Study on Corrosion Resistance of Pulse Laser Welded Joints of Hastelloy C-276

Ying Wang¹, a, Lei Du², b, Dawei Liu², c, and Desheng Xu¹, *

¹School of Jilin University, Chang Chun 130022, China
²Harbin Electric Power Equipment Co. Ltd, Harbin 150006, China

*Corresponding author e-mail: xuds@jlu.edu.cn, a1224156841@qq.com,
b411374767@qq.com, chpcliudawei@harbin-electric.com

Abstract. Laser welding is an ideal method to join hastelloy C-276 for the good characters. Presently, there are few studies on corrosion resistance of the weld joint of hastelloy C-276. The corrosion resistance of hastelloy C-276 pulse laser welded joints was studied in this paper. The results of the electrochemical testing both in neutral and acidic solution show that the corrosion resistance of the weld is better than the base metal. The microstructure was analyzed by using SEM, EDS and XRD, it is found that the grain of the weld obviously is refined and the size reduces to 2-5μm, which is benefit to the corrosion resistance, and slight micro-segregation of Mo occurs and no second phase formation in the weld which has little effect on the corrosion resistance. The change of the microstructure makes it that the corrosion resistance of the weld is superior to that of the base metal.

1. Introduction

The AP1000 nuclear power plant adopting a shielded motor is the third-generation nuclear power plant introduced by China for the 2020 nuclear power using plan. The material of the shielding sleeve must have good corrosion resistance in terms of security because rich boric acid, sulfate, chloride ions and other corrosive component distributing around the sleeve [1]. Hastelloy C-276 is ideal material which has high content of Cr and Mo so it’s easy to form passive film on the surface and has good corrosion resistance [2, 3]. TIG welding, manual GTAW, GMAW and plasma arc welding are often used in China for the connection of the alloy, and there are obvious precipitates at the weld [4, 5, 6], which would reduce the corrosion resistance and limit using the material.

Laser welding is an ideal welding method for laser’s good characters of high energy density, small heating range and heat input, which could make the weld small and decrease the range of heat affected zone (HAZ) to increase the properties of the joints. Some studies have found that 304 stainless steel laser welded joints have no obvious heat affected zone, and no second phase is formed [7], and the Hastelloy C-276 laser welded joints are the same [8], and the welded joint has good performance. The nuclear power plant benefit for us, but it could destroy us if the joints fail to meet the corrosion resistance requirement. There are few studies on the corrosion resistance of the joints at home and abroad [9]. Therefore, it is necessary to further study the corrosion resistance of the laser welded joint, which is of great significance for using safely nuclear power.
2. Materials and Methods
The welding material is 0.381 mm thick Hastelloy C-276, which is treated by solution annealing and
water cooling, and its chemical composition is shown in Table 1. The welding equipment is a HKW-
1050 pulse laser welding system. The welding current is 78A, pulse width is 7.5ms, frequency is 9Hz,
welding speed is 190mm/min, and defocusing amount is 0mm.

| sample | Ni   | Cr     | Mo    | Fe    | Mn    | Co    | W     | C     | Si   |
|--------|------|--------|-------|-------|-------|-------|-------|-------|------|
| C-276  | Bal. | 14.5-16.5 | 14.0-17.0 | 5.0-7.0 | 1.0 | 2.5 | 3.0-4.5 | 0.02 | 0.08 |

2.1. Electrochemical measurement
The base metal and the welded joint were cut into 15 mm × 12 mm × 0.381 mm, wherein the welded
joint samples were cut along the center of the weld, as shown in Fig 1, and the cross section at the weld
side is the test surface, and the test surface of the base metal is any cross section. The test surface of the
weld and base metal is ground to 2000# and polished. The copper wire tightly connected to the sample.
Apply nail polish to the copper wire and the sample except the test surface of 10mm. The corrosion
resistance was tested by using three-electrode electrochemical test method. The auxiliary electrode (AE)
was a platinum plate electrode, the reference electrode (RE) was a calomel electrode, and the working
electrode (WE) was the sample, the schematic diagram is shown.

Figure 1. Cutting diagram of weld sample

Figure 2. Electrochemical test schematic diagram

In Fig 2. In the experiment, the scanning potential range of the polarization curve is -1.5V to 1.5V,
the scanning rate is 5mv/s, and the electrochemical impedance spectroscopy (EIS) measurement is a
sinusoidal voltage with a maximum value of 10mv, and the scanning frequency range is 100 KHz-10
MHz. The testing solution was a 3.5% NaCl solution and 100H2O + 5 ml HCl + 3 g NaCl respectively.

