515 Enhancement in Corrosion Resistance of Laser-Melted Stainless Steel by Passivation Treatment

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Summary

Martensitic stainless steel AISI 440C was surface melted by a 2.5-kW CW Nd:YAG laser, followed by 50 vol-% nitric acid passivation treatment at 50 °C for further improvement in corrosion resistance. The corrosion behavior in 3.5% NaCl solution of various specimens before and after passivation was studied by potentiodynamic polarization technique. It was found that the pitting corrosion resistance of the laser-melted specimens was significantly improved by HNO₃-passivation as evidenced by a shift of the pitting potential in the noble direction, a wider passive range, and a lower passive current density. After passivation treatment, the laser-melted specimens possess higher pitting corrosion resistance than that of as-received and conventionally hardened 440C which were passivated under the same conditions. The pitting corrosion characteristics of the passivated 440C specimens were strongly dependent on the microstructures. The enhanced pitting corrosion resistance is due to the combined effect of dissolution or refinement of carbide particles by laser surface melting and removal of carbides inclusions and free iron by passivation treatment.

Keywords : Laser surface melting; Passivation; Pitting corrosion; Martensitic stainless steel

1. Introduction

Martensitic stainless steels are widely used in many engineering applications such as steam and water valves, pumps, turbines, compressor components, shafting, cutlery, surgical instruments, bearings and plastics moulds, etc, which demand high hardness, wear and corrosion resistances. Among the martensitic stainless steels, 440C has the best mechanical properties and the highest chromium and carbon content. The mechanical strength increases but the corrosion resistance decreases as the carbon content in the martensitic stainless steels increases. Thus it is not easy to achieve both high mechanical strength and high corrosion resistance. The corrosion resistance of 440C is the lowest among this stainless group because of its high carbon content which leads to the precipitation of a large amount of carbide phases.

Laser surface melting (LSM) has been proven to be a promising method for improving the pitting corrosion resistance ⁽¹⁾⁻⁽⁵⁾ of martensitic stainless steels by dissolution of large carbides, refinement of the microstructure, and homogenization of chemical compositions. The superficial layer of the steels is modified while the bulk properties of the substrate are preserved, thus providing a possible solution to the conflicting effects due to high carbon content. In a previous paper by the present authors, the pitting corrosion resistance

of laser-melted 440C was found to increase significantly and depend on the scanning speed which results in different amounts of carbide particles and retained austenite remaining in the melt layer ⁽¹⁾. A low scanning speed would result in higher pitting corrosion resistance due to more carbon in solid solution and a higher degree of decarburization. However, it is unavoidable that a small amount of precipitated carbide remains in the laser-melted 440C and weakens the passive film.

Passivation, according to ASTM A380-99, is "the removal of exogenous iron or iron compounds from the surface of stainless steel by means of a chemical dissolution, most typically by a treatment with an acid solution that will remove the surface contamination, but will not significantly affect the stainless steel itself" ⁽⁶⁾. In addition, it also describes passivation as "the chemical treatment of stainless steel with a mild oxidant, such as a nitric acid solution, for the purpose of enhancing the spontaneous formation of the protective passive film" ⁽⁶⁾. Chemical passivation is an inexpensive way for further improvement in pitting corrosion resistance by removing free iron or other anodic contaminants from the surfaces of 440C. These contaminants are potential corrosion sites that result in premature corrosion and ultimately result in deterioration of the component if not removed.

Studies relating to the combined effect of LSM and passivation on the pitting corrosion behavior of martensitic stainless steel 440C are scarce in the literature. The present work thus aims at improving the pitting corrosion resistance of laser-melted martensitic stainless steel 440C in 3.5% NaCl solution by nitric acid passivation.

2. Materials and Methods

The as-received AISI 440C (designated as AR-440C) was in annealed condition and in the form of round bar. The nominal chemical composition in weight % was : 17% Cr, 0.75% Mo, 1% Mn, 1.1% C, 1% Si, 0.049% P, 0.03% S, balance Fe. Hardened specimen of 440C (designated as HT-440C) was achieved by conventional heat treatment for comparison with the laser-melted specimens. Specimens were preheated to, and kept at, 850 °C for 45 minutes and then heat-treated through the austenitizing temperature (1060 °C) for 30 minutes, followed by quenching in liquid nitrogen. Tempering was achieved by keeping the specimens at 250 °C for 210 minutes followed by air cooling.

