

Article

Cerium Addition Enhances Impact Energy Stability in S355NL Steel by Tailoring Microstructure and Inclusions

Jiandong Yang^{1,2}, Bijun Xie^{1,3,*} and Mingyue Sun^{1,3,*}¹ Shenyang National Research Center for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China² School of Mechanical Engineering and Automation, Dalian Polytechnic University, Dalian 116034, China³ Key Laboratory of Nuclear Materials and Safety Evaluation, Institute of Metal, Chinese Academy of Sciences, Shenyang 110016, China

* Correspondence: bijunx@uci.edu (B.X.); mysun@imr.ac.cn (M.S.)

Abstract

S355NL structural steel is extensively employed in bridges, ships, and power station equipment owing to its excellent tensile strength, weldability, and low-temperature toughness. However, pronounced fluctuations in its Charpy impact energy at low temperatures significantly compromise the reliability and service life of critical components. In this study, vacuum-induction-melted ingots of S355NL steel containing 0–0.086 wt.% rare earth cerium were prepared. The effects of Ce on microstructures, inclusions, and impact toughness were systematically investigated using optical microscopy (OM), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and Charpy V-notch testing. The results indicate that appropriate Ce additions (0.0011–0.0049 wt.%) refine the average grain size from 5.27 μm to 4.88 μm , reduce the pearlite interlamellar spacing from 204 nm to 169 nm, and promote the transformation of large-size Al_2O_3 -MnS composite inclusions into fine, spherical, Ce-rich oxysulfides. Charpy V-notch tests at -50°C reveal that 0.0011 wt.% Ce enhances both longitudinal (269.7 J) and transverse (257.4 J) absorbed energies while minimizing anisotropy ($E_t/E_l = 1.01$). Conversely, excessive Ce addition (0.086 wt.%) leads to coarse inclusions and deteriorates impact performance. These findings establish an optimal Ce window (0.0011–0.0049 wt.%) for microstructural and inclusion engineering to enhance the low-temperature impact toughness of S355NL steel.



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Keywords: S355NL steel; rare earth microalloying; grain refinement; inclusion modification; impact toughness

1. Introduction

S355NL steel, a high-strength low-alloy (HSLA) steel composed of a ferrite–pearlite microstructure, exhibits exceptional load-bearing capacity with superior corrosion resistance in harsh environments, making it widely applicable in offshore wind turbines, bridge construction, and marine engineering [1–3]. However, despite its high baseline toughness, S355NL exhibits pronounced scatter in Charpy V-notch impact energies at cryogenic temperatures (-40°C to -60°C) [4]. This variability has been traced chiefly to two microstructural factors: large size and irregular Al_2O_3 -MnS inclusions—formed during conventional deoxidation and sulfide precipitation—that serve as crack nucleation sites and amplify local stress concentrations; and heterogeneous distributions of ferrite and pearlite grains, which foster localized strain accumulation and premature fracture in weaker regions of the matrix [4,5].

Rare earth elements serve to purify the steel melt, modify inclusions, microalloys, and refine grains, thereby effectively enhancing the mechanical properties of steel and improving economic efficiency. Li et al. [6] developed a “dual low-oxygen rare earth steel” technology and demonstrated that adding an appropriate amount of rare earth can dramatically boost the fatigue performance of bearing steel [7–9]. They showed that the root cause of performance variability in rare earth steels is oxygen content: only under low-oxygen conditions can rare earth stably deliver deep melt purification, inclusion modification, and vigorous microalloying effects. This finding subsequently sparked numerous studies on rare earth microalloying to further improve the mechanical properties of different steels. For example, it is demonstrated that microalloying peritectic-grade steels with 0.045 wt.% Ce can significantly boost Charpy impact toughness at $-40\text{ }^{\circ}\text{C}$ while raising yield strength from 431 to 483 MPa through refined inclusions and grains [10]. In P110 oil-casing steel [11], adding Ce up to ~ 294 ppm reduced inclusion sizes to $\sim 2.82\text{ }\mu\text{m}$ and lifted the tensile strength to 784 MPa before performance declined at higher levels. Xiaofeng Zhang et al. [12] investigated the effects of adding 0.0028–0.0048 wt.% Ce to Al-killed Q355B steel and observed a marked decrease in inclusion size and quantity, concurrent grain refinement, and significant enhancements in impact toughness and tensile strength relative to the Ce-free baseline. Similarly, in a secondary-hardening steel, Ce additions from 0 to 66 ppm suppressed MnS inclusions in favor of uniform Ce–O–S complexes, yielding a 20% increase in yield strength and a 15% boost in elongation under tensile loading [13]. Recent inclusion modification studies on Q355ME steel demonstrated that Ce addition (≈ 15 ppm) transformed MgAl_2O_4 spinels into fine Ce_2O_3 and CeS dispersoids, lowering the ductile-to-brittle transition temperature by $20\text{ }^{\circ}\text{C}$ and improving upper shelf energy by 30% [14]. Moreover, mechanistic thermodynamic analyses indicate that cerium preferentially forms stable Ce–O and Ce–S compounds at high temperatures, which act as nucleation sites for fine inclusions and inhibit the growth of MnS clusters [15]. Comparative studies of La, Ce, and Y microalloying in weathering steels demonstrate that Ce yields superior grain refinement and inclusion spheroidization, doubling upper shelf energy and stabilizing the brittle-to-ductile transition [16]. A comprehensive review on rare earth inclusion modification underscores that optimal Ce windows generally lie between 0.002 and 0.01 wt.% to maximize mechanical benefits without inducing detrimental inclusion coarsening [17].

