



# Article Effect of Yttrium-Based Rare Earth on Inclusions and Cryogenic Temperature Impact Properties of Offshore Engineering Steel

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**Abstract:** EH36 offshore engineering steels with varied yttrium-based rare earth content were prepared by trials in industrial production. The effects of yttrium-based rare earth on the inclusions and cryogenic temperature impact properties of EH36 offshore engineering steel were investigated by scanning electron microscopy, automatic statistics of inclusions, thermodynamic analysis and fracture morphology analysis. Yttrium-based rare earth could refine the inclusions and modify irregular Al<sub>2</sub>O<sub>3</sub> and MnS inclusions into small, spherical, regular rare earth inclusions. The optimal impact properties were found in EH36 steel with 0.020 wt.% yttrium-based rare earth. Compared with 0RE steel, the RE-inclusions were within 3  $\mu$ m (91.95% of total inclusions) in diameter and were spherical or quasi-spherical when dispersed in 200RE steel. Meanwhile, the cryogenic temperature impact properties significantly increased: 200RE steel impact properties were increased by 245.1% at -80 °C.

**Keywords:** offshore engineering steel; yttrium-based rare earth; inclusions; thermodynamic; cryogenic temperature impact properties

# 1. Introduction

With the continuous development of marine resources, China's shipbuilding and offshore oil industry has ushered in a new period of rapid growth, which has an increasing demand for shipbuilding steel and offshore engineering steel. EH36 steel is an offshore engineering steel widely used in major projects for the development of marine resources, such as offshore platforms, polar tankers, polar sea platforms, etc. [1,2]. Remarkable cryogenic temperature impact toughness, strength, weldability, fatigue resistance, fine corrosion resistance, large thickness and large standardization are the development direction of offshore engineering steel [3–5]. However, in the harsh marine environment, offshore engineering steel is easily affected by cryogenic temperature conditions and can undergo cleavage or tearing fracture modes [6]. Therefore, in order to better serve the field of marine engineering and promote the development of the industry, there is an urgent need to develop the offshore engineering steel with the sufficient impact energy absorption at lower temperatures. In recent years, many published papers have shown that the addition of alloying elements (Zr, Ti, Mg, etc.) has been effective in improving the toughness for offshore engineering steel [7–9].

Rare earth (RE) as microalloying elements, have been widely used in the field of the steelmaking process [10–15]. A number of scholars have shown that the addition of rare earth elements to the test steel can significantly improve the mechanical properties of materials [16–20]. In addition, it has been reported that rare earth yttrium could improve the ductility and magnetic properties of the Fe-6.5 wt.% Si alloy [21,22]. With the addition of rare earth, the impact toughness and ultra-high cycle fatigue properties of high-carbon



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). chromium bearing steel are obviously improved [23,24]. Chen and co-workers [25,26] also reported that it is beneficial for refining the prior austenite grain size, block size, lath size and improving the fracture behavior, work-hardening the ability of H13 die steel to add yttrium. Moreover, rare earth elements lanthanum and cerium have a remarkable effect on inhibiting the initial marine corrosion behavior of offshore engineering steel [27,28].

In this paper, the role of yttrium-based rare earth on inclusions and cryogenic temperature impact properties of EH36 offshore engineering steel were systematically analyzed by means of scanning electron microscopy (SEM), automatic statistics of inclusions and thermodynamic analysis, with the aim to develop excellent cryogenic temperature impact toughness in offshore engineering steel and to lay the foundations for broadening the application of rare earth in high-performance offshore engineering steels.

