Study on corrosion mechanism of high-nitrogen steel laser-arc hybrid welded joints

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Abstract
In this paper, the electrochemical microcorrosion behavior of High-nitrogen steel hybrid weld joints with different wires addition were investigated. Polarization curves measurement was conducted to evaluate the corrosion feature in 3.5% NaCl solution. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were used to analyze the specific corrosion behavior and pitting deepening mechanism induced by precipitated ferrite-dendrites. The experimental results showed that the addition of nitrogen-containing welding wire improved the corrosion resistance of whole weld joint. As a transitional region, the HAZ exhibited relative weak pitting resistance and severe shedding behavior. The coherent dendrites and similar complex geometries led to the accumulation of continuous corrosion channels. The XPS spectra results indicated that the additional nitrogen in the welding wire optimized oxide composition of the surface passive film.

1. Introduction
Nitrogen can be used as a potential candidate to replace expensive nickel in steel to produce high-nitrogen stainless steel (HNSS), an inexpensive material with a combination of excellent mechanical properties and high corrosion resistance [1, 2]. With the general orientation of extensive application in resource saving metal materials, the manufacturing material product from HNSS experienced a long period of extreme environments, the corrosion resistance of vulnerable welding parts has received increasing attentions.

Conventional stainless welded joints are more susceptible to intergranular corrosion and crevice corrosion than their parent metal due to their heterogeneous second phase. The partial-crystallize HAZ, as transition region in welded joints, may exhibit a poor corrosion defense depending on different weld temperature gradient and solidification mode. Nitrogen, as austenite-stabilizing element [3–5], has the synergistic effect with molybdenum, which enhances the stability of passive films [6–8]. The infiltrated nitrogen in weld puddle from base metal indirectly optimized the pitting corrosion resistance and repassivation ability of welded joints [9, 10]. However, the welding process of HNSS accompanied by huge difficulties, some non-metallic elements overflow from the weld puddle under supersaturation effect which result in a less nitrogen content and poor comprehensive mechanical properties of the weld seams. The solidification process of HNSS welds also contribute to harmful secondary phase segregation and deteriorates the intergranular corrosion resistance [11].

The microstructure of HNSS welds contains typically Austenite phase inclusions with a small amount of δ-Ferrite phase [12–14] precipitated along the dendrites. Studies by Moon J et al [15] demonstrated that the segregation of δ-ferrite had a significant effect on the pitting corrosion resistance, the corrosion behavior is strongly affected by the fraction of chromium-depletion zone and sedimentation formed at 1200 °C to 1350 °C.
The microstructural evolution and corrosion behavior of friction high-nitrogen stainless welded joint were proposed by H Zhang et al [16]. A high corrosion rate was confirmed in thermomechanically affected zone (TMAZ) via electrochemical corrosion test, which was mainly attributed to the high defect density. Nitrogen and molybdenum created a beneficial synergistic effect and formed passive film on the metal surface [17–21]. However, the excessive amounts of molybdenum and chromium induce the accumulation effect of chromium-depleted zone [22, 23].

The corrosion characteristic of multiphase HNSS weld joints with dendritic structures is still in the research phase. This paper attempts to study the understanding of the corrosion mechanism of different microstructures by analyzing corrosion-susceptible zones of HNSS welded joint. Laser-arc hybrid welding with low residual stress and high efficiency was used to fit the characteristics of HNSS [24]. Furthermore, the effects of chromium-depleted zone and dendrites geometry on corrosion resistance were studied in detail.

2. Materials and experimental

2.1. Welding experiment

Welding experiment was performed using HL4006D solid-state laser of TRUMPF Company and a Panasonic MIG/MAG welding machine. The paraxial welding mode was guided by arc welding in front, and laser in the rear. A schematic of the hybrid welding process is shown in figure 1. The composition of the HNSS and 1.2 mm austenitic stainless welding wire are listed in tables 1 and 2. The chemical components of welding wire was selected at the element like N, Mo and Ni which is lack in the base metal. The changes of welding wire composition induce different solidification modes of welded joints, whose final metallography can be compared to study the various corrosion behaviors induced by different recrystallized weld microstructures. And the addition of elements such as N and Mo in the welding wire is also likely to change the passivation ability of the welded joint.