Despite the demonstrable benefits of rare earth microalloying in a variety of steels, a comprehensive study addressing the effect of controlled Ce additions on the microstructure, inclusion evolution, and mechanical performance of S355NL has not yet been reported. In this study, by correlating detailed measurements of inclusion chemistry and morphology, average grain size, pearlite interlamellar spacing, and mechanical response, we obtain an optimal Ce window (0.0011–0.0049 wt.%) for enhancing the mechanical properties and elucidate the mechanisms by which Ce refines microstructure and enhances toughness in S355NL. The findings provide both theoretical and practical foundations for optimizing the performance of S355NL steel, paving the way for advancing the industrial application of rare earth-modified steels.

2. Experimental Section

Using pure cerium (Ce) as the rare earth source, 15 kg of S355NL steel with varying Ce contents was produced using an intermediate-frequency vacuum induction furnace. Operating under a vacuum of 1.5–2 Pa and at a pressure around 8–9 MPa, this process ensures a clean, controlled melt with minimal contamination. After the steel was completely melted, it was kept at 1550–1570 $^{\circ}\text{C}$ for 2 h to ensure uniform composition. Then, the molten steel was transferred into preheated ingot molds (300 $^{\circ}\text{C}$) using a vacuum bottom-pouring

system designed to minimize secondary oxidation. The molds were placed in a sand box to facilitate slow cooling to room temperature (cooling rate about 5–10 °C/min), thereby reducing thermal stress and segregation during solidification. During forging, the ingots were heated to 1200 °C and held for 2 h, then forged into square bars with a cross-section of 70 mm × 70 mm, followed by air cooling to room temperature (cooling rate after forging is about 20 °C/min.) Finally, a normalizing heat treatment was conducted by heating the bars to 910 °C and holding for 25 min; the air cooling rate after normalizing treatment was about 15 °C/min. The chemical compositions of the investigated S355NL steel are summarized in Table 1. The cerium contents listed in the table represent the final residual concentrations measured in the steels after melting, solidification, and forging. The actual amounts of Ce added to the charge were higher due to inevitable losses (e.g., oxidation or slag entrapment) during high-temperature processing. Specifically, the initial additions of Ce to the charge for Steel No. 2 to No. 5 were approximately 0.003 wt.%, 0.007 wt.%, 0.030 wt.% and 0.130 wt.%, respectively. These additions resulted in the final retained Ce contents of 0.0011 wt.%, 0.0049 wt.%, 0.019 wt.% and 0.086 wt.%, as reported in Table 1. For analysis, gas rods and iron filings were taken from the same position at the mid-radius of the ingot. Alloying elements, including Ce, were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) and a carbon–sulfur analyzer, while oxygen, nitrogen, and hydrogen were analyzed using an oxygen–nitrogen–hydrogen analyzer. Each S355NL steel with different Ce contents was tested twice to verify the accuracy of the contents.

Table 1. Chemical compositions of S355NL steel with different Ce contents (wt.%).

Steel No.	C	Si	Mn	P	S	Nb	V	Al	Ti	Cr	Ni	Mo	Cu	H	N	TiO	Ce
1	0.15	0.14	1.39	<0.005	0.0027	0.034	0.037	0.036	<0.001	<0.03	<0.03	0.019	<0.03	<0.0001	0.002	0.0009	0
2	0.15	0.15	1.39	<0.005	<0.001	0.034	0.040	0.046	<0.001	<0.03	<0.03	0.020	<0.03	<0.0001	0.002	0.0008	0.0011
3	0.15	0.20	1.38	0.006	0.0018	0.037	0.035	0.047	<0.001	<0.03	<0.03	0.020	<0.03	<0.0001	0.0015	0.0008	0.0049
4	0.15	0.15	1.39	<0.005	<0.001	0.035	0.040	0.049	<0.001	<0.03	<0.03	0.019	<0.03	<0.0001	0.0021	0.0006	0.019
5	0.15	0.15	1.40	<0.005	<0.001	0.034	0.039	0.050	<0.001	<0.03	<0.03	0.019	<0.03	<0.0001	0.002	0.0007	0.086

For microstructure and inclusion analysis, metallographic specimens (10 mm × 10 mm × 10 mm) were sectioned from the ingots. These specimens were ground using SiC abrasive paper up to 2000 grit and polished with SiO₂ paste. The composition and morphology of inclusions were characterized using a MIRA3-LMH, TESCAN (Brno, Czech Republic) scanning electron microscope (SEM) equipped with an UltimMax40 energy-dispersive X-ray spectroscopy (EDS) system (Oxford Instruments, Abingdon, UK). Inclusion size and quantity were statistically analyzed using Image-Pro Plus software (v. 6.0). Polished specimens were etched with a 4% nitric acid alcohol solution, and the metallographic structure was observed via optical microscopy (OM). For electron backscatter diffraction (EBSD) analysis, specimens were mechanically ground, polished, and electropolished in a 10% perchloric acid solution at 30 V. Grain structure was characterized using a Zeiss Sigma 300 EBSD system with a step size of 0.23 µm, and grain size was measured and statistically evaluated using AZtecCrystal software (v. 3.3).

The influence of Ce content on the impact properties of heat-treated S355NL steel was investigated via Charpy impact testing. Square bars (70 mm × 70 mm × 65 mm) were sectioned from the mid-length region of the forged ingots and subsequently subjected to normalizing heat treatment at 910 °C for 25 min, followed by air cooling to room temperature at an approximate rate of 15 °C/min in an air atmosphere. Standard Charpy V-notch specimens (10 mm × 10 mm × 55 mm) were then machined from these square bars, and their transverse and longitudinal impact properties at −50 °C were evaluated using ZBC3302-B, MTS Systems (Eden Prairie, MN, USA). To ensure statistical reliability, at least three parallel specimens were tested for each Ce content condition in accordance

with the Chinese standard GB/T 229-2020 [18]. Fracture surfaces of the tested specimens were examined using the MIRA3-LMH SEM, and inclusions within the fracture zones were analyzed using the UltimMax40 EDS system.