# 2. Materials and Methods

The raw materials are the offshore engineering steels of grade EH36 produced by the trials in the industrial field. The production of offshore engineering steel is as shown in Figure 1. In this process, the yttrium-based rare earth (60 wt.% Y, 40 wt.% Ce/La) was added into the molten steel in the form of cored wires (BXX-S1, 556 g/m, Longnan Longyi, Ganzhou, China) during the ladle furnace (LF) refining stage and ladle bottom argon blowing technology was employed to ensure the homogeneity of molten steel. The final rare earth content in the design test steels is 100 ppm, 200 ppm and 300ppm, respectively. The chemical compositions of test steels are presented in Table 1. The chemical compositions in the hot rolled plate were measured by ICP-MS, (PE ELAN 9000; PerkinElmer, Waltham, MA, USA). The continuous casting billets with thickness of 248 mm were heated to 1150 °C. Each billet was then hot rolled by thermo-mechanical control process into a steel plate of the thickness of 25 mm. The detail of thermo-mechanical control process of EH36 grade offshore engineering steel was described in the previous study [3].



Figure 1. Industrial production process of the grade EH36 offshore engineering steels.

Sample	С	Si	Mn	Р	S	0	Al	Cr	Ni	Мо	Cu	As	RE	Fe
0RE	0.10	0.28	1.42	0.017	0.003	0.0020	0.029	0.04	0.01	0.010	0.05	< 0.01	0	Bal.
90RE	0.10	0.24	1.27	0.019	0.001	0.0015	0.022	0.07	0.02	0.005	0.04	< 0.01	0.009	Bal.
200RE	0.10	0.32	1.43	0.010	0.001	0.0011	0.017	0.08	0.01	0.013	0.04	< 0.01	0.020	Bal.
280RE	0.10	0.31	1.33	0.014	0.001	00010	0.015	0.03	0.01	0.007	0.03	< 0.01	0.028	Bal.

**Table 1.** Chemical compositions of test steels (wt.%).

The specimens were mechanically polished and etched with a 4% nitric acid solution for SEM analysis. Inclusions of the samples were analyzed by TESCAN MIRA3 LMH scanning electron microscope (Tescan, Czech Republic) equipped with a field emission gun (FEG). The inclusion behaviors of the steel, such as particle size, composition and species were investigated via an automated scanning electron microscope (ASPEX explorer, Hillsboro, OR, USA). We could find the inclusion by EDS scanning automatically and calculate the inclusion's center. Then, the equipment scanned towards eight dimensions from the center to obtain the spinning line. The inclusion structure and size was determined via this information. Moreover, the non-aqueous solution electrolytic specimen was cut into cylinders 10 mm in diameter and 120 mm in length. The electrolyte mainly consists of 5 vol % glycerine, 5 vol % triethanolamine, 90 vol % absolute methanol, and a small amount of tetramethylammonium chloride [29]. Inclusions could be extracted after electrolysis and prepared for scanning electron microscopy analysis.

The impact properties samples were prepared along their rolling directions according to the GB/T 229-2020 standard with the dimensions of 55 mm × 10 mm × 10 mm and processed into Charpy V-notch at the 1/4 width and 1/4 length direction of steel plates edge. They were then tested on a pendulum impact testing machine (SANS, ZBC2452, Shenzhen, China), which could generate a standard strike energy of 450 J, using the Charpy V-notched impact test method for metals. The impact properties were tested at -40 °C, -60 °C and -80 °C. To obtain accurate test data, the impact samples for each temperature state were tested three times to obtain the average values. The fracture morphology of the specimens was also analyzed using the TESCAN MIRA3 SEM operated in the secondary electron imaging mode.

#### 3. Results and Discussion

# 3.1. Effect of Rare Earth on Inclusions

#### 3.1.1. Inclusions Morphology and Type

Figures 2–5 show the morphology and EDS analysis of inclusions in EH36 steel plates after rolling with different rare earth contents. From the analysis of the morphology and energy spectrum of inclusions in Figure 2, it can be seen that  $Al_2O_3$  and MnS, which are the main inclusions in 0RE EH36 steel, could exist alone or in composite inclusions as well. It can be seen from Figure 2a that the oxides in 0RE steel mainly exist as irregular squares and the particles' sizes are less than 3  $\mu$ m. Figure 2b is an independent MnS inclusion with a long cross section and a long axis diameter of about 4  $\mu$ m. Figure 2c shows the characteristics of composite inclusions. According to the results of element surface scanning analysis, composite inclusions should exist in the form of a small amount of MnS-wrapped  $Al_2O_3$  and a small amount of MgO.