Butt welding with a clearance of 0.8 mm was performed used with a Y type 30° groove angle and welding blunt edge of 4 mm was retained. In order to comply with the uniform variable principle and eliminate errors caused by the welding process, the same hybrid welding optimized parameters were used for each welding process and the specific welding parameters are shown in table 3.

![Figure 1. Schematic of Laser-arc hybrid welding.](image)

**Table 1. Chemical composition of HNSS/wt%.

| Number | C   | Si  | Mn  | Cr  | Ni  | N   | Mo | S  | P  |
|--------|-----|-----|-----|-----|-----|-----|----|----|----|
| N01    | 0.148 | 0.49 | 16.0 | 22.07 | 0.47 | 0.56 | —  | 0.002 | 0.029 |

**Table 2. Chemical composition of welding wires/wt%.

| Number | C   | Si  | Mn  | Cr  | Ni  | N   | Mo | S  | P  |
|--------|-----|-----|-----|-----|-----|-----|----|----|----|
| N02    | 0.06 | 0.45 | 1.2 | 20.0 | 10.0 | —   | 1.0 | 0.003 | 0.013 |
| N03    | 0.004 | 0.02 | 1.3 | 23.2 | 59.7 | —   | —  | 0.004 | 0.011 |
| N04    | 0.018 | 0.48 | 1.5 | 22.7 | 8.1  | 0.16 | 3.0 | 0.003 | 0.021 |
2.2. Electrochemical test

The weld parts were cut into disc-shaped pieces to fit the electrochemical corrosion mold, the specific cutting positions and oleoresin treatments are shown in Figure 2. Two kinds of corrosion area were selected. One is to expose the center weld seam but seal other areas with oleoresin (3 mm wide region in the center of overall weld joint), while the other method is to expose the overall surface (1 cm$^{-2}$) of the welded joint to electrolyte which including the whole weld joint surface.

The division of HAZ in welded joints mainly depends on the degree of grain growth. After many times of measurement by metallographic microscope, the width of HNSS weld heat-affected zone (HAZ) is mostly maintained at 0.85 mm $\sim$ 1.16 mm, it is difficult to guarantee the accuracy by directly measuring the region of HAZ. However, by comparing the electrochemical results of above two select modes, the corrosion resistance of the HAZ and weld seam edge can be obtained accurately. To ensure a measurable flat surface, the irregular residual height of the weld joint should be removed. The exposed weld surface should be polished to the mirror to eliminate the effect of grease and residue on the electrochemical corrosion test.

The corrosion instrument adopted three-electrode ZENNIUM electrochemical workstation with the calomel electrode of reference electrode. The 3.5 wt% (0.6 mol l$^{-1}$) NaCl solution was used as electrolyte. The range of test voltage and current select $-2.5$ V $\sim$ $+2.5$ V and $-1$ A $\sim$ $+1$ A. The solvent was deoxygenated with Ar gas for 40 min, and specimens soaked for 40 min until the open circuit potential showed no significant fluctuate. Then the potentiodynamic polarization curve was collected in room temperature.

2.3. Morphology and composition analysis

The microscopic corrosion morphology and pitting distribution were analyzed by Scanning electron microscopy (SEM) and metalloscope. The metallographic structure and microcorrosion morphology were analyzed by x-ray diffraction (XRD). The pitting hole bottom and exposed dendritic microstructure was analyzed by energy dispersive spectrum (EDS).

The most stable surface of the passivation layer was obtained by transient interception during the passivation zone in electrochemical experiments. The potential is maintained at the passivation pause position and soaked in the electrolyte for at least 2 h to ensure the integrity of the passivation film. To ensure that each weld sample with different wires can be compared under same statistical selection condition, the selected potential to be observed were unified from $-0.2$ V/SCE to 0.3 V/SCE, and the distance between the interception positions limited not exceed 0.2 V compared with OCP. The composition of the passive film formed by reaction on the surface of the weld was analyzed by x-ray photoelectron spectroscopy (XPS) technology from Escalab 250 Xi electronic energy spectrometer. The XPS scanning position selected at the center of the weld, as circular radius of 2.5 mm.

