EVALUATION OF LASER SURFACE MELTING TO MITIGATE CHLORIDE STRESS CORROSION CRACKING IN AN AUSTENITIC STAINLESS STEEL

by

Michael P. Brady

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APPROVED:

[Signatures]

R.W. Hendricks, Co-Chairman

M.R. Louthan, Jr., Co-Chairman

N.E. Dowlng

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(ABSTRACT)

This thesis evaluates the ability of laser surface melting to mitigate chloride stress corrosion cracking (SCC) of type 304 stainless steel. The effects of laser surface melting on microstructure, mechanical state, and corrosion behavior were examined. The major effect of laser surface melting of 304 stainless steel was found to be the introduction of tensile residual stresses on the order of the yield strength in the surface of the laser-melted regions. Exposure of laser-melted coupons to boiling magnesium chloride at 154°C revealed that the residual stresses were sufficient to cause failure by SCC processes in the absence of an external load. It was concluded that unless measures could be found to eliminate or reverse the residual stresses introduced by the laser melting process, the technique is not viable for mitigating chloride SCC in these alloys.
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Chapter 1
INTRODUCTION

Stress corrosion cracking (SCC) may be considered to be a synergy between stress, environment, and material [1]. Stress corrosion cracking failures of austenitic stainless steel in chloride ion containing environments are a major problem in industrial water and steam systems in general and the chemical industry in particular [2]. Several possible approaches to alleviating the problem are:
1) to modify the environment,
2) to modify the state of stress, or
3) to modify the material.

Elimination of the environmental factors that promote SCC is often not possible. For example, low levels of the chemical ion $Cl^-$ (as low as several ppm) can cause SCC failures [3]. Environmental control at this level is not practical for many applications.

Both applied and residual stresses can be present in a structure. Design improvement can minimize tensile loading of parts exposed to the environment. Control of residual stress is possible by methods such as post-weld cooling, heat sink welding, and shot peening [4]. However, loading and fabrication stresses cannot be eliminated completely. As with environmental factors, it is not practical to eliminate tensile stresses in many applications.
Materials modification can take several forms. Proper materials selection could eliminate many potential SCC failures. The "workhorse" austenitic stainless steels, grades 304 and 316, are highly susceptible to chloride SCC [5]. Replacement of these alloys by high-alloy content SCC-resistant stainless steel grades or other classes of materials may reduce the incidence of SCC failures but is often not economically feasible because of the high cost of chromium and nickel [6]. Very few materials combine the corrosion resistance and formability of austenitic stainless steels and they are not easily replaced by other classes of materials [7].

One possible approach to alleviating SCC is surface modification. The ASM Handbook defines surface modification as "the alteration of surface composition or structure by the use of energy or particle beams [8]." Several advantages of such treatments have been identified in terms of corrosion protection [9]. Among the are:

1) the alteration of the surface without sacrifice of bulk properties,
2) the conservation of scarce, critical, or expensive alloying elements,
3) the production of novel surface alloys (unattainable by conventional metallurgical techniques) with superior properties, and
4) avoidance of coating adherence problems.

One such surface modification treatment is laser surface melting. It is the purpose of this thesis research to evaluate the ability of laser surface melting to mitigate chloride SCC in 304 stainless steel.
Chapter 2

LITERATURE REVIEW

2.1 Laser Surface Treatments

The three major categories of laser surface treatments are:[10]

1) shocking,

2) heating, and

3) melting.

Laser shocking treatments attempt to work harden the material and induce compressive residual stress. The laser produces a high power, short duration pulse which vaporizes a thin surface layer of material [11]. Atom movement resulting from vaporization generates a mechanical shock wave which work hardens the material and generates compressive residual stress [12]. The effect of the process is analogous to shot peening. Thermal effects are negligible. Possible benefits include improved wear and fatigue resistance. The main drawbacks of the process are cost and difficulty in controlling surface tolerance. No industrial applications have yet been developed [13].
Laser surface heating processes can be divided into two categories: annealing and transformation hardening [14]. Laser annealing is primarily applicable to the electronics industry where rapid, high temperature heating for short periods of time can be used to remove defect structures in semiconductor materials. Most metallic annealing applications require heating of thick cross-section workpieces for long periods of time. For example, a stress relief anneal of 304 stainless steel requires a four hour anneal at 900 degrees celsius per inch of cross-section. Laser processes are usually cost effective only if the interaction time is short, and are not practical for bulk cross-section heating.

Laser transformation hardening is applicable to any material hardened by conventional means [15]. The laser rapidly heats the surface of the material above the critical phase transformation temperature. Because the heated layer is very thin, self quenching follows by conduction of heat into the bulk material [16]. The process potentially holds two advantages over conventional quenching. If the nose of the TTT curve for the material is far to the left, laser processing may be the only means to produce cooling rates sufficiently high to retain a high temperature phase and/or promote a martensitic-like transformation (refer to Figure 1). The other advantage of the laser is the potential to localize and control the depth of hardening in the near surface regions, which may be desirable for some applications. Despite these possibilities, neither laser annealing nor laser transformation hardening are widely used in industry [17].

Laser surface melting processes (glazing, grain refining, alloying, and cladding) incorporate many of the most promising laser processing techniques [18]. During the process, the laser melts a thin surface layer of material. As with laser surface heating, the bulk metal acts as a heat sink and the surface layer quickly resolidifies and cools. Laser parameters such as beam power, size, speed, and coupling mode, etc. offer a wide range of melt depth and solidification rate ranges.

Laser glazing refers to the rapidly solidified product of pulsed laser melting [19]. A rapid laser pulse heats and melts a thin, localized surface region. Cooling rates can approach $10^{10}$ kelvins per second [20]. The formation of very fine microstructures is promoted by the high solidification and cooling rates. The formation of new metastable phases is possible in metallic systems where the nose of the TTT curve is far to the left, beyond the cooling rates attainable by conventional
quenching processes (refer to Figure 1). Laser glazed material has been reported to exhibit improved mechanical properties such as higher yield strength and greater corrosion resistance than conventionally processed material [21].

Grain refining is the application of laser surface melting to produce refined, homogeneous microstructures at the surface of a metal. The process uses continuous wave (cw) laser output instead of the pulsed output used for laser glazing, which results in greater heat input to the workpiece. Solidification and cooling rates are, therefore, orders of magnitude slower. The process is often applied to cast material [22]. The melting of the surface layer and subsequent high cooling rates help alleviate segregation and break up inclusions in the surface [23]. The goal is to produce quality surfaces (fine scale structure and minimal segregation) characteristic of a higher cost material on a less expensive bulk cast material. Cast material processed in this manner has been reported to exhibit improved corrosion, wear, and fatigue behavior as compared with un-treated material [24].

