Experimental preparation and property analysis of rare earth modified impact resistant steel

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Abstract. To further improve the comprehensive performance of existing impact-resistant steel, rare-earth-modified steel samples were experimentally prepared and their performance was analyzed. Different amounts of mixed rare earths were added into the 30MnCrNiMo impact-resistant steel, followed by vacuum smelting, forging, and rolling to prepare the steel plate. The effects of rare earths on the phase transformation critical points, high-temperature deformation behavior, microstructure, and mechanical properties were studied. The results show that rare earths can play a purifying role in the test steel. The Ac1-Ac3 phase transition temperatures were increased, and those of the Bs-Bf phase transition were decreased significantly. When compressed at 1000 °C, the deformation resistance of the test steel with rare earth became higher. Thus, the added rare earths improve the microstructural morphology and inclusions in the steel, as well as the comprehensive mechanical properties.

1. Introduction
Impact protection steel is the most important structural and protective material for armored vehicles used in the military and for transporting valuables [1]. Recent rapid technological development has raised the performance requirements of impact protection steel. In addition to higher strength and hardness, they should also possess a level of impact toughness to ensure that the material in the no back fall or brittle rupture during impact protection [2-5].

The effect of rare earth in steel is mainly manifested as metamorphic inclusions, improved microstructure, or strong microalloying. Adding trace amounts of rare earth elements to steel can significantly improve the microstructure and properties of the material. The application of rare earth in impact protection steel has been discussed. Fang [6] and Yu et al. [7] showed that adding rare earth elements into an impact-protective steel plate improved the steel structure, refined the grains, deteriorated the inclusions, and effectively improved mechanical properties such as the tensile and impact toughness. Due to the influence of rare earths on the phase transition points of steel [8-10], the heat treatment process should be adjusted after adding the rare earth. To provide useful references, this research examines the preparation of rare earth-modified impact-resistant steel, and the influence of rare earth addition on the phase transition point, high-temperature deformation behavior, microstructure, and mechanical properties.

2. Test materials and methods
The experimental materials were smelted in a 25-kg vacuum melting furnace at the Central Iron & Steel Research Institute. Two materials were studied: steel 1# did not contain rare earth, while steel 2# contained La and Ce (for compositions see Table 1). After completion of smelting, the test steel was forged as follows. The steel was first placed in a heat treatment furnace at 1250°C and kept warm for 10 h. When the temperature was greater than 1150°C, the steel was taken out of the oven for forging into a final ingot dimension of 800 mm × 120 mm × 20 mm. Then, the ingot was put into a heating furnace and kept at 1150°C for 1 h. Finally, the ingot at 1150°C was rolled into 10-mm thick steel plate in 8 passes, and the final rolling temperature was 932°C.

| No. | C   | Si | Mn | P  | O   | S   | Cr  | Ni  | Mo | V  | Nb | Ce | La |
|-----|-----|----|----|----|-----|-----|-----|-----|----|----|----|----|----|
| 1#  | 0.34| 0.34| 1.00| 0.010| 0.0046| 0.004| 1.05| 2.03| 0.43| 0.19| 0.033| -  | -  |
| 2#  | 0.36| 0.33| 0.98| 0.008| 0.0024| 0.002| 1.02| 2.01| 0.43| 0.19| 0.032| 0.0059| 0.0043|

According to the requirements of standard YB/T5127-93 “Method for the determination of critical points of steel (expansion method)”, cylindrical samples (Φ5 mm×10 mm) were collected from the steel plate and used for the thermal simulation test with a LinSeth L78 automatic quench dilatometer. In the thermal test, the sample was first heated to 1180°C at the rate of 0.05°C/s, and then cooled to room temperature at the same rate. The test process flow chart is shown in Figure 1.

The microstructure examination followed GB/T13298-2015 “The method for the examination of microstructure of metals”. The metallographic sample was prepared by resin inlay method, and the microhardness was tested by a 402 MVD Vickers hardness tester.

For high-temperature compression tests, samples Φ8 mm×15 mm were measured with a Gleeble-1500-d thermal simulation testing machine. The samples were heated at 10°C/s to 1000°C or 1100°C and held for 3 minutes. Then, a strain rate of 1 s⁻¹ was used for single-pass compression test, the deformation was 20% at 1000°C and 30% at 1100°C, and then the samples were air-cooled to room temperature. The stress-strain curves at different temperatures and the deformation quantities were obtained.

