

PITTING OF LASER WELDED STEELS

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ABSTRACT

Pitting corrosion dominates the early stages of corrosion of steels exposed to chloride solutions. In order to rapidly locate regions of greatest corrosion susceptibility in laser welded steels the passive film that causes localized corrosion was reduced prior to inducing corrosion. A number of interesting observations were made. Removing the oxide film showed that the weld itself was highly susceptible to corrosion. On polarizing the steel after removing the passive film produced a non-protective film which enabled general corrosion to develop. The growth of the film was observed using a difference technique that enhances changes taking place in surface images. Pretreatment the passive film at potentials of -0.7 V in chloride solution markedly improved the pitting resistance.

INTRODUCTION

Laser welding is being widely used in metal working industries to produce, automobiles, pacemakers, and cigarette lighters¹⁻³. While the initial cost of this technique is higher than other conventional techniques such as tungsten arc welding (TIG), the reduced surface finishing requirements and the ability to join different thicknesses of steels lower labor costs and have led to increased interest by manufacturers in investing in this technology. In addition, the narrow weld beads and heat affected zones (HAZs), have been identified as features that might improve corrosion resistance of a component. These improvements have resulted in greater use of laser welding in the automotive industry that aims to improve corrosion resistance, particularly in produce lightweight fuel-efficient cars.

There is limited available literature on the corrosion of laser welded galvanized high-strength steels. The narrow laser welded region increases the protection of the steel by the zinc until the sacrificial dissolution of the zinc leads to insufficient electrochemical throwing power to protect the steel. The present investigation employs electrochemical measurements and novel optical

observations^{4,5} to study the development of corrosion of laser-welded steel sheets to determine the susceptibility of the weld and the sequence and location of corrosion sites after the zinc is removed.

The objective of the work was to develop a rapid test to locate the most susceptible areas as no such test was found in the literature. Initial open circuit tests showed that almost random pitting dominated the early stages location corrosion and extended period of time and statistics would be required to determine the most susceptible areas for welded steels.

EXPERIMENTAL WORK

Galvanized high strength low alloy steel 1.5 mm thick sheets were Nd:YAG laser welded at the speed of 5.2m/minute with an input energy of 3000W. Samples of size 20 x 15mm were cut from the sheet. The samples were abraded to remove the Zn and prepare a surface with a 600 grit finish. The area of exposure was 6 x 6 mm limited by 3M type 5 adhesive tape applied on the surface⁶. The sample were mounted vertically and tested in air saturated 0.5 M NaCl. All potential are relative to a saturated calomel reference electrode.

Three sets of experiments were performed. The first set involved measuring open circuit potentials of the laser welded steels with an oxide formed in air and in a borate solution. The oxide was grown as the potential was to +0.5 V in pH 8.4 borate buffer at 5mV/s. This preparation was used for all subsequent tests that were carried out in the chloride solution. In the second set of the experiments, the samples were pretreated at a single potential of -1000mV for 3 minutes hoping to remove the passive oxide. Then, the potential was stepped to a higher potentials ranging from -500 to -300mV for an hour to observe the corrosion characteristics of the different metallurgical structures present in the welded samples. In the third set of experiments the samples were potentiostatically polarized at potentials ranging from -1200mV to -500mV for 3 minutes, and then, stepped to -500mV for an hour^{7,8}. Cathodic reduction has been used for to remove air formed oxide layers on a sample's surface to obtain a film free surface⁹⁻¹³. The objective of this set of tests was to observe the influence of the altering or removing the oxide potential on the corrosion characteristics.

