------|---------------|----------------|
| 1#     | 1732        | 1438            | 5.6    | 37.5   | 0.83          | 64950          |
| 2#     | 1739        | 1444            | 8.9    | 38     | 0.83          | 66082          |
| 3#     | 1745        | 1492            | 10.1   | 40.5   | 0.85          | 70672.5        |

It can be seen that the strength index of the test steel increases with the increase of the amount of rare earth solid solution. After adding rare earth, the plastic index of the test steel also increases, and the reduction of area is the most significant. After calculation, after adding rare earth, the test steel The yield-strength ratio of the steel is almost unchanged, but the strong plastic product is significantly increased. Therefore, after adding the mixed rare earth La and Ce to the test steel, the strength of the steel is increased and the plasticity is significantly improved, thereby effectively improving the comprehensive mechanical properties of the steel.

4. Conclusion

(1) The addition of rare earth can significantly refine the as-cast grains of 30MnCrNiMo alloy steel;
(2) Rare earth can well improve the morphology of inclusions in 30MnCrNiMo alloy steel;
(3) With the increase of rare earth content, $Ac_1$ and $Ac_3$ of the test steel increased, while $Bs$ and $Bf$ decreased.
(4) The microstructure of the impact-resistant rare earth alloy steel plate is tempered sorbite; the crystal grains are uniform and fine, the size of the crystal grains is about 10μm, and the grain size grade is 9-10.
(5) Adding mixed rare earth La and Ce to 30MnCrNiMo steel can effectively refine the structure and inclusions to improve the impact performance of the steel.
(6) After adding the mixed rare earth La and Ce to the test steel, the strength of the steel is increased and the plasticity is significantly improved, thereby effectively improving the comprehensive mechanical properties of the steel.

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