According to GB/T2975-2018 “Sampling location and sample preparation for mechanical properties test of steel and steel products”, a transverse billet (10 mm×12 mm×60 mm) was taken at 1/4 of the width of the steel plate. U-shaped impact samples were prepared in accordance with GB/T229-2007 “Charpy pendulum impact test methods for metallic materials”. The sample size was 7.5 mm×10 mm×55 mm. Proportional tensile samples were prepared according to GB/T228.1-2010 “Tensile tests for metallic materials – Part 1: Methods for testing at room temperature”. The original diameter of the sample was d₀ = 5 mm, the original range was L₀ = 25 mm, and the total length of the sample was L₁ = 60 mm. Three samples were tested under each condition, and their average value is reported. An Observer A1m metallographic microscope (ZEISS) was used to observe the metallographic structure and evaluate the grain size. A QUANTA400 scanning electron microscope was used to observe the impact and tensile fracture morphology. The composition of inclusions on the impact fracture was examined using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Influence of mixed rare earth La-Ce on phase transition point of test steel

The expansion curves of the two types of steel during heating and cooling were analyzed using the tangent method. The phase transition critical points Ac1, Ac3, Bs, and Bf are shown in figure 1. For the steel without rare earth (1#), Ac1 and Ac3 were at 646°C and 805°C, respectively. After adding the rare earths, the corresponding temperatures were 12°C and 7°C higher (658°C and 812°C). Because
The austenitic transformation is a diffusion-dominated process, the rare earth atoms with larger sizes than iron atoms are hardly dissolved in the matrix. Rather, they tend to be concentrated at grain boundaries and crystal defects to hinder the diffusion of carbon atoms. As a result, a higher temperature is required to provide enough driving force for the phase transition [10].

The critical points of Bs and Bf were at 586°C and 340°C for 1# and 560°C and 316°C for 2#, respectively. The mixed rare earths significantly lowered these two critical points by 26°C and 24°C. This is because the bainite transition is a semi-diffusion phase transition, in which carbon atoms diffuse while the iron atoms do not. As mentioned above, the solid-soluble rare earth in steel tends to be concentrated at grain boundaries and crystal defects. This hinders the carbon atom diffusion and thereby the phase transition temperature of bainite [11,12].

After the phase transition critical points, the Vickers hardness of samples was measured. As shown in figure 2, the hardness was higher at the core of the cylinder than at the edge. This suggests that the core was bainitic with a higher hardness while the edge was a mixture of ferrite and bainitic tissues. In general, solid-state phase transition of metal crystal nuclei is always stylish phase in the formation of crystal defects. There are more crystal defects at the edge of the cylinder relative to the core. As the sample cools slowly, there is a radial temperature gradient with a cooler edge and a hotter core. So, during the phase transition, edges by austenite grain boundary ferrite microstructure, and then, surrounded by ferrite bainite microstructure. With its slower cooling rate, the cylinder core easily enters the bainitic transition zone during cooling. Here, the carbon atoms can diffuse while the iron atoms have difficulty doing so, resulting in a non-layered structure with ferrite as matrix and cementite, that is, the bainitic structure [13].
In addition, 2# generally has higher hardness than 1#, especially Vickers hardness in the bainite. In 1#, the average hardness of bainite at the core and the edge are 303.9 and 230.2 HV, respectively, as shown in Figure 2(a) and 2(b). The corresponding values in 2# are 326.8 HV (22.9 HV higher than 1#) and 245.6 HV (15.4 HV higher), as shown in Figure 2(c) and 2(d). This was because adding the mixed rare earths decreased the bainite phase transition temperature, while the carbon supersaturation in bainite was mainly affected by its formation temperature. The lower the formation temperature, the greater the carbon supersaturation, and the higher the hardness of bainite. In addition, at a fixed steel composition, a lower phase transition temperature implies smaller and more numerous cementite particles, and the shape of cementite also changes from intermittent rod or lamellar to fine sheet, which increases the hardness of bainite [12].

3.2. Influence of rare earth on the deformation resistance of steel
Figure 3 shows the true stress-strain curves of the steel samples with and without rare earth. The curves have similar trends for the two steels under different temperature and compression deformations. At fixed deformation temperature and strain rate, the stress increased rapidly with increasing strain (ε) when ε ≤ 0.05, showing a strong work hardening characteristic. When ε > 0.05, the stress increase slowed down with increasing strain, and dynamic recovery and recrystallization softening occurred in conjunction with the work hardening, so that the curve tended to be flat. In addition, a comparison of figure 3(a)–(d) reveals that under the same amount of compression deformation, the deformation resistance significantly decreases when the temperature rises from 1000°C to 1100°C. As the deformation temperature increases, the dislocation slip resistance caused by plastic deformation decreases, and dynamic recovery and recrystallization are more likely to occur, thus reducing the deformation resistance.

