Corrosion Study on Ni-based Alloy in Acidic Environment

Yuejuan Shi¹, Yanling Liu¹, Xuepeng Wang¹, Yongxing Zhou¹, Jun Ma¹ and Shuai Zhang²*

¹Wuzhong Instrument Co. Ltd, China
²School of mechanical engineering, Ningxia University, Yinchuan, China
*Corresponding author

Abstract. Ni-based alloys have excellent corrosion resistance and are widely used in the petrochemical industry. In this study, the effects of sulfuric acid concentration on the corrosion resistance of Ni-based alloys were analyzed by software simulation and electrochemical tests. The results show that the corrosion rate of the alloy is gradually increased with the increase of sulfuric acid concentration, and the influence of sulfuric acid concentration on the corrosion rate of 304 stainless steel is greater than that of nickel-based alloy. In a 10% sulfuric acid solution, the corrosion rate of the four nickel-base alloy samples is only one-twentieth of that of the 304 stainless steel substrate.

Keywords: ni-based alloy; corrosion resistance; electrochemical analysis.

1. Introduction
Ni-based alloys have excellent corrosion resistance and are widely used in the petrochemical industry, especially in the manufacture of key components of equipment [1, 2]. There are many systems for Ni-based alloys. Common systems include Ni-Mo system, Ni-Cr-Mo-Cu system, Ni-Fe-Cr-Mo-Cu system and Ni-Cr system. Different systems of Ni-based alloys have been developed for different corrosive environments[3]. Hastelloy Hastelloy B-2, Hastelloy C-2000, Hastelloy G-30 and Incoloy 925 have excellent corrosion resistance in an acidic environment. These alloy components contain a large amount of Mo, Cr and other elements that improve the corrosion resistance of the alloy, such as Cu, rare earth, etc., to ensure the excellent corrosion resistance of the alloy in an acidic environment. Many research work shows[4,5], in a corrosive environment, the Ni-based alloy indicates that a passivation film is formed to prevent the corrosive medium from entering the inside of the solution to protect the alloy, but some of the precipitated phases in the alloy also have an bad effect on the corrosion resistance of the alloy. Zhao Xuehui et al [6] studied the effect of precipitation on the corrosion resistance of nickel-based alloys, and found that Cr₂₇C₆ and Cr₆C and other high chromium carbides precipitated in the alloy after aging treatment significantly reduced the corrosion resistance of the alloy.
This paper mainly studies the corrosion resistance of Ni-based alloys in acidic environment, and explores the effects of Ni-based alloy composition and precipitation on the corrosion resistance of alloys.

2. Materials and Methods
Purchased 304 stainless steel and nickel-based alloy materials at Shanghai Chenghuai Special Alloy Co., Ltd. The composition of the alloy was tested in Tables 1 and 2. Sulfuric acid solutions with concentrations of 1.5%, 3%, 5%, and 10% were separately disposed, and the corrosion resistance of the alloy samples was tested using an electrochemical workstation. The sample was prepared and tested according to the requirements of GB/T24196-2009.
Table 1. Elemental composition of the 304 stainless steel (wt%)

|        | C   | B   | Cr   | Si  | Ni  | Mn  | P   | Fe   |
|--------|-----|-----|------|-----|-----|-----|-----|------|
| 304 Steel | ≤0.08 | 0   | 18-20 | ≤1  | 8.0-10.5 | ≤2  | ≤0.05 | Bal. |

Table 2. Elemental composition of the Ni-based alloy (wt%)

| Ni-based alloy | Ni        | Cr   | Mo  | Fe  | Si   | Al  | Cu  | Co  | Mn  | C    | Bal. |
|----------------|-----------|------|-----|-----|------|-----|-----|-----|-----|------|------|
| G-30           | 57.61     | 22.3 | 15.5 | 1.1 | 0.45 | 0.31 | 0.5 | 1.08 | 0.62 | 0.01 |       |
| C-2000         | 56.46     | 22.56 | 15.8 | 2   | 0.03 | 0.35 | 1.45 | 1.02 | 0.32 | 0.01 | W: 0.5 |
|                |           |      |      |     |      |      |     |      |      |      | P: 0.01 |
|                |           |      |      |     |      |      |     |      |      |      | S: 0.008 |
| Incoloy 925    | 43.2      | 21.2 | 2.6  | 24.58 | 0.2 | 0.35 | 2.83 | 2.4 | 0.45 | 0.01 | S: 0.01 |
|                |           |      |      |      |     |      |     |      |      |      | Ti: 2.18 |
|                |           |      |      |      |     |      |     |      |      |      | P: 0.01 |
|                |           |      |      |      |     |      |     |      |      |      | S: 0.01 |
| B-2           | 65.3      | 0.8  | 28.02 | 4.45 | 0.08 | 0.5 | 0   | 0.62 | 0.5  | 0.01 |       |

3. Testing of Samples
Using the material thermodynamic calculation software and the corresponding Ni-based alloy database, the precipitation rule of the alloy equilibrium phase is simulated and calculated. The alloy composition (listed in Tables 1 and 2) and temperature parameters were used as the input conditions of the simulation to calculate the possible equilibrium phase (Fig. 1).