The addition of an appropriate amount of rare earth could modify the inclusions in offshore engineering steels plates and form rare earth inclusions. Figures 3 and 4 show the scanning electron microscope images and corresponding energy spectrum analysis and element surface scan results of typical inclusions in 90RE steel and 200RE steel after adding 0.009 wt.% and 0.020 wt.% rare earth, respectively. It can be seen from Figures 3 and 4 that with the addition of rare earth, the inclusions in steels were modified from irregular  $Al_2O_3$  and MnS inclusions without rare earth treatment to spherical or quasi-spherical RE-O-S inclusions, and the diameter of inclusions were refined to less than 2  $\mu$ m.

When the rare earth content in EH36 steel was further increased to 0.028 wt.%, some RE-O-S inclusions in 280RE steel were transformed into RE-O-S-As-P composite inclusions with a particle size of about 2  $\mu$ m, as shown in Figure 5. The above reaction order of rare earths in steel could basically be measured by describing the electronegativity of the gain and loss of the electron chemical reactivity of atoms [23]. The electronegativity of La, Ce and Y is 1.10 eV,1.12 eV and 1.22 eV, respectively, which is almost the same as that of alkaline earth metals, and it is easy to lose electrons in the process of a chemical reaction. On the other hand, the electronegativity of non-metallic inclusion elements O and S in steel is very large, and the element S of O up to 3.50 eV is 2.58 eV, which usually has a strong

ability to attract electrons in chemical reactions. From the comparison of the possibility of reaction of a combination of O and S with rare earth metals, the difference between the electronegativity of O and that of rare earth metals is larger than that of S and rare earth metals, which is close to 1 eV; so, under the same conditions, O will react first with rare earth metals, followed by S. The electronegativity of As and P is 2.20 and 2.06 eV, respectively. Therefore, when the O and S in the steel are consumed by the reaction with rare earth metals, if there are any remaining rare earths, they will combine with As and P reactions.



Figure 2. Morphology and type of (a-c) inclusions formed in ORE steel.

It can be seen that after the addition of rare earth to the EH36 steel plates, the oxygen and sulfur in the steel interact with the rare earth elements, and the rare earth oxide compounds, rare earth sulfur oxide inclusions, are formed, and the morphology and size of the inclusions are changed. Rare earth elements play an excellent role in modifying inclusions. The thermal expansion coefficient of MnS and  $Al_2O_3$  inclusions is  $18.1 \times 10^{-6}$ /°C and  $8.0 \times 10^{-6}$ /°C, respectively, which are quite different from those of steel matrix ( $12.5 \times 10^{-6}$ /°C), while the thermal expansion coefficient of rare earth inclusions is  $11.5 \times 10^{-6}$ /°C, which are similar to those of steel matrix [30], and most of them are spherical or ellipsoidal, which could reduce stress concentration [31]. Therefore, there is a good adaptability between rare earth inclusions and steel matrix. In the process of the hot working deformation of steel, rare earth inclusions still maintain a small spherical or spindle shape that are uniformly distributed in the steel, which could avoid the large additional stress around the inclusions during hot working and cooling. Therefore, the modification of inclusions in steel could increase the ability of inclusions and grain boundaries to resist crack formation and propagation, which are beneficial to improve the impact properties of steel.



Figure 3. Morphology and type of (a–c) inclusions formed in 90RE steel.



Figure 4. Morphology and type of (a,b) inclusions formed in 200RE steel.



Figure 5. Morphology and type of (a,b) inclusions formed in 280RE steel.