2.2. Intergranular corrosion test
Cut the welded joint to test samples of size of 11mm × 12mm × 0.381mm, and polish the samples to
2000grid, rinsed them with water and blow dry, and soak them in a mixed solution of 7% H2SO4 + 3%
HCl + 1% FeCl3 + 1% CuCl2, of which the temperature was controlled at 90 °C and the time was 72h.

3. Result and discussion
3.1. Potentiodynamic Polarization and EIS Results
Fig 3 showed the polarization curves of the base metal and weld. It was seen that the corrosion potential
\(E_{corr}\) of weld was closed to that of the base metal, but the corrosion currents \(i_{corr}\) had a difference. In
the neutral solution, as shown Fig 3(a), the anodic current of the base metal and the weld increased with
the voltage, and the current reached the maximum at -0.5 V, and then the current slightly decreased. As we know, the surface of the alloy with big content of Cr easily forms passive film, which would decrease charge transfer and reduce current, and forms a passive zone of 0V ~ 1.0V, the current is almost steady. As the voltage continues to increase, the passive film is broken down or the element is oxidized further [10], making the metal exposed to the etching solution, and the current increases again.

In the acidic solution, as shown Fig 3(b), the trend of anodic current was consistent with that in the neutral solution, and the current decreased at 0V, and it decreased faster than that in the neutral solution, which indicated that the formation rate of the passive film was greater than the dissolution rate in the acidic solution. That is that it would form the films more easily in harsh solution. The values of corrosion potential and corrosion current density in the two solutions are shown in Table 2, it is found that the corrosion potential of the weld is close to that of the base metal, and the corrosion current is smaller than that of the base metal in neutral and acidic solutions. According to the result above, it conclude that the corrosion resistance of the weld is superior to that of the base metal.

![Figure 3](image-url)

**Figure 3.** Polarization curve of base metal and weld in (a) neutral and (b) acidic solution.

**Table 2.** Corrosion current and potential of base metal and weld in neutral and acidic solution.

| Sample  | Neutral solution | Acidic solution |
|---------|------------------|-----------------|
|         | $I_{corr} / (A \cdot \text{cm}^{-2})$ | $E_{corr} / V$ | $I_{corr} / (A \cdot \text{cm}^{-2})$ | $E_{corr} / V$ |
| Weld    | 0.384425         | -0.8692         | 0.099875         | -0.3637         |
| Base metal | 2.04675         | -0.8948         | 0.27915          | -0.3473         |

Fig 4 showed the Nyquist plots of the base metal and the weld in neutral and acidic solutions. In the neutral solution, as shown in Fig 4(a), the capacitive reactance arc of the weld was larger than that of the base metal, and there is a small capacitive reactance arc at the medium-high frequency. It could be seen that the impedance appeared 45° upward trend at the low frequency, which showed that the electrode reaction process would be changed from the original charge transfer process control to the material transfer process control at low frequency [1]. The corrosion product could cause the dispersion effect, so there would be a variable $W$ and CPE in the equivalent circuit, as shown the circuit diagram of Fig 4. The EIS data were fitted with the fitting software Zsimpwin, as shown red plot. The fitting data are shown in Table 3, of which $R_s$ is the solution resistance between the reference electrode and the working electrode, CPE is the electric double layer capacitance formed between the working electrode and the solution. The expression of its impedance is

$$Z_{CPE} = 1 / [(j\omega)^n \cdot C]$$  \[1\]
Wherein the coefficient $n$ in this circuit component represents the strength of the dispersion effect, and the closer $n$ is to 1, the closer CPE is to pure capacitance. $R_{ct}$ is a charge transfer resistor and $W$ is a semi-infinite diffusion impedance. The corrosion resistance of the working electrode depends on the charge transfer resistance $R_{ct}$, and the larger the $R_{ct}$, the stronger the corrosion resistance. It can be seen from the data in the table 3 that the $R_{ct}$ of the base metal is smaller than the resistance of the weld, which corresponds to the result of the polarization curve, and the corrosion resistance of the weld is good.

Table 3. Value of each circuit element of Equivalent circuit

|                | $R_s$ (Ω·cm$^{-2}$) | CPE, Y$_0$ (S·sec$^{1/2}$·cm$^{-2}$) | $n$ | $R_{ct}$ (Ω·cm$^{-2}$) | $W$ (S·sec$^{1/2}$·cm$^{-2}$) | $C$ (F·cm$^{-2}$) | $R_1$ (Ω·cm$^{-2}$) |
|----------------|---------------------|-------------------------------------|-----|------------------------|-----------------------------|----------------|---------------------|
| neutral solution | C-276                | 0.1482                              | 0.0081 | 0.7657                | 97.2                     | -             | -                   |
| weld           | 0.6474          | 6.635E-5                            | 0.8379 | 101.2                 | 0.1227                  | -             | -                   |
| acidic solution | C-276              | 0.0841                              | 0.02134 | 0.4991              | 0.6696                  | 0.953         | 0.00025          |
| weld           | 0.0614             | 0.01297                             | 0.5394 | 3.684                 | 0.1027                  | 0.00018       | 12.17              |

