Preparation and corrosion resistance properties of duplex stainless steel (00Cr22Ni6MnMoCu)

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Abstract

In the present paper, a new kind of duplex stainless steel (DSS, 00Cr22Ni6MnMoCu) was prepared. Cr30 was chosen as a comparison of microstructures and mechanical properties with 00Cr22Ni6Mn-MoCu. Corrosion tests with 3.5% NaCl solution and electrolytic solution for 00Cr22Ni6MnMoCu were carried out to analyze the corrosion pattern of test materials. It can be concluded that: (1) Austenitic and ferrite duplex stainless steel has an optimized phase distribution, high toughness and strength when the ratio of two-phase content is 1:1. (2) Corrosion tests show that the corrosion resistance of 00Cr22Ni6MnMoCu is 12 times compared to ferrite stainless steel Cr30. (3) Electrolytic corrosion tests show that for 00Cr22Ni6MnMoCu, the corrosion is caused by intergranular corrosion. For Cr30, it is mainly caused by pinholes. However, Cr30 has a poor corrosion resistance because of the presence of a large amount of carbides and their phase boundaries caused by the electric potential difference between the carbide and the matrix.

1. Introduction

Erosion-corrosion of metal materials often exists in modern industry, such as petrochemical, machinery, metallurgy, energy transport, accounting for about 9% of the total amount of corrosion, which is equal to 5% of the total amount of wear [1–3]. The direct economic losses caused by corrosion account for around 4% of GDP expenditures of such countries as United States, United Kingdom, Japan, Germany [4–8]. For mineral pumps, petrol industrial buildings, offshore buildings, marine hulls, and other equipment, they all suffered serious erosion, corrosion, stress corrosion, and so on [9–11]. Nowadays, erosion-corrosion stainless steels are hard to meet the requirements of working conditions [12, 13]. For example, 0Cr18Ni9Ti austenite steel has a high anti-corrosion property, but poor wear resistance and ferrite stainless steel Cr30 has a good erosion resistance property, but poor anti-corrosion property. It has been noticed that stainless steels with an even distribution of ferrite and austenite have better anti-erosion and corrosion properties [14–16]. More ferrite contents in stainless steel can be considered as an unsuitable design in corrosion-erosion environment nowadays. In the present authors’ viewpoint, increasing austenite content is, however, beneficial to improve the distribution to austenite and ferrite phases. Finally, it will also improve resistance of corrosion and erosion for duplex stainless steel [17, 18].

In order to improve the mechanical properties DSSs are alloyed with various chemical compositions such as Cr, Ni, and Mo [19]. Nitrogen is added to stainless steels to improve mechanical properties and corrosion [20, 21]. In the present paper, ferrite stainless steel Cr30 was chosen as comparative material to new duplex stainless steel 00Cr22Ni6MnMoCu. This study designed a chemical composition of duplex stainless steel which was resistant to erosion, abrasion and corrosion, then performed a special solution treatment on the prepared samples, evaluated the mechanical properties and the corrosion properties of the test materials, analyzed and concluded the mechanism of anti-corrosion failure, which could be a reference for industrial application. This experiment focuses on the preparation and corrosion resistance of new duplex stainless steel materials.
2. Experimental procedures

Chemical compositions of duplex stainless steel named 00Cr22Ni6MnMoCu and ferrite stainless steel Cr30 are shown in table 1.

Solution treatment is of great significance in improving mechanical properties of DSS. When the volume fraction of austenite and ferrite is of great difference, the micro-stress concentration will be very high. It is suggested that the best volume ratio of austenite and ferrite is 50%, which can be achieved through suitable adjustment of chemical compositions and pouring process controls to prevent introducing micro-stress concentration.

The hardness, tensile strength, yield strength and elongation of duplex stainless steel gradually increase with the increase of solution treatment temperature, because as the solid solution temperature increases, the number of harder α phases increases and the coarse dendrites of the alloy decreases in the α/γ dual phase structure, the carbides in the as-cast structure all dissolve into the matrix, the widmanstatten structure almost disappear, and

| Material          | C    | Si  | Mn  | Cr   | Ni  | Mo  | Cu  | N    |
|-------------------|------|-----|-----|------|-----|-----|-----|------|
| 00Cr22Ni6MnMoCu   | 0.048| 0.91| 0.85| 21.46| 6.02| 2.79| 2.34| 0.015|
| Cr30              | 0.012| 0.36| 0.48| 29.05| —   | 1.79| —   | —    |

* The contents for phosphorus and sulfur aren’t given here.
the ratio of \( \alpha \) to \( \gamma \) phase is close to 1:1. It is generally believed that the duplex stainless steel with this ratio has better overall performance.