RESULTS AND DISCUSSION

Open circuit measurements

During open circuit exposure in the chloride solution, corrosion, seen by darkening of the surface spread from random pitting sites that showed no clear preference for the weld area. With abraded steel welds the darkening depended on the history of the specimen prior to immersion. Recently abraded surfaces darkened rapidly accompanied by a rapid drop in potential whereas surfaces air aged for a day remained at potentials around -0.5 V for longer periods of time before decreasing slowly to about -0.65 V as shown in 1938¹⁴. The differences in the air

aging results from thickening of the passive oxide film. In an attempt to evade the necessity to wait a fixed amount of time after surface abrasion, a relatively thick oxide film was grown in borate^{9,10}. During immersion this procedure showed extended times at -0.5 V similar to extended air exposure, but the initial pitting sites from which corrosion spread were still random.

An example of the observed surface changes for a borate treated surface is shown in Figure 1. Figure 1a is a real image of the surface immediately after immersion. Figure 1b is a difference image. The image was obtained by digital subtraction of 1a from 1c recorded after 270s of immersion. The difference between the figures shows where changes have taken place and is enhanced by amplifying the difference and setting it against a gray background. Figure 1c showed no clear indication of where corrosion was taking place whereas the difference image shows many distinct areas of change not visible to the naked eye demonstrating the sensitivity of the technique.

The extended period of time that the potential remained close to -0.5 V following the growth of the passive oxide in borate proved to be an advantage when other surface treatments were investigated. During open circuit exposure in chloride the initiation of corrosion is rapid as seen from Figure 1. The corrosion products formed then interfered with other surface treatments that were being investigated. It was not possible to reduce these corrosion products as they were not in electrochemical contact with the surface.

Pretreatment to Remove the Passive Oxide Prior to Potentiostatic Polarization

Experiments were carried out to determine if the dissolution of iron was sensitive to metallurgical differences of the steel. If these effects existed the passive oxide film on iron clearly would play a role in masking them. Hence, the approach was to remove or alter the passive oxide and enable the metal characteristics to influence the metal dissolution rather than allowing domination by breakdown of the highly protective oxide.

Many investigators have monitored the potential during galvanostatic reduction of oxide films on Fe in borate buffer. The oxide dissolves leaving a bare metal surface at potentials of about -1.0 V (vs sce.)^{9,10} In chloride it is difficult to carry out the same experiment because invariably there is corrosion and precipitation of corrosion products on the surface. In our experiments a potential of -1.0 V was chosen as a base potential, expecting the oxide film to be reduced and dissolve on reaching this potential. At more negative of -1.2 V hydrogen bubbles formed which interfered with the visual observation of the surface and detracted from running many experiments with this pretreatment.

The experiments were run by first removing the borate grown oxide at -1.0 V for 3 minutes after which the potential was stepped to a higher value and the current was monitored. Figure 2 shows the current variations with time. At and below -0.55 V the currents were negligible in comparison to those at potentials from -0.5 to -0.3 V. Three stages were observed at -0.3 V. The first was a transient

that extended for a few seconds, a period greater in time and a magnitude of current larger than would be expected if due to double layer charging. The surface during this early stage of the process darkened to a degree just perceptible when closely observed but distinctly seen using the difference imaging technique. (This behavior is again seen in Figure 4 below) The second stage was an attempted plateauing at 4 mA/cm² followed by a distinct plateau due to solution resistance control after 1500 s. At -0.4 V the current showed the same stages but each extended in time and lower currents. At -0.5 V the first stage where the darkening took place was further extended and can be easily seen in Figure 2. At all potentials from -0.5 to -0.3 the darkening of the surface was also seen to be dependent on properties of the metal as it was less intense on the weld than the remaining metal.

Very obvious differences in corrosion developed at the higher potentials due to a distinctly greater susceptibility of the weld to attack in the chloride solution. This is seen from images in Figure 3 after 1800 s for samples exposed at -0.5 and -0.4 V. It was also observed to be the case at -0.3 V but could no longer be discerned as the entire surface had blackened except for the fusion lines on each side of the weld.

From this set of experiment two features are of definite interest. The first is that there is indeed a dependence of the corrosion behavior on the structure of the metal which can be brought out by first removing the passive oxide film. Similar results were obtained when only an air formed passive film was present. Therefore, the initial thickened passive oxide film did not induce the differences in this susceptibility.