3.1.2. Thermodynamic Analysis on Formation of Inclusions

To determine the formation sequence for different oxides and sulfides of yttrium-based rare earth in EH36 steel plates, the amount of yttrium in the calculations was set as 1 mol to compare the Gibbs free energy of formation for various inclusions, which could be derived as [32,33]

$$2[Y] + 3[O] = Y_2O_3(s), \ \Delta G_1^{\theta} = -1792600 + 658.0T \tag{1}$$

$$2[Y] + 2[O] + [S] = Y_2 O_2 S(s), \ \Delta G_2^{\theta} = -1521000 + 536.0T$$
<sup>(2)</sup>

$$2[Y] + 3[S] = Y_2 S_3(s), \ \Delta G_3^{\theta} = -1171000 + 441.0T \tag{3}$$

$$[Y] + [S] = YS(s), \ \Delta G_4^{\theta} = -433800 + 151.2T \tag{4}$$

In the EH36 liquid steel, the reaction equation of RE element reacts with non-metal element N to generate  $RE_aN_b$ , which can be expressed through Equation (5).

$$aRE + bN = RE_a N_b(s) \tag{5}$$

According to the isothermal equation of chemical reaction, the Gibbs free energy of formation is obtained as

$$\Delta G = \Delta G^{\theta} + RT lnJ \tag{6}$$

For Equation (6)

$$J = \frac{\left(a_{RE_aN_b}\right)^{\frac{1}{a}}}{a_{RE} \cdot (a_N)^{\frac{b}{a}}}$$
(7)

The relationship between activity and concentration could be expressed by

а

$$_{i} = f_{i} \cdot w[i] \tag{8}$$

where the activity coefficient  $f_{[i]}$  was calculated from metal composition with interaction coefficients

$$lgf_i = \sum_{i=1}^n e_i^j \times w[i]$$
<sup>(9)</sup>

where *J* denotes the reaction quotient (unitless),  $\Delta G$  is the Gibbs free energy change of reaction (J·mol<sup>-1</sup>),  $\Delta G^{\theta}$  denotes the Gibbs free energy change of reaction for unmixed reactants and products at standard conditions (J·mol<sup>-1</sup>), *R* is the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>), *T* is temperature (K),  $a_i$  is the activity of component *I*,  $f_i$  is the activity coefficient of element *I* and w[i] is the concentration of the element *i* in EH36 liquid steel;  $e_i^j$  is the interaction coefficients of the element *j* to solute *i*.

Table 2 presents the first-order interaction coefficient  $e_i^j$  of various solute elements in the molten EH36 steel [32-34]. Substituting the data in Table 2 into Equations (8) and (9), the activity and activity coefficients of O, S and Y in the molten EH36 steels are calculated and presented in Table 3. The Gibbs free energy of inclusions in EH36 steels at 1873 K are shown in Figure 6. When the rare earth content in the steel was 0.009 wt.%, the free energy of yttrium-containing inclusions in the steel were as follows:  $\Delta G(Y_2S_3)$  was 137,549.92 J·mol<sup>-1</sup>,  $\Delta G(YS)$  was 36,678.29 J·mol<sup>-1</sup>, so  $Y_2S_3$  and YS inclusions cannot be precipitated in 90RE steel;  $\Delta G(Y_2O_3)$  was -61,470.41 J·mol<sup>-1</sup>,  $\Delta G(Y_2O_2S)$  was -23,755.97 J·mol<sup>-1</sup>, so  $Y_2O_3$  and  $Y_2O_2S$  inclusions precipitate in 90RE steel. When the rare earth content in the steel was 0.020 wt.%, the free energy of yttrium-containing inclusions in the steel were as follows:  $\Delta G(Y_2S_3)$ was 110,678.69 J·mol<sup>-1</sup>, and  $\Delta G(YS)$  was 23,143.56 J·mol<sup>-1</sup>, so  $Y_2S_3$  and YS inclusions were not precipitated in 200RE steel; the  $\Delta G(Y_2O_3)$  was -55,678.25 J·mol<sup>-1</sup>,  $\Delta G(Y_2O_2S)$  was -28,851.61 J·mol<sup>-1</sup>, so the inclusions of Y<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>2</sub>S precipitate in 200RE steel. When the rare earth content in the steel was 0.028 wt.%, the free energy of yttrium-containing inclusions in the steel were as follows:  $\Delta G(Y_2S_3)$  was 99,739.61 J·mol<sup>-1</sup>, so  $Y_2S_3$  inclusion was not precipitated in 280RE steel; the  $\Delta G(Y_2O_3)$  was -49,789.92 J·mol<sup>-1</sup>,  $\Delta G(Y_2O_2S)$  was -28,572.41 J·mol<sup>-1</sup> and  $\Delta G(YS)$  was -17,642.84 J·mol<sup>-1</sup>, so the inclusions of  $Y_2O_3$ ,  $Y_2O_2S$ and YS precipitate in 280RE steel. It can be seen from the above thermodynamic calculation, that rare earth oxides and rare earth oxysulfides can be formed in 90RE, 200RE and 280RE steels. Rare earth sulfides are only formed in 280RE steel.