![Figure 2. Preparation of specimen and selection principle of test areas.](image)
3. Results and discussion

3.1. Weld forming and microstructure
The new recrystallized metallographic structure of the weld joint will produce plural interphase potential difference and a different corrosion mechanism, it is necessary to analyze the microstructure distribution of hybrid welds. Figure 3 shows the XRD energy spectrum results, macroscopic weld joint morphology and metallographic distribution of each weld section. According to correspondence peak position of XRD in figure 3(a), the recrystallized metallographic of N02 and N04 welds showed the peak position feature of ferrite peak and austenite phase, the metallographic structure of these weld seam belongs to F&A. On the contrary, the N03 weld showed pure austenite peak, which was recrystallized single austenite phase structure.

In figure 3(b), the weld section was immersed and corroded by 10% oxalic acid solution. For N02 and N04, the dark dendritic phase distributed at the cross section of the weld is the secondary ferrite phase. The region inside the weld fusion line was full of columnar crystals. When position shifts to the center part, the microstructure is gradually refined into equiaxed crystals. For pure recrystallized single-austenite phase in N03 weld, the distribution feature was similar to that of N02/N04 which also exhibit obviously refinement behavior. However, the distribution of single-phase austenite dendrites was more extensive.

The different microstructures of weld seam correspond to their diversity of the crystallization states. The solidification mode of HNSS weld joint make a great difference by the addition of different welding wire. Since the welded part contained the infiltrated nitrogen element from the parent material, the prediction solidification equation WRC-1992 was adopted for nitrogen-containing stainless steel evaluation [25]. The solid-state transformations process, reactions and final metallographic structure were shown in table 4. The specific solidification mode were determined by the value of Creq/Nieq [26] in weld joint. The specific
The nitrogen content in weld seams was collected using the re-melting method. The non-metallic elements were transformed at the fusion ratio of 0.6 calculated by chemical component of each welding wire. Then, it was substituted into the weld composition corresponding to \( C_{req}/N_{eq} \) value of: 

- \( H_02 = 1.512 \), 
- \( H_03 = 0.608 \), and 
- \( H_04 = 1.549 \).

It is obvious that the solidification mode of \( H_02 \) and \( H_04 \) belong to the FA mode, the \( H_03 \) weld joint underwent pure A-solidification mode. The final metallographic composition of each weld seam consistent with the XRD feature in figure 3(a). As shown in table 4, during the fluid-solid reaction of FA mode, the ferrite phase was first precipitated from \( L + \delta \) weld puddle, and the austenite phase precipitated next. On the contrary, for \( H_02 \), the \( L + \gamma \) states in A mode just precipitate a pure austenite phase in weld seam.

### 3.2. Electrochemical test characterization

The anodic potentiodynamic polarization curves measured by electrochemical corrosion experiments are shown in figure 4. N02-1 to N04-1 indicate the center weld seam corrosion, and N01 to N04-2 were aimed to represent the overall surface of welded joints. The passivation zone was observed in each simple, starting approximately at \(-1\ V/SCE\). This indicated a protective passivation layer formed both on the HNSS base metal and weld microstructure. The values obtained from electrochemical measurements are presented in table 5. In

![Figure 4. Anodic polarization curves of N01, N02-2, N03-2, N-4-2: (a) Center weld seam; (b) Overall welded joint.](image)