The second feature of interest, was seen using the difference technique, where some type of film was formed in the chloride solution on stepping from -1.0 V to the higher potential. From the initial transient at -0.5 V starting at about 0.5 mA/cm² and decaying in about 100 s (Figure 2 and Figure 3) it can be deduced that a film, say FeOOH, which formed would be about 14 nm thick. It is possible that films may have compositions that incorporate chloride but it is very unlikely that it was a chloride salt film. The high chloride solubility would necessitate much higher currents. The calculated thickness is far greater than the 4nm expected for a passive oxides formed on Fe. The formation of the semiprotective film in the chloride solution was unexpected but accounts for the initial decay on stepping the potential and a slow breakdown at the surface and build up of the current observed in Figure 2.

Passive Oxide Pretreatment Prior to Potentiostatic Polarization

The film formed on stepping the potential may also be related to a passive film but in a reduced state. Reduction of a passive film takes place over a wide range of potentials that may alter its properties. In order to study this relation anodic films were pretreated at different potentials ranging from -1.2 to -0.5 V, and then polarized to -0.5V in the chloride solution recording the currents.

The behavior of the current after the different pretreatments is show in Figure 4. The appearance of the samples after 1800 s is shown in Figure 5. The

minimum in the current after stepping the potential, that was discussed above is more clearly seen after the -1.2 to -1.1 V pretreatments. The darkening of the surface due to film formation was seen again on the difference viewer following stepping of the current. For samples pretreated at -1200 mV and -1100 mV, the minimum points are rather closed to each other which indicated that the surfaces were similar after the pretreatment and the original passive film had been removed. The current at -1.0 V was notably smaller which in turn suggest incomplete removal of the passive film. On increasing the pretreatment potential to -0.9 and -0.8 V the currents dropped significantly but they began to increase after about 1000 s associated with pitting corrosion predominantly along the weld. After -0.7 V no current increase is seen but one pit was observed after 1800 s. With a less negative potentials of -0.6 V pitting susceptibility appears to be greater which was definitely the case when the potentials was only held at -0.5 V.

The results in Figures 5 and 6 demonstrate that distinct changes are induced in the passive film by pretreatments at different potentials after immersion of the sample, and before any corrosion has initiated at open circuit. The most interesting change occurred after the pretreatment at -0.7 which produces a distinct improvement in the pitting resistance. Pretreatments at and below -1.0 V led to more general corrosion. The corrosion following the pretreatments below -1.0 V are complicated because the cathodic currents that flow and produce distinct pH increases that probably lead to the appearance of a pitting type of corrosion seen in Figure 5.

CONCLUSIONS

1. The laser weld nugget is highly susceptible to corrosion. The presence of the passive oxide reduces the probability of its attack but over long period of time and spreading of corrosion it will probably become the location of most rapid attack.
2. The method of pretreating a steel at potential close to where the passive film is removed, and then stepping it to a high value can be used to differentiate the corrosion susceptibility due to different metallurgical structures.
3. A thick film is formed on iron and steel when the metal is polarized after the oxide film is removed. The film has poor protective properties and leads to general corrosion.
4. Pretreatment of iron or steels at potentials around -0.7 V alters the properties of the passive film and leads to a protective behavior and increased resistant to pitting corrosion.

