High-temperature corrosion behavior of TP91, C22 alloy and C22 based on laser coatings in simulated reducing corrosion environment

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Abstract

To explore corrosion characteristics of TP91, C22 alloy and C22 laser coatings in reducing environment caused by low-nitrogen combustion at 500 °C–600 °C, a synthetic corrosive medium containing 0.2 vol% H2S-0.1 vol% O2–N2 were selected. Results showed that the order of corrosion resistance is: C22 laser coatings > C22 alloy > TP91. 550 °C was the limit temperature for C22 alloy and C22 laser coatings. The reason for the strong corrosion resistance of C22 alloy and C22 laser coatings is that a dense layer of Cr-rich corrosion products due to the is produced in the inner layer, thus protecting the matrix from direct corrosion by corrosive gas. Finer grains before corrosion tests and the formation of dense Cr2O3 inner layers in much speedier process were the main reasons for the best corrosion resistance of C22 laser coatings.

1. Introduction

Low nitrogen combustion technology is widely used in coal power plants to reduce the emissions of NOx. However, the use of nitrogen combustion technology generates a large amount of H2S and the deposits are mainly composed of sulfides of various elements, leading to a reducing environment in boiler area. It is well known that corrosion in reducing environment is more severe than in oxidizing environment due to the formation of the porous, nonadherent and unprotected sulfide scales on the surface of water wall [1–3]. Materials used for the boiler water wall, superheater tube and low-NOx burners are particularly susceptible to sulfidation attack by both H2S in the gas and sulfides (such as pyrite) in the deposits, which gives rise to the severe failure of them.

Therefore, to extend the service life of materials for boiler water wall, superheater tube and low-NOx burners, various approaches have been used, such as using more corrosion-resistant materials and employing surface modification technology. Ni–Cr–Mo alloys are widely used in modern industry because of their outstanding resistance to pitting corrosion [4], crevice corrosion [5] and stress-corrosion cracking [6–8]. A large number of studies have shown that Ni–Cr–Mo alloys has strong corrosion resistance in oxidized environment at high-temperature [9, 10]. Element Cr plays an important role in ensuring better corrosion resistance of Ni–Cr–Mo alloy by forming a dense protective oxide scale [11–14] and preventing intergranular corrosion [15]. Mo shows resistance to localized corrosion because it can promote fast repassivation by forming Mo insoluble compounds [14, 16]. However, there haven’t been much studies aimed at high-temperature corrosion of Ni–Cr–Mo alloys in reducing atmosphere.

As a surface modification technology, laser-cladding technology has excellent properties of high energy density, metallurgical bonding, low dilution rate, refined microstructure and small heat affected zone [17–19], which is an effective means to obtain excellent surface properties. Using laser cladding technology to prepare a corrosion resistant laser coatings on the surface of the material, not only can improve the corrosion resistance,
but also reduce the cost effectively [9, 20–23]. Furthermore, studies [9, 10] show that the high-temperature corrosion resistance of C22 laser coatings is better than that of C22 alloy (a typical Ni–Cr–Mo alloy) due to its fine grain size. In previous work [24], the corrosion resistance of C22 laser coatings in reducing atmosphere at 450 °C was studied. Results show that C22 laser coatings show excellent corrosion resistance in reducing environment at 450 °C. However, the corrosion resistance of laser coatings at higher temperature needs to be further studied to meet the challenge of increasing boiler temperature.

In this work, in order to better understand the influence of high-temperature (500 °C, 550 °C and 600 °C) on the corrosion resistance in reduction atmosphere, a comparative study was carried out between TP91, C22 alloy and C22 laser coatings in reduction atmosphere simulating H2S corrosive environment caused by low-NOx combustion. The phase of corrosion products and the morphology of corrosion layers were discussed thoroughly, and the corresponding corrosion behaviors and chemical reactions of TP91, C22 alloy and C22 laser coatings during corrosion tests were presented in detail.

2. Materials and experimental methods

Bulk specimens with 20 mm × 10 mm × 3 mm in size of TP91 stainless steel, C22 alloy and C22 laser coatings were prepared in this study. TP91 samples were cut from a commercial superheater tube and C22 alloy samples were cut from a forged piece made of pure C22 alloy. C22 laser coatings samples were fabricated using a self-assemble coaxial laser cladding device equipped with 2000W high-power fiber laser with beam spot diameter of 1.4 mm and the focal length of 30 mm (ZKZM-2000, ZKzM Laser Technology Co., Ltd, Xi'an, China), a self-designed coaxial powder feeding nozzle ejecting three powder streams and an argon shielding system (the nozzle diameters is 5 mm and angle of nozzles with respect to laser beam is 20°). The photograph of the cladding system is presented in previous work [24]. Chemical compositions of samples are shown in table 1 including the C22 powders used in the cladding process for preparing the laser coatings. Commercial C22 powders with a diameter in the range of 46–150 μm were offered by Beijing General Research Institute of Mining and Metallurgy (BGRIMM), Beijing, China.