3. Results and Discussion

3.1. Microstructural Evolution

Figure 1 illustrates the typical microstructural morphology of S355NL steel with varying Ce contents under normalized conditions. After normalizing, the microstructure of S355NL steel consists of ferrite (light regions) and pearlite (dark regions). Finely dispersed carbides within the ferrite matrix contribute to strengthening, while the refinement of pearlite colonies enhances the toughness. The Ce-free Steel No. 1 (Figure 1a) exhibits a coarser microstructure with prominent pearlite colony clusters. In contrast, the addition of 0.0011 wt.% Ce (Steel No. 2, Figure 1b) results in significant microstructural refinement, characterized by reduced pearlite colony size and more homogeneous phase distribution. This refinement effect becomes increasingly pronounced with higher Ce contents (Steel No. 3 to No. 5, Figure 1c–e), demonstrating the role of Ce in inhibiting grain growth and promoting phase uniformity during normalizing.

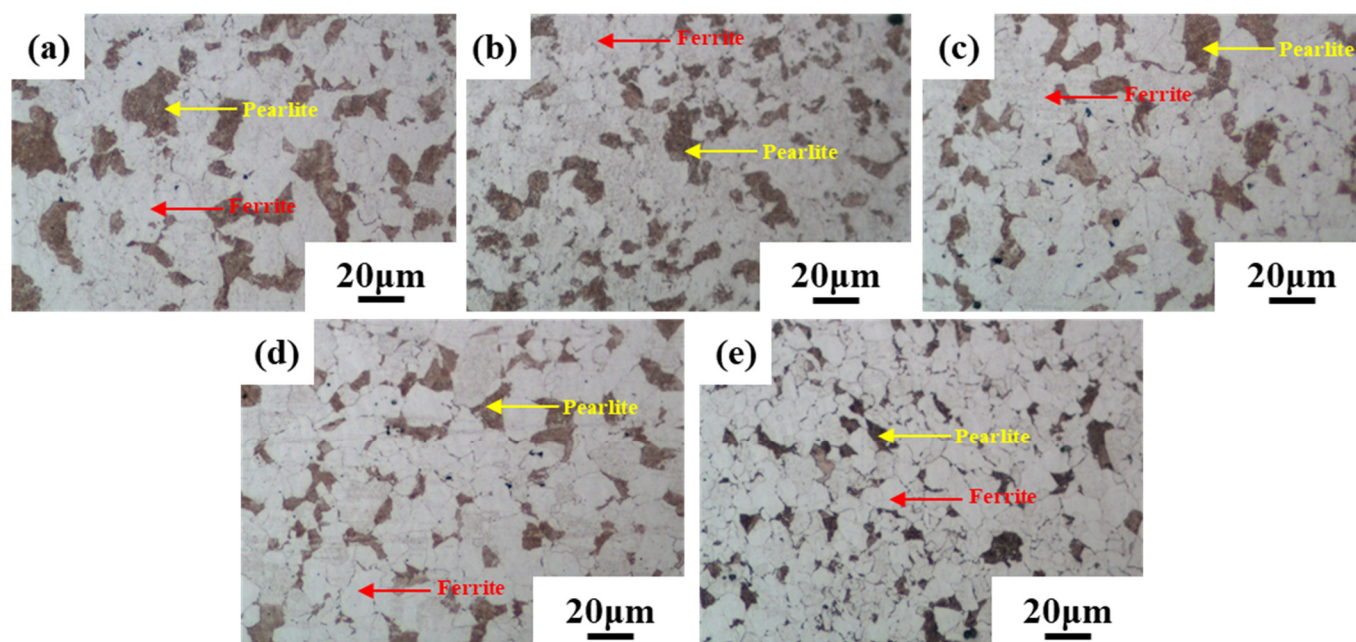


Figure 1. OM image shows the typical metallographic structure of S355NL with different Ce contents: (a) Steel No. 1; (b) Steel No. 2; (c) Steel No. 3; (d) Steel No. 4; (e) Steel No. 5.

Figure 2 demonstrates the lamellar morphology evolution of pearlite in S355NL steel with increasing Ce content. The SEM micrographs (a–e), correspond to Steel No. 1 (Ce-free), No. 2, No. 3, No. 4, and No. 5 (Ce-added), respectively. Quantitative analysis reveals that Ce addition induces progressive refinement of pearlite structure, as evidenced by the measured interlamellar spacing decreasing from 204 ± 15 nm in Steel No. 1 to 156 ± 12 nm in Steel No. 5 (24% reduction, see Table 2). This confirms that Ce addition effectively reduces pearlite interlamellar spacing. The refinement mechanism may be attributed to the sensitivity of pearlite nucleation kinetics to structural factors, as nucleation preferentially occurs at grain boundaries. In hypoeutectoid low-carbon steels, for instance, the early formation of proeutectoid ferrite expels carbon into the untransformed austenite. The ferrite-austenite interfaces then serve as nucleation sites for pearlitic cementite, from which pearlite grows. The significant reduction in pearlite interlamellar spacing with Ce addition

could arise from two factors: (1) The addition of Ce may directly regulate pearlite growth by altering carbon atom diffusion behavior at grain boundaries. This phenomenon is attributed to Ce segregation at grain boundaries and its subsequent control over boundary diffusion processes. Concurrently, Ce addition significantly modifies the microscopic architecture of pearlite. (2) Ce segregation at grain boundaries, coupled with its capacity to modify inclusions, plays a pivotal role in determining pearlite interlamellar spacing. The preferential segregation of Ce at boundaries alters carbon diffusion pathways, thereby governing the kinetics of pearlite growth [13,19].