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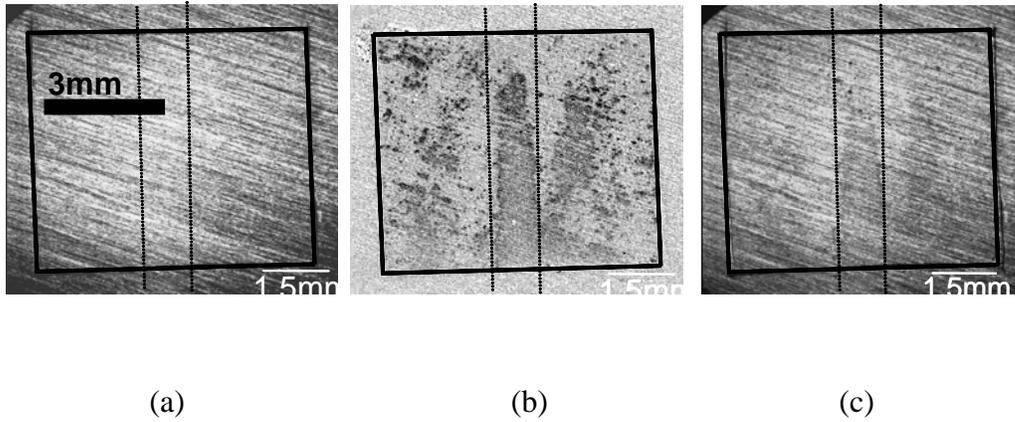


Figure 1. Surface images during open circuit exposure of laser welded steel in 0.5 M NaCl. (a) Shows the surface after immersion. (b) A difference image that clearly shows where corrosion had occurred in 270 s. (c) Shows the surface after 270 s. The difference image was obtained by digital subtraction of image in (a) from the image in (c) followed by amplification of the difference and adding a gray background.

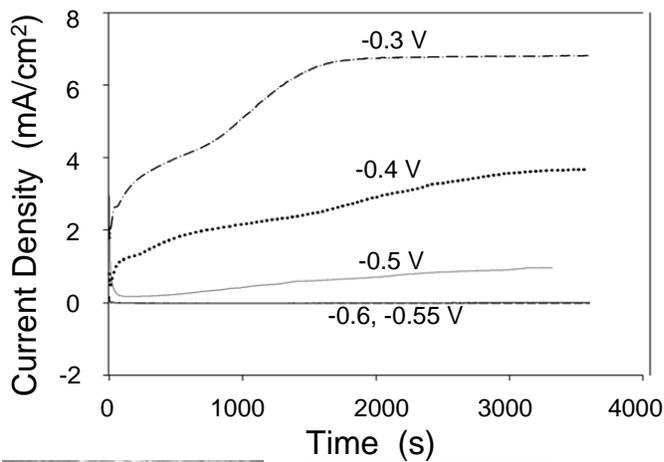


Figure 2. Variation in current in 0.5 M NaCl for a laser welded steel at different applied potentials following a 180 s pretreatment at -1.1 V.

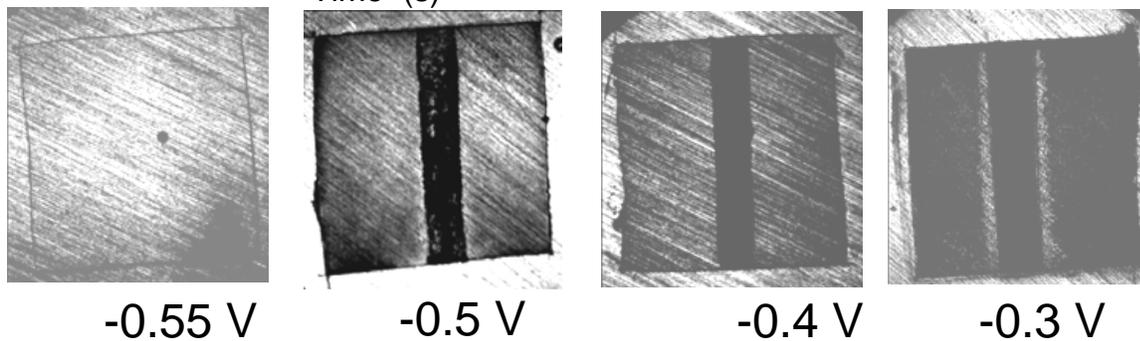


Figure 3. *In situ* images of laser welded steel after 1800 s at the potentials shown following a pretreatment at -1.1 V in 0.5 M NaCl. The images were recorded during the measurements shown in Figure 2.