### Table 4. Solidification mode.

| Solidification mode | Equivalent ratio | Reaction | Microstructure                  |
|---------------------|------------------|----------|---------------------------------|
| (A): Fully Austenitic Cr\(_{eq}\)/Ni\(_{eq}\) < 1.25 | \( L \rightarrow L + \gamma \rightarrow \gamma \) | Fully Austenitic |
| (AF): Austenitic Ferritic | 1.25 < Cr\(_{eq}\)/Ni\(_{eq}\) < 1.48 | \( L \rightarrow L + \gamma \rightarrow L + \gamma + (\gamma + \delta)_{cut} \rightarrow \gamma + \delta_{cut} \) | Austenite matrix with grain boundary Ferrite |
| (FA): Ferritic Austenitic | 1.48 < Cr\(_{eq}\)/Ni\(_{eq}\) < 1.95 | \( L \rightarrow L + \delta \rightarrow L + \delta + (\gamma + \delta)_{per/cut} \rightarrow \gamma + \delta \) | Skeletal Ferrite resulting from Austenite |
| (F): Fully Ferritic | 1.95 < Cr\(_{eq}\)/Ni\(_{eq}\) | \( L \rightarrow L + \delta \rightarrow \gamma + \delta \) | Ferrite matrix with grain boundary Austenite |

### Table 5. The results of polarization curve.

| Center weld seam | Overall weld joint surface | Base metal |
|------------------|---------------------------|------------|
| Unite | N02-1 | N03-1 | N04-2 | N02-2 | N03-2 | N04-2 | N01 | N01 |
| \( I_{corr} \) \( \mu A.cm^{-2} \) | 4.184 | 4.022 | 3.084 | 5.751 | 7.873 | 3.746 | 3.013 |
| \( I_{p} \) \( \mu A.cm^{-2} \) | 31.87 | 47.05 | 31.27 | 42.46 | 75.83 | 33.58 | 65.66 |
| \( E_{corr} \) V/SCE | −1.043 | −0.998 | −1.015 | −1.108 | −1.005 | −1.221 | −0.973 |
| \( E_{p} \) V/SCE | 1.25 | 1.07 | 1.2 | 1.37 | 1.0 | 1.42 | 0.5 \( \sim \) 1.0 |

The nitrogen content in weld seams was collected using the re-melting method. The non-metallic elements were transformed at the fusion ratio of 0.6 calculated by chemical component of each welding wire. Then, it was substituted into the weld composition corresponding to \( C_{req}/N_{eq} \) value of: \( H_02 = 1.512 \), \( H_03 = 0.608 \), and \( H_04 = 1.549 \). It is obvious that the solidification mode of \( H_02 \) and \( H_04 \) belong to the FA mode, the \( H_03 \) weld joint underwent pure A-solidification mode. The final metallographic composition of each weld seam consistent with the XRD feature in figure 3(a). As shown in table 4, during the fluid-solid reaction of FA mode, the ferrite phase was first precipitated from \( L + \delta \) weld puddle, and the austenite phase precipitated next. On the contrary, for \( H_02 \), the \( L + \gamma \) states in A mode just precipitate a pure austenite phase in weld seam.

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| Center weld seam | Overall weld joint surface | Base metal |
|------------------|---------------------------|------------|
| Unite | N02-1 | N03-1 | N04-2 | N02-2 | N03-2 | N04-2 | N01 | N01 |
| \( I_{corr} \) \( \mu A.cm^{-2} \) | 4.184 | 4.022 | 3.084 | 5.751 | 7.873 | 3.746 | 3.013 |
| \( I_{p} \) \( \mu A.cm^{-2} \) | 31.87 | 47.05 | 31.27 | 42.46 | 75.83 | 33.58 | 65.66 |
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addition, the corrosion current density \( I_{\text{corr}} \) of N01 to N04 fitted by Tafel slope extrapolation plays a crucial role in evaluating the corrosion resistance. The collected data were normalized according to the exposed test area.

The center weld seam was analyzed first. For multiphase N04-1 weld with nitrogen-containing welding wire, \( I_{\text{corr}} \) was fitted relative to the minimum than that of weld joint without extra N addition. In contrast, the N03-1 center weld seam with single austenite phase showed the highest \( I_{\text{corr}} \), which corresponding the lowest corrosion electrical resistance. In figure 4, the passive current densities \( I_{p} \) of N02-1 to N04-1 all stay around \( 0.31 \times 10^{-4} \) A cm\(^{-2}\) without excessive fluctuation, while N03-1 exhibited a relatively negative breakdown potential \( E_{\text{p,t}} \) and narrower passive range as shown in table 5. This indicated an earlier rupture process of the passive film on the N03-1 subsurface layer.

