EFFECT OF Ce ON THE MICROSTRUCTURE AND PROPERTIES OF 27Cr-4Mo-2Ni SUPER-FERRITIC STAINLESS STEEL WITH 800 °C AGING

VPLIV DODATKA CERIJA NA MIKROSTRUKTURO IN LASTNOSTI SUPER FERITNEGA NERJAVNEGA JEKLA VRSTE 27Cr-4Mo-2Ni PO STARANJU NA 800 °C

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The influence of Ce additions on the microstructure and properties of 27Cr-4Mo-2Ni super-ferritic stainless steel during 800 °C aging was systematically investigated via thermodynamic calculations, microstructural characterizations, impact and corrosion measurements. The results indicated that with an increase of Ce content from 0.00 w/% to 0.050 w/%, Al2O3 wrapped by TiNb(CN) were gradually modified into CeAlO3 wrapped by TiNb(CN), spheroidal Ce2O3, and Ce2O2S, the ferrite grain was noticeable refined, the \( \sigma \) phase changed from continuously distributed with a coarser size to dispersedly distributed with a tiny size accompanied by an increase in number, the impact toughness of super-ferritic stainless was improved at 25 °C, and the cleavage facets at the morphology of a fully brittle fracture becomes smaller, the uniform corrosion resistance of super-ferritic stainless steel to 40 w/% H2SO4 were enhanced especially at 60 °C.

Keywords: cerium, microstructure, properties, ferritic stainless steel

1 INTRODUCTION

27Cr-4Mo-2Ni super-ferritic stainless steel (SFSS) exhibits excellent thermal conductivity, lower linear expansion, and outstanding resistance to stress corrosion cracking, which is widely used as the pipeline, heat exchanger, and condenser to replace more expensive super austenitic stainless steel (SASS) and nickel-based alloy.1,2 However, two factors limit the extensive usage of SFSS. First, due to the high content of alloying elements, several brittle and hard intermetallics such as \( \sigma \) and Laves phases are easily formed in the microstructure during industrial production, which are enriched in Cr or Mo.3–5 Second, because of the ultra-low content of C, SFSS maintains a BCC ferrite structure below the melting temperature, this eliminates the possibility of grain refinement through phase transition.6 Therefore, the precipitation of intermetallics and structure coarsening are the main factors increasing the risk of brittle fracture and uniform corrosion degradation of the final products, which is urgently in need of a solution.

The dependence of mechanical properties and corrosion resistance on precipitation behavior for SFSS was discussed,7 the \( \sigma \) and Laves have been found after aging at 950 °C for 0.5h, which decreased the ductility and hardness of the materials and can dissolve into the matrix after solution treatment at 1100 °C for 0.5 h.8 This demonstrates that solution treatment is an effective method to control the segregation of alloying elements, but it’s not conducive to ensure the uniformity and refinement of ferrite microstructure. In fact, the precipitation of all of 25Cr-3Mo-4Ni,7 25Cr-4Mo-3Ni,9 28Cr-2Mo-4Ni-Nb,10 29Cr-4Mo,11 and 29Cr-4Mo-2Ni SFSS have already been studied, aiming to report the systematic effects of the precipitation behaviour for SFSS and their negative effects over the past several decades; however, there is little research on the precipitation behaviours and properties of SFSS containing rare earths (REs).
RE elements in steel can purify molten steels, modify inclusions and act as micro-alloying elements, which are widely known. RE transforms the angular inclusions such as Al₂O₃, and MnS into spherical ReₓOᵧ and ReₓOᵧS, which disperse as solid particles to trigger any grain refinement.¹⁴ Solute RE can also improve the elemental segregation and purify the grain boundary. So far, several research works have focused on the application of RE on the precipitation of intermetallics in super duplex stainless steel (SDSS) and SASS,¹⁵–¹⁹ and whether the rare earth Ce can play a beneficial role in improving the microstructure, precipitation behaviors and properties of 27Cr-4Mo-2Ni SFSS during 800 °C aging is worth systematically studying.

