Corrosion behavior of plasma transferred arc and laser cladding Ni-based alloy coatings in different acid solutions

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Abstract. The Ni-based coatings were prepared by laser cladding (LC) and plasma transferred arc (PTA) welding, respectively. The corrosion behavior of the coatings were tested by scanning electron microscopy (SEM), X-ray diffraction (XRD), electrochemical corrosion, long-term immersion tests and X-ray photo electron spectroscopy (XPS) analysis. The results of XRD showed that the composite coatings comprised Ni, Cr and Mo. The electrochemical corrosion tests included polarization curves and electrochemical impedance spectroscopy (EIS). The XPS analysis presented samples included Ni, Fe, Cr and Mo oxides, which protected the substrate from corrosion by acid solutions. The results also presented that the Ni-based PTA coating is more resistant to corrosion than the Ni-based LC coating. In the immersion tests, the coatings changed from pitting to general corrosion as the immersion time prolonged.

1. Introduction
Generally, Ni-based coatings exhibit outstanding mechanical properties and wear performances, so it is commonly used in the field of deep sea oil drilling, an acidic environment containing H⁺, SO₄²⁻ and Cl⁻. The method for preparing Ni-based coatings is called surface engineering technology [1,2]. For flame spraying with a mature process and low processing cost, this method has some disadvantages. Flame spray coatings are prone to corrosion because these resulting pores, microcracks, and oxide layers at the interface between the coating and the substrate are susceptible to corrosion channels in the corrosive medium for serious damage. These pores or defects cause fatigue cracks to occur and produce more cracks. Corrosion is often exacerbated by the formation and expansion of fatigue cracks [3,4].

At present, in order to improve the performance of components, three methods are commonly used to extend the service life of metal components [5]. First, the method is adjusting the composition of the metal to improve the nature of the metal. Second, it is easily form a protective film layer on the component surface. Third, covering the surface of the part with a corrosion-resistant and wear-resistant metal matrix composite (MMC). Compared with the first two methods, the third method can produce a coating having excellent properties such as corrosion resistance, abrasion resistance, and
high temperature resistance. LC is a surface engineering process that provides energy by laser. PTA is developed from the most traditional tungsten inert gas shielded welding process. They are commonly used in the art of metal matrix composites [6].

The corrosion behavior was studied by Yang et al. of Ni on laser surface-clad Fe-based alloy in H$_2$SO$_4$ solution. Different amounts of Ni have different effects on the substrate, and the higher content is more resistant to corrosion. Ni-based alloy coating enhances corrosion resistance of materials [7]. Coatings with denser layers of fabrication and fewer voids greatly improve corrosion resistance [8]. The development of PTA and LC technology has improved coating compactness, improved bond strength and reduced porosity [9]. However, there is currently little information on the corrosion of Ni-based coatings in different acid solution [10].

The purpose of this paper is to explore the corrosion resistance of Ni-based coatings in different acid solutions, and contribute to the study of corrosion of Ni-based coatings. The corrosion behavior of the Ni-based coatings were clarified by the polarization curve, EIS measurement, long-time immersion test and XPS analysis. This article provides an in-depth introduction to the use of Ni-based coatings in different acidic solution.

2. Experimental

2.1. Materials

In this study, Ni-based powders were used, the chemical composition of the Ni-based powders are shown in Table 1. The Ni-based alloy power morphology and particle size distribution are shown in Figure 1. It can be seen from the SEM image that the Ni-based powders were spherical, and spherical powder had good fluidity. It can be seen from the figure that its particle size was mainly distributed at 60-240 μm.