In the later passivation zone before \( E_{\text{p,t}} \), the N02-1/N03-1 weld sample exhibit a significant step-transition interval at 0.8 V/SCE. This rapid increase in current density was attributed to their unstable erosion of heterogeneous passive film. H03-1 and H03-2 in figure 3 both display an unstable transitional phenomenon in the later passive zone that will be analyzed in the following section. Instead, the transpassivation zone in H04-1/H04-2 with nitrogen-containing wire was relatively smooth, accompanied by tiny \( I_{p} \) fluctuation before \( E_{\text{p,t}} \). This fluctuation phenomenon belonged to the nucleation symbol of miniature metastable pitting. The passive film above the H04 weld surface went through transient processes of destruction and repair. Bore Jegdić [12] and Tian [27] both obtained similar metastable pitting corrosion characteristics in austenitic stainless steel (X5CrNi18-10) weld joints and 304 stainless steel respectively. It can be seen that the weld with nitrogen-containing welding wire showed the minimum passivation fluctuations, which represent the best passivation stability.

The polarization curves of the overall welded joint are shown in figure 3(b), whose test regions include the center weld seam, fusion line transition area, and HAZ. Each surface of welded joint all exhibited similar resistance order as the center weld seam. The comparison in table 5 indicated that the \( I_{\text{corr}} \), increased by 37.45% (N02), 95.74% (N03) and 21.47% (N04) as the exposed test area expanded to the peripheral microstructure of the weld. The divergence between the degrees of passivation also widened, according to the \( I_{p} \) values in table 5. N04-2 has the lowest \( I_{p} \) followed by N02-2, and N03-2 which represent the protective ability of passive film. On one hand, the HAZ and weld edge zone inside the fusion-line diminished the comprehensive corrosion resistance and passive ability of the weld joint. On the other hand, the lowest \( I_{\text{corr}} \), and \( I_{p} \) of N04-2 demonstrated that each part of the weld joint with nitrogen-containing welding wire own better passivation property and pitting resistant. The larger \( I_{\text{corr}} \) and unstable passivation phase transition of the pure recrystallized austenitic phase N03 weld structure indicated a poor passivation property and pitting resistance.

### 3.3. Corrosion behavior in dendrites

Figure 5 shows the micro-corrosion morphology of weld seam observed by SEM. The corrosion channel appeared as skeleton shape in N02-1 and N04-1 weld seam due to their similar F&A type solidification mode. As shown in figure 5(a), the corrosion traces of the center weld seam part appear to be comprised of uniform equiaxed crystals. The corrosion traces of the edge part of weld seam were characterized by large columnar crystals and dense branch crystals as shown in figures 5(b), (c), these kinds of complex geometric corrosion traces generally own high degree of continuity. Compared with conventional elliptical pitting in HNSS base metal, the skeleton corrosion traces on weld surface had the same geometric distribution characteristics as the generated second ferrite-dendrites [28]. It indicated that the ferrite phase induced special corrosion with the adjacent austenitic phase, finally the entire ferrite-dendrites shed and left skeleton traces. For F&A type weld seam, the density of ferrite-dendrites was directly proportional to the degree of weld corrosion.

As shown in figures 5(c), (d), the dendritic corrosion traces of N04-1 were more dispersed than those of N02-1. In the transition region of the fusion line, the corrosion channel of N04-1 gradually narrowed and the microstructure show a trend of refinement. This phenomenon ameliorated the aggregation of dendrites and indirectly reduced the corrosion sensitivity. And this is also the fundamental reason for the better corrosion behavior of the N04 weld with nitrogen-containing wire.