Laser alloying and cladding take the process one step further by modifying surface composition. Material is added to the laser-melted surface layer before solidification or is deposited on the surface prior to melting. In this manner, the surface composition can be altered [25]. For example, it may be possible to create a plain carbon steel piece with a stainless steel surface by alloying the laser melt pool with chromium [26]. Again, the goal is to produce surfaces characteristic of higher cost materials on lower cost bulk materials. For the work performed in this thesis, laser surface melting was used.

### 2.2 Laser Parameters

The five parameters necessary to describe a particular cw laser treatment are beam power, beam diameter, traverse speed, depth of focus, and type of gas shielding [27]. Laser beam power and beam diameter determine the power density applied to the workpiece. The high power density of the laser separates it from conventional heating sources. The laser melts the surface before much
Figure 1. Hypothetical TTT curve. In materials where the nose of the TTT curve is far to the left on the time axis, rapid solidification processing such as laser surface melting may be the only means to retain a high temperature phase and/or produce a martensitic-like transformation.
heat can be conducted into the bulk of the workpiece. This limits the size of the heat-affected zone (HAZ) and results in high cooling rates. Conventional heating sources produce larger heat-affected zones because the bulk of the workpiece is heated before the surface melts. The bulk heating of the workpiece also lowers cooling rates.

The laser power input to the workpiece determines the melt depth [28]. The beam diameter determines the width of the laser-melted region. The beam traverse or sweep speed determines the local interaction time and can alter melt depth penetration by an order of magnitude [29].

A stream of protective shroud gas (usually argon or helium) follows the laser beam as melt passes are made. The shroud gas serves two purposes. It minimizes oxidation of the workpiece during the laser process and it can aid in beam absorption. For example, the addition of a reactive gas such as oxygen to an argon shroud can increase melt depth 100% by promoting an endothermic reaction. This results in greater heat input into the workpiece [30].

There are two beam-workpiece coupling modes: conduction-limited melting and keyhole melting [31]. The beam focus determines which mode is active. To achieve conduction limited melting, the laser beam is focused above or at the surface of the metal. Heat is transferred from the surface of the workpiece into the bulk by conduction. Efficiency is low because the absorptivity of most metals is less than 15% [32]. Melt profiles are crescent shaped and limited in depth (see Figure 2).

The keyhole coupling mode produces deep penetration melting, characterized by a keyhole shaped melt profile (see Figure 3). To achieve keyhole formation, the laser beam is focused below the surface of the workpiece [33]. The beam vaporizes a column of base metal and the vapor pressure displaces the molten metal surrounding the column which forms a cavity or keyhole [34]. This cavity greatly increases beam power absorption into the workpiece. The absorption mechanism is not completely understood, but is believed to involve multiple internal reflections of the beam from the molten metal inside the cavity [35].
Figure 2. Cross-section micrograph of conduction melted 304 stainless steel. The grains are equiaxed and approximately the same size as the base metal grain size.
Figure 3. Cross-section micrograph of keyhole melted 304 stainless steel. The grains are columnar (Micrograph courtesy of K.L. Rohr).
2.3 Microstructure

Laser melting is characterized by high solidification and cooling rates. When the laser heats the material sufficiently, a molten front is established [36]. The front moves down from the free surface into the bulk material. As the laser beam moves away along the surface, the melt front slows, stops, and moves back toward the free surface [37]. The depth of the molten region (which is controlled by laser parameters and material properties) seldom extends beyond four or five hundred microns and is often only tens of microns in depth. The bulk of the metal acts as a heat sink. The ratio of the volume of melted material to the volume of cool un-melted material is many orders of magnitude less than one. Therefore, cooling and solidification rates are high and steep temperature gradients are formed. The ramifications of this in terms of microstructure again can be illustrated by the hypothetical TTT curve shown in Figure 1. In material systems where the nose of the TTT curve is far to the left, laser processing may produce unique microstructures not attainable by conventional means (if the cooling rates are high enough).

Laser processing generally affects microstructure in any of three ways [38]. There may be:

1) redistribution of major alloy components,
2) changes in the morphology of second phases, or
3) changes in crystalline structure.

Laser melting of austenitic stainless steels has been reported to refine grains, coarsen grains, form dendrites, form cellular dendrites, form a columnar structure, form an equiaxed structure, favor primary austenite solidification, result in the formation of ferritic regions, result in the formation of martensitic regions, nucleate new grains, and favor epitaxial regrowth [39-43]. In short, a wide variety of microstructures can be formed. Laser parameters, which determine the cooling and solidification rates, are the controlling factors.

Laser melting can be divided into two general cases. The molten region depth may be on the order of the grain size of the material prior to melting, or the molten region depth may be much greater than the grain size of the material prior to melting [44]. When the laser melts to a depth
on the order of the grain size, grain coarsening occurs [45]. This melting regime favors epitaxial growth of the partially melted substrate grains [46]. Texture effects also result. When the depth of the molten region is much greater than the grain size, refinement is possible under certain cooling rate and solidification conditions because new grains are nucleated. Both columnar and equiaxed structures can be formed. In all cases, when 304 stainless steel is laser-melted, a dendritic structure is formed as a result of the steep temperature gradients and the high degree of undercooling.

Several researchers have reported the formation of duplex structures of austenite and ferrite [47, 48]. The solidification mode was primary austenite. The ferrite formed in the interstices of dendrites. The ferrite morphology was found to vary with laser parameters, but under all conditions examined, the solidification mode was always primary austenite [49].

Martensite has also been reported to form in laser-melted 304 stainless steel [50]. Its formation was attributed to a stress-induced transformation as a result of residual stress introduced by the laser melting process. It may also be possible that nickel was locally depleted in some regions as a result of undercooling. In the absence of the austenite stabilizer, martensite would form because of the high cooling rates.

2.4 Residual Stress

The rapid local heating and cooling inherent in laser surface melting generates residual stress. The nature of the residual stress depends on a number of complex interacting processes (thermal expansion, plastic deformation, temperature gradients, phase changes, workpiece shape and constraint, melt profile, etc.) which act during the laser-induced thermal cycle [51]. The heated material expands while the surrounding cool material constrains this expansion. This generates compressive stress in the surface layer. Both compressive plastic deformation and liquid state flow occur at this high temperature [52]. Rapid cooling follows by conduction of heat into the bulk. In the absence of a phase change, the last material to cool will be placed in tension. In a laser melting process, the
last material to cool is the surface region that was melted. Therefore, one would expect tensile residual stresses at the surface of the laser-melted materials.

A phase change in the laser-melted material, which is normally accompanied by volume expansion or contraction, may affect the final state of surface residual stress. For example, the volume expansion associated with a martensitic transformation can place the last material to cool in compression. It should be noted that the volume integral of residual stresses in a material balance to zero. If a state of compressive residual stress exists in one region of a sample, tensile residual stress must be present in a different region of the sample. The location of residual stresses, whether surface or subsurface, can influence such behavior as SCC and fatigue, and must be considered.