Figure 6. Experimental steels inclusions Gibbs free energy at 1873K.

**Table 2.** First-order interaction coefficients  $e_i^j$  of various elements in molten EH36 steel at 1873K.

e_i^j	С	Si	Mn	Р	S	0	Al	Cr	Ni	Мо	Cu	Y
0	-0.45	-0.131	-0.021	0.07	-0.133	-0.2	-3.9	-0.04	0.006	0.0035	-0.013	-16.3
S	0.112	0.063	-0.026	0.029	-0.028	-0.27	0.035	-0.011	0	0.0027	-0.0084	-0.55
Y	-0.22	-	-	-	-7.34	-90.7	-	-	-	-		-0.006

Table 3. Activity and activity coefficients of O, S and Y in the molten EH36 steels.

Sample	$f_{[O]}$	$a_{[O]}$	$f_{[S]}$	$a_{[S]}$	$f_{[Y]}$	$a_{[Y]}$
90RE	0.45916	0.00069	0.97294	0.00097	0.68321	0.00615
200RE	0.30724	0.00034	0.96064	0.00096	0.74263	0.01485
280RE	0.23480	0.00023	0.95680	0.00096	0.75821	0.02123

Figure 7 shows the schematic of the evolution process of inclusions in the steel during the rare earth modification process. Before the addition of rare earth, inclusions in the steel were mainly  $Al_2O_3$ -MnS. With the increase in rare earth content in EH36 steel, rare earth oxides, rare earth oxygen sulfides and rare earth sulfides are formed successively. When the rare earth content in steel reaches 0.028 wt.%, the excess rare earth reacts with residual arsenic in steel to form rare earth arsenide.



**Figure 7.** Schematic of the evolution process of inclusions in the steel during the rare earth modification process.

### 3.1.3. Inclusions Size and Number Evolution

In order to explore the effect of different rare earth contents on the behavior of inclusions in EH36 steel plates, the metallographic samples were scanned and analyzed by an ASPEX explorer automatic scanning electron microscope and energy dispersive spectrometer. The region where the samples area was  $25.27 \text{ mm}^2$  was automatically analyzed and detected for non-metallic inclusions, and the total number density and average diameter of inclusions could be obtained with different rare earth contents, as shown in Figure 8. It can be concluded from Figure 8 that the total number density of inclusions in EH36 steel plate without rare earth treatment was 105.62/mm<sup>2</sup>. When the rare earth content in EH36 steel plates was 0.009 wt.%, 0.020 wt.% and 0.0280 wt.%, the quantity density of the total number of inclusions was 117.29/mm<sup>2</sup>, 191.97/mm<sup>2</sup> and 144.99/mm<sup>2</sup>, respectively. By comparison, the total number of inclusions in 200RE samples with rare earth content of 0.020 wt.% in steel were higher than those of other samples. Meanwhile, the average diameter of inclusions in 90RE and 200RE samples decreased by 9.25% and 14.45%, respectively compared with the 0RE sample, but the average diameter of inclusions in the 280RE sample increased by 5.3%, indicating that when rare earth in EH36 steel plates is in an appropriate range, the inclusions can be obviously refined and dispersed in steels.