The substrate of C22 laser coatings was TP91 stainless steel, which was polished and then cleaned with acetone before cladding. In order to reduce the negative influence of Fe diffusion, the thickness of C22 laser coatings prepared on the TP91 substrate was more than 5 mm through a multi-track and multilayer cladding process. Schematic diagram of laser cladding process was shown in [23]. The optimum working parameters determined by previous experiments were as follows: beam spot was 1.4 mm in diameter, laser power was 2000 W, overlap ratio was 40%, laser scan speed was 8 mm s⁻¹ and flow rate of argon was 5 l min⁻¹.

Isothermal corrosion tests were carried out in a horizontal tube furnace for 168 h (24 h × 7) at 500 °C, 550 °C and 600 °C. To simulate the reducing environment caused by low-nitrogen combustion in coal power plants, a synthetic gas mixture containing 0.2 vol% H2S-0.1 vol% O2—N2 was selected as the corrosive medium. The gas flow rate was set at 100 ml min⁻¹ and temperature accuracy of the furnace was ±1 °C. Before corrosion test, all samples were grounded using SiC sandpaper from 200# to 1200#, then degreased using an ultrasonic cleaner with medium of acetone followed by being cleaned with deionized water and dried in a desiccator. Each sample had three specimens. In order to keep experimental reproducibility and data consistency, three specimens of each samples were placed in the same position in crucible boat and the crucible boat was also placed in the same position in tube furnace during every corrosion cycle. A balance with accuracy of 0.0001 g was used to measure the mass gain after every corrosion cycle. The final mass gain data of each samples was the average value of three specimens.

Table 1. Chemical compositions of TP91, C22 alloy and C22 powders in wt%.

| Element | Ni | Cr | Mo | Mn | Fe | Si | Co | V | W | C |
|---------|----|----|----|----|----|----|----|---|---|---|
| TP91    | 0.4| 8.75| 0.95| 0.45| Bal| 0.35| —  | 0.22| — | 0.105 |
| C22 alloy | Bal | 20.0| 13.8| 0.45| 5.0 | 0.08| 1.83| 3.2 | 0.08 |
| C22 powders | Bal | 21.3| 13.2| —  | 2.93| —  | 2.0 | —  | 3.0 | 0.08 |

The phase constitution of corrosion products was detected by Rigaku D-max-rA X-ray diffract meter with Cu Kα radiation, between 20 angles of 10° and 110° at a scanning rate of 8°/min. The morphology of corrosion layers was analyzed by scanning electron microscopy (SEM, FEI Quanta 200 F) combined with energy dispersed X-ray spectroscopy (EDS, EDAX). The specimens for the observation of cross section after corrosion test were embedded in the epoxy resin to protect the corrosion layer from spalling. All XRD and SEM specimens were wet ground through SiC sandpaper to 1200# followed by polishing and cleaning used alcohol.
3. Results

3.1. Corrosion mass gain curves and products of TP91 stainless steel

Figure 1 presents the mass gain of TP91 corroded in 0.2 vol% H2S-0.1 vol% O2–N2 for 168 h at 500 °C, 550 °C and 600 °C. As shown in figure 1, the mass gain increases rapidly at beginning and then the increasing trend slows down. The mass gain curves of TP91 at 500 °C–600 °C all show a near-parabolic law. At 500 °C, the final corrosion mass gain is only about 13.26 mg cm$^{-2}$. However, the final corrosion mass gains at 550 °C and 600 °C are 20.9 mg cm$^{-2}$ and 23.63 mg cm$^{-2}$, respectively, which are almost twice than that at 500 °C. This phenomenon indicates the corrosion resistance decreases rapidly when the corrosion temperature exceeds 550 °C. The detailed corrosion mechanism will be discussed in section 4.1.

Figure 2 displays the XRD patterns of corrosion products formed on the surfaces of TP91 corroded in 0.2 vol% H2S-0.1 vol% O2–N2 for 168 h at 500 °C–600 °C. Peaks from FeS2, Fe7S8, Fe2O3 and Fe0.98O phases are detected. At 500 °C, the main phases on the surface are Fe7S8 and FeS2 with a small amount of Fe2O3. At 550 °C, the phases are mainly Fe7S8. At 600 °C, the corrosion products are mainly Fe2O3 and Fe0.98O, no sulfides of iron are detected. It can be concluded from the XRD patterns that the corrosion scale formed at surface at 500 °C–550 °C are mainly composed of Fe-rich sulfides, while that at 600 °C are composed of Fe-rich oxides.
At low corrosion temperature of 500 °C, the slope of mass gain curves becomes small and the increase tendency becomes slow, showing a parabolic law.