The curve of 2# was always above that of 1# without rare earth. However, the curve deviation of the two groups of test steel with 30% compression deformation was less than 20% compression deformation. At 1000°C, the peak stress of 2# was 9.6% and 23.8% higher than that of 1# when the compression deformation was 30% and 20%, respectively. At 1100°C, the true stress-strain curves of 1# and 2# basically agree, as shown in figure 3(c) and 3(d). These results indicate that the addition of rare earth increased the deformation resistance of steel at 1000°C, and the degree of compression deformation varied with the amount of compression deformation, while rare earth had little effect on the deformation resistance at 1000°C.

When the steel was compressed and deformed at 1000°C, rare earths can reduce the activity coefficient of carbon and alloying elements in austenite, hinder their diffusion, and de-aggregate at or near the grain boundaries. Thus, the movement of dislocations is hindered and the deformation resistance is increased [13]. When the compression deformation increases, the dislocation density increases. At a higher temperature of compression deformation, more dislocations will participate in the slip, reducing the deformation resistance. From 1000°C to 1100°C, the effect of rare earth on
carbon and alloying elements is weakened due to the increase of deformation temperature. Meanwhile, the enhanced thermal vibration of atoms facilitates the dislocation slip and atomic diffusion. A higher temperature is also conducive to dynamic recovery and recrystallization, thus reducing the deformation resistance [13].

![Figure 3](image3.png)

**Figure 3.** True stress-strain curves of steel with and without rare earths.

### 3.3. Effect of mixed rare earth La-Ce on the microstructure of test steel

The quenching heating temperature of the subeutectoid steel is generally 30–50°C above Ac3. According to the phase transition critical point of the test steel, a heat treatment process (850°C, 1 h) followed by oil cooling, and air cooling at 200°C×1 h was adopted. The metallographic structure of the steel after heat treatment is shown in figure 4. Both steels were mainly tempered martensite. The tempered martensite microstructure of 1# has flakes and distinct black acicular characteristics, while that of 2# has smaller flakes and thinner and less marked needle shapes, indicating that the rare earth can refine the tempered martensite microstructure of steel.

![Figure 4](image4.png)

**Figure 4** Microstructure of steel before and after adding rare earth.  
**a:** 1#, **b:** 2#.
Previous studies [14] showed that low-carbon martensite would decompose and precipitate flake carbides in the process of low-temperature tempering, while the addition of rare earth elements in steel could inhibit this behavior, as well as hinder the precipitation of plate cementite and delay its growth. Other data [15] show that rare earths concentrated at grain boundaries easily combine with carbon to form rare earth carbides such as ReC3 and Re2C3 with high melting points. However, rare earth carbides are difficult to stabilize; therefore, the only way to prepare fine carbides is by replacing Fe atoms in the cementite to form an cementite. This may be the reason why the tempered martensite structure in 2# was small and not pronounced.

Modification with rare earth reduces the size martensite lath and therefore enhances the strength of the steel. According to the modified Nalver formula \( \sigma = 1 + K \sqrt{d/m} \) (dm is the effective grain martensite strip bundle size), a smaller strip bundle size means a greater strengthening effect, and the linear relationship with dm is shown [16]. Xu et al. [17] also showed that the addition of rare earth in steel can narrow the martensite strip width and refine the austenite grains, thus playing a role of fine grain strengthening. In steels with a carbon content greater than 0.3%, the addition of rare earth could also increase the amount of residual austenite and improve the toughness of steel.

The grain morphology of the two groups of steels is shown in figure 5. It is not difficult to find that the grain size of 1# was significantly different from 2#. The austenitic grain of 2# was more uniform than that of 1#. The steel grains were analyzed using Image-Pro Plus software, and the result is shown in Figure 6. In both steel samples, the grain size was concentrated in the range of 10–30 \( \mu \text{m} \) (45.2% for 1# and 58.1% for 2#), followed by 30–50 \( \mu \text{m} \) (36.7% for 1# and 23.8% for 2#). The average grain size of 2# was 17.1% less than that of 1# (21.8 vs. 26.3 \( \mu \text{m} \), a difference of 4.5 \( \mu \text{m} \), indicating that the addition of mixed rare earths La and Ce can refine the grain size and structure of the steel. The reason is that as active materials, the rare earths readily adsorb on the grain boundary, reducing the surface tension and therefore the driving force required to form crystal nucleus in the grain boundary. Thus, it facilitates nucleation [6,10]. On the other hand, fine rare earth inclusions have a nailing effect on the grain boundaries, and rare earth polysegregation in steel may also have a dragging effect on the grain boundaries, which hinder the migration of grain boundaries and thus inhibit grain growth [11].