In austenitic stainless steels, laser surface melting has been reported to introduce tensile residual stresses on the order of the yield strength in the surface of the melted regions [53-55]. The sign and magnitude of the residual stress has been reported to be independent of laser parameters [56]. The laser-melted regions in these studies were found to be austenitic. Martensite was not formed. Tensile residual stresses on the order of the yield strength in laser-melted regions have been reported for other non-hardenable ferrous materials [57]. In experiments where the laser only heated the surface of the metal, the magnitude of the residual stress was found to be related to the surface temperature. The higher the temperature to which the surface was heated, the greater the resultant residual stress [58]. Therefore, it is unlikely that the laser can be used to stress relieve material. Residual stresses of thermal origin (ie. no phase changes) are always tensile in the surfaces of the laser-melted regions [59].

Laser melting of hardenable materials, for example 420 stainless steel, has been reported to produce compressive surface residual stresses in the surface of single melt tracks [60]. This result was attributed to the formation of martensite. The overlapping of melt tracks, which is necessary for large scale surface coverage, was found to produce tensile residual stresses in the surface melted regions despite the formation of martensite [61]. The effect was attributed to high temperature plastic flow from adjacent tracks [62]. Surface heating effects may also play a role in the production of tensile residual stresses in overlapping melt tracks. The heating of a martensitic layer to a high temperature, but below the austenitic transformation temperature, is equivalent to surface heating.
of a non-hardenable material. Heat transfer from subsequent tracks would supply this surface heating. Therefore, differential cooling between the surface and the bulk resulting from surface heating of adjacent tracks, as well as plastic flow, could explain this effect.

Residual stress in all but the last overlapped melt tracks in the 420 stainless steel were found to be tensile. Isolated melt tracks always possessed compressive residual stresses in surface of the melted regions [63]. The residual stresses were found to be a function of laser parameters. Parameters which favored greater melt track overlap (and, therefore, greater heating and plastic flow in previously melted regions) promoted tensile residual stresses. The authors concluded that proper selection of parameters to minimize heating effects from overlapping melt tracks is necessary to form martensitic layers possessing compressive surface residual stresses.

### 2.5 Stress Corrosion Cracking (SCC)

As will be seen, this thesis is not a fundamental study of the phenomena of chloride SCC in 304 stainless steel. Rather, it evaluates the ability of laser surface melting to mitigate chloride SCC in this material. This section is, therefore, limited to an examination of the ways in which laser melting may potentially impact the SCC behavior of 304 stainless steel.

Stress corrosion cracking is the result of the synergistic effects among stress, environment, and microstructure. The exact cracking mechanism of austenitic stainless steels under tensile stresses (either applied or residual) in chloride environments is not completely understood [64]. A number of metallurgical factors have been observed to affect SCC behavior. They include crystal structure, anisotropy, grain size and shape, dislocation density and geometry, yield strength, composition, stacking fault energy, ordering, and phase composition [65].

Laser surface melting potentially impacts SCC behavior in two manners (refer to Figure 4). The process affects material microstructure. First, laser melting potentially alters grain size, phase presence and distribution, and composition. Fine grain sized materials have been reported to exhibit
improved SCC resistance [66]. Non-austenitic stainless steels are resistant to chloride SCC. The formation of phases other than austenite in the laser-melted regions such as duplex structures of austenite/ferrite or austenite/martensite may impart a degree of SCC resistance [67]. Second, the rapid heating and cooling of the laser surface melting process significantly alters the state of residual stress. The introduction of a surface state of compressive residual stress may impart a degree of SCC resistance. However, the introduction of tensile surface residual stresses would degrade SCC resistance.

Because this thesis examines the ability of cw laser surface melting to mitigate chloride SCC of 304 stainless steel, a known, well-documented SCC producing environment (boiling magnesium chloride at 154°C) was chosen (ASTM practice G 36) [68]. According to the practice, "The boiling magnesium chloride test is applicable to wrought, cast, and welded stainless steels and related alloys. It is a method for detecting the effects of composition, heat treatment, surface finish, microstructure, and stress on the susceptibility of these materials to chloride SCC [69]." All austenitic stainless steels are susceptible to SCC in this environment [70]. Type 304 stainless steel fails rapidly in this environment under a tensile stress of 15 ksi or greater [71]. This testing environment is extremely severe and is not an accurate simulation of field conditions [72]. However, it is believed to be ideal for evaluating the effects of laser surface melting on chloride SCC in 304 stainless steel.

2.6 Scope of thesis

Continuous wave laser surface melting was used in the present work because of the anticipated need for large scale workpiece surface coverage that would be encountered in practical applications. Laser melting under such conditions does not produce amorphous or microcrystalline microstructures in 304 stainless steel. The literature search indicates that the microstructures produced by the laser surface melting conditions used in the present work will be dendritic, and
Figure 4. Areas of effects of laser melting on SCC factor relationships.
primarily consist of austenite. Fine dispersions of ferrite or martensite may also be present. Such microstructures may impart a degree of SCC resistance.

Laser melting of non-hardenable ferrous metals, such as 304 stainless steel, was reported to introduce high tensile residual stresses in the laser-melted regions. The introduction of such residual stresses might negate any microstructural improvements in SCC resistance that may result from the laser process. One group of researchers reported the formation of martensite in laser-melted 304 stainless steel. The formation of martensite may result in a state of surface compressive residual stress in the melted regions, thereby, imparting a degree of SCC resistance. However, the formation of martensite in laser-melted 304 stainless steel is not widely cited in the literature.

Finally, both conduction and keyhole laser beam/workpiece coupling modes were studied. They are intended to represent a wide range of possible cw laser parameters. Shallow penetration, conduction limited melting represented the upper range of possible cooling and solidification rates. Deep penetration keyhole melting represented the lower end of possible cooling and solidification rates. These choices were made because of the almost unlimited number of combinations of laser parameters that are possible and were believed to be the only practical way to determine the extent to which microstructure and residual stress may be functions of cw laser conditions in 304 stainless steel.
Chapter 3

METHODS AND MATERIALS

Laser surface melting was studied as a surface modification technique to mitigate chloride SCC in type 304 stainless steel. Because stress corrosion cracking is the result of the synergy between microstructure, stress, and environment the work was divided into three parts: characterization of microstructure, determination of mechanical state, and study of corrosion behavior.

3.1 Materials

3.1.1 Material Preparation

As-received 304 stainless steel was heat treated in air at 900°C for four hours and furnace cooled. This heat treatment was used to provide stress free samples for laser processing and corro-
sion studies. A black oxide film was formed as a result of the heat treatment. The oxide film was removed by immersion in a pickling bath of HCl and HF.