Table 2: EDS spot scan results for TP91 in figure 3.

| Temperature | Spot | Elements (at%) |
|-------------|------|---------------|
| 500 °C      | A    | S 5.92, Fe 29.07, O 60.32, Cr 0.79, Mo 4 |
| 550 °C      | B    | S 44.9, Fe 44.29, O 5.74, Cr 1.89, Mo 3.18 |
| 600 °C      | C    | S 0.12, Fe 35.19, O 61.38, Cr 0.13, Mo 3.1 |

Figure 3 shows the SEM images for the corrosion surface of TP91 corroded in 0.2 vol% H2S-0.1 vol% O2−N2 at 500 °C–600 °C. Table 2 displays the EDS results for typical phases in figure 3. As shown in figure 3(a) spot A, the corrosion surface at 500 °C is covered by bulk-shaped phases containing 60.3 at% O and only 5.9 at% S. This result indicates that there is an oxide layer on the surface of TP91 at 500 °C rather than a sulfides layer as detected in XRD patterns shown in figure 2. This phenomenon is due to the peeling of oxides layer during XRD test. The binding between the outermost oxides layer and the inner sulfides layer is not strong enough. As a result, the outermost oxides layer was easy to be peeled off during XRD test and the inner sulfides are detected in XRD patterns. The multi-layer structure of corrosion products can be observed in the cross-section of corroded TP91 which will be discussed in section 4.1.

When the test temperature rises to 550 °C, lamellar-shaped corrosion products can be observed on the surface as shown in figure 3(b). The lamellar-shaped product contains a large amount of S and a small amount of O (spot B) indicating the surface corrosion products are mainly sulfides. This result is in agreement with XRD patterns. The sulfides layer grows outward during corrosion test resulting in a porous and loose corrosion surface which plays a negative role in hindering the further corrosion progress. This conclusion is also confirmed by the cross-sections of corrosion layer discussed later.

At 600 °C, the cracks and pores are more obvious than that at 550 °C as shown in figure 3(c). The lamellar-shaped morphologies become thicker and are covered with irregular-shaped phases. Spot C shows elements distribution of the irregular-shaped phase, containing 62.38 at% O and only 0.12 at% S. This phenomenon is due to the oxidation of sulfides at 600 °C. The lamellar-shaped sulfides were oxidized into Fe2O3 and Fe0.98O (mainly loose and porous Fe2O3) and a Fe-rich oxides layer were formed during corrosion test. The EDS results are consistent with the XRD phase constitution.

3.2. Corrosion layer and behavior of C22 alloy and C22 laser coatings

Figure 4 presents the mass gain curves of C22 alloy and C22 laser coatings corroded in 0.2 vol% H2S-0.1 vol% O2−N2 for 168 h at 500 °C, 550 °C and 600 °C. It can be seen that the mass gain increases rapidly at first and then the slope of mass gain curves becomes small and the increase tendency becomes slow, showing a parabolic law. At low corrosion temperature of 500 °C, the final corrosion mass gain of C22 alloy and C22 laser coatings are only 0.26 mg cm−2 and 0.38 mg cm−2, respectively. However, at high corrosion temperature of 550 °C and 600 °C, the final corrosion mass gain of C22 alloy (2.87 mg cm−2 at 550 °C and 3.60 mg cm−2 at 600 °C) and C22 laser coatings (2.75 mg cm−2 at 550 °C and 3.01 mg cm−2 at 600 °C) increase significantly, which is almost 10 times higher than that at 500 °C as shown in figure 4. Therefore, corrosion temperature plays an important role on the corrosion resistance ability. The limit corrosion temperature of C22 alloy and C22 laser coatings at reducing atmosphere of 0.2 vol% H2S-0.1 vol% O2−N2 is 500 °C. Compared with the final mass gain of TP91 (20.9 mg cm−2 at 550 °C and 23.63 mg cm−2 at 600 °C) in figure 1, it can be concluded that, although the mass gain of C22 alloy and C22 laser coatings increase rapidly above 500 °C, the corrosion resistance ability of C22 alloy and C22 laser coatings is still much better than TP91. What’s more, as shown in figure 4, the final mass gain...
of C22 laser coatings at 550 °C and 600 °C is lower than C22 alloy and the mass gain curves of C22 laser coatings are gentler, indicating a better corrosion resistance of C22 laser coatings compared with C22 alloy.

Figure 5 displays the X-ray diffraction patterns of surface corrosion products of C22 alloy and C22 laser coatings. Peaks from NiS, NiS₂, Cr₂O₃, Cr₃O₄, Cr₂S₃ and [Fe,Cr]₂O₃ phases are detected. At 500 °C, the corrosion products of C22 alloy and C22 laser coatings are the same. The corrosion layer is mainly composed of NiS phase and little Cr₂O₃. The peaks of the matrix (Ni-Cr-Mo-Co) is also detected. At 550 °C, the main phases of corrosion products of C22 alloy are NiS and NiS₂ while the main phases of C22 laser coatings is NiS₂ and Ni₂S₃. [Fe,Cr]₂O₃ phase is also observed both in C22 alloy and in C22 laser coatings. At 600 °C, both C22 alloy and C22 laser coatings contain NiS, Cr₂S₃ and Cr₃O₄ phases. In general, the corrosion surface of C22 alloy and C22 laser coatings at 500 °C−600 °C is mainly composed of kinds of Ni-rich sulfides.