![Figure 5. Grain size of steel samples.](image1)
a: 1#, b: 2#.

![Figure 6. Grain size distribution of test steels.](image2)
3.4. Effect of La-Ce on the impact properties of test steel

From Table 2, it could be seen that the impact performance of the steel at room temperature and at 
-40°C was improved after the addition of mixed rare earths. The impact work at room temperature 
was increased from 25.6 to 29.9 J (an increase of 16.8%), and that at -40°C increased from 23.5 to 27.6 J 
(increasing by 17.4%).

Figure 7 shows the morphology of impact fracture at room temperature and the EDS profile of the 
inclusions. The impact fracture of 1# presented quasi-cleavage and mixed fracture with a few shallow 
dimples. There were long strips of inclusions in the dimples, the lengths of which was approximately 6 
μm, as shown in figure 7(a). Sample 2# showed the characteristics of dimmer fracture, and there were 
small granular inclusions in the dimmer. The diameter of the dimples in 2# was approximately 2 μm, 
and the size of the inclusions was significantly smaller than that of 1#, as shown in figure 7(b). Energy 
spectrum analysis in figure 7(d) indicates that the inclusions in 2# are mixed rare earth Re-O-S-Al 
inclusions. From the impact performance at room temperature, the addition of mixed rare earths could 
form fine rare earth metamorphic inclusions in the steel, which is conducive to the formation of 
dimples, thereby increasing the number and depth of dimples, and improving the impact performance 
at room temperature.

In addition, compared with rare earth inclusions, the MnS and Al₂O₃ inclusions show poorer fusion 
with the matrix. The thermal expansion coefficients of the MnS and Al₂O₃ inclusions are 18.1 × 10⁻⁶ 
and 8.0 × 10⁻⁶/°C, respectively, while that of the iron matrix (12.5 × 10⁻⁶/°C) is fairly different. During 
the cooling and heating of the steel, the complex stress field formed at the interface between the 
inclusions and the matrix became the source of crack formation, reducing the steel performance. 
Meanwhile, the thermal expansion coefficient of rare earth inclusions (11.5 × 10⁻⁶/°C) matches better 
with that of the iron matrix. Therefore, the tiny rare earth inclusions do not easily break from the steel 
substrate during hot working processes, thereby weakening the cracks and concentrated stress under 
the impact load. Only under the effect of large strain, only in the form of inclusion/matrix interface 
separation nucleation generated cavitation, as toughening, thereby boosting the impact performance 
of steel [18, 19].

| Table 2. Impact energy absorbed by each test steel. |
|-----------------|--------|--------|
| Samples         | 1# average | 2# average |
| Room temperature impact, AKU/J | 24.8, 26.9, 25.3 (25.6) | 29.3, 28.9, 31.5 (29.9) |
| -40°C impact, AKU/J | 22.8, 23.6, 24.2 (23.5) | 27.5, 28.1, 27.3 (27.6) |
Figure 7. SEM impact fracture morphology at room temperature of (a) 1# and (b) 2#. (c and d) The respective EDS profiles of inclusion.

The fracture of the steels under low-temperature impact (-40°C) is shown in figure 8. In this case, both samples show characteristics of quasi-cleavage fracture, which is a kind of microscopic fracture in the brittle fracture range, as a transitional form between cleavage fracture and dimple fracture. There are a few intergranular dimples in the area of quasi-cleavage fracture, indicating the presence of a small amount of plastic deformation there. In figure 8(a), there were few intergranular dimples on the quasi-cleavage fracture of 1#, implying that the steel shows less plastic deformation and almost pure brittle fracture at low-temperature impact. In 2#, there are relatively more intergranular dimples on the quasi-cleavage fracture, and a relatively large plastic deformation at low-temperature impact. The spherical rare earth inclusion in the dimple will not produce significant stress concentration when it bears impact load (figure 8(b)), and the impact toughness at a low temperature is relatively high. When the impact occurs at a low temperature of -40°C, the spherical inclusions of the rare earth in 2# could reduce the stress concentration and increase the number of intergranular dimples on the quasi-cleavage fracture, thus improving the low-temperature impact performance of the steel [19].
3.5. Influence of mixed rare earth La-Ce on tensile properties of test steel