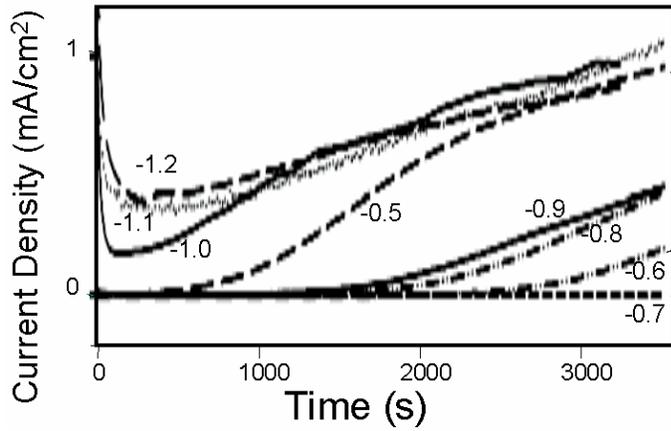


Figure 4. Variation in current for laser welded steel in 0.5 M NaCl at $-0.5 V_{scc}$ after pretreatment for 180 s at the potentials shown.

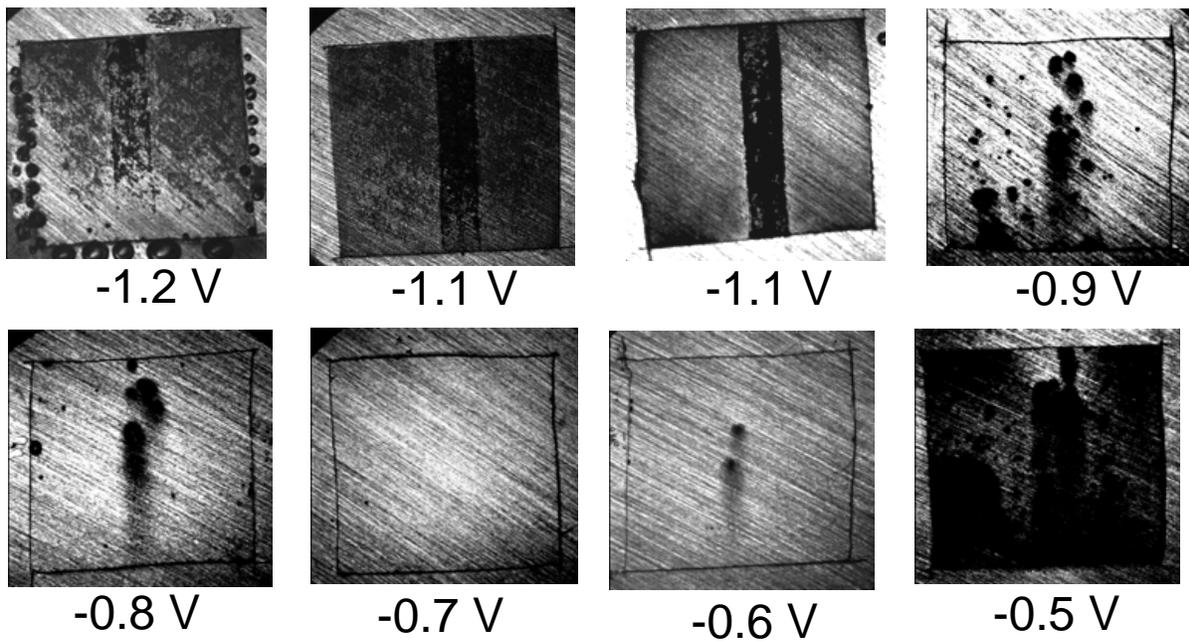


Figure 5. *In situ* mages of laser welded steel after 1800 s at $-0.5 V$ shown after pretreatment at the potential shown in 0.5 M NaCl. The images were recorded during the measurements shown in Figure 4