**Figure 8.** Comparison of the total number density and average diameter of inclusions with different rare earth contents.

In addition, from the particle size distribution of inclusions in the samples with different rare earth content shown in Figure 9, it can be seen that the inclusions in the industrial EH36 steel plates all show a small distribution, in which the inclusions  $\leq 3 \mu m$  in 0RE steel plate without rare earth treatment account for 86.89% of the total, while, after rare earth treatment, the inclusions less than 3  $\mu m$  in 90RE, 200RE and 280RE samples account for 87.48%, 91.95% and 82.14% of the total, respectively. The proportion of inclusions  $\leq 3 \mu m$  in 200RE samples is the highest, indicating that the refinement effect of inclusions in the EH36 steel plate is the best under this rare earth content (0.020 wt.%).



**Figure 9.** Comparison of the (**a**) number density and (**b**) size distribution of inclusions with different rare earth contents.

The 200RE sample was selected for non-aqueous solution electrolysis analysis. Figure 10 shows the microscopic morphology of inclusions in 200RE steel after non-aqueous solution electrolysis under scanning electron microscope. Combined with the energy spectrum analysis of the non-aqueous solution electrolytic inclusions in Figure 10, it is found that there are a large number of small rare earth inclusions in 200RE steel with a size less than 3  $\mu$ m, which is consistent with the statistical results of ASPEX inclusions. Composition analysis shows that these inclusions are mainly composite inclusions containing rare earth oxides or rare earth oxygen sulfides, and the morphology is spherical or quasi-spherical dispersed in the steel.



**Figure 10.** Analysis of morphology and EDS of electrolytic inclusions in non-aqueous solution of 200RE steel.

# 3.2. Effect of Rare Earth on the Cryogenic Temperature Impact Properties

3.2.1. Impact Properties at Different Temperatures

The cryogenic temperature impact properties of EH36 steels with different rare earth contents are shown in Figure 11. According to the requirements of the national standard GB/T 712-2011, EH36 grade offshore engineering steels are required to have good impact properties under the condition of low temperature at -40 °C. From the results of Figure 11,

it can be seen that the impact absorption energy of steel increases with the increase in rare earth content at a cryogenic temperature of -40 °C. When the rare earth content is 0.020 wt.%, the impact absorption energy reaches the highest value of 300.7 J. However, when the rare earth content in the steel continues to increase to 0.028 wt.%, the impact energy absorption of the steel decreases rapidly to 93 J at this temperature, indicating that rare earth has an inhibitory effect on the impact properties of steel under this rare earth content.

In addition, the comparison of impact properties of EH36 steel with different rare earth contents at -60 °C and -80 °C are shown in Figure 11. It can be seen that after adding yttrium-based rare earth, EH36 steel still has good impact toughness at -60 °C and -80 °C under an appropriate rare earth content (0.009 wt.% and 0.020 wt.%). The impact properties exceed the national standard of steel plate of the same level by two levels. In particular, when the test temperature was -80 °C, the impact absorbed energy of 0RE steel increased by 245.1% from 78.7 J to 271.6 J (200RE steel). It has been reported that cerium and lanthanum could increase the impact properties by 74.7% for GCr15 bearing steel [23] and by 90% for H13 die steel [35]. It seems that yttrium-based rare earth increased the impact properties of the steel more effectively than cerium and lanthanum.



Figure 11. Comparison of cryogenic temperature impact properties of test steels.

Figure 12 shows the relationship between the impact properties at -80 °C and the proportion of inclusions  $\leq 3 \mu m$ . It can be concluded from Figure 12 that the more inclusions within 3  $\mu m$ , the better the cryogenic temperature impact properties of the steel plate. These fine spherical particles are dispersed in the steels, which realizes the rare earth oxide metallurgy function and effectively improves the cryogenic temperature impact properties of offshore engineering steel [36,37].