Solution treatment procedure is as follows: samples with \( \Phi \)25mm in diameter were kept at 1100 \( ^\circ \)C for 2 h to get more ferrite volume. Then, they were pre-cooled to 1040 \( ^\circ \)C for 2 h. Finally, they were quenched into water till room temperature. The samples after heat treatment were cleaned in HCl solution with FeCl3.

Microstructures of the materials are shown in figure 1. Figure 2 shows that the microstructures of 00Cr22Ni6MnMoCu with austenite and ferrite, in comparison with Cr30 with ferrite and carbides. The phase volume ratio of 00Cr22Ni6MnMoCu is with 52.1% (austenite):47.9% (ferrite). Steel Cr30 is with carbides whose amount is in 13.6%vol. Above data were obtained from Laica image analyzer.

Table 2. Phase microhardness in test materials.

| Material          | 00Cr22Ni6MnMoCu | Cr30 |
|-------------------|-----------------|------|
| Micro-rigidity/HV | 226             | 418  |

Table 3. Mechanical properties for test materials.

| Materials          | Yield strength \( \sigma_{0.2} \)/MPa | Tensile strength \( \sigma_b \)/MPa | Elongation/% | Toughness/(J/cm\(^2\)) | Harness/HB |
|--------------------|----------------------------------------|-----------------------------------|--------------|-------------------------|------------|
| 00Cr22Ni6MnMoCu    | 455                                    | 720                               | 24           | 113                     | 206        |
| Cr30               | 520                                    | 780                               | 14           | 78                      | 286        |

Table 4. Chemical composition of phosphorus solution (wt%)\(^a\).

| Component | \( P_2O_5 \)(%) | Fe(%) | Al(%) | Mg(%) | Cl(%) | F(%) | \( SO_4^{2-} \)(%) |
|-----------|----------------|-------|-------|-------|-------|------|-------------------|
| Content   | 48             | 0.7–0.8 | 0.3–0.4 | 0.4–0.5 | 0.2–0.4 | 1–1.2 | 1–1.5             |

\(^a\) The solid content is 31%–34%, pH \( \approx \) 1.

Table 5. Corrosion rate of tested materials.

| Materials          | Corrosion velocity (g/mm\(^2\)\cdot a) | Anti-corrosion property |
|--------------------|----------------------------------------|-------------------------|
| 00Cr22Ni6MnMoCu    | \( 1.24 \times 10^{-6} \)              | 1.00                    |
| Cr30               | \( 1.60 \times 10^{-3} \)              | 12.90                   |

the ratio of \( \alpha \) to \( \gamma \) phase is close to 1:1. It is generally believed that the duplex stainless steel with this ratio has better overall performance.

Solution treatment procedure is as follows: samples with \( \Phi \)25mm in diameter were kept at 1100 \( ^\circ \)C for 2 h to get more ferrite volume. Then, they were pre-cooled to 1040 \( ^\circ \)C for 2 h. Finally, they were quenched into water till room temperature. The samples after heat treatment were cleaned in HCl solution with FeCl3. Microstructures of the materials are shown in figure 1. Figure 2 shows that the microstructures of 00Cr22Ni6MnMoCu with austenite and ferrite, in comparison with Cr30 with ferrite and carbides. The phase volume ratio of 00Cr22Ni6MnMoCu is with 52.1% (austenite):47.9% (ferrite). Steel Cr30 is with carbides whose amount is in 13.6%vol. Above data were obtained from Laica image analyzer.

Table 2 shows the phase microhardness of test material. It can be seen that microhardnesses of the two phrases for DSS are lower than that for Cr30. Carbide has a higher microhardness in Cr30 which can be considered as a main phase of erosion resistance.

Mechanical properties of test materials are shown in table 3. We can see that DSS has better toughness than steel Cr30.

3. Corrosion results and discussions

3.1. The chemical and water corrosion tests

According to Chinese standard GB/T 19291–2003, weight increment of corrosion is adopted as a measurement of material corrosion after corrosion test. In the test, corrosive medium in phosphorus chemical industry solution was applied with more \( Cl^- \), \( F^- \), and \( SO_4^{2-} \) ions in it (as shown in table 4). That kind of solution is with more serious corrosion characteristics and a higher content of solid. Therefore, it is also with more serious erosion characteristic. A corrosion temperature 81 \( \pm \) 1 \( ^\circ \)C was chosen and corrosive time lasted 72 h.