The corrosion behavior of N03 weld (Pure A) was quite different from F&A type weld. In figure 6, the N03 surface exhibit large-scale shedding marks along the heat crystallization direction. As shown in figure 6(a), the region of central weld optimized by laser shows severe microstructure shedding which attributed to a lack of intergranular stability. Combined with figure 6(b), large elliptical pitting can be obtained in the transition structure. However, this extensive shedding performance on N03 is the mostly harmful corrosion behavior. The pure recrystallized austenite without steady second phase may lost the effect of precipitated-phase strengthening which finally degrade the corrosion resistance drastically.

Alexander Schmid [29] investigated the interphase corrosion behavior of similar metallographic structure of double-phase structural steel and austenitic steel, the experiment result showed that ferrite phase of the duplex steel is selectively attacked, while the austenite phase remained without severe corrosion. In this paper, however,
the recrystallized secondary austenite phase formed under pure A solidification mode did not restore the excellent properties of the parent material due to its poor intercrystalline binding ability.

3.4. Corrosion characteristics in each region
To compare the corrosion-weak zone of overall weld, the micro-corrosion behavior at each region is summarized. The corrosion resistance distribution diagram for N02 and N04 (F&A weld) were constructed in figure 7 based on the statistics of microscopic corrosion degree and shedding feature in figure 8.

For center weld seam, the laser keyhole effect and the metal vapor reflected from the bottom, and promoted the fluidity ability of the central weld puddle. As shown in figure 7, the center weld seam with a small temperature gradient eventually crystallized into uniform fine equiaxed crystals [28]. This refined distribution

Figure 5. Microscopic corrosion morphology of the weld seam of N02 and N04: (a) Equiaxed crystals traces in the center weld; (b) Columnar crystal traces on the exterior of the weld seam; (c) Branch crystal traces of N02-1; (d) Branch crystal traces of N04-1.

Figure 6. Corrosion morphology of N03 welded joint: (a) Weld center; (b) Weld-fusion line.
pattern of dendrites reduces the accumulation phenomenon of corrosion channels, which optimize the resistance property directly.

The inner side of the fusion line exhibited the severe accumulation of skeleton shape corrosion channels in figure 7, while the adjacent HAZ appeared large-shedding corrosion behavior. With further comparation in figure 8, the corrosion mechanism in HAZ was significantly different from the interior microstructure of the fusion line. The HAZ does not undergo the re-melting and recrystallization process as molten puddle, which led to a different corrosion deterioration mechanism between the HAZ and the dendritic structure. This is owning to the high welding temperature had a local sensitizing effect on the peripheral structure of the weld puddle [30]. The closest part of HAZ experience the grain coarsening [31]. The heated grains deteriorated the segregation behavior of Cr at the grain boundary and aggravated the chromium-depletion effect [32]. Eventually, the grown grain with weak grain boundary was eroded rapidly and shed, the structure on the side of the molten puddle exhibit banded shedding traces as shown in figures 7 and 8(a).

The statistical diagram of weld seam and HAZ are represented in figure 8(b). The specific corrosion characteristics of each regions were counted and the measurement errors were marked. There is a large number of corrosion pits at the weld seam edge but the independent area is relatively small. In contrast, HAZ own the less pits number but accompanied by huge shedding area. From comparison result, it further confirmed that the HAZ and weld seam edge were the corrosion weakest region susceptible to corrosive electrolyte. M Dadfar [33]
also pointed out a similar results in 316L weld joint that the adjacent zones of weld seam and HAZ will be attacked preferentially when exposed to corrosive environments.

3.5. Pitting corrosion of F&A welded joints

The corrosion pitting behavior is an important criterion for evaluating the properties of metal; After the metastable pitting stage and $E_{pit}$ point, the pitting gradually nucleate and experienced stable growth with sharp increase in polarization current density. Compared with the shedding observed in H03, the stable pitting characteristics can be observed in H02 and H04 as corrosion increases in severity. The N04 with better resistance was selected to analyze the pitting deepening mechanism in the F&A type weld with dendrites structure. Figure 9 shows the pitting morphology. Compared with traditional stainless steel, the pitting hole in the dendrites weld structure are not deepening in the shape of an ellipsis. In figure 9(a), the pitting of equiaxed crystal in weld seam were mainly formed by gradual shedding of granular grains. The bottom of the pitting holes still retained obvious grain structure and signs of continuous erosion along the grain boundary. With the dendrite density increased in figure 9(b), this special ‘grain shedding’ characteristic increased in severity.