3.1.2 Laser Processing

American Research Corporation of Virginia, the industrial sponsor of this work, supplied the equipment and expertise for laser melting. The laser source was a Spectra-Physics Model 810, 600 Watt CO$_2$ fast-axial flow laser operated in the continuous wave (cw) output mode. The beam delivery system was designed to direct a horizontally projected beam of light to a vertical position above the sample and then focus it downward for materials processing. This system consisted of a molybdenum mirror beam-bender, a circularly polarizing silicon mirror, and a fine focus assembly. A welding gas jet nozzle assembly provided an argon cover gas shield to minimize oxidation of the sample during the laser melting process. Sample coverage was achieved by passing the test sample under the beam and overlapping the melt track passes. The sample was moved on a computer-controlled X-Y stage under a fixed beam. Laser melting parameters were considered proprietary and are not available.

3.2 Microstructural Characterization

3.2.1 Metallography

Specimens were sectioned and prepared for observation by standard metallographic techniques. Type 304 stainless steel was etched electrolytically at 6 volts in a 10% aqueous oxalic acid
solution. This etch was used to reveal general austenitic structure. Optical microscopy was performed using an Aus Jena Neophot 21 metallograph.

3.2.2 Phase Analysis

Lambda Research Inc. of Cincinnati, Ohio provided a qualitative phase analysis by X-ray diffraction. The diffraction patterns were obtained by step-scanning from 10 to 165° 2θ in steps of .05°/second. Chromium Kα radiation was used. As-received 304 stainless steel, keyhole melted, and conduction melted samples were analyzed.

3.3 Mechanical Testing

Impact behavior, microhardness, and residual stress were examined in laser-melted 304 stainless steel. Impact behavior and microhardness of laser-melted M2 tool steel were also studied to provide a basis for comparison to the mechanical behavior of laser-melted 304 stainless steel. The M2 tool steel was chosen as a comparison material because laser melting significantly altered its mechanical properties.

3.3.1 Impact Testing

Impact testing was performed using a Tinius Olsen Model 74 Impact Machine equipped with a Dynatup Model 500 computer-based data acquisition system. The system measures load vs. time and energy vs. time data during the course of the impact test. Crack initiation and crack propagation
energies as well as the total impact energy absorbed by the test sample are then calculated. The energy needed to initiate a crack corresponds to the area under the load vs time curve up to the point of maximum load. The remaining energy represents the energy needed to propagate the crack. The test bars were machined from .635 cm thick rolled plate. Samples with identical orientations with respect to the rolling direction were tested. The test sample configuration is shown in Figure 5. A 1.6 mm. hole was drilled in one end of each sample to a depth of 3.2 mm to allow thermocouple monitoring of the temperature during testing. The samples were immersed in liquid nitrogen, cooled to -196°C, and impacted when they warmed to the desired testing temperature. Laser-melted and as-received M2 tool steel were tested at -78, -28, 0, and 25°C. Keyhole melted, conduction melted, and as-received 304 stainless steel were tested at -50, -25, 0, and 25°C. M2 tool steel and 304 stainless steel samples were not tested at identical temperatures because of difficulties in placing samples in the test holder before they warmed to room temperature.

It is important to note that the test samples were subsized and un-notched. Thus, the results are valid only as a relative intercomparison between laser-melted and as-received material. The test results suggest whether or not the laser-melted material acts as a notch.

3.3.2 Microhardness

Vicker's microhardness profiles across the depth of the melted regions were made using a Leco DM-400 microhardness tester. Base metal and laser-melted regions of 304 stainless steel and M2 tool steel were examined. A load of 500 grams and an indent time of 15 seconds was used.

3.3.3 Residual Stress

Residual stresses were calculated from X-ray diffraction data using a TEC Model 1610 portable X-ray stress analysis system. The X-ray system measures the change in lattice (d) spacing
Figure 5. Impact test specimen configuration.
caused by the residual stress. These strain measurements are converted to stress using known X-ray elastic constants for the alloy. Data were recorded at several ψ angles (the degree of tilt between the specimen and the X-ray beam) and plotted as d-spacing vs sin²ψ. The normal stress in the direction of the diffractometer tilt is obtained from the slope of this plot. A split in the plot between positive and negative ψ angles indicates the presence of shear stresses in the planes perpendicular to the sample surface. A typical run output for laser-melted 304 stainless steel is shown in Figure 6. The absence of sin²ψ split and the excellent straight line fit of the data are consistent with a biaxial state of stress. Shear stresses were not observed. Although the analysis is straightforward in the case of simple biaxial stresses, several complexities can be introduced in examining some materials. Further details are described by Noyan and Cohen [73].

X-ray measurements were made on the (311) austenite reflections using Cr Kα radiation at 149 degrees 2θ. A 3 mm diameter pinhole was used. Acquisition time was 100 seconds. ψ angles were -40, -30, -20, 0, +20, +30, +40 degrees with an oscillation of 2 degrees. The test samples (see Figure 7) were rectangular coupons 1.5" by 1" by the coupons. Residual stresses in keyhole melted, conduction melted, and as-received 304 stainless steel were studied. Residual stresses were measured both parallel (X direction) and perpendicular (Y direction) to the beam scan direction.

3.4 Corrosion Testing

Laser-treated and as-received 304 stainless steel samples were subjected to boiling magnesium chloride at 154°C (ASTM practice G36). This environment is known to produce transgranular SCC in austenitic stainless steel under tensile loads greater than 15 ksi. A reflux condenser apparatus chilled with tap water was used to prevent evaporation of the test solution (see Figure 8). Two types of sample configuration were tested: coupons (same design as the residual stress test coupons) and externally loaded bar samples.
Figure 6. Typical residual stress output run. The excellent straight line fit of the data are consistent with a biaxial state of stress. The absence of a \( \sin^2\psi \) split indicates that shear stresses are not present.
Figure 7. Residual stress test coupon configuration. These test coupons were also used as corrosion test specimens.
Figure 8. Reflux condenser. Reflux condenser apparatus used to maintain constant temperature conditions in the boiling magnesium chloride bath [74].
The coupons were exposed to the environment for periods up to 72 hours. At various intervals, the coupons were removed for residual stress measurement. Liquid dye penetrant and metallographic sectioning were used to determine the presence of cracking.