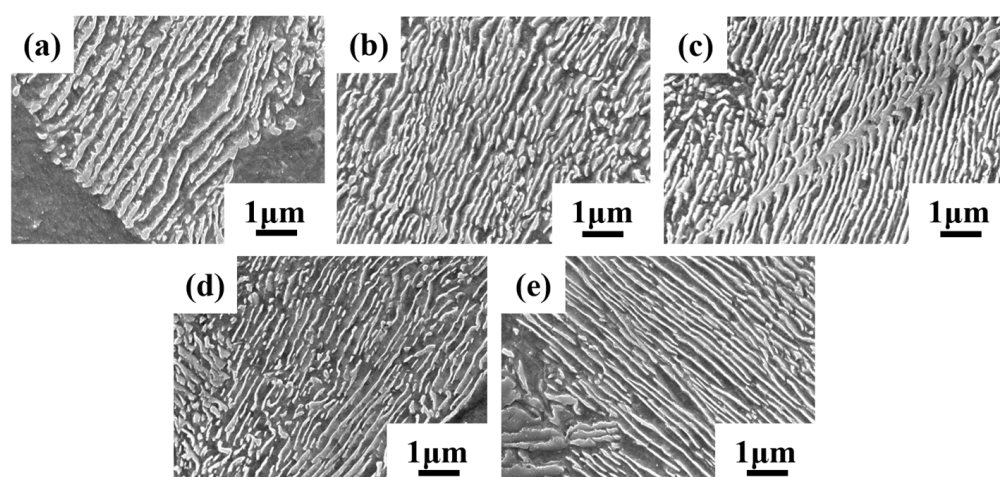


Figure 2. SEM images of pearlite S355NL with different Ce contents: (a) Steel No. 1; (b) Steel No. 2; (c) Steel No. 3; (d) Steel No. 4; (e) Steel No. 5.

Table 2. Average grain size and pearlite layer spacing statistics of S355NL with different Ce contents.

Steel No.	Ce Content/wt.%	Average Grain Size/ μm	Interlamellar Spacing of Pearlite/ μm
1	0	5.27	204
2	0.0011	4.88	169
3	0.0049	4.98	159
4	0.019	4.97	150
5	0.086	4.65	156

Figure 3a–e presents the electron backscatter diffraction (EBSD) analysis of grain morphology evolution in S355NL steel with Ce contents ranging from 0 to 0.086 wt.%. The inverse pole figure maps (scale bars: 25 μm) demonstrate a progressive refinement of equiaxed grains with increasing Ce addition. Steel No. 1 (Ce-free) exhibits coarse grains with heterogeneous size distribution (Figure 3a), whereas Steel Nos. 2–5 (0.0011–0.086 wt.% Ce) display refined microstructures characterized by uniformly distributed fine grains. Quantitative analysis in Figure 3f confirms that Ce addition increases the population of grains <5 μm by 41.7% (223 in Steel No. 1 to 316 in Steel No. 5). The introduction of rare earth metals, such as Ce, into the molten steel generates heterogeneous nucleation sites primarily composed of Ce_2O_3 due to their high melting points. These nucleation sites influence the grain size of ultra-low carbon steel. The increased density of nucleation sites results in a marked reduction in grain size and a corresponding enhancement in yield strength [20].

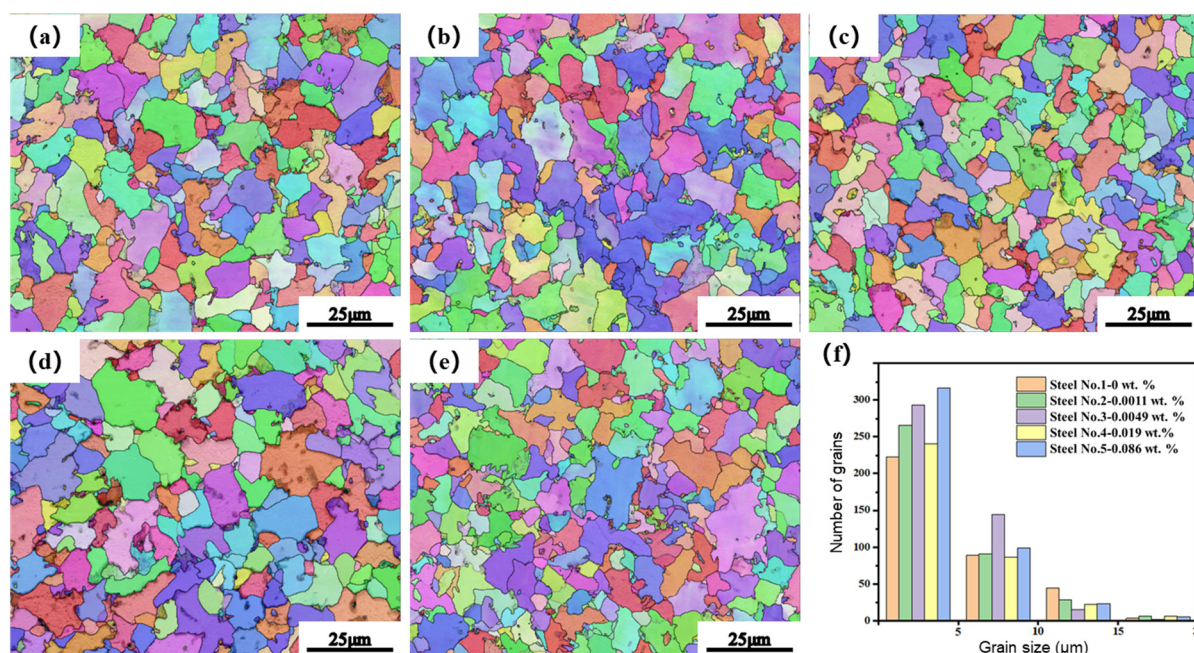


Figure 3. EBSD diagram of S355NL with different Ce contents: (a) Steel No. 1; (b) Steel No. 2; (c) Steel No. 3; (d) Steel No. 4; (e) Steel No. 5; (f) statistical graph of grain size distribution of S355NL with different Ce contents.