The Tafel curve of the Ni-based alloy was tested using an RST 5200 electrochemical workstation. The Tafel curve of the sample was tested by using a three-electrode potentiometric scanning method and operated in the H₂SO₄ solution as the electrolyte. The sample to be tested was used as the working electrode, the platinum wire electrode was used as the auxiliary electrode, A saturated calomel electrode (SCE) was used as a reference electrode for testing. The parameters setting are shown in Table 3.

Table 3. Electrochemical workstation related parameters

| Parameter            | Value |
|----------------------|-------|
| Rest time(s)         | 10    |
| Scan rate(V/s)       | 0.0005|
| sampling interval(V) | 0.0001|
| Electrode area (cm²) | 1     |
| Curve points         | 2001  |

4. Results and Analysis.

4.1. Analysis of Software Simulation Results
The equilibrium phase diagrams of each alloys were simulated by software. The simulation result is shown as fig.1.
As can be seen from Fig. 3, a large amount of \( \gamma \) phase was precipitated in the a, b, c and d alloy samples. The hard phase such as carbide and boride is less in the alloy, which is mainly related to the content of carbon and boron in the alloy\(^7\). Combined with the software simulation results and related research conclusions, On the one hand, the precipitation of carbides in the alloy acts as a dispersion strengthening, which has a positive effect on the strength and hardness of the alloy. On the other hand, the precipitation of carbides will lead to the reduce of the alloy corrosion resistance. It can be seen from the software simulation results. The content of the carbide phase in the nickel-based alloy is within 5%. During the solidification process, the carbon element preferentially reacts with Cr, Mo, etc. in the alloy, and precipitates metal carbides such as M\(_2\)C\(_6\) and M\(_6\)C, which cause aggregation of Cr and Mo elements, causing intercrystalline chromium depletion\(^8\). It has a great influence on the properties of the alloy. The 304 stainless steel material has a higher carbon content than the nickel-based alloy, so there are more carbide phases.
4.2. Analysis of Electrochemical Test Results

![Polarization curves of samples in different concentrations of sulfuric acid solution](image)

**Figure 2.** Polarization curves of samples in different concentrations of sulfuric acid solution (a-1.5%H$_2$SO$_4$; b-3%H$_2$SO; c-5%H$_2$SO; d-10%H$_2$SO)

It can be seen from Fig. 4 that the corrosion potential of the four nickel-base alloy samples is higher than the corrosion potential of 304 stainless steel in different concentrations of sulfuric acid solution. The corrosion potential can reflect the corrosion tendency of the alloy to some extent$^{[9]}$. The closer the corrosion potential is to the positive direction, the less the tendency of the alloy to corrode in solution. In the test of the 304 stainless steel sample, the corrosion potential fluctuated between -0.29 V and -0.31 V, and the corrosion potentials of the other four nickel-base alloys fluctuated between -0.22 V and 0.1 V. The corrosion potential anomaly of the C-2000 sample in Figure 2(c) may be related to experimental error.

As can be seen from Fig. 3 and Table 4, with the concentration of sulfuric acid increases, the corrosion rate of the sample also added. It can be seen from the test data, that the corrosion current density of the Ni-based alloy in sulfuric acid is very small, and the corrosion rate of the material fluctuates within a certain range. The higher the concentration of the sulfuric acid solution, the faster the corrosion rate of the alloy. Moreover, in the 10% H$_2$SO$_4$ solution, the corrosion rate of the Ni-base alloy sample is only one-twentieth of that of the 304 stainless steel sample.

By analysis of the composition of each alloy, it was found that the influence of Cr and Mo elements on the corrosion resistance of the alloy has a positive effect, but the content of both elements does not exceed 30%. The Cr is an element which makes nickel non-rust and has good corrosion resistance in an oxidizing medium. From an electrochemical point of view, a higher Cr content not only makes the alloy easy to passivate, but also reduces passive current density of the alloy. Thereby reducing the alloys...
dissolution rate and imparting passivation ability to the alloy and rapidly repairing the damaged passivation film, which is the root cause of the high corrosion resistance of the nickel-based alloy with high Cr content. Therefore, although the Mo content of Incoloy 925 alloy is only 2.6%, the higher Cr content and the addition of elements such as Cu and Fe ensure that the alloy has strong corrosion resistance in the lower concentration of sulfuric acid. The Mo element can significantly improve the corrosion tendency of nickel-based alloys in pitting and crevice corrosion environments, and improve the corrosion resistance of the alloy in reducing acid. The content of Cr in Hastelloy B-2 alloy is only 0.8%, but the extremely high Mo content in the alloy can effectively improve the corrosion resistance of the alloy. The addition of a small amount of Al, Ti, Cu, Co and rare earth elements in the alloy can also improve the corrosion potential of the alloy, reduce the corrosion tendency, promote the generation of passivation film on the surface of the alloy, refine the grain size. Further, the content of the C element in each of the Ni-based corrosion resistant alloys is extremely low. It can significantly reduce the intercrystalline chromium deficiency caused by the precipitation of carbide phases such as M₂₃C₆ and M₆C during solidification. This can also be verified from software simulation results, so nickel-based corrosion-resistant alloys have strong corrosion resistance[10].