Two types of bar samples were tested. Figure 9 shows a three-point bend sample and loading configuration. The laser melted samples were laser processed prior to loading. Loading conditions varied from sample to sample, but all were loaded well past yield. The test was considered complete when widespread cracking was observed. The four point bend samples and loading configurations are shown in Figure 10. Loading conditions were duplicated by measuring the deflection of the bar. Two samples were tested: as-received and a sample with one surface completely laser melted. This sample was laser processed prior to loading. The samples were exposed to the environment for 18 hours and examined for evidence of cracking by visual inspection and sectioning.
Figure 9. Three-point bend test specimen configuration. All components are made of 304 stainless steel. The bar was laser-melted prior to loading. After loading beyond the yield strength (by tightening the bolts), the specimen was exposed to boiling magnesium chloride. A wide range of exposure times was examined.
Figure 10. Four-point bend test specimen configuration. All components are made of 304 stainless steel. Materials were laser-melted prior to loading. Two specimens were tested: as-received and laser-melted. After loading beyond the yield strength, the samples were exposed to boiling magnesium chloride for 18 hours.
Chapter 4

RESULTS AND DISCUSSION

4.1 Microstructure

Microstructure plays a key role in stress corrosion cracking susceptibility. Laser melting may create SCC resistant microstructures by creating a fine grain size and/or altering the crystal structure. The microstructural effects of both keyhole mode and conduction mode laser melting were evaluated by both optical microscopy and X-ray diffraction.

4.1.1 Metallography

The cross-section micrographs of laser-melted 304 stainless steel (refer to Figures 2 and 3) show that the melted zone is clearly not microcrystalline or highly refined. The grain size of laser-melted material and as-received material is approximately the same. There is a heat affected zone at the melted region/base metal interface, but the grain growth is confined to grains immediately
adjacent to this interface. This effect was observed in both keyhole and conduction melted samples, but can best be seen in Figure 2. Small heat affected zones are characteristic of laser melting.

A micrograph of the surface of two overlapping laser-melted tracks produced by the keyhole coupling mode show that the microstructure consists of cellular dendrites (see Figure 11). The formation of dendrites is controlled by the ratio of temperature gradient to solidification rate. Laser melting is characterized by large temperature gradients and high solidification rates. In an alloyed material such as 304 stainless steel, this results in a great deal of undercooling which produces the dendritic structure. In the melt track overlap region (where the metal was exposed to two laser passes) the dendrites are refined. Figure 12 shows a surface track melted in the conduction mode. The structure is also cellular dendritic, but slightly more refined than the keyhole mode melting. Conduction mode melting cooling rates are greater than the cooling rates produced by keyhole melting, and produce greater refinement. A number of researchers report similar microstructures in laser-melted austenitic stainless steels [75, 76, 77].

A major difference in the microstructures between keyhole and conduction melting was the morphology of grains formed. Figure 2 shows that the microstructure produced by conduction melting predominantly exhibits a random, equiaxed grain structure. The microstructure produced by keyhole melting (refer to Figure 3) is columnar. This effect is also attributed to the cooling rate differences between conduction melting and keyhole melting. The melt front travels a shorter distance in conduction melting than keyhole melting which results in higher solidification rates. The lower heat input results in larger temperature gradients and higher cooling rates. These effects combine to produce a greater degree of undercooling in conduction melting than keyhole melting, which favors the formation of equiaxed structures. The slower cooling rates of keyhole melting allow for preferential grain growth parallel to the direction of maximum heat flow, which results in a columnar structure.

Laser melting has been reported to redistribute alloying elements [78]. The microstructure shown in Figure 13 supports this observation. The 304 stainless steel test samples were heat treated for stress relief prior to laser melting. The resulting structure was found to be sensitized. The micrograph of Figure 13 was made by polishing etched cross-sections. Sensitized structures etch
deeply in an electrolytic oxalic acid etch because the grain boundaries are no longer protected by sufficient chromium. The laser-melted regions did not etch as deeply and were quickly polished away. Therefore, it is likely that the chromium was redistributed during the melting and the passive protective layer was restored. This effect also explains the solute dumping lines (hemispherical lines present in the melt zone of keyhole melted samples) which can also be seen in Figure 13 [79].

4.1.2 X-Ray Phase Analysis

X-ray diffraction indicated that laser melting produced no major phase changes in 304 stainless steel (refer to Tables 1-3). As expected, as-received material was completely austenitic. Conduction melted 304 was primarily austenitic. A small amount of ferrite was present. This result is consistent with microstructures produced by conventional welding. Keyhole melted material was also austenitic. Additionally, the presence of oxides and preferred orientation were found in the keyhole sample. This result is consistent with visual inspection of the sample. Oxidation is a problem in keyhole mode melting because of the relatively slow cooling rates and high heat input, which gave additional time for oxidation to occur despite the Argon shield gas. An insufficient number of oxide peaks were present for complete identification. Only the strongest peaks registered on the diffraction pattern because of the bulk of the X-ray sample volume was metal (the oxide film wasn’t very thick). The large size of the d-spacings (2.549 to 4.905 A) are consistent with Fe, Ni, and Cr oxides. The ratio of strong peaks in the keyhole sample as compared with the other two samples (as received material and conduction melted) and Joint Committee on Powder diffraction standards (JCPDS) indicate a preferred orientation in the (200) reflection. This result confirms the observations of optical microscopy which showed columnar structure in microstructures produced by keyhole melting.
Figure 11. Surface micrograph of keyhole melted 304 stainless. This 304 stainless shows cellular dendrites. Refinement occurs in the pass overlap region shown in the right hand side of the micrograph.
Figure 12. Surface micrograph of conduction melted 304 stainless steel.
Figure 13. Etched and polished cross-section of keyhole melted 304 stainless steel. The structure was sensitized prior to laser melting. Laser melting may have normalized the sensitized structure by redistributing the chromium. The region is featureless in this micrograph. Further evidence of the redistribution of alloying elements is given by the hemispherical solute dumping lines of impurities which are present in the laser-melted regions.
Table 1. X-ray phase analysis of as-received 304 stainless steel.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>2θ (deg.)</th>
<th>d(A)</th>
<th>I/Jo</th>
<th>Identification</th>
<th>JCPDS 2θ</th>
<th>I/Jo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.01</td>
<td>2.075</td>
<td>100</td>
<td>austenite (111)</td>
<td>66.79</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>79.01</td>
<td>1.801</td>
<td>26</td>
<td>austentite (200)</td>
<td>78.99</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>128.66</td>
<td>1.271</td>
<td>15</td>
<td>austentite (220)</td>
<td>128.7</td>
<td>50</td>
</tr>
</tbody>
</table>
Table 2. X-ray phase analysis of conduction melted 304 stainless steel.

The microstructure is primarily austenitic. A small amount of ferrite is present.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>$2\theta$ (deg.)</th>
<th>d(A)</th>
<th>I/Io</th>
<th>Identification</th>
<th>JCPDS 2\theta</th>
<th>I/Io</th>
</tr>
</thead>
<tbody>
<tr>
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<td>66.96</td>
<td>2.076</td>
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<td>austenite (111)</td>
<td>66.79</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>68.56</td>
<td>2.034</td>
<td>1</td>
<td>ferrite (100)</td>
<td>68.6</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>79.11</td>
<td>1.799</td>
<td>36</td>
<td>austenite (200)</td>
<td>78.99</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>128.61</td>
<td>1.2721</td>
<td>27</td>
<td>austenite (220)</td>
<td>128.7</td>
<td>50</td>
</tr>
</tbody>
</table>
Table 3. X-ray phase analysis of keyhole melted 304 stainless steel.