Figure 6 shows the surface micrographs for C22 alloy and C22 laser coatings corroded in 0.2 vol% H₂S−0.1 vol% O₂−N₂ for 168 h at 500 °C, 550 °C and 600 °C. Table 3 displays the EDS results for typical phases in figure 6. As shown in figure 6(a1), the C22 alloy surface after corroding at 500 °C is covered by discontinuous particle-shaped corrosion products. EDS results of spot A1 show that the particle-shaped corrosion products contain 39.2 at% Ni and 40.2 at% S with less Cr and O. Combining with the XRD patterns in figure 5, it can be concluded that the particle-shaped corrosion products is NiS. The corrosion surface of C22 laser coatings at 500 °C is shown in figure 6(a2). Considering EDS results of spot A2 and XRD patterns in figure 5, the little irregular particles-shaped corrosion products as shown in spot A2 is NiS. The big particles-shaped corrosion products contain element O, S, Ni, Cr and Mo. It is speculated that it is the mixed particles of sulfides of Ni and oxides of Mo and Cr. In general, the corrosion surfaces of C22 alloy and C22 laser coatings at 500 °C are mainly covered with discontinuous particle-shaped NiS.

At 550 °C, the surfaces of C22 alloy and C22 laser coatings are both covered with polygonal shaped products. The corrosion products are sulfides of Ni with small amount of Mo according to the EDS results of spot C1 and
The NiS phases grow up at 550°C and the space between NiS particles become small as compared with 500°C. When the temperature reaches 600°C, particle-shaped corrosion products are formed on the surface of C22 alloy and C22 laser coatings. The elements of the corrosion products are mainly Ni, S, Cr, Mo and O as shown in spot D1 and D2. The particle-shaped corrosion products are speculated to be mixed particles of NiS, Cr2S3 and Cr3O4.

It should be noted that, at low corrosion temperature 500°C, the corrosion surface of C22 laser coatings has more pores than C22 alloy. However, at high corrosion temperature 550°C and 600°C, the corrosion surface of C22 laser coatings is much denser than C22 alloy. This phenomenon is consistent with the mass gain curves in figure 4. The final mass gain of C22 laser coatings is higher than C22 alloy at 500°C while the final mass gain of C22 laser coatings is lower than C22 alloy at 550°C and 600°C. The C22 laser coatings is more suitable for high-temperature application as compared with C22 alloy. The better corrosion resistance of C22 laser coatings is mainly due to finer grains which will be discussed in the following.

### 4. Discussion

#### 4.1. Corrosion mechanism of TP91

To explore corrosion mechanisms of TP91 under the reducing atmosphere of 0.2 vol% H2S-0.1 vol% O2–N2 at 500°C–600°C, the cross-sections of specimens after corrosion tests are investigated shown in figure 7. Corrosion products with multi-layer structure are observed at three different test temperature. However, the elements distribution are different as the test temperature rising from 500°C to 600°C. Table 4 shows the EDS results of different corrosion layer in figure 7.

![Figure 6. Surface micrographs of the corrosion products corroded in reducing corrosive atmosphere for 168 h: (a1)500 °C, (b1)550 °C and (c1)600 °C for C22 alloy; (a2)500 °C, (b2)550 °C and (c2)600 °C for C22 laser coatings.](image)

| Materials         | Temperature | Spot | Elements (at%) |
|------------------|-------------|------|---------------|
|                  |             |      | O  Fe  Ni  W  Mo  S  Cr  Mn |
| C22 alloy        | 500 °C      | A1   | 5.1  1.6 39.22 0.32 6.76 40.22 3.6 3.18 |
|                  |             | B1   | 33.81 2.3 20.6 0.26 3.61 23.72 13.1 2.7 |
|                  | 550 °C      | C1   | 2.78 0.83 43.62 0.48 8.82 41.64 1.42 0.72 |
|                  | 600 °C      | D1   | 9.9  3.18 40.39 1.2 6.2 39.06 0.4 0.5 |
| C22 laser coatings| 500 °C      | A2   | 8  0 40.1 0.25 5.72 40.83 2.48 1.72 |
|                  |             | B2   | 30.48 4.5 17.92 0.8 6.3 25.91 10.42 3.76 |
|                  | 550 °C      | C2   | 2.13 0.3 41.04 1.47 5.6 48.08 0.9 0.59 |
|                  | 600 °C      | D2   | 8.8 1.02 37.85 0.9 7.7 42.45 0.6 0.7 |

C2. The NiS phases grow up at 550°C and the space between NiS particles become small as compared with 500°C.

When the temperature reaches 600°C, particle-shaped corrosion products are formed on the surface of C22 alloy and C22 laser coatings. The elements of the corrosion products are mainly Ni, S, Cr, Mo and O as shown in spot D1 and D2. The particle-shaped corrosion products are speculated to be mixed particles of NiS, Cr2S3 and Cr3O4.