**Table 4.** Characteristic values of Tafel curves of Ni-based alloys and stainless steels in H₂SO₄ solution

|             | 10% H₂SO₄   | 5% H₂SO₄   | 3% H₂SO₄   | 1.5% H₂SO₄ |
|-------------|-------------|-------------|-------------|-------------|
|             | Vₘ₈₉₉ / V  | Iₘ₈₉₉/ (μA·cm²) | Vₘ₈₉₉ / V  | Iₘ₈₉₉/ (μA·cm²) | Vₘ₈₉₉ / V  | Iₘ₈₉₉/ (μA·cm²) | Vₘ₈₉₉ / V  | Iₘ₈₉₉/ (μA·cm²) |
| B-2         | -0.0335     | 0.658       | -0.0084     | 0.424       | -0.035      | 0.2044      | -0.042      | 0.335       |
| C-2000      | -0.0357     | 0.536       | -0.2252     | 0.44        | -0.0804     | 0.529       | 0.0326      | 0.389       |
| G30         | -0.0306     | 0.273       | -0.039      | 0.212       | -0.0392     | 0.227       | -0.0122     | 0.241       |
| Incoloy 925 | -0.0327     | 0.89        | -0.0528     | 0.204       | 0.0107      | 0.135       | 0.023       | 0.302       |
| 304 steel   | -0.3043     | 32          | -0.2914     | 10.19       | -0.2979     | 9.33        | -0.2944     | 6.46        |

**Figure 3.** Corrosion rate line chart of sample in solution

5. **Conclusion**
1. Ni-based alloy has stronger corrosion resistance than 304 stainless steel in sulfuric acid. With the increase of sulfuric acid concentration, the corrosion rate of each alloy also increased. Among them, the corrosion rate of 304 stainless steel sample in sulfuric acid solution was about 20 times that of nickel-based corrosion resistant alloy.
2. The main precipitate in the nickel-based alloy is the $\gamma$ phase, and the carbide phase in the alloy is mainly precipitated in the form of M23C6 and M6C phases, which has an effect on the corrosion resistance of the alloy.

3. The Cr and Mo elements in the nickel-based alloy have the greatest influence on the corrosion resistance of the alloy, while the addition of elements such as Cu, Al and rare earth can improve the corrosion resistance of the alloy to some extent.

Acknowledgements
This works was supported by Collaborative Innovation Center of Advanced Control Valve Project (Grant No.WZYB-XTCX-003).

References
[1] A J Sedriks. Nickel Alloys: Corrosion[J]. Encyclopedia of Materials Science & Technology, 2001:6140-6141.
[2] W Z Friend. Corrosion of nickel and nickel-base alloys[M]. 1980.
[3] X L Shang, Z J Wang, Q F Wu, et al. Effect of Mo Addition on Corrosion Behavior of High-Entropy Alloys CoCrFeNiMo_ x in Aqueous Environments[J]. Acta Metallurgica Sinica (English Letters), 2019, 32(1):41-51.
[4] Y V Deshpande, A B Andhare, P M Padole. How cryogenic techniques help in machining of nickel alloys? A review[J]. Machining Science & Technology, 2018, 22(1):1-42.
[5] D Gervasio, H Elsentriecy . Corrosion of Hastelloy in Molten Salt Used As High Temperature Heat Transfer Fluids[J]. Nature Medicine, 2015, 9(8): 1076-1080.
[6] X H Zhao, Z Q Bai, Y R Feng, et al. Effects of heart trement and precipitates phase on corrosion resistance of Ni-based alloy[J]. Transactions of Materials and Heart Treatment, 2012, 33(08):39-44.
[7] C L Hu. Corrosion Resistance Dependence of Rare Earth NiCrMoY Alloy Coatings[J]. Applied Mechanics & Materials, 2014, 665:107-110.
[8] T Hong, M Nagumo. The effect of SO 4 2− concentration in NaCl solution on the early stages of pitting corrosion of type 430 stainless steel[J]. Corrosion Science, 1997, 39(5):961-967.
[9] K. S RAJA, NAMJOSHI, et al. Improved corrosion resistance of Ni-22Cr-13Mo-4W Alloy by surface nanocrystallization[J]. Materials Letters, 2005, 59(5):570-574.
[10] J H Chang, J M Chou, R I Hsieh, et al. Corrosion behaviour of vacuum induction-melted Ni-based alloy in sulphuric acid[J]. Corrosion Science, 2010, 52(7):2323-2330.