Finer-grained microstructures inherently exhibit superior strength and hardness due to their increased total grain boundary area. These boundaries act as effective barriers to dislocation motion, while the diversity in grain orientations necessitates coordinated deformation across adjacent grains, collectively enhancing resistance to plastic deformation. Furthermore, grain refinement increases the number of grains per unit volume, enabling more uniform deformation by distributing strain across a larger population of grains. This promotes extended plastic deformation prior to fracture, demonstrating that the Hall–Petch strengthening mechanism can simultaneously enhance both strength and ductility. The resultant improvement in energy absorption during deformation also elevates fracture toughness. The enhanced energy absorption before fracture also improves toughness. The addition of rare earth elements achieves this grain refinement effect, effectively elevating both strength and toughness, thereby addressing the limitation of solid solution strengthening, which improves strength at the expense of ductility [21].

As shown in Table 2, the addition of Ce to S355NL steel reduces the average grain size progressively from 5.27 μm (Ce-free) to 4.65 μm (0.086 wt.% Ce), with intermediate Ce concentrations (e.g., 0.0011–0.019 wt.%) yielding grain sizes between 4.88–4.97 μm. This refinement is attributed to Ce segregation at grain boundaries, which suppresses grain growth via Zener pinning while promoting nucleation during phase transformation. This distortion enhances solid solution strengthening, further improving the mechanical properties of the steel [22,23]. These findings confirm that rare earth Ce refines the microstructure of the studied steel, likely through its role in providing nucleation sites that facilitate solidification and grain boundary stabilization [20].

3.2. Inclusion Modification

The addition of Ce replaces conventional inclusions with well-dispersed, geometrically regular complex rare earth inclusions, accompanied by reductions in inclusion size and volume fraction [24]. Ren et al. demonstrated the sequential evolution of inclusion composition as follows: $\text{Al}_2\text{O}_3 \rightarrow \text{CeAlO}_3 \rightarrow \text{Ce}_2\text{O}_2\text{S} \rightarrow \text{Ce}_2\text{O}_2\text{S} + \text{CeS}$. With further increases in Ce content, rare earth-containing inclusions exhibit lower lattice mismatch with α -Fe and

disperse uniformly in the steel, facilitating ferrite formation [25,26]. Rare earth addition optimizes and refines the microstructure. Specifically, rare earth metals enhance mechanical properties, particularly impact toughness. The size and distribution of inclusions critically influence toughness, as spherical inclusions induce less stress concentration compared to elongated ones. The spheroidization and dispersion of inclusions improve their ability—along with grain boundaries—to resist crack initiation and propagation while mitigating stress concentration [27].

As shown in Figure 4, the morphology and composition of inclusions in S355NL steel evolve significantly with increasing Ce content. In Steel No. 1 (Ce-free), inclusions predominantly comprise angular MnS and Al_2O_3 particles averaging 5 μm in size. With minor Ce addition (0.0011 wt.%), these inclusions are progressively modified into finely dispersed spherical rare earth oxysulfides (Ce-O-S). Further increasing the Ce content to 0.019 wt.% results in compositionally heterogeneous inclusions characterized by carbon enrichment at their peripheries, suggesting interfacial reactions during solidification. At the highest Ce concentration (0.086 wt.%), irregularly shaped As-containing inclusions form, likely due to interactions between Ce and arsenic impurities. In contrast, rare earth inclusions predominantly adopt spherical or elliptical morphologies with favorable distribution. Compared to sulfide inclusions, rare earth inclusions exhibit thermal expansion coefficients and elastic moduli closer to the matrix, effectively reducing stress concentration around inclusions during impact testing [28,29].

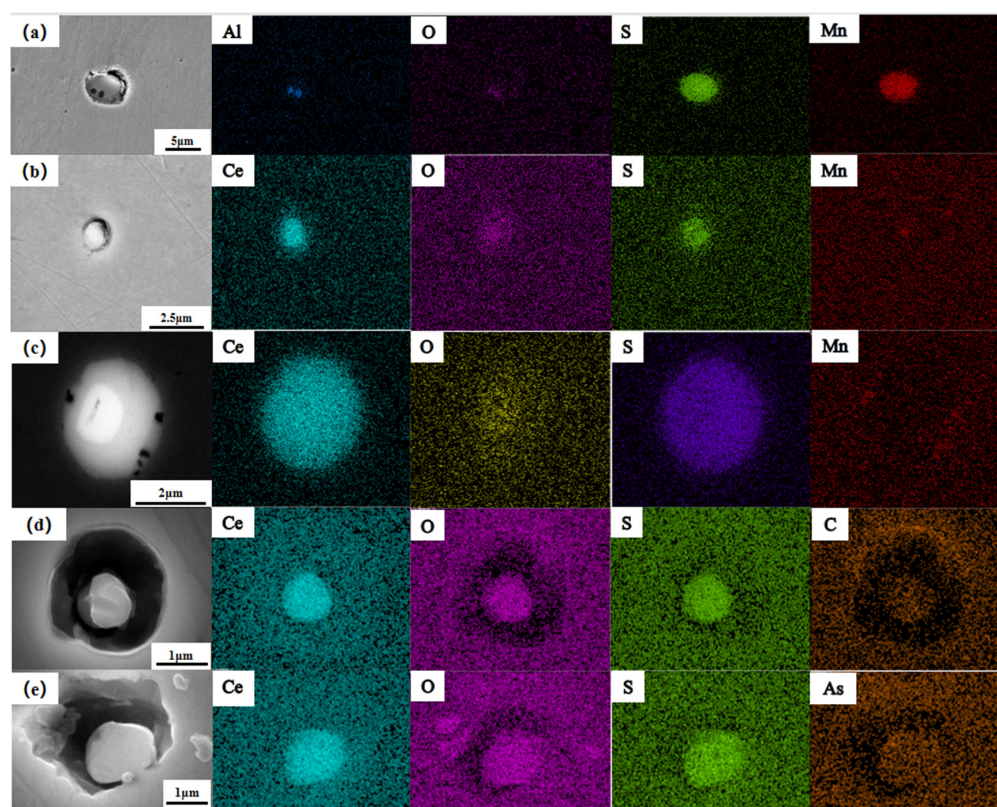


Figure 4. SEM and EDS analysis of inclusions with different Ce contents in S355NL: (a) Steel No. 1; (b) Steel No. 2; (c) Steel No. 3; (d) Steel No. 4; (e) Steel No. 5.