From Table 3, adding the mixed rare earth increased the tensile strength of the steel by 266 MPa (1752 to 2018 MPa, an increase of 15.2%). The yield strength increased by 64 MPa (from 1426 to 1490 MPa, an increase of 4.5%). Also, elongation after fracture increased from 12.0% to 13.0%, a relative increase of 8.3%. The calculated strength and plastic volume of the test steel increased significantly from 21024 to 26234 MPa*% after the addition of rare earth, an increase of 24.8%. Therefore, adding La-Ce to the test steel significantly improved the strength and plasticity of the steel as well as its comprehensive mechanical properties. As mentioned above, the austenite grain was refined after adding La-Ce, the strength and plasticity of the steel were improved, and the tensile property was improved through the fine grain strengthening. From our calculation, the flexo-strength ratio of the test steel decreased from 0.81 to 0.74 after the addition of rare earth, a change of 8.6%. The research of Pradipta Kumar Jena et al. [20] showed that armored steel with a low flexo-strength ratio usually has good elastic energy.

The tensile fracture morphology of the two steels (Figure 9) shows dimple fracture characteristics. In an material under external force, the strong slip dislocations accumulate to form more deformation mouth in toughening. Therefore, on a large interface area with many micro holes or broken inclusions and matrix metal interface with many tiny holes, the size and concentration of the holes grow under the action of external force, leading to cracks and ductile fracture separations. Comparing Figure 9(a) and 9(b), the dimples in 2# are clearly deeper, larger in size, more numerous, and denser than those in 1# without rare earth, thus showing better tensile properties.

Previous reports show that the size and distribution of particles in the second phase have a great influence on the size of dimples, and the size and spacing of those particles determine the size and distribution of dimples [21]. The stretching process creates a lot of space between the second phase particles and the matrix. With increasing tensile stress, the gaps in all directions increase and gradually develop into micro cracks. In the end, micro cracks along the direction of maximum extension reach the surface of specimen. Less tensile off the testing of rare earth in steel containing rare earth better.

**Figure 8.** SEM impact fracture morphology at -40°C of steel before and after adding rare earth.

a: 1#, b: 2#.

**Table 3.** Average values of tensile properties of experimental steel at room temperature.

| No. | Tensile strength $R_m$ / MPa | Yield strength $R_{0.2}$ / MPa | Elongation $A$ / % | Strength*Elongation $R_m*A$ (MPa*%) | Yield ratio $R_{0.2}/R_m$ |
|-----|-----------------------------|--------------------------------|-------------------|-------------------------------------|---------------------|
| 1#  | 1752                        | 1426                           | 12.0              | 21024                               | 0.81                |
| 2#  | 2018                        | 1490                           | 13.0              | 26234                               | 0.74                |
Figure 9. Tensile fracture morphology of steel before and after adding rare earth.
   a: 1#, b: 2#.

4. Conclusions
(1) After adding mixed La-Ce, the Ac1 and Ac3 phase transition points of 30MnCrNiMo steel were improved from 646°C to 658°C and from 805°C to 812°C, respectively. Meanwhile, those of Bs and Bf were significantly reduced (from 586°C to 560°C and from 340°C to 316°C). After the addition of mixed rare earths, the microhardness of bainite was increased from 303.9 to 326.8 HV.

(2) At the temperature of 1000°C, rare earth could increase the deformation resistance of the steel, and the degree of increase varied with the amount of compression deformation. At 1100°C, the rare earth elements had no significant effect on the deformation resistance. When the deformation temperature rose from 1000°C to 1100°C, the deformation resistance decreased distinctly.

(3) After adding mixed La-Ce to the impact protection steel, the microstructure of tempered martensite was improved, the austenite grain was refined, and the microstructure sheet of tempered martensite became smaller. The acicular shape became fine, and the average austenite grain size was reduced from 26.3 to 21.8 μm.

(4) The original impact protection steel contained long MnS inclusions. After adding rare earths, small metamorphic rare earth inclusions with a spherical shape appeared.

(5) After adding mixed rare earths, the comprehensive mechanical properties of impact protection steel were improved. For impact performance, the impact energy at room temperature increased by 16.8%, and that at -40°C increased by 17.4%. At the same time, the tensile strength, yield strength, and elongation after fracture were all improved to different degrees.

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