2 EXPERIMENTAL PART

In this study, three 27Cr-4Mo-2Ni SFSS cast ingots with different Ce contents were melted in a 30-kg vacuum induction furnace. The smelting process was as follows. Firstly, pure Fe, Ni, Mo, and Cr were melted in a crucible at 1550–1600 °C under a vacuum. Secondly, adding Al, Si, Nb, and Ti in this order in small amounts. Thirdly, Mn was added after 3 min. Finally, Ce was added to the molten steel and cast into an ingot after 2.5 min.

The ingots with a diameter of 100 mm were hot forged to slabs of 40 mm × 220 mm × 65 mm at 1150–1200 °C. The slabs were hot rolled into 6-mm plates at 1250 °C. The chemical compositions of three SFSS samples were measured by inductively coupled plasma mass spectrometry, as shown in Table 1.

Samples with dimension of 10 mm × 10 mm × 6 mm were cut from the centre of each hot-rolled plate. After a solution treatment at 1080 °C for 5 min followed by water quenching, three SFSS samples were aged at 800 °C for 10 min. The samples were ground using 320-2000# SiC sandpapers and polished with diamond pastes (5 μm and 1 μm), then etched in 10 wt% oxalic acid (H₂C₂O₄) solution at 3.0 V for 90 s.

Table 1: Chemical compositions of SFSS samples, w/%

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>N</th>
<th>O</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce0</td>
<td>0.012</td>
<td>0.007</td>
<td>0.0024</td>
<td>27.0</td>
<td>2.1</td>
<td>4.0</td>
<td>0.24</td>
<td>0.22</td>
<td>0.06</td>
<td>0.007</td>
<td>0.0031</td>
<td>0</td>
</tr>
<tr>
<td>Ce0.035</td>
<td>0.013</td>
<td>0.006</td>
<td>0.0022</td>
<td>27.1</td>
<td>2.0</td>
<td>3.9</td>
<td>0.26</td>
<td>0.22</td>
<td>0.05</td>
<td>0.007</td>
<td>0.0026</td>
<td>0.035</td>
</tr>
<tr>
<td>Ce0.050</td>
<td>0.013</td>
<td>0.006</td>
<td>0.0015</td>
<td>27.1</td>
<td>2.1</td>
<td>3.9</td>
<td>0.27</td>
<td>0.23</td>
<td>0.05</td>
<td>0.006</td>
<td>0.0020</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Microstructural characterizations were performed utilizing several complementary analysis techniques, such as OM, SEM along with chemical analysis by EDS and TEM. The impact toughness was evaluated using plate impact test samples (thickness of 5 mm) with a Charpy-V notch, as shown in Figure 1. Samples for uniform corrosion tests were machined according to GB 10124 - 88 with a size of 5 mm × 25 mm × 50 mm, and a hole with a diameter of 3 mm in the upper part of the samples was drilled. Samples were abraded with 600# SiC paper and immersed in 40 wt% H₂SO₄ for 24 h at 25 °C and 60 °C, then the weight loss was calculated from measurements before and after the experiment.

3 RESULTS AND DISCUSSION

3.1 Inclusion analysis

The relationship between Ce content and types of inclusions was calculated by thermodynamic database of FactSage 7.2 based on the chemical composition of experimental steels. As shown in Figure 2a, CeAlO₃ has
the most stable region to generate, and under the condition of low-S content ($S < 0.004$ wt%), the transition behaviour of the inclusion is $\text{CeAlO}_3 \rightarrow \text{CeAlO}_3 + \text{Ce}_2\text{O}_3 \rightarrow \text{Ce}_2\text{O}_3$ with a decrease of O content. When $S > 0.004$ wt%, $\text{CeAlO}_3$ tends to transform into $\text{Ce}_2\text{O}_3$ with a decrease in O content. In the Ce0.050 steel (Figure 2b), with increasing Ce content, the stable region of $\text{CeAlO}_3$ tends to disappear while the stable region of $\text{Ce}_2\text{O}_3$ and $\text{Ce}_2\text{O}_2\text{S}$ appears. The necessary condition for $\text{Ce}_2\text{O}_2\text{S}$ precipitation was that the S content is higher than 0.0019 wt%. The red dots in Figure 2a and Figure 2b corresponds to the O and S contents in the Ce0.035 steel and Ce0.050 steel, respectively. Changes in the locations of the red dots show that $\text{CeAlO}_3$ will transform to $\text{Ce}_2\text{O}_3$ within the scope of the calculation in experimental SFSS.