It should be noted that, at low corrosion temperature 500°C, the corrosion surface of C22 laser coatings has more pores than C22 alloy. However, at high corrosion temperature 550°C and 600°C, the corrosion surface of C22 laser coatings is much denser than C22 alloy. This phenomenon is consistent with the mass gain curves in figure 4. The final mass gain of C22 laser coatings is higher than C22 alloy at 500°C while the final mass gain of C22 laser coatings is lower than C22 alloy at 550°C and 600°C. The C22 laser coatings is more suitable for high-temperature application as compared with C22 alloy. The better corrosion resistance of C22 laser coatings is mainly due to finer grains which will be discussed in the following.
The middle layer is loose with cracks and pores. The inner layer is the densest and closely attached to the matrix. The EDS results of spot A1, B1 and C1 in table 3 show the elements information of the three sub-layers. The outer and inner layers mainly contain Fe, Cr, and O. Element S is not detected. The \( \frac{\text{Fe} + \text{Cr}}{\text{O}} \) atomic ratio is about 2:3, which is the same M/O atomic ratio as metal oxide \( \text{M}_2\text{O}_3 \), indicating the main composition of the outer and inner layers is \( \text{Fe}_2\text{O}_3 \). The main elements of the middle layer are Fe and S with small amount of O and Cr. This result is consistent with XRD patterns, indicating the main composition of the loose corrosion products of middle layers is \( \text{Fe}_7\text{S}_8 \). In general, the corrosion layer at 500 °C includes three different sub-layers: the outer layer is \( \text{Fe}_7\text{S}_8 \), the middle layer is \( \text{Fe}_7\text{S}_8 \) and the inner layer is \( \text{Fe}_7\text{S}_8 \).

At 550 °C, the thickness of the corrosion layer increases to 450 μm with two sub-layers (figure 7(b)). The outer layer is loose with a large number of pores and cracks. The inner layer is dense but has a thin belt full of cracks in the middle. EDS scan results of spot A2 show that the main elements of the outer layer are Fe and S. According to XRD analysis in section 3.1, the main phase in outer layer at 550 °C is \( \text{Fe}_7\text{S}_8 \). EDS results of spot B2 and D2 show that the main elements of inner layer are Fe, Cr, and O with the same \( \frac{\text{Fe} + \text{Cr}}{\text{O}} \) atomic ratio as spot C1, indicating the main phase of inner layer at 550 °C is \( \text{Fe}_7\text{S}_8 \). What’s more, element S is detected in the inner layer at 550 °C while no S is found at 500 °C. In general, the corrosion layer at 550 °C includes two different sub-layers: the loose outer layer \( \text{Fe}_7\text{S}_8 \) and the dense inner layer \( \text{Fe}_7\text{S}_8 \). As the temperature increasing from 550 °C to 600 °C, the dense \( \text{Fe}_7\text{S}_8 \) corrosion layer cannot completely prevent the diffusion of S from outside to matrix. The reaction between S and \( \text{Fe}_7\text{S}_8 \) results in the formation of sulfides in inner layer, leading to pores and cracks as shown in spot C2 and accelerating the corrosion process.

At 600 °C, the cross-section micrographs of the corrosion layer are similar to that at 550 °C (figure 7(c)). The corrosion layer is composed of two sub-layers: the loose outer layer and the dense inner layer. EDS results of C3 show that the inner layer is mainly composed of \( \text{Fe}_7\text{S}_8 \) with a small number of sulfides, which is the same as the inner layer at 550 °C. However, EDS results of A3 and B3 show that the O content in outer layer is much higher than that at 550 °C and the O content decreases with inward diffusion from 56.98 at% at spot A3 to 37.05 at% at B3. The outer layer should be composed of loose sulfides. However, as the temperature increasing from 550 °C to 600 °C, O becomes more active and the outermost sulfides in outer layer are oxidized into iron oxide. The iron oxide at outermost layer at 600 °C are also observed by XRD results in section 3.1. The iron oxide at the surface of outer layer is loose because it is transformed from loose sulfides. In general, the corrosion layer at 600 °C includes two different sub-layers: the inner layer is dense \( \text{Fe}_7\text{S}_8 \) and the outer layer is loose sulfides together with oxides.

| Temperature | Spot | Elements (at%) |
|-------------|------|---------------|
| 500 °C      | A1   | 0 21.09 62.32 14.47 1.72 |
|             | B1   | 53.26 41.84 1.55 0.32 2.83 |
|             | C1   | 0 17.13 65.08 14.08 3.63 |
| 550 °C      | A2   | 45.88 49.42 2.63 0.51 1.58 |
|             | B2   | 9.17 36.22 40.69 12.9 1.2 |
|             | C2   | 29.53 52.16 11.72 1 5.59 |
|             | D2   | 2.38 34.93 42 18.31 2.28 |
| 600 °C      | A3   | 0.51 41.94 56.98 0.18 0.4 |
|             | B3   | 27.20 35.27 37.05 0.15 0.14 |
|             | C3   | 5.83 33.81 48.64 11.60 0.13 |

The SEM images of cross-sections of TP91 stainless steel corroded in reducing corrosive atmosphere for 168 h at (a) 500 °C, (b) 550 °C and (c) 600 °C.
Generally, the main corrosion process of TP91 under the reducing atmosphere of 0.2 vol% H₂S-0.1 vol% O₂–N₂ at 500° C–600° C consists of three different stages.