Figure 12. Relationship between impact properties and proportion of inclusions.

3.2.2. Morphology of Impact Fracture

Figure 13 displays the morphology of the impact fracture surface of test steels exposed at -80 °C. It can be seen from Figure 13a that the impact fracture surface of the 0RE steel was mainly characterized by a cleavage surface river pattern, and the impact fracture surface of the 280RE steel from Figure 13d shows similar characteristics. This indicates that when the cryogenic temperature impact absorption energy is at a low value, the impact fracture extends along the crystal surface, the cracks in the 0RE and 280RE steels resulted mainly from transgranular expansion when the steels impacted. In addition, the arsenide formed in 280RE steel has an adverse effect on the impact properties [38]. With the appropriate rare earth addition, many dimples are formed in the fracture surface area of 90RE and 200RE steels. Small equiaxial dimples are distributed near the large deep dimples and many small spherical inclusions lie in the bottom of the dimples. As shown in Figure 13b,c the impact fracture surface consists of dimples, and petal-shaped fracture edges exist between these dimples, indicating that the 90RE and 200RE steels have undergone significant plastic deformation prior to fracture.

In Figure 13b,c it can be seen that with the addition of yttrium-based rare earth, the 90RE and 200RE steels contain small spherical inclusions that are distributed on the matrix interface of the steel. Figure 14 shows that these spherical inclusions are mainly rare earth complex inclusions. Compared with irregular shape inclusions, these spherical rare earth inclusions reduce the stress concentration of inclusions during crack expansion. It can be seen that the dimples of 200RE steel are larger and deeper than those of 90RE steel, so it can absorb more impact energy. In summary, with the appropriate yttrium-based rare earth addition, the spherical rare earth inclusions on the interface of the 90RE and 200RE steels yield increased crack expansion work and a considerable improvement in the cryogenic temperature impact toughness of the steel. The impact fracture of the steels transitions from a cleavage fracture to a dimple fracture.



**Figure 13.** Fracture morphology of impact specimens with different yttrium-based rare earth contents at -80 °C of (a) 0RE steel; (b) 90RE steel; (c) 200RE steel; (d) 280RE steel.



Figure 14. Impact fracture morphology and EDS of (a) 90RE steel and (b) 200RE steel.

The above results and analyses indicate that adding appropriate yttrium-based rare earth to EH36 offshore engineering steel can increase the number density and refine the particle size of inclusions, and improve the cryogenic temperature impact properties of EH36 steel, but excessive rare earth will result in an undesired increase in the average diameter of inclusions and a deterioration in impact properties.

#### 4. Conclusions

In this study, the effect of yttrium-based rare earth on inclusions and cryogenic temperature impact properties of EH36 offshore engineering steel was investigated. The main results are summarized as follows:

- (1) Yttrium-based rare earth addition could modify irregular Al<sub>2</sub>O<sub>3</sub> and MnS inclusions into spherical or quasi-spherical rare earth inclusions. With the increase in rare earth content, the reaction sequence of RE and potential inclusion forming elements should be O, S, As and P.
- (2) The addition of yttrium-based rare earth refines the inclusions. Comparatively, the proportion of inclusions  $\leq 3 \mu m$  in 200RE steel is the highest, which account for 91.95% of total inclusions, and the dispersion effect is optimal.
- (3) The cryogenic temperature impact properties of EH36 steels increased along with increasing RE content (0~0.020 wt.%), the impact fracture changes from a typical cleavage fracture to a dimple fracture containing small, spherical, regular rare earth inclusions, and the excess rare earth (0.028 wt.%) reacts with the residual arsenic in steel to form the rare earth arsenide, causing the impact energy absorption of the 280RE steel to decrease rapidly.
- (4) The optimal impact toughness is found in EH36 offshore engineering steel with 0.020 wt.% yttrium-based rare earth, and the cryogenic temperature impact properties were increased by 245.1% at -80 °C.

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