Statistical analysis of inclusion characteristics (Table 3) demonstrates a direct correlation between inclusion refinement/dispersion and improved mechanical performance. In Steel No. 1 (Ce-free), 254 inclusions with an average size of 2.62 μm are observed, including detrimental large inclusions (>10 μm). With 0.0011 wt.% Ce, the inclusion count sharply decreases to 74 (average size: 2.11 μm), accompanied by complete elimination of large

inclusions and enhanced spheroidization, which strengthens inclusion–matrix interfacial bonding. At 0.0049 wt.% Ce, the inclusion count rises to 376 (average size: 2.28 μm), but large inclusions remain absent, suggesting retained refinement efficacy. However, at 0.019 wt.% Ce, both inclusion count and average size increase moderately, though large inclusions are still suppressed. Notably, excessive Ce addition (0.086 wt.%) causes a dramatic surge in inclusion count (1071) and average size (2.81 μm), coupled with reappearance of large inclusions. These trends highlight that 0.0011 wt.% Ce optimally refines inclusions, promotes spheroidization, and mitigates stress concentration, thereby enhancing toughness. Conversely, excessive Ce induces inclusion coarsening due to oversaturation and agglomeration, reversing the beneficial effects. The decline in steel toughness at high Ce levels may stem from large inclusions disrupting matrix continuity and degrading performance [30].

Table 3. Inclusion statistics of S355NL with different Ce contents.

Sample	Number	1–2 μm /%	2–5 μm /%	5–10 μm /%	>10 μm /%	Average / μm	Max / μm	Density / mm^{-2}
No. 1	254	37.01	58.72	3.54	0.73	2.62	10.70	9.45
No. 2	74	55.41	41.89	2.70	0	2.11	7.68	2.47
No. 3	376	40.14	56.65	3.2	0	2.28	8.82	14.24
No. 4	689	41.83	48.88	9.29	0	2.42	9.81	24.47
No. 5	1071	47.18	51.07	1.49	0.26	2.81	12.49	38.03

3.3. Impact Performance Optimization

As shown in Figure 5a, the $-50\text{ }^{\circ}\text{C}$ Charpy impact absorbed energy exhibits a pronounced dependence on Ce content. For longitudinal samples, the energy increases from 181.05 J in Steel No. 1 (Ce-free) to a peak of 269.67 J in Steel No. 2 (0.0011 wt.% Ce), representing a 49% enhancement. Steel No. 3 (0.0049 wt.% Ce) and No. 4 (0.019 wt.% Ce) display intermediate values of 242.10 J and 215.33 J, respectively, remaining higher than Steel No. 1 but 10–20% lower than the optimal Steel No. 2. A drastic decline to 64 J occurs in Steel No. 5 (0.086 wt.% Ce), indicating detrimental effects of excessive Ce. Transverse impact energy follows a similar trend: rising from 226.11 J (Steel No. 1) to 257.39 J (Steel No. 2), with Steel No. 3 (238.44 J) and No. 4 (221.17 J) maintaining superior performance relative to Steel No. 1 but falling short of Steel No. 2. Steel No. 5 again exhibits the lowest transverse energy (109.09 J), underscoring the non-monotonic relationship between Ce content and toughness.

Isotropy, a critical performance requirement for S355NL steel closely tied to service life, is evaluated using the ratio of transverse-to-longitudinal impact energy [31]. As illustrated in Figure 5b, moderate Ce addition (0.0011 wt.% in Steel No. 2) significantly reduces anisotropy, lowering the isotropy ratio from 1.24 (Ce-free Steel No. 1) to 1.01, achieving near-isotropic mechanical behavior. Steel No. 3 (0.0049 wt.% Ce) and No. 4 (0.019 wt.% Ce) exhibit slightly elevated ratios of 1.08 and 1.12, respectively, while Steel No. 5 (0.086 wt.% Ce) shows a sharp resurgence in anisotropy (ratio: 1.45). This improvement is attributed to Ce-induced grain refinement, dispersion of fine inclusions (reducing stress concentration sources), and enhanced grain boundary cohesion, collectively improving toughness. However, excessive Ce promotes harmful inclusions, degrading impact performance [32]. Overall, Ce addition significantly stabilizes the impact energy variability of S355NL steel. These results demonstrate that 0.0011 wt.% Ce optimizes impact stability, offering substantial benefits for the steel's mechanical reliability.