The structure is austenitic. A preferred orientation is present in the (200) reflection. A number of small peaks were present that most likely correspond to oxides (a black oxide film formed on this sample). There are insufficient number of intense peaks for identification of the oxides.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>2θ (deg)</th>
<th>d(A)</th>
<th>I/Io</th>
<th>Identification</th>
<th>JCPDS 2θ</th>
<th>JCPDS I/Io</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.01</td>
<td>4.905</td>
<td>12</td>
<td>oxide</td>
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<td></td>
</tr>
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<td>2</td>
<td>45.06</td>
<td>2.990</td>
<td>4</td>
<td>oxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50.11</td>
<td>2.705</td>
<td>2</td>
<td>oxide</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>53.41</td>
<td>2.549</td>
<td>8</td>
<td>oxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>66.91</td>
<td>2.078</td>
<td>63</td>
<td>austenite (111)</td>
<td>66.79</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>79.11</td>
<td>1.799</td>
<td>100</td>
<td>austenite (200)</td>
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<td>128.61</td>
<td>1.271</td>
<td>47</td>
<td>austenite (220)</td>
<td>128.7</td>
<td>50</td>
</tr>
</tbody>
</table>
4.1.3 Discussion

Optical microscopy and X-ray diffraction showed that laser melting 304 stainless steel did not significantly refine the grain size or alter the crystal structure as compared with the as-received material. Therefore, it appears that no major microstructural improvement resulted from laser surface melting. The major microstructural effect of laser melting was the formation of cellular dendrites. It should be noted that it has been postulated that the cellular dislocation tangles associated with the formation of cellular dendrites produced by laser melting may impart SCC and hydrogen embrittlement resistance by providing sites for hydrogen and preventing planar slip [80]. Further work is needed to verify this hypothesis. Substructure analysis was not performed in this thesis.

4.2 Mechanical Testing

The mechanical properties of the laser-melted region influence susceptibility to SCC and may limit practical applications. A successful surface modification treatment must impart SCC resistance without degrading the mechanical state of the material. For example, tensile residual stress increases susceptibility to SCC and shortens fatigue life. A state of compressive residual stress has the opposite effect. To detect changes in the mechanical state of the material, impact behavior, microhardness, and residual stress were examined as a function of laser processing.

4.2.1 Impact Testing

Impact testing was used to determine if laser-melted material would behave as a notch. Notch sensitivity is a characteristic of many brittle materials. A crack or notch in a ductile material deforms
to a large radius, minimizing the stress concentration effect. 304 stainless steel is a ductile material. In a brittle material, the radius of curvature of a crack or notch remains sharp, and the stress concentration effect is great. The notch sensitivity of M2 tool steel was examined because M2 tool steel is a brittle material. In 304 stainless steel, the possibility that laser melting may promote the formation of a brittle phase or harden the material in a manner that reduces ductility was investigated by a band of overlapping laser melt tracks (shown in Figure 5) to simulate a notch. The notch sensitivity of laser-melted M2 tool steel was examined as a comparison material because M2 tool steel is a brittle material.

Experiments which measured the total impact energy absorbed as a function of temperature showed that laser melting severely degraded the impact behavior of M2 tool steel, but that laser melting did not affect the impact behavior of 304 stainless steel (see Figures 14 and 15). There were some variations in the impact energy of the 304 stainless steel specimens tested, but the results are well within the scatter expected with austenitic stainless steels [81].

The ratio of crack initiation energy to crack propagation energy remained constant for room temperature testing of both laser-melted and control M2 tool steel (see Table 4). Therefore, laser melting affected both crack initiation and crack propagation in the tool steel (i.e. the low energy initiation of a sharp crack).

Complete data on the energy needed to initiate and propagate cracks in the 304 stainless steel samples is not available because the samples did not crack to failure. Ductility was such that the samples bent sufficiently to pass through the holder when struck by the impact hammer before fracture could occur. The results suggest that laser melting did not affect crack initiation in 304 stainless steel. Again, conclusions about crack propagation are not possible because the samples were so ductile that cracks did not propagate. The great ductility observed in the laser melted samples indicate that laser surface melting does not degrade toughness in 304 stainless steel. The results of the testing of the M2 tool steel attest to the sensitivity of the impact testing to detect degradation in toughness as a result of laser processing.
Figure 14. Impact energy vs temperature for M2 tool steel. The samples were cooled by immersion in liquid nitrogen. Laser melting severely degraded the impact energy necessary for fracture.
Figure 15. Impact energy vs temperature for 304 stainless steel. It appears that laser melting did not significantly degrade impact behavior. The scatter in the data is characteristic of impact testing of austenitic stainless steels.
Table 4. Crack initiation and crack propagation energies.

Crack initiation and crack propagation energies for laser-melted and as-received M2 tool steel tested at room temperature. Laser melting affected both crack initiation and crack propagation.

<table>
<thead>
<tr>
<th>Test sample</th>
<th>Crack initiation energy (ft-lb)</th>
<th>Crack propagation energy (ft-lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received</td>
<td>21.78</td>
<td>27.85</td>
</tr>
<tr>
<td>laser-melted</td>
<td>0.50</td>
<td>1.15</td>
</tr>
</tbody>
</table>
4.2.2 Microhardness

Laser melting had little effect on microhardness in 304 stainless steel (see Figures 16 and 17). The slight increase in hardness in the melted region is attributed to the formation of cellular dendrites and/or work hardening as a result of the melting process. The similarity in hardness of the laser-melted regions to the base metal suggests that the laser melting did not produce any significant structural effects in 304 stainless steel.

Figure 18 shows a typical microhardness profile for a cross-section of laser-melted M2 tool steel. The laser melted region shows a dramatic hardness increase over the base metal (Vickers 800 to 250). This effect has been attributed to a fine dispersion of carbides in the melted region [82]. A Vicker's microhardness of 800 is comparable to that obtained in the as-quenched condition for this material [83]. The testing of the M2 tool steel showed that microhardness measurements are capable of detecting changes which may result from laser melting.