The velocity of the corrosion is shown in table 5. It shows that the corrosion rate of 00Cr22Ni6MnMoCu is much lower than that of Cr30. The corrosion rate of Cr30 is in 12 times of DSSs.

Figure 3 shows the surface corrosive morphology after corrosion tests. Corrosive products were evenly distributed in surface of the two DSSs with a few holes. The compacted film of anti-oxidation (Cr2O3, NiO) was formed from elements, such as Cr, Ni, Mo and Cu. That is the main reason why the two DSSs have a better corrosion resistance (as shown in figure 3(a). Compared with DSS, Cr30 is corroded more seriously with much
more and deeper corrosive holes in the surface. That results in poor corrosion resistance because of a lot of carbides and phase interphase corrosion caused by the different electric potential between matrix and the carbide.

### 3.2. Results of electrolytic corrosion and discussions

Electrolytic corrosion is another way to characterize corrosion resistance of the materials. Its procedure is as follows: anode process (metal dissolved and electrons lost), the current flow and cathode process (e-absorption).

The experiment was conducted in electrolyte-3.5%NaCl solution at ambient temperature. Firstly, a 0.4 V voltage was kept for 5 min during electrolytic corrosion test. After that, the samples were dried to obtain corrosive data. Then, the samples were put back to electrolyte and voltage was kept at 0.6 V for 10 min. Following that, the samples were dried again to obtain data. Finally, the test was performed for another 10 min. Then, the third group data were obtained.

The electrolyte became yellow green color after 5-min. test for Cr30 when the voltage is 0.4 V, whereas the color of other two tests did not change. It shows that there are many metallic ions in the electrolyte for Cr30, causing more material losses. With higher voltage, or the longer time of corrosion, other electrolytic solutions were also changed to yellow green color and this shows that corrosion increases.

Figure 4 shows the SEM morphology of test materials after electrolytic corrosion tests in 3.5%NaCl solution.

It is concluded that the failure of 00Cr22Ni6MnMoCu is mainly caused by intergranular corrosion. The failure of Cr30 is caused by intergranular corrosion and also by pinholes because there is poor corrosion resistance for carbides in matrix. Therefore, Cr30 is corroded more seriously. With increasing voltage or the longer time of corrosion, the grain boundaries of 00Cr22Ni6MnMoCu is corroded thicker.
The electrolyte is neutral tested by pH test paper before test ($\text{pH} = 6.9$). After the experiment, pH value of 00Cr22Ni6MnMoCu electrolyte was changed to pH 3, and pH value of Cr30 electrolyte became 2~3. With pH value decreasing, the dissolution of the anode was accelerated. A smaller pH value means stronger acidity. From following reaction (1) and (2), it can be concluded that the more Fe$^{2+}$ the solution contains, the greater weight the material loss after the electrolytic corrosion.

\begin{align*}
Fe^{2+} + 2Cl^- & \rightarrow FeCl_2 \\
FeCl_2 + 2H_2O & \rightarrow Fe(OH)_2 + 2HCl
\end{align*}

(1) (2)

4. Conclusions

(1) Newly prepared austenitic and ferrite duplex stainless steel has an even distribution and the equal volume ratio of two-phases. It is with good toughness and high strength.

(2) Corrosion tests show that new material is with similar good erosion resistance. It is 12 times higher than ferrite stainless steel Cr30. The compacted anti-oxidation film (Cr$_2$O$_3$, NiO) formed by elements, such as, Cr, Ni, Mo and Cu becomes a main reason why two DSSs have better corrosion resistance. Compared with DSSs, Cr30 is corroded more seriously with more and deeper corrosive pinholes in the surface because of higher electric potential difference between carbides and matrix, causing intergranular corrosion.

(3) The failure pattern of 00Cr22Ni6MnMoCu is also an intergranular corrosion. The corroded surface is with a little pinhole corrosion, and vice versa, and intergranular and pinholes corrosion are coexist for Cr30.

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Data availability statement

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

Author contributions

Chong Zhang: Investigation and Validation, Writing-original draft preparation. Prof. Chonggao Bao: Supervision, Methodology, Validation and Writing-review. The authors declared that they have no conflicts of interest to this work.

Compliance with ethical standards

The authors declared that they have no conflicts of interest to this work.

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