At the first stage, O₂ reacts with the matrix material to form a dense inner (Fe+Cr)₂O₃ layer. The slope of mass gain curves becomes small and then the mass gain curves show a near-parabolic law after the formation of dense (Fe+Cr)₂O₃ layer shown in figure 1. The reaction equation including in this stage is below:

\[ \text{xM} + \frac{1}{2} \text{yO₂} = \text{M_xO_y} \]

Where M refers to Fe and Cr.

At the second stage, the H₂S in the atmosphere reacts with the iron oxide from inner layer to form a loose sulfides layer. The reaction equation including in this stage is below:

\[ \text{FeO + H₂S} \rightarrow \text{FeS + H₂O} \]
\[ \times (\Delta G_{\text{500 °C}-\text{600 °C}} = -50.2 \sim -50.4) \]

The transformation from iron oxides to iron sulfides can be confirmed from the SEM images shown in figure 8. The corrosion surface of TP91 at 600 °C after 24 h is shown in figure 8. It can be seen that the granular sulfides grow on the surface of oxides. When the corrosion time extends, the sulfides increase and then a loose iron sulfides layer is formed as shown in figure 7.

At the third stage, the loose sulfides layer can’t stop the diffusion of O₂ and H₂S. O₂ reacts with sulfides layer to form another loose oxide layer on the surface of sulfides layer (shown in figure 7(c)). H₂S diffuses inside to react with inner oxide, forming porous sulfides (shown in figure 7(b)) and accelerating the corrosion process. The reaction equation including in this stage is below:

\[ 4\text{FeS} + 3\text{O₂} \rightarrow 2\text{Fe₂O₃} + 4\text{S} \]
\[ \times (\Delta G_{\text{500 °C}-\text{600 °C}} = -108.5 \sim -104.5) \]

4.2. Corrosion mechanism of C22 alloy

H₂S-containing reduction environments are well known to cause accelerated corrosion due to the generation of porous sulfide scales on the metal surface, resulting in increased corrosion, metal wastage and internal attack. However, C22 alloy possesses excellent corrosion resistance at 0.2 vol% H₂S-0.1 vol% O₂–N₂ at 500° C–600° C, which is attribute to the formation of protective scales. The cross-sections of C22 alloy after corrosion tests are shown in figure 9. A loose outer layer and a dense inner layer can be observed at three different test temperature. EDS results of corrosion products are shown in table 5.

As shown in figure 9(a), the thickness of the corrosion layer of C22 alloy at 500 °C is 10 μm. The corrosion products in outer layer (spot A) are particle-shaped protrusion. EDS results show that it mainly consists of Ni-rich sulfides, with little O and Cr element. The dense inner layer, as pointed by B, is mainly composed of O, Cr and Mo with little Ni and S as compared with spot A, indicating the formation of oxides of Cr and Mo. The phase constitution of cross-section of C22 laser coatings at 500 °C is the same as C22 alloy.

When test temperature increases to 550 °C, the thickness of corrosion layer for C22 alloy (figure 9(b)) is more than 40 μm, which is much thicker than that at 500 °C. Increasing test temperature accelerates corrosion process, resulting in a higher mass gain as shown in figure 4. The corrosion layer of C22 alloy has two sub-layers. The outer corrosion layer is block-shaped structure. EDS results of spot C show that the main element of outer layer is Ni, S with a little Mo, and the content of Cr and O is less than 1 at%. The inner layer becomes denser and more continuous. Therefore, the inner layer can effectively prevent the direct contact between the corrosive medium and the substrate and slow down the corrosion rate. According to EDS results of D and E, the content of Cr and O in inner layer increases, while the Ni and S elements decreases.
Cross-sections of C22 alloy at 600 °C are shown in figure 9(c). According to the EDS results in F, G, H and P, the discontinuous particle-shaped corrosion products in outer layer are Ni-rich sulfides, with little O and Cr. The dense inner layer is oxides of Cr and Mo with little Ni and S.

In general, the corrosion layer of C22 alloy possesses two sub-layers. The outer layer is Ni-rich sulfides and the inner layer is oxides of Cr and Mo. With the increase of corrosion depth, the element S decreases while the element O increases.

During corrosion process of C22 alloy, Ni tends to react with S and Cr tends to react with O. The O$_2$ in the atmosphere firstly reacts with Ni and Cr diffused from matrix to form a mixed oxide inner layer of NiO and Cr$_2$O$_3$. At this step, the corrosion rate is controlled by the chemical reaction rate, the mass gain increases rapidly until a dense oxides inner layer formed. The chemical reaction in this step includes:

\[
2\text{Ni} + \text{O}_2 = 2\text{NiO} \quad (\Delta G_{500 \text{ oC} \cdots 600 \text{ oC}} = -336.9 \sim -319.3)
\]

\[
4\text{Cr} + 3\text{O}_2 = 2\text{Cr}_2\text{O}_3 \times (\Delta G_{500 \text{ oC} \cdots 600 \text{ oC}} = -1857.4 \sim -1806.6)
\]

As the corrosion process goes on, NiO phase prefer to react with H$_2$S to form NiS particles in the outer layer (figure 9). In this step, the corrosion rate is controlled by the diffusion of Ni through the inner oxides layer [25].