Ni-based coating were prepared by LC and PTA surfacing processes, respectively. Define the Ni-based LC coating as S1 coating, and the Ni-based PTA coating as S2 coating. The processed samples were cut into 10mm×10mm×5mm. Then, the obtained samples were immersed, sanded to 1500# with water-resistant sandpaper, deionized water, alcohol degreased and cold air dried, and placed in a drying dish for use. Particularly, the samples processing required for electrochemical experiments was formed by first, the samples need to be sanded to 400# with water-resistant sandpaper. Then, one of the 10mm×10mm faces of the sample was selected as the work surface, and its back surface was welded with a copper wire. In addition, the other five faces of the removal face were encapsulated in epoxy in a Teflon tube. Next, after drying the working surface of the packaged sample, it is ground to 1000#, and then washed with deionized water. Finally, it is washed in anhydrous ethanol for 10 minutes using an ultrasonic cleaner, and then dried and taken out.

| Table 1. Chemical composition of Ni-based powders [wt. %]. |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| C        | P        | Mo       | W        | Fe       | Mn       | Cr       | Si       | O        | V        |
| 0.12     | 0.016    | 15.9     | 4.6      | 2.9      | 1.3      | 15.6     | 0.6      | 0.03     | 0.6      | Bal.     |

2.2. Electrochemical tests

Electrochemical workstations (CHI600E Series Electrochemical Analyzer / Workstation, Shanghai Chenhua Instrument Co., Ltd.) were used, and the standard three-electrode system was used. These samples were respectively immersed in the HCl solution electrolyte and H$_2$SO$_4$ solution electrolyte for 1 hour to reach a steady state before the measurement. The potentiodynamic-polarization curves and EIS measurement results were obtained by this these tests.

2.3. Immersion tests

The samples were immersed in HCl solution duration of 1, 3 and 7 days in order to find out the corrosion parameters. After the test, the corroded surfaces were observed by SEM. Further, the Ni-based LC composite coating surface product after 3 days of immersion was analyzed by XPS.
Figure 1. SEM image and particle size distribution of Ni-based powders.

3. Results and discussion

3.1. Phase Composition and Microstructure
The XRD patterns of Ni-based coating and Ni-based powders are shown in Figure 2. It can be observed that NiFe, Cr4Ni15W and MoNi4 phases existed on the coatings. The SEM images obtained at the cross-sectional positions of the S1 coating and the S2 coating are shown in Fig. 3. Compared to S1 coating (Figure 3a), S2 coating (Figure 3b) has a clear dividing line, which indicates that the heat affected zone of laser cladding is small, and the area affected by plasma transferred arc welding is large. In the Figure 3, the coatings had a good metallurgical bond with the substrate steel by the thin white layer [11]. The SEM images of the S1 coating and S2 coating are shown in Figure 4. The surface of the coatings are dispersed with many tiny pores, and the presence of small pores can offset the influence of energy and improve the impact resistance.

3.2. Electrochemical measurements
Figure 5 shows the potentiodynamic-polarization curves of the substrate, S1 coating and S2 coating. The data obtained from the potentiodynamic-polarization were presented in Table 2. Combine Figure 5 and Table 2, the corrosion current $I_{corr}$ of S2 coating maximum. The polarization resistance value of S2 coating was great. The substrate steel exhibited the lowest self-corrosion potential value in H2SO4 solution. Typical passivation can be observed in both the S1 coating and the S2 coating. Compared to LC technology, PTA technology had a uniform temperature change during the surfacing process, was less prone to deformation, and the coating surface was smoother to reduce subsequent processing cycles and tool wear. In the Figure 5b, the S2 coating still had a noble direction, but S1 coating exhibited the lowest self-corrosion potential in HCl solution, confirming the impact of PTA technology. Consequently, in different acid solutions, the S2 coating has better corrosion resistance than the S1 coating.

Figure 6 shows the EIS results and Figure 7 shows the equivalent electrical circuits of EIS. S2 coating and the substrate steel Nyquist curve consists of only one capacitive loop, while S1 coating consists of two capacitive loop, and the low frequency capacitive anti-arc is caused by the corrosion product film appearing on the surface of the sample. The adsorption of corrosion products on the surface of the sample causes a low frequency induction loop, and the charge transfer reaction results in a high frequency capacitor loop [12]. For better adaptability, the capacitor was replaced by a constant phase element [13]. The equivalent circuit of the substrate steel, S1 coating, and S2 coating Nyquist plots can be expressed by Figures 7(a), 7(b) and 7(c), respectively. In the equivalent circuit (Figures 7) $R_s$ was the solution resistance, $C_i$ was the capacitive behavior of the passivation film formed, $R_t$ was the resistance caused by passivation layer, $C_{dl}$ was the resistance behavior of electric double layer, $R_{ct}$ was the charge transfer resistance, $R_i$ was the adsorption of intermediate products on the electrode.
process, W was an impedance element containing information reflecting corrosion products and L was the reactance. Tables 3, 4 and 5 presented equivalent circuit parameters of the samples, respectively.