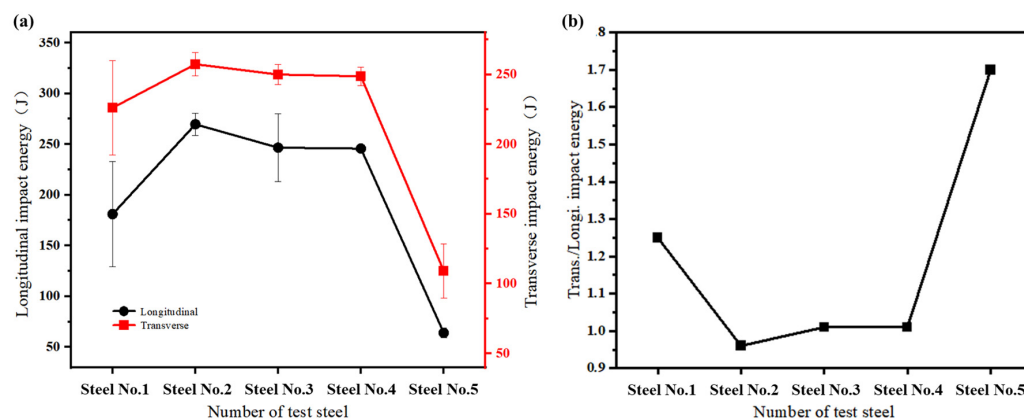


Figure 5. Influence of Ce content on impact performance of S355NL at $-50\text{ }^{\circ}\text{C}$: (a) Lateral and longitudinal shock absorption energy at $-50\text{ }^{\circ}\text{C}$ for Steel Nos. 1–5, corresponding to Ce contents of 0, 0.0011, 0.0049, 0.019, and 0.086 wt.%, respectively. (b) Ratio of transverse and longitudinal impact energy at $-50\text{ }^{\circ}\text{C}$ for the same steel series.

3.4. Impact Fractography Analysis

The impact fracture morphologies of S355NL steel with varying Ce contents are compared in Figure 6. In Ce-free steel (Figure 6a), the fracture surface exhibits a bimodal failure mode, combining ductile and brittle fracture mechanisms. The upper region displays classic ductile fracture characteristics, including elongated dimples and fibrous structures, indicative of localized plastic deformation. In contrast, the lower region transitions to brittle fracture patterns, featuring radial markings and flat cleavage facets characteristic of low-energy crack propagation. High-magnification imaging (Figure 6a) further resolves a heterogeneous microstructure where dimples are interspersed with quasi-cleavage facets, reflecting competing deformation mechanisms under cryogenic conditions.

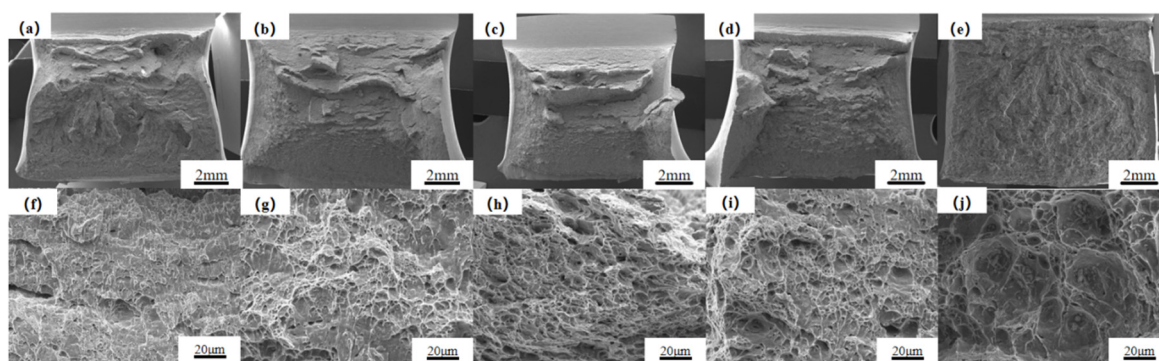


Figure 6. Effect of Ce content on the impact fracture morphology of S355NL: (a,f) Steel No. 1 with Ce content of 0 wt.%; (b,g) Steel No. 2 with Ce content of 0.0011 wt.%; (c,h) Steel No. 3 with Ce content of 0.0049 wt.%; (d,i) Steel No. 4 with Ce content of 0.019 wt.%; (e,j) Steel No. 5 with Ce content of 0.086 wt.%.

At 0.0011 wt.% Ce (Figure 6b), the fracture surface exhibits prominent tear ridges, indicative of enhanced plastic deformation resistance. High-magnification imaging reveals a dense population of fine, equiaxed dimples, confirming a transition to dominant ductile fracture behavior. As Ce content increases to 0.0049–0.019 wt.% (Figure 6c,d), ductile characteristics intensify, with dimples becoming deeper and more uniformly distributed, reflecting improved strain accommodation through grain refinement and inclusion spheroidization. However, at 0.086 wt.% Ce (Figure 6e,j), the fracture morphology shifts abruptly to a flat, quasi-cleavage pattern marked by radial cracks and river markings. High-magnification analysis identifies oversized inclusions, primarily Ce-As-O-S complexes, embedded within

large, irregular dimples (Figure 6j). These inclusions act as stress concentrators, initiating microcracks under impact loading and propagating brittle fracture pathways, which directly correlate with the drastic reduction in impact energy observed in Steel No. 5 (64 J).

Analysis of Ce-free fracture surfaces (Figure 7a) reveals coarse, irregularly shaped inclusions (~50 μm in diameter), identified via EDS as Al_2O_3 -MnS composite inclusions. These large heterogeneities act as preferential sites for crack initiation due to their angular morphology and weak interfacial bonding with the matrix. With Ce addition, oxygen and sulfur preferentially react with Ce to form finely dispersed submicron-sized rare earth oxysulfides (Ce-O-S, <1 μm), effectively replacing the brittle Al_2O_3 -MnS inclusions. This chemical modification eliminates coarse inclusions (>10 μm) and reduces stress concentration sources, as evidenced by the refined inclusion distribution in Steel No. 2 (0.0011 wt.% Ce). The transition to Ce-O-S inclusions enhances interfacial cohesion and mitigates localized strain mismatch, thereby suppressing crack propagation and improving fracture resistance. Notably, Al_2O_3 and MnS exhibit thermal expansion coefficients of $18.1 \times 10^{-6}/^\circ\text{C}$ and $8.1 \times 10^{-6}/^\circ\text{C}$, respectively, significantly diverging from the matrix ($12.5 \times 10^{-6}/^\circ\text{C}$). This mismatch disrupts matrix–inclusion continuity during solidification [33]. In contrast, rare earth inclusions adopt spherical morphologies with a thermal expansion coefficient of $11.5 \times 10^{-6}/^\circ\text{C}$, closely matching the matrix. Their lower hardness (compared to Al_2O_3) and reduced plasticity (relative to MnS) ensure minimal stress concentration at inclusion–matrix interfaces during low-temperature impact testing, effectively suppressing crack initiation [34,35].