Figure 3 shows the typical inclusions analysed by SEM. In the Ce0 steel (Figure 3a), the main type of inclusion is TiNb(CN)$\cdot$Al$_2$O$_3$. Al$_2$O$_3$ is wrapped by TiNb(CN) with a size of approximately 2.5 μm. In the Ce0.035 steel (Figure 3b), TiNb(CN)$\cdot$Al$_2$O$_3$ is modified into TiNb(CN)$\cdot$CeAlO$_3$ by Ce. With the Ce content increasing, inclusions in the Ce0.050 steel (Figure 3c and Figure 3d) are completely modified into globular $\text{Ce}_2\text{O}_3$ and $\text{Ce}_2\text{O}_2\text{S}$ with a size of 1 μm. In addition, typical TiNb (CN) inclusions are found in three samples (Figure 3e) due to the strong affinity of C or N with Ti and Nb, its size is smaller than the composite inclusions of TiNb(CN)$\cdot$Al$_2$O$_3$ and TiNb(CN)$\cdot$CeAlO$_3$.

Figure 4 shows the formation mechanism of typical inclusions with different Ce content in SFSS. In the smelting process, Ce will react with Al$_2$O$_3$ to form CeAlO$_3$, $\text{Ce}_2\text{O}_3$ and $\text{Ce}_2\text{O}_2\text{S}$ successively with the increase of Ce content. And in the solidification process, Nb, Ti, C, N elements are enriched in the liquid phase of the solidification front, as the solidification process continues, the actual activity product of TiNb(CN) becomes larger than the equilibrium activity product of TiNb(CN). Therefore, single TiNb(CN) inclusions start to precipitate at the solidification front, meanwhile, the vast majority of Al$_2$O$_3$ and CeAlO$_3$ act as the nucleation core of TiNb(CN) to form the wrapped composite inclusion, while Ce$_2$O$_3$ and Ce$_2$O$_2$S hardly acts. Therefore, the inclusions in the Ce0.050 steel are mainly single TiNb(CN), Ce$_2$O$_3$ and Ce$_2$O$_2$S, which results in a decrease in the size of the inclusion.

3.2 Microstructure analysis

Figure 5 presents the microstructure of samples during 800 °C aging for 10 min followed by water quenching. All three samples contain a single ferrite phase due to the high Cr and Mo and the ultra-low contents of C and N. The statistic of grain size was measured by using image analysis according to GB/T 6394-2002. Figure 5d shows that the average grain size decreases, apparently by 22.16 % (from 127.3 μm to 99.1 μm) with Ce content.
increasing from 0% to 0.050%, which indicates that a small amount of Ce can refine the ferrite grain.

The refinement mechanism of Ce addition on aged-ferrite grain can be discussed from two aspects. For one thing, Ce₂O₃, Ce₂O₂S can exist stably in molten steel and act as nucleation particles to refine the ferrite grains, which depends on the lattice disregistry between them, according to the two-dimensional lattice disregistry proposed by Bramfitt, when the disregistry is less than 12%, heterogeneous nucleation will occur, and when less than 6%, it is extraordinarily favourable for heterogeneous nucleation. The lattice disregistry between (0001) Ce₂O₃, (0001) Ce₂O₂S and (111) δ-Fe is 6.19% and 3.5%, this indicates that both Ce₂O₃ and Ce₂O₂S can effectively improve the aged-ferrite grain. For another thing, the radius of Ce atoms is 50% larger than that of Fe atoms, when Ce atoms are mixed in the solid state with Fe matrix, stress fields are created around each Ce atom, this will hinder the coarsening of grains during aging. In summary, the ferrite grain of aging-treated SFSS is effectively refined by a Ce addition.