Figure 2. XRD pattern of S1 coating, S2 coating and Ni-based alloy powders.

Figure 3. SEM images S1 coating (a) and S2 coating (b) at locations of cross section.

Figure 4. SEM images of S1 coating (a) and S2 coating (b).
Figure 5. Potentiodynamic-polarization curves of the substrate, S1 coating and S2 coatings in H$_2$SO$_4$ solution (a) and HCl solution (b).

Table 2. Corrosion data determined from the potentiodynamic-polarization curves of the coatings.

|                | H$_2$SO$_4$ |           | HCl      |           |
|----------------|-------------|-----------|----------|-----------|
|                | $E_{\text{corr}}$ [V] | $I_{\text{corr}}$ [A] | $E_{\text{corr}}$ [V] | $I_{\text{corr}}$ [A] |
| Substrate      | -0.492      | 9.207×10$^{-4}$ | -0.474   | 8.103×10$^{-5}$ |
| S1 coating     | -0.461      | 6.668×10$^{-4}$ | -0.422   | 1.777×10$^{-4}$ |
| S2 coating     | -0.282      | 9.511×10$^{-5}$ | -0.184   | 1.347×10$^{-5}$ |

Figure 6. (a) Nyquist plots and (b) Bode impedance plots of the substrate, S1 coating and S2 coatings in H$_2$SO$_4$ solution; (c) Nyquist plots and (d) Bode impedance plots of the substrate, S1 coating and S2 coatings in HCl solution.
Figure 7. Equivalent electrical circuits of EIS for substrate (a) and S1 coating (b) and S2 coating (c) in different acid solutions.

Table 3. EIS fitting results of the substrate in different acid solution.

| Solution | Rs/[$\Omega \cdot \text{cm}^2$] | $C_f/[$$\Omega \cdot \text{cm}^{-1} \cdot \text{cm}^2$] | $R_{ct}/[$$\Omega \cdot \text{cm}^2$] | $L/[$H$ \cdot \text{cm}^2$] | $R_{ind}/[$$\Omega \cdot \text{cm}^2$] |
|----------|-----------------|-----------------|-----------------|--------------------|-----------------|
| H$_2$SO$_4$ | 2.583 | 5.013x$10^{-5}$ | 42.70 | 14.76 | 24.41 |
| HCl | 2.709 | 4.463x$10^{-5}$ | 2.348x$10^{-7}$ | 186.5 | 55240 |

Table 4. EIS fitting results of the S1 coating in different acid solution.

| Solution | Rs/[$\Omega \cdot \text{cm}^2$] | $C_f/[$$\Omega \cdot \text{cm}^{-1} \cdot \text{cm}^2$] | $R_{f}/[$$\Omega \cdot \text{cm}^2$] | $C_{dl}/[$$\Omega \cdot \text{cm}^{-1} \cdot \text{cm}^2$] | $R_{ct}/[$$\Omega \cdot \text{cm}^2$] | $W/[$$\Omega \cdot \text{cm}^2$] |
|----------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|
| H$_2$SO$_4$ | 2.209 | 8.158x$10^{-5}$ | 25.51 | 6.830x$10^{-5}$ | 124.5 | 7.944x$10^{-3}$ |
| HCl | 5.314 | 9.366x$10^{-5}$ | 13.91 | 1.109x$10^{-4}$ | 32.24 | 8.028x$10^{-2}$ |

Table 5. EIS fitting results of the S2 coating in different acid solution.