In order to explore the pitting deepening mechanism, the point EDS of different region were performed on dendrite structure exposed at the bottom of the N04 pitting hole. According to the EDS results in table 6, the dendrites were chromium-rich and Nickel-depleted phase, while the Cr content of the adjacent microstructure was obviously lower than that of the dendrites. From precipitation order of FA solidification mode, the preferential segregation of dendritic ferrite leads to the chromium deficiency in the post-crystallized austenite structure [34]. It can be found that the erosion against at the chromium-depleted zone is the main cause of skeletal corrosion, which result in the incessant shedding phenomenon of the whole ferrite-dendrites.

3.6. XPS analysis of passive film

To directly compare the effect of different welding wires on the composition of the weld passive film, the surface layer of the passive film was sampled and analyzed by XPS spectra. Samples welds N02 and N04 with nitrogen-containing wire was adopted, and N03 was abandoned due to its unstable interface during passivation zone. Figure 10 indicated the presence for Cr2p3/2, Fe2p3/2 and Mo3d states. The peaks of the oxide component were smoothed and normalized according to the fitted peaks.

In the fitted spectra of figure 10, the peaks at 711.45 eV and 710.3 eV corresponded to the valence states of Fe$^{3+}$ of Fe$_2$O$_3$ and FeOOH. However, the relative proportion of FeOOH in H02 was higher than that of N04, while Fe$_2$O$_3$ showed the opposite trend. The Cr$^{3+}$ of Cr2p3/2 formed Cr$_2$O$_3$ at 576.2 eV and Cr(OH)$_3$ at 577.3 eV both in N02 and N04. Compared with free CrO$_2^{2-}$ appeared at a higher binding energy in the N02 weld, a newly formed oxide CO$_3$ in N04 played an additional protective role in passive film. Mo3d in the HNSS weld passive film was mostly Mo$^{4+}$ and Mo$^{6+}$ at 232.3 eV and 235.5 eV respectively, while the relative intensity of...
Mo\(^{4+}\) of N04 passive film was stronger than N02, and Mo\(^{6+}\) had a similar intensity. However, there are reports showed that the enrichment degree of Mo element plays an important role in affecting the isolation ability of the passive film \([35]\).

These results indicated that the higher proportion of unstable FeOOH and the lower amount of Mo\(^{4+}\) lead to a relatively low passivation protection ability of N02 without extra N. In contrast, due to the protection of sufficient MoO\(_2\), a dense metallic oxide layer rich with Cr\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) showed the best passivation performance \([36]\) of the N04 weld surface with nitrogen-containing welding wire.

4. Conclusions

The micro-corrosion characteristics and corrosion-susceptible areas of HNSS laser-arc hybrid welded joints were studied in this paper. The pitting deepening mechanism and corrosion behavior of different weld metallographic structure were analyzed. The conclusion are as follows:

(1) The nitrogen-containing welding wire can optimize the corrosion resistance and passivation ability of welded seam. Compared with single phase recrystallized austenite, the welded joint with FA-solidification mode showed better pitting resistance.

(2) The chromium-depleted zone induced skeletal corrosion traces along the dendrites structure. The refined equiaxed crystals in the center weld seam exhibited less accumulation of corrosion channel.
(3) The erosion along the dendritic structure is the direct reason for the deepening of pitting corrosion. The complex geometric characteristics of dendrites exhibited severe shedding corrosion, and the HAZ and weld edge were the most corrosion-susceptible region.

(4) The additional nitrogen into the welding wire produced dense oxides passive film with a higher degree of oxidation on the weld surface.

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