In the acidic solution, as shown in Fig 4(b), the impedance arc of the base metal and the weld has changed from one to two that adding a resistor and a capacitor, and the increasing resistance should be the resistance of the passive film. Not only the Cr element, but the Mo and Win the alloy also promote formation of passive film in the acidic solution [2, 3, 12, 13]. And the result of polar curve proves that the film would form faster in the solution, so the film could be the resistor, and the increased capacitor is formed between the film and the material itself. Table 3 shows the values of the different circuit components fitted. It is found that the values of both the resistance of the film and the charge transfer resistance $R_{ct}$ of the welds are large, and the welds exhibit high corrosion resistance.

3.2. Immersion Corrosion

Immersion corrosion was carried out to study the corrosion resistance of the weld joint further. Fig 5 shows the surface morphology after immersion corrosion of the welded joint. Fig 5(b) and 5(c) are the weld center and boundary micrographs respectively. It could be seen that the grain boundary is corroded severely at the weld and severe intergranular corrosion occurs. We need to analyze the microstructure to explain the reason.

Figure 4. The Nyquist spots of base metal and weld in (a) neutral and (b) acidic solution
4. Microstructures of the Weld joints

Fig 6 and Fig 7 show the metallographic structure of the welded joint and the base metal structure respectively. Combined with the microstructure of the weld and the base metal, the grain size in the weld is significantly refined. The grain size of the base metal calculated by Image Pro plus software is 30-50μm, and of the weld at least is 2-5μm. It has found that the material easy to form a passive film will increase its corrosion resistance as the grain size decreases, and vice versa [14, 15]. The grain refinement increases the grain boundary density to provide the favorable position to formation of a film [16]. So the corrosion resistance of the weld is better than that of the base metal in the electrochemical measurement.
Slight element segregation was observed by SEM analysis and energy spectrum analysis (EDS) of the weld, as shown in Fig 8. The content of Mo in the fusion line is significantly reduced, and the other elements are evenly distributed, as shown in Fig 8(a). It can be seen that Ni and Mo elements fluctuate significantly in the weld by line scanning, as shown in Fig 8(b). Further scanning, shown in Fig 9, it can be seen that the elements of the grain boundary of the weld segregated, and the content of Mo is decreased, and the grain internal elements slightly segregated, which is not obvious.

Laser welding is a good method connecting the sheet of Hastelloy C-276 of which the laser energy density is high, and the temperature gradient of the weld boundary is large. According to the solidification theory, element segregation would occur when the solidification speed is fast, whereas the cooling rate is fast enough to limit the elements diffusion, so the segregation of the elements in the center of the weld is not serious. It was found that the Mo element mainly segregated based on

![Figure 8](image_url)

**Figure 8.** (a) Map and (b) line scanning near fusion-line.
ED’s analysis. It has found that Mo can increase the corrosion resistance of materials in reducing acids, and can also benefit the pitting resistance [17, 18]. Nickel-based alloys with high content of Mo
have high corrosion resistance in HCl solution [11], and Mo in the alloy easily reacts with O dissolved in the solution to form MoO$_4^{2-}$ which adhere to the surface of the film to prevent Cl transport, and improves the properties of the film[19,20]. But it would increase the driving force for the formation of the second phase if the content of the Mo is too high, which could reduce corrosion resistance [21]. In this paper, the Mo content of Hastelloy C-276 is proper, 14wt%-17wt%, and the corrosion resistance increases with the increase of Mo content. Therefore, the segregation of the Mo element adversely affects the corrosion resistance of the weld and has a tendency to intergranular corrode. In the center of the weld, the grain size is refined, the element segregation is not serious, and the corrosion resistance at the center of the weld is superior to that of the base metal.

Fig 10 shows the XRD pattern of the welded joint. It was found that the composition of the base metal and the weld did not change, that is, no new phase was formed. The phase of each peak is Ni-Cr-Co-Mo, which is austenite structure, that is, the difference of corrosion resistance of the weld and the base metal is independent of the second phase.

5. Conclusion

(1) The grain of the laser welding weld is refined, and the minimum size of the weld center is 2μm. There is slight element segregation, and no formation of second phase, and there is a tendency of intergranular corrosion at the weld.

(2) It is found that the corrosion current of the laser welding weld center is lower than that of the base metal in the neutral and acidic solution, and the corrosion voltage of both are close in electrochemical tests. So the corrosion resistance of the weld is better than that of the base metal. The main reason is refinement of the grain of the weld. The EIS test results show that the material form a passive film more easily in an acidic solution.