4.2.3 Residual Stress

A tensile residual stress of greater than 15 ksi is sufficient to cause cracking by SCC processes in 304 stainless steel. X-ray residual stress measurements made on the surface of the laser-melted regions (X-ray penetration depth of 10 microns) showed biaxial tensile residual stresses 3 to 4 times greater than this critical level (see Figures 19 and 20). High tensile residual stresses were observed in both the keyhole melted and the conduction melted samples. The generation of this residual stress is attributed to shrinkage during solidification and cooling. Unmelted material at a lower temperature surrounded the melted material. The constraint provided by the unmelted material as the melted material shrank as it solidified and cooled gave rise to the residual stress. The surface of the melted regions were placed in tension because it was the last material to solidify and cool.
Figure 16. Microhardness vs depth for keyhole melted 304 stainless steel.
Figure 17. Microhardness vs depth for conduction melted 304 stainless steel.
Figure 18. Microhardness vs depth for laser-melted M2 tool steel.
The absence of compressive surface residual stress in the melted regions suggest that no volume expansion phase changes such as a martensitic transformation occurred.

Compressive residual stresses were present in the surface of the unmelted regions near the melted/unmelted material interface (see point D in Figures 19 and 20). The compressive residual stresses are necessary to help balance the tensile residual stresses present in the surface of the melted regions. A sharp stress gradient was observed at the melted/unmelted material interface (see points C and D in Figures 19 and 20). The interface is sharp because the heat-affected zone produced by laser melting is very small. The switch from tensile to compressive residual stresses occurred within several millimeters of the melted/unmelted region interface. It was difficult to map the interface residual stresses because the X-ray beam size was also on the order of several millimeters.

Shear stresses were not observed in either the conduction melted or the keyhole melted samples. The absence of sin 2ψ split and the excellent straight line fit of the data are consistent with a biaxial state of stress. A typical run output which shows the data fit is shown in Figure 6.

The major difference between the residual stress distributions produced by keyhole melting and conduction melting is the difference between the σx stress and the σy stress in the center of the laser-melted region (point A in Figures 19 and 20). The σx stress was found to be twice the σy stress in the keyhole melted sample, but essentially identical in the conduction melted sample. The high heat input of keyhole melting was sufficient to warp the test coupon along the X direction axis. Because the test coupon was rectangular, the constraint along the width axis (the X direction) was less than the constraint provided along the length axis (the Y direction). Conduction melting also warped the test coupon in the same manner, but not to the same degree. This conclusion is based on both visual inspection and residual stress measurements made on the backside of the test coupons.

Figure 21 shows that the magnitude of backside residual stress (the face opposite the laser-melted face) is greater in the keyhole melted coupon than the conduction melted coupon. Therefore, keyhole melting warped the test coupons more than conduction melting. Visual inspection of the coupons confirms this. The warping of the test coupon relieved some of the residual stress in the keyhole sample in the X direction. The effect is seen to a lesser degree in the conduction melted
Figure 19. Residual stresses in a conduction melted 304 stainless steel test coupon. Measurements were made using Cr $\lambda_\alpha$ radiation in orientations both parallel to and perpendicular to the laser beam scan direction.

<table>
<thead>
<tr>
<th>Point</th>
<th>$\sigma_x$ (ksi)</th>
<th>$\sigma_y$ (ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>+61.0</td>
<td>+70.5</td>
</tr>
<tr>
<td>B</td>
<td>+40.3</td>
<td>+30.8</td>
</tr>
<tr>
<td>C</td>
<td>+17.0</td>
<td>+15.0</td>
</tr>
<tr>
<td>D</td>
<td>-4.0</td>
<td>+1.0</td>
</tr>
</tbody>
</table>
Figure 20. Residual stresses in a keyhole melted 304 stainless steel test coupon. Measurements were made using Cr $\mathcal{K}$ radiation in orientations both parallel to and perpendicular to the laser beam scan direction.

<table>
<thead>
<tr>
<th>Point</th>
<th>$\sigma_x$</th>
<th>$\sigma_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>+33.0 ksi</td>
<td>+57.0 ksi</td>
</tr>
<tr>
<td>B</td>
<td>+15.0 ksi</td>
<td>+17.0 ksi</td>
</tr>
<tr>
<td>C</td>
<td>+45.0 ksi</td>
<td>+36.0 ksi</td>
</tr>
<tr>
<td>D</td>
<td>-17.0 ksi</td>
<td>+14.0 ksi</td>
</tr>
</tbody>
</table>
samples. This result implies that increase in constraint (which would decrease warpage during the process) would result in higher magnitudes of tensile residual stress in the surface of the laser-melted regions. Therefore, residual stresses will likely be higher in field applications where the degree of constraint will certainly be higher (due to larger size and mass as well as design imposed constraints) than that of the small test coupons examined in this study.

4.2.4 Discussion

Microhardness and impact measurements made on 304 stainless steel suggest that laser melting did not induce major structural changes. Similar tests performed on laser-melted M2 tool steel show that these tests were sensitive to changes resulting from laser melting. The most important effect of laser melting on 304 stainless steel was identified as the introduction of high tensile residual stresses in the surface of the melted regions. This effect was produced by both coupling modes.

The two coupling modes represent a range of melting depth penetrations and solidification and cooling conditions. It is, therefore, unlikely that modification of the laser parameters would produce a less severe state of residual stress. The residual stresses in the melted regions and at the interfaces of the melted/unmelted regions were well in excess of the minimum stress (15 ksi) necessary to promote SCC cracking of 304 stainless steel in a chloride environment.

A final point to be noted is that the nominal yield strength of annealed 304 stainless steel plate is 35 ksi [84]. The ultimate strength is 80 ksi [85]. The measured residual stress values at some locations exceed twice the yield strength. Similar magnitudes of residual stress have been reported for laser-melted 316 stainless steel [86]. The mechanical properties of 316 stainless steel are similar to the mechanical properties of 304 stainless steel. The high values of residual stress observed in laser-melted 316 stainless steel were attributed to dislocation buildup in the melted region [87]. The author emphasized that laser-melted material is comparable to the severely cold worked state, not the annealed starting condition [88]. The values of residual stress determined by X-ray measurements in this study are below the ultimate strength of the material and are therefore reasonable.
Figure 21. Residual stresses. Residual stresses in the face opposite the laser-melted face for both the conduction melted and keyhole melted test coupons.

<table>
<thead>
<tr>
<th>Point</th>
<th>Sample</th>
<th>$\sigma_x$</th>
<th>$\sigma_y$</th>
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<tr>
<td>A</td>
<td>Keyhole</td>
<td>+ 19.7 ksi</td>
<td>+ 25.9 ksi</td>
</tr>
<tr>
<td>A</td>
<td>Conduction</td>
<td>+ 10.4 ksi</td>
<td>+ 9.8 ksi</td>
</tr>
</tbody>
</table>
4.3 Corrosion Testing

An initial qualitative evaluation of the SCC behavior of laser-melted 304 stainless steel was made by three-point bend testing. Exposure times to the boiling magnesium chloride environment varied from 12-24 hours. Widespread visible cracking marked the end of the test. Loading levels varied from sample to sample, but all were loaded well beyond yield. A typical test sample after exposure is shown in Figure 22. The sample failed a distance away from the point of highest external loading (the strip of laser-melted material across the middle of the bar) at the melted/unmelted region interface. Untreated control samples suffered widespread cracking (refer to Figure 23). The deepest crack penetration was always found to correspond to the point of maximum initial loading.