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### Table 5. EDS spot results of the corrosion layers for C22 alloy in figure 9.

| Materials          | Temperature | Spot | Elements (at%)         |
|--------------------|-------------|------|------------------------|
|                    |             |      | O  | Fe | Ni | W | Mo | S  | Cr | Mn |
| C22 alloy          | 500 °C      | A    | 0.91 | 0.5 | 44.19 | 0.30 | 6.81 | 45.69 | 0.49 | 1.01 |
|                    |             | B    | 50.61 | 0.11 | 0.71 | 0.87 | 5.57 | 13.71 | 27.51 | 0.81 |
|                    | 550 °C      | C    | 0.7 | 1.09 | 37.02 | 1.09 | 5.09 | 51.08 | 0.81 | 0.41 |
|                    |             | D    | 5.45 | 1.12 | 9.51 | 0.71 | 3.61 | 50   | 28.51 | 1.08 |
|                    |             | E    | 36.21 | 1.11 | 2.61 | 1.52 | 11.14 | 22.81 | 23.83 | 0.77 |
|                    | 600 °C      | F    | 6.71 | 0.7 | 44.87 | 0.24 | 1.08 | 45.91 | 0.23 | 0.26 |
|                    |             | G    | 14.06 | 0.6 | 35.47 | 0.16 | 1.26 | 40.66 | 5.28 | 0.25 |
|                    |             | H    | 44.49 | 0.99 | 4.04 | 2.18 | 16.73 | 9.79 | 21.17 | 0.61 |
|                    |             | P    | 24.01 | 4.09 | 39.40 | 1.45 | 9.06 | 1.79 | 19.88 | 0.41 |

### Table 6. EDS spot results of corrosion layers for C22 laser coatings in figure 11.

| Materials          | Temperature | Spot | Elements (at%)         |
|--------------------|-------------|------|------------------------|
|                    |             |      | O  | Fe | Ni | W | Mo | S  | Cr | Mn |
| C22 laser coatings | 500 °C      | A    | 10.91 | 1 | 38.52 | 1.11 | 4.71 | 41.92 | 1.53 | 0.3 |
|                    |             | B    | 59.42 | 0.88 | 2.86 | 1.3 | 6.41 | 7.57 | 20.9 | 0.66 |
|                    | 550 °C      | C    | 2.27 | 4.81 | 32.72 | 1.21 | 4.41 | 53   | 1   | 0.48 |
|                    |             | D    | 7.62 | 3.53 | 13.15 | 1.71 | 6.22 | 54.3 | 10.21 | 0.8 |
|                    |             | E    | 8.65 | 2.51 | 7.81 | 2.92 | 9.62 | 25   | 41.61 | 2.08 |
|                    | 600 °C      | F    | 38.19 | 1.38 | 6.88 | 2.07 | 8.89 | 10.3 | 32.9 | 1.01 |
|                    |             | G    | 11.63 | 0.56 | 35.33 | 0.2 | 2.22 | 45.99 | 1.05 | 0.31 |
|                    |             | H    | 58.76 | 0.63 | 2.21 | 1.1 | 6.31 | 12.86 | 16.13 | 0.2 |
|                    |             | K    | 12.23 | 4.28 | 48.34 | 2.10 | 6.37 | 1.03 | 21.31 | 0.48 |
The dense oxides layer can hinder the diffusion of Ni. As a result, the mass gain curves show a parabolic law. The chemical reaction in this step includes:

\[
\text{NiO + H}_2\text{S} = \text{NiS} + \text{H}_2\text{O} \\
\times (\Delta G_{500 \, \text{°C} - 600 \, \text{°C}} = -68.7 \sim -69.3)
\]  

To better understand the elemental enrichment phenomenon at different corrosion layers, map scanning results of C22 alloy cross-section at 500 °C are shown in figure 10. It can be seen that the outer layer is Ni-rich and S-rich zone, indicating the selective corrosion between Ni and S. The inner layer is O-rich zone and Cr-rich zone without Ni, indicating the selective corrosion between Cr and O. It should be noted that the content of Cr in inner layer is much higher than matrix. This phenomenon indicates that element Cr diffuses outward from matrix to inner layer and reacts with O resulting in a dense Cr oxides layer during corrosion test.