References

[1] G MA. Foundation of thin hastelloy C-276 sheet laser welding for nuclear reactor coolant pump can. Dalian: Dalian university of technology, 2013.

[2] A C Lloyd, J J Noël, S McIntyre and D W Shoesmith. Cr, Mo and W alloying additions in Ni and their effect on passivity, Electrochim. Acta. 2004, 49 (17-18): 3015 - 27.

[3] A Mishra. Corrosion Study of Base Material and Welds of a Ni–Cr–Mo–W Alloy, Acta Metall. Sinica (English Letters). 2017, 30 (4): 326 - 32.

[4] L Shang, Z Huang, H Xu. Study on microstructure and properties of welded joint for C-276 alloy, Electric. Welding. Mach. 2018, (5): 29.

[5] G Ren, X Guo, Z Liu, J Xu and Y Zhang. Effect of different welding process on weld microstructure and intergranular corrosion resistance for hastelloy C-276, Mater. Dev. Appl. 2016, 31 (5): 40 - 44.

[6] P Subramani, S Shetty, R Anirudhapandit, P R Hari, K Gokul Kumar, M Manikandan, N Arivazhagan and N Siva Shanmugam. Investigations on the Microstructure, Microsegregation and Hardness Properties of Bead on Plasma Arc Welded C-276 Alloy. Mater, Today. Proc. 2018, 5 (5): 13628 - 36.

[7] W Zhang. Research on Laser Welding 304 Austenitic Stainless Steel Sheet. Dalian: Dalian university of technology, 2009.

[8] G Ma, D Wu, F Niu and H Zou. Microstructure evolution and mechanical property of pulsed laser welded Ni-based superalloy. Opt. Lasers .Eng. 2015, 72: 39 - 46.

[9] G Ma, F Niu, D Wu and Y Qu. Electrochemistry corrosion properties of pulsed laser welding Hastelloy C-276, Phys. Procedia. 2013, 41: 31 - 37.

[10] C Fan. Mechanical and corrosion properties of hastelloy C-276/316L laser dissimilar welding. Dalian: Dalian university of technology, 2014.

[11] K Sarkar, A Mondal, A Chakraborty, M Sanbui, N Rani and M Dutta. Investigation of microstructure and corrosion behavior of prior nickel deposited galvanised steels, Surf. Coat. Technol. 2018, 348: 64 - 72.
[12] A Mishra. Performance of Corrosion-Resistant Alloys in Concentrated Acids, Acta Metall. Sinica (English Letters). 2017, 30 (4): 306 - 18.

[13] P Crook. Corrosion characteristics of the wrought Ni-Cr-Mo alloys, Mater. Corros. 2005, 56 (9): 606 - 10.

[14] Y Feng, X Zhang, Y Hong, Y Liu, S Hao and L Cui. Corrosion behavior of electrodeposited Ni with normal and bimodal grain size distribution, Trans. Nonferrous. Met. Soc. CHN. 2019, 29 (2): 424 - 436.

[15] K D Ralston and N Birbilis. Effect of grain size on corrosion: a review. Corros, 2010, 66 (7): 075005-075005-13.

[16] V Pandey, J K Singh, K Chattopadhyay, N S Srinivas and V Singh. Optimization of USSP duration for enhanced corrosion resistance of AA7075. Ultrason. 2019, 91: 180 - 92.

[17] H Wang. A study on laser welding joint corrosion resistance performance of hastelloy C-22. Shanghai: Shanghai Jiao Tong University, 2009.

[18] Y Li, S Wang, J Yang, D Xu, Y Guo, L Qian and W Song. Corrosion characteristics of a nickel-base alloy C-276 in harsh environments, Int. J. Hydrogen Energy. 2017, 42(31): 19829-35.

[19] S Zhou, G Ma, D Chai, F Niu, J Dong, D Wu and H Zou. Nickel-based alloy/austenitic stainless steel dissimilar weld properties prediction on asymmetric distribution of laser energy, Opt. Laser Technol. 2016, 81: 33 - 39.

[20] B Yang, C Shi, J Teng, X Gong, X Ye, Y Li, Q Lei and Y Nie. Corrosion behaviors of low Mo Ni-(Co)-Cr-Mo alloys with various contents of Co in HF acid solution, J. Alloys. Compd. 2019, 791: 215 - 224.

[21] S Zhang, H Li, Z Jiang, B Zhang, Z Li, J Wu, S Fan, H Feng and H Zhu. Effects of Cr and Mo on precipitation behavior and associated intergranular corrosion susceptibility of superaustenitic stainless steel S32654, Mater. Charact. 2019, 152: 141 - 150.