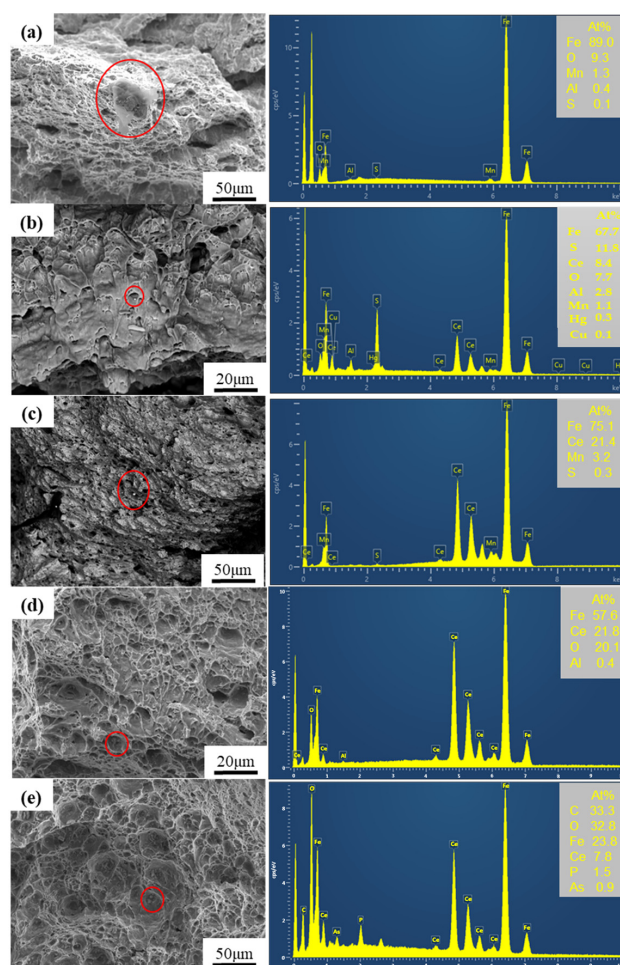


Figure 7. SEM morphology of inclusions and EDS analysis of inclusions in the fracture surfaces of S355NL steel with different Ce contents: (a) Steel No. 1; (b) Steel No. 2; (c) Steel No. 3; (d) Steel No. 4; (e) Steel No. 5.

3.5. Mechanism Analysis of Performance Improvement

As summarized in Table 1, the sulfur (S) content in the steel decreases markedly from 0.0027 wt.% to <0.001 wt.% following rare earth (RE) addition, achieving a reduction of >63.03%. This dramatic decline underscores the strong thermodynamic affinity between RE elements and sulfur, which facilitates the formation of stable RE sulfides during solidification. These compounds effectively scavenge sulfur from the molten steel, significantly enhancing cleanliness by eliminating residual sulfur-induced impurities.

Regarding inclusion modification mechanisms, non-RE steel contains predominantly Al_2O_3 and MnS inclusions. RE addition suppresses MnS formation by drastically lowering sulfur content, while transforming oxide inclusions into rare earth-based variants. RE inclusions exhibit thermal expansion coefficients and elastic moduli closely matching the matrix. Under external loading, their low deformability minimizes stress concentration, effectively suppressing crack initiation. Furthermore, their strong interfacial continuity with the matrix hinders crack propagation, collectively enhancing overall performance [36].

The strengthening effects of RE arise from two primary mechanisms: grain refinement strengthening and solid solution strengthening. Grain refinement strengthening: Increased grain boundary density impedes dislocation motion and delays grain elongation, enhancing toughness. Solid solution strengthening: Rare earth atoms dissolved in the matrix induce lattice distortion, elevating alloy strength. As a surfactant, RE tends to segregate at grain boundaries. This preferential segregation reduces interfacial tension and energy, diminishing the driving force for grain growth and pinning boundary migration, thereby inhibiting grain coarsening [37]. The dual effects of dislocation pinning and grain refinement significantly enhance both strength and toughness.

In summary, optimal RE addition refines grains, suppresses inclusion precipitation at boundaries, and strengthens grain boundary cohesion. Moreover, during hot processing, RE compounds retain small spherical/globular morphologies with uniform distribution, substantially improving impact toughness.

4. Conclusions

This study systematically investigated the influence of cerium addition on the microstructure, inclusion characteristics, and mechanical performance of S355NL steel. The main conclusions are as follows:

1. An optimal Ce addition window (0.0011–0.0049 wt.%) in S355 NL steel is obtained. Within this range, the addition of Ce significantly improves impact toughness and suppresses fluctuations in Charpy impact energy.
2. Ce addition promotes grain size reduction and narrows pearlite interlamellar spacing. At 0.0011 wt.% Ce, the total inclusion count drops by $\approx 70\%$, and the mean diameter decreases to 2.11 μm , entirely eliminating coarse ($>10 \mu\text{m}$) inclusions. With the addition of Ce at 0.086 wt.%, however, the inclusion density rises to over 1000 inclusions with a mean diameter of 2.81 μm , leading to the re-emergence of large-size inclusions that act as crack initiation sites.
3. Charpy V-notch tests show that the 0.0011 wt.% Ce-added steel exhibits the highest absorbed energies (257 J transverse, 270 J longitudinal) and achieves an isotropy ratio of ~ 1.01 . Steels with higher Ce addition suffer reduced absorbed energies and increased anisotropy due to the presence of coarse and stress-concentrating inclusions.

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