4.3. Corrosion mechanism of C22 laser coatings

Figure 11 displays the cross-sections of C22 laser coatings after corrosion tests and the EDS results are shown in table 6 at 500 °C, 550 °C and 600 °C. As shown in figure 11(a), at 500 °C, the outer layer (spot A) is Ni-rich sulfides with a small amount of Mo, and the inner layer (spot B) is oxides of Cr and Mo with little Ni and S. When test temperature increases to 550 °C, the outer corrosion layer is block-shaped NiS (spot C) with a little Mo and the inner layer is oxides of Cr (spot D, E and F). At 600 °C, the discontinuous particle-shaped corrosion products in outer layer are Ni-rich sulfides, with little O and Cr (spot G). The dense inner layer is oxides of Cr and Mo with little Ni and S (spot H and K). In general, the corrosion layer of C22 laser coatings also has two sub-layers which is the same as C22 alloy. Ni-rich sulfides are the main phases of outer layer and oxides of Cr and Mo are the main phases of inner layer.

Chemical reactions including in corrosion process of C22 laser coatings are the same as C22 alloy. As shown in equations (4)–(6), element Cr and Ni prefer to react with O to form oxides of Cr and Ni in inner layer. Then
element Ni is sulfided into NiS in the outer layer. To confirm the formation of NiO and Cr₂O₃ in the inner, figure 12 shows the SEM images for the surface after corrode 24 h at 600 °C. As shown in figure 12, the oxides particles grow on the surface of matrix containing 41.2 at% O, 15.5 at% Cr and 27.7 at% Ni. This result indicates that the inner layer is composed of oxides of Ni and Cr at beginning. As the corrosion process goes on, NiO phase is consumed by H₂S to form NiS particles in the outer layer while the Cr₂O₃ phase remains unchanged and stay in the inner layer.

It is well known that both phase constitution of corrosion products and morphology of corrosion layers play important roles in corrosion resistance ability. It is obvious that C22 alloy and C22 laser coatings show better corrosion resistance than TP91 as evidenced by mass gain curves shown in figures 1 and 4. This phenomenon is due to the difference of corrosion products. As shown in figure 10, the Ni content in Cr-rich zone is very low. The dense Cr oxides layer in C22 alloy and C22 laser coatings can hinder the outward diffusion of Ni from matrix to outer layer. However, as shown in figure 13, the Fe content in inner layer, middle layer and outer layer of TP91 is high indicating the dense (Fe,Cr)₂O₃ layer in TP91 can’t prevent the outward diffusion of Fe. This is the main reason for the worse corrosion resistance and higher mass gain of TP91.

What’s more, it should be figured out that the corrosion resistance of C22 laser coatings is better than C22 alloy at 550 °C–600 °C as shown in figure 4. The composition and corrosion products of them are similar, but C22 laser coatings has finer grains due to laser cladding technology. As shown in figure 14, the grain size of C22 alloy is about 100 μm while the grain size of C22 laser coatings is about 5–10 μm. Refined grains can accelerate the short-circuit diffusion of Cr along grain boundaries, resulting a lower critical concentration of Cr for selective oxidation [26]. As result, selective oxidation of Cr is easier to happen in C22 laser coatings than C22 alloy, forming a protective Cr oxide inner layer in much speedier progress, reducing the oxygen activity at oxide layer/alloy interface and resulting in a lower corrosion rate [9]. However, the final mass gain of C22 laser
coatings at 500 °C is higher than C22 alloy. The opposite corrosion resistance is speculated to be caused by a porous morphology of corrosion layer for C22 laser coatings shown in figure 6(a2).

5. Conclusion

The corrosion characteristics of boiler steels TP91, C22 alloy and C22 laser coatings at 500 °C−600 °C at reducing atmosphere of 0.2 vol% H₂S-0.1 vol% O₂–N₂ caused by low-NOx combustion were investigated. The mass gain curves were obtained and the phase constitution and microstructure evolution of corrosion products were analyzed. The main conclusions are summarized as follow:

(1) A multi-layer structure with three sub-layers after corrosion tests for TP91 are observed. The main phases of outer layer, middle layer and inner layer are Fe-rich oxides, pores sulfides and dense (Fe,Cr)₂O₃, respectively.

(2) The corrosion layer of C22 alloy and C22 laser coatings contains two sub-layers. The outer layer is NiS particles due to selective reaction between Ni and S. The inner layer is dense Cr₂O₃ due to selective reaction between Cr and O.

(3) The order of corrosion resistance at 550 °C−600 °C is: C22 laser coatings>C22 alloy>TP91. Better corrosion resistance of C22 alloy and C22 laser coatings is due to the formation of dense Cr₂O₃ layer, which can hinder the outward diffusion of Ni while the (Fe,Cr)₂O₃ layer can’t hinder the diffusion of Fe. Furthermore, dense Cr oxide inner layer of C22 laser coatings can be formed in much speedier process than C22 alloy due to fine grains, resulting in a lowest mass gain and best corrosion resistance. Therefore, in view of corrosion resistance and cost, the preparation of C22 laser coatings on the surface of water-cooled wall can greatly enhance the corrosion resistance of boiler tube in low nitrogen combustion environment without high cost.

(4) Corrosion weight increases with increasing temperature, and the mass gain increases rapidly for C22 alloy and C22 laser coatings above 550 °C, indicating their limit corrosion temperature at reducing atmosphere is 550 °C.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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