The precipitation of intermetallic phases was also observed. It can be seen that numerous dark and irregular precipitates are formed at ferrite grain boundaries. In the Ce₀ steel (Figure 5a), precipitates distribute concentrated, with a larger size and smaller quantity. When the Ce content is 0.035% (Figure 5b), precipitates become fine and dispersed with larger amounts. With increasing Ce content, precipitates at the grain boundary become less noticeable, the size of precipitates is small with a scattered distribution (Figure 5c). To further clarify the variation of the equivalent diameter (d) and number den-
sity \((N_b)\) of intermetallic precipitates at grain boundaries with Ce content, the number and size of precipitates were measured by metallographic image-analysis software, at least 50 particles in each steel were measured and averaged to reduce the experimental errors. As can be seen obviously (Figure 6), Ce addition leads to a noticeable decrease by 42.9 % (from 19.8 μm to 11.3 μm) in the size of precipitates. On the contrary, the number density of precipitates increases by 44.0 % (from 121.2 mm² to 174.5 mm²). It can be concluded that the addition of Ce leads to a decrease in the equivalent diameters and an increase in the number density of precipitates.

In order to further observe and analyse the effect of Ce on the precipitates, SEM along EDS was applied. With the increasing Ce content, precipitates at the grain boundary develop from continuous networks with coarser size into discontinuous distribution, as shown in Figure 7a to 7b. When the Ce content is 0.050 % (Figure 7c), the precipitates at grain boundaries become less, and the colour of the precipitates at boundary changes from dark to lighter. In addition, rod or elliptical precipitates are observed and randomly distributed in the grain interior of all three samples. Table 2 and Table 3 present, respectively, the elemental compositions of precipitates at the grain boundary and in the grain interior, at least 25 particles in each steel were measured and averaged to reduce experimental errors. Previous studies found that the \(\sigma\) phase mainly consists of Fe, Cr, and Mo, whereas the Laves phase is enriched with Nb and Mo. In this study, precipitates at the grain boundary are enriched in Cr, and for precipitates in the grain interior, apart from enriched in Mo, Nb and Si, elements are dissolved, where the Nb content is up to 12 %. Figure 8 shows the TEM images and SAD of typical intermetallics in aged SFSS. The results show that precipitates at grain boundaries are \(\sigma\) phases (Figure 8a), \(\sigma\)-phase possesses a tetragonal structure (P42/mmc space group) with lattice parameters of \(a = 0.88–0.92\) nm, \(c = 0.45–0.48\) nm and \(C = 0.52\) nm, precipitates in the grain interior are identified as Laves phases (Figure 8b). The Laves phase is approximatively \((\text{Fe,Cr,Ni})_2(\text{Mo,Nb,Si})\) with a hexagonal structure (P63/mmc space group) and lattice parameters of \(a = 0.473\) nm and \(c = 0.772\) nm. It is worth noting that some \(\sigma\) phases precipitating around Ce\(_2\)O\(_3\) in Ce-bearing SFSS were observed, the lattice disregistry between \((\#)\text{Ce}_2\text{O}_3\) and \((111)\sigma\) is about 5.0 %, this indicates that Ce\(_2\)O\(_3\) remaining in residual liquid phase can serve as heterogeneous nucleation sites for \(\sigma\)-phase. Few Laves phases precipitated around Ce\(_2\)O\(_3\) were also observed (Figure 9a), but the relationship between Laves phase and Ce content is not obvious in this study.