The specimens for polarization studies were machined to discs 12.7 mm in diameter and 3.2 mm thick. The surface of the specimens for LSM was sandblasted in order to reduce the reflectivity to the laser beam. Prior to passivation procedures, the surface of as-received, hardened and laser-melted specimens was mechanically polished with 1- μ m diamond paste in order to keep the surface roughness consistent. The specimens were then passivated in nitric acid, cleaned, degreased and dried before the polarization test.

LSM was carried out using a 2.5-kW CW Nd:YAG laser. The laser beam was focused onto the specimen by a BK-7 glass lens with focal length of 100 mm. Laser power (P) of 0.8 kW (2.8 kW/cm²) at workpiece with a laser spot size of 6 mm in diameter and beam scanning speed (v) of 25 mm/s were used. Argon flowing at 15 l/min was used as shielding gas. The designation of the laser-melted specimen is P08-440C-25. The melt surface was achieved by overlapping of successive melt tracks at 50% track width interval.

The passivation procedures were based on ASTM Standard A380-99 ⁽⁶⁾. The specimens were immersed

in ethanol in an ultrasonic cleaner to remove organic or metallic residues. The specimens were then placed into 50 vol-% nitric acid at constant temperature (50 ± 1 °C) for 30 minutes. After immersion in the passivation bath, the specimens were cleaned by running tap water and then placed into a copper sulfate solution for verification. Absence of pink spots indicated that no residual iron was present on the surface of all the specimens.

Polarization studies were performed in 3.5% NaCl solution to investigate the electrochemical corrosion behavior of the laser-melted, the as-received and the hardened specimens. Cyclic potentiodynamic polarization scans were carried out using an EG&G PARC 273 corrosion system according to ASTM Standard G61-94⁽⁷⁾. The NaCl solution was maintained at 23 ± 1 °C open to air. A constant scan rate of 5 mV s^{-1} was used. All potentials were measured with respect to a saturated calomel electrode (SCE, 0.244V versus SHE at 25 °C) as the reference electrode. Two parallel graphite rods served as the counter electrode for current measurement. Potential scans started after an initially delay of 30 minutes for the specimen to reach a steady state. The scan was reversed when a current density of 5 mA/cm^2 was reached.

3. Results and discussion

The cross-sectional appearance and microstructure of the laser-melted specimen P08-440-25 is shown in Fig. 1. The surface layer of P08-440-25 is free of cracks and pores. The melt depth is 0.29 mm. In the melted zone (MZ), the M_{23}C_6 carbide was dissociated to form a homogeneous structure. Primary austenitic dendrites (bright in contrast) and interdendritic regions which consist of martensite and secondary M_{23}C_6 and M_7C_3 carbides (darker in contrast) are observed in Fig. 1(b). Beneath the MZ, a heat-affected zone (HAZ) with a depth of about 0.21 mm was observed. The HAZ corresponded to complete austenitization of the steel together with dissolution of M_{23}C_6 carbide and a final martensite transformation upon rapid cooling, with some undissolved carbide particles.

Potentiodynamic polarization curves of the laser-melted specimens (for MZ and HAZ), as-received and hardened specimens before and after passivation treatment in 3.5% NaCl solution (open to air) at 23 °C are shown in Figs. 2 and 3. The corrosion parameters are summarized in Table 1.

Prior to passivation treatment, AR-440C did not passivate, HAZ of P08-440C-25 and HT-440C had a low pitting potential, both being attributable to the large amount of carbide particles present in the ferritic or martensitic matrix, respectively (Table 1). The carbide particles had very high chromium content so that the matrix was depleted of chromium, especially in the region next to the carbide particles. The boundaries between the carbide particles and the metal matrix then acted as the nucleation and anodic sites for pitting corrosion in a chloride medium⁽⁹⁾. For P08-440C-25, the pitting corrosion potential became higher and the passive current density was lower than those of AR-440C, HT-440C and the HAZ of P08-440C-25 as shown in Fig. 3 and Table 1. In the present study, the scanning speed for LSM was 25 mm/s, resulting in a constant proportion of retained austenite^(1,8). LSM of 440C is capable of improving the pitting corrosion resistance by reducing the amount and the size of the M_{23}C_6 carbides and increasing the amount of retained austenite⁽⁸⁾.