| Solution | Rs/[$\Omega \cdot \text{cm}^2$] | $C_f/[$$\Omega \cdot \text{cm}^{-1} \cdot \text{cm}^2$] | $R_{f}/[$$\Omega \cdot \text{cm}^2$] | $C_{dl}/[$$\Omega \cdot \text{cm}^{-1} \cdot \text{cm}^2$] | $R_{ct}/[$$\Omega \cdot \text{cm}^2$] |
|----------|-----------------|-----------------|-----------------|--------------------|-----------------|
| H$_2$SO$_4$ | 2.223 | 1.805x$10^{-4}$ | 0.884 | 15660 | 4.337x$10^{-4}$ | 1 |
| HCl | 3.182 | 3.010x$10^{-4}$ | 1 | 3609 | 7.931x$10^{-5}$ | 0.919 |

In these tables, n was a parameter of no unit. These data showed that the S2 coating has a significantly higher resistance value than the substrate and the S1 coating. The $R_f$ value of the S2 coating is about one hundred times higher than that of the S1 coating, which indicated that Ni-based coating is more resistant to corrosion than the substrate steel, and compared with Ni-based composite coatings made by LC process, Ni-based composite coatings made by PTA process can prevent corrosion more effectively. The diameter d of the capacitor ring gradually became smaller in the order of the S2 coating, the S1 coating, and the substrate steel, and this tendency also indicated that the corrosion resistance was lowered in this order.

3.3. Surface analysis after corrosion

Define the Ni-based LC coating in H$_2$SO$_4$ solution as Sample 1, and in HCl solution as Sample 2, the Ni-based PTA coating in H$_2$SO$_4$ solution as Sample 3, and in HCl solution as Sample 4. Figure 8 shows SEM images of the coatings surfaces. After 1 day of immersion, the coating of the Ni-based composition on the surface appeared to be unaffected by the solution. After 3 days of immersion, the Ni-based composition coating on the surface was pitting. After 7 days of immersion, the Ni-rich phase was dissolved. It has been found that physical or chemical inhomogeneities can have a severe impact on pitting corrosion [14]. Metals with lower potentials produce dissolution or pits faster.

The XPS analysis of the S2 coating obtained after 3 days of immersion is shown in Figure 9. Ni$_2$p$_{3/2}$ spectrum consisted of four peaks located at 825.598eV, 873.884eV, 856.000eV and 861.357eV,
corresponding to the presence of Ni, NiO, Ni$_2$O$_3$ and NiOOH, respectively. Cr $2p_{1/2}$ spectrum consisted of three peaks located at 586.837 eV (Cr$_2$O$_3$) and 577.315 eV (Cr(OH)$_3$). Fe$2p_{3/2}$ spectrum consisted of two peaks located at Fe$_2$O$_3$ (712.368eV), and FeOOH (725.921eV). In Mo $3d_{3/2}$ spectra, the peak of MoO$_3$ (235.533eV), MoO$_2$ (232.051eV) and Mo (227.807eV) can be detected on the surface of the coating.

4. Conclusion

The Ni-based composite coatings respectively formed by LC and PTA have a good metallurgical effect on the substrate steel. The composite coating is considered to be a Ni-rich phase containing [Ni, Fe], Cr$_3$Ni$_5$W, and MoNi$_4$. Compared with Ni-based composite coatings made by LC process, Ni-based composite coatings made by PTA process can prevent corrosion more effectively, due to the PTA technology makes the coating more compact. The corrosion resistance of the Ni-based coating in the H$_2$SO$_4$ solution is superior to in HCl solution, due to the H$_2$SO$_4$ solution is an oxidizing acid, and it is easier to form a passivation film protective substrate. As the immersion time is extended, the surface of the Ni-based coating changes from pitting to general corrosion.

![Figure 8. SEM images of corroded surface of S1 coating and S2 coating in H$_2$SO$_4$ solution and HCl solution for 1, 3 and 7 days.](image)
Figure 9. Detailed XPS spectra of Ni 2P3/2, Cr 2P1/2, Fe 2P3/2, and Mo 3d3/2 of coating surface on S1 coating in HCl solution for 3 days.

Acknowledgments
This work was financially supported by the Ocean Public Science and Technology Research Fun Projects of China (201405013-3).

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