![Figure 7: SEM images of Ce bearing SFSS samples after aging at 800 °C for 10 min: a) Ce0 steel; b) Ce0.035 % steel; c) Ce0.05 % steel](image-url)
The effect of Ce on the formation and distribution of the \( \sigma \) phase in SFSS during 800 °C can be inferred from Figure 10. Firstly, Ce could refine the size of the ferrite grains because of a superb mismatch between Ce\(_2\)O\(_3\) and Ce\(_2\)O\(_2\)S and \( \delta \)-Fe, and it is well known that intermetallic phases in steels preferentially precipitate at crystal defects, such as the boundaries of grains, particles and vacancies,\(^{22}\) the smaller the grain of SFSS, the higher the grain density, which means the larger the number of crystal boundaries. This makes \( \sigma \) phase have a larger quantity and smaller size (Figure 10b and Figure 10d). Secondly, it is worth noting that the \( \sigma \) phase tends to precipitate around Ce\(_2\)O\(_3\) in Ce-bearing SFSS, as shown in Figure 9.
Ce2O3 inclusions could serve as points of heterogeneous nucleation for the α phase. Moreover, the data in Table 2 show a trend that the addition of Ce reduces the composition of Cr and Mo in the α phase. This may be due to that solute Ce elements segregating at the grain boundaries, which improves the segregation of Cr and Mo (Figure 10a and Figure 10c). Since the growth of α was inhibited due to the insufficient Cr supply and the increased density of grain boundaries, adding Ce into SFSS could suppress the formation of the α-phase.

3.3 Impact properties and corrosion resistance

Figure 11d presents the impact energy of three samples aged at 800 °C for 10 min. With the increasing content of Ce, the impact performance of the material has been improved from 26.5 J to 35.2 J, which suggests that the impact toughness of aged SFSS has been enhanced by the Ce element. The fracture morphology of aged SFSS at 25 °C was observed (Figure 11a to Figure 11c). All three samples show a fully brittle fracture, and there are many river patterns and cleavage facets on the surface of samples. It should be noted that adding Ce leads to a reduction of cleavage facets and steps.

For SFSS, the number of effective slip lines in the BCC structure is less than that of in the FCC structure, which causes a higher probability of crack formation and propagation. Cracks mostly begin with grain boundaries and metallurgical defects, after adding Ce, inclusions become globalized, which could withstand more stress con-
4 CONCLUSIONS

The effect of Ce in the range of 0–0.050 wt.% on the microstructure, mechanical properties and corrosion resistance of 27Cr–4Mo–2Ni SFSS during 800 °C aging were studied. According to the experimental results, the following conclusions could be drawn:

1. With the increase of Ce content from 0 to 0.050 wt.%, TiNb(CN)·Al2O3 will transform into TiNb(CN)CeAlO3, CeO2 and Ce3O7 in order, and the TiNb(CN)·Al2O3 inclusions with the diameter of 2.5 μm are effectively refined to 1 μm. Al2O3 and CeAlO3 inclusions could serve as the nucleation core of TiNb(CN) to form TiNb(CN)Al2O3 and TiNb(CN)CeAlO3 inclusions during the solidification process, while Ce2O3 and Ce2O5 hardly serves.

2. The ferrite grain of 800 °C aging-treated SFSS is effectively refined by Ce addition from 127.3 μm to 99.1 μm, which could be attributed to the combined actions of Ce-bearing inclusions and solute Ce.

3. The addition of Ce promotes σ-phase at grain boundaries more dispersed with smaller size from 19.8 μm to 11.3 μm, it also increases the number of σ-phase from 121.2 / mm² to 174.5 / mm². For one thing, the grain refinement makes the precipitation area of the σ phase more dispersed and limits its grow space; for another, this could be attributed to a superb matching degree between the Ce2O3 and the σ phase.

4. The addition of Ce improves the impact toughness of 800 °C aging-treated SFSS from 26.5 J to 35.2 J (25 °C), and leads to a reduction of cleavage facets and steps at the morphology of a fully brittle fracture. At the same time, Ce additions enhance the uniform corrosion resistance to 40 φ/%H2SO4, especially at 60 °C. The impact-toughness improvement could be caused by the combined influence of refinement in the ferrite grain and the σ-phase, as well as the modification of inclusions by Ce. The strengthening of the uniform corrosion resistance of SFSS could be attributed to the effect of the solute Ce, which is conducive to refine the grains and alleviate the segregation of Cr and Mo and enhance the uniformity of the grain and alloying element.

Acknowledgments

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