After the passivation treatment, the pitting corrosion resistance of the laser-melted specimens (for MZ and HAZ), as-received and hardened specimens was significantly improved as evidenced by a shift of the pitting potential in the noble direction, a wider passive range, and a lower passive current density (in the

order $\mu\text{A}/\text{cm}^2$) (Table 1). Under the same passivation conditions, MZ of P08-440C-25 possess higher pitting corrosion resistance than that of conventionally hardened and as-received 440C, and the HAZ of P08-440C-25. The pitting corrosion characteristics of the passivated 440C were strongly dependent on the microstructures prior to passivation treatment. The enhanced pitting corrosion resistance of laser-melted 440C after passivation is due to the combined effect of dissolution or refinement of carbide particles by LSM and removal of carbides inclusions and free iron by passivation treatment. The ranking of pitting corrosion resistance of the laser-melted 440C before and after passivation is consistent. In descending order, the ranking is : P08-440C-25 (MZ) > HT-440C > P08-440C-25 (HAZ) > AR-440C.

P08-440C-25 had a pitting potential of 260 mV before passivation, and increased to 900 mV after passivation. At such a low scanning speed (25 mm/s), more carbides dissolved into the matrix due to a longer laser interaction time and the remaining carbides were then removed by passivation. Vayer and his coworkers reported that chromium carbide inclusions are present on the surface of the martensitic stainless steel and pitting corrosion yields elimination of these inclusions⁽¹⁰⁾. The pitting potential of martensitic stainless steels (X20Cr13, X30Cr13 and X40Cr14) after HNO_3 -passivation in Hexanios solution (containing 43 ppm Cl⁻, pH =7.3) was more noble than air-passivated specimens⁽¹¹⁾. The HNO_3 -passivated film was enriched in oxidized chromium and hydroxide. Oxidized chromium and oxidized iron were uniformly distributed all over the passive layer. The beneficial effect of HNO_3 -passivation for pitting corrosion resistance of laser-melted 440C is in agreement with the work by Vayer et al⁽¹¹⁾.

On the other hand, the repassivation capability of the laser-melted specimen with and without passivation is poor as indicated by the low protection potential (below the corrosion potential). This indicates that the amount of Cr present in solid solution in the treated layer was still not sufficiently high to effect rapid repassivation.

4. Conclusions

- (1) LSM of 440C results in an increase the pitting corrosion resistance, as demonstrated by a higher pitting potential and a lower the passive current density (of the order of $\mu\text{A}/\text{cm}^2$) compared with the as-received and conventional hardened 440C.
- (2) After passivation treatment, the pitting corrosion resistance of all the specimens was improved. The ranking of pitting corrosion resistance both before and after passivation is the same. In descending order, the ranking is : P08-440C-25 (MZ) > HT-440C > P08-440C-25 (HAZ) > AR-440C.
- (3) After passivation treatment, the pitting potential of the melted zone of laser-melted 440C was increased from 260 mV to 900 mV (SCE), which was much higher than that of the annealed 440C (287 mV) and the heat-affected zone of laser-melted 440C (430 mV) passivated under the same conditions.
- (4) The enhanced pitting corrosion resistance of laser-melted specimens with passivation treatment is due to the combined effect of dissolution or refinement of carbide particles by LSM and removal of chromium carbide inclusions and free iron by HNO_3 -passivation.

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Specimens	Corrosion potential (mV) SCE	Pitting potential (mV) SCE
AR-440C	-482	active
AR-440C (passivated)	-270	287
HT-440C	-280	-150
HT-440C (passivated)	-161	840
P08-440C-25 (MZ)	-206	260
P08-440C-25 (MZ, passivated)	-277	900
P08-440C-25 (HAZ)	-287	-163
P08-440C-25 (HAZ, passivated)	-206	430

Table 1. Corrosion parameters of as-received, hardened and laser-melted 440C (for MZ and HAZ) before and after passivation in 3.5% NaCl solution at 23 °C.

Fig. 1. (a) Cross-sectional view & (b) microstructure of laser-melted specimen P08-440C-25.

Fig. 2. Potentiodynamic polarization curves of as-received and hardened 440C before and after passivation in 3.5% NaCl at 23 °C.

Fig. 3. Potentiodynamic polarization curves of laser-melted 440C (MZ and HAZ) before and after passivation in 3.5% NaCl at 23 °C.