The patterns of cracking shown in Figures 22 and 23 indicate that the microstructure produced by laser melting may be more resistant to SCC than untreated material. This apparent improved SCC behavior as a result of laser melting is surprising. The residual stress introduced by the process would be expected to severely degrade SCC behavior. The residual stress measurements predict that the melted regions would be most susceptible followed by the interfaces (based on magnitude of tensile surface residual stress). Additionally, the process does not appear to significantly alter the microstructure. The cracking pattern suggests two possibilities. Either laser melting 304 stainless steel imparts chloride SCC resistance or laser melting degrades chloride SCC resistance at the melted/unmelted region interface making those regions more susceptible, perhaps as a result of the severe stress gradient. Coupon testing and four-point bend testing were designed to attempt to provide the answer.

Coupons with no externally applied load were exposed to the test environment for periods ranging from 27 to 72 hours. Red liquid penetrant and sectioning were used to determine the presence of cracks. Cracking was not observed in as-received coupons. Laser melted coupons exposed for 67 hours suffered widespread cracking (see Figures 24-26).
Figure 22. Typical three-point bend test result. The sample failed after 18 hours exposure to boiling magnesium chloride (154 Celsius) at the interface of the melted/unmelted regions. This micrograph shows the surface of the bar sample. The laser-melted material did not crack.
Figure 23. Cross-section of an as-received 304 stainless steel bend sample. This sample was exposed to boiling magnesium chloride (154 Celsius) for 20 hours. The material is as-received 304 stainless steel. The crack are primarily transgranular.
Cracks observed in the conduction melted samples were oriented in a grid-like pattern along the A and B directions. Because cracks form perpendicular to the stress, this grid pattern of cracking supports the biaxial state of surface stress measured by X-ray diffraction. The keyhole melted samples cracked preferentially along the A direction. Cracking extended further beyond the melted/unmelted region interface in the keyhole melted sample than the conduction melted sample. This cracking pattern is also consistent with the results of the residual stress measurements.

Coupon cross-sections (see Figures 27 and 28) confirm that in both keyhole melted and conduction melted samples, the cracking is primarily transgranular. Transgranular cracking is a characteristic of chloride SCC in austenitic stainless steels. The cracking does not extend beyond the melt depth in the keyhole melted sample. Little crack branching is evident in the plane examined. Cracks grow perpendicular to the maximum tensile stress. The straight, deep penetrating cracks indicate tensile residual stress exists through the melt depth. There is some evidence of undulating cracking (cracks that appear disconnected). The effect is not widespread. This indicates the absence of a strong tensile residual stress oriented perpendicular to the free surface at this depth.

Cracking in the conduction melted sample differs from cracking in the keyhole melted sample only in crack penetration depth. It is assumed that the thick surface oxide that formed on the surface of the keyhole sample delayed crack initiation. Therefore, crack penetration is deeper in the conduction melted sample.

The driving force for cracking was found to be the reduction of residual stress. Figures 29 and 30 show that after 27 hours exposure to boiling magnesium chloride, residual stress in both the keyhole melted and conduction melted samples were relieved. Stress relief occurred to a greater extent in the orientation of the highest residual stress prior to environmental exposure. After 72 hours exposure, there is virtually no tensile residual stress left in the laser-melted regions of either sample.

The compressive residual stress observed in the keyhole melted sample after 72 hours exposure is surprising (see Figure 30). It may result from the wedging of corrosion products [89]. The wedging of corrosion products during SCC of austenitic stainless steels was first quantitatively measured by Pickering, Beck, and Fontana in 1962 [90]. The wedging action of solid corrosion products found in notches or cracks was found to produce tensile stress in excess of 7 ksi. Tensile

RESULTS AND DISCUSSION
Figure 24. Surface macrographs. Surface macrographs of test coupons after exposure to boiling magnesium chloride for 67 hours. Cracks are highlighted by a red liquid penetrant. Tensile residual stresses introduced by the laser-melting process were of a sufficient magnitude to promote SCC. a) Keyhole melted  b) Conduction melted.
Figure 25. Keyhole melted test coupon from Figure 24(a). Cracks generally grew preferentially along the beam scan (X) direction. a) polished surface section  b) surface micrograph of last pass region.
Figure 26. Conduction melted test coupon from Figure 24(b). Cracks generally grew in a grid pattern oriented parallel to (X direction) and perpendicular to (Y direction) the beam scan direction. 

a) polished surface section  b) surface micrograph of last pass region.
Figure 27. Cross-section micrograph. Cross-section micrograph of keyhole 304 stainless steel exposed to boiling magnesium chloride for 67 hours. Cracking is primarily transgranular.
Figure 28. Cross-section micrograph. Cross-section micrograph of conduction melted 304 stainless steel exposed to boiling magnesium chloride for 67 hours. Cracking is primarily transgranular.
wedging between successive parallel cracks formed in the keyhole melted coupon would produce compression in the material between the cracks and may account for this compressive residual stress (see Figure 25).

The four-point bend testing was designed to eliminate the two main limitations of the three-point bend testing: the presence of a melted/unmelted material interface and the duplication of initial loading conditions. The melted/unmelted region interface was eliminated in the laser-melted sample by laser melting one entire surface of a test bar (see Figure 10). Because the three-point bend testing was designed as a qualitative initial evaluation of the SCC behavior of laser-melted material, no attempt was made to duplicate the extent of loading between the many samples tested, although all samples were loaded well past the yield strength. Therefore, direct comparison between three-point bend samples was not possible. Additionally, only a small area of material can be subjected to the maximum load in three-point bend. The four-point bend allowed for a large area of the test bars to be exposed to the maximum load. A spacer bar was used to measure the extent of deflection applied to the test bars in order to duplicate loading conditions and thus allow direct comparison of sample behavior. Figure 31 shows that both the untreated and laser-melted samples failed after 18 hours exposure. The untreated sample failed in the region of highest external loading. One major crack is present. The laser-melted sample failed in two regions. The major cracks are located outside the region of highest initial external loading as occurred in the three-point bend testing. The cause of this effect is unknown. The important point is that externally loaded laser-melted material failed to the same extent as untreated material in this test environment.

4.3.1 Discussion

The results of the corrosion tests indicate that laser-melted material 304 stainless steel is susceptible to chloride SCC. The key factor is residual stress. Laser melted coupons with no external loading failed in the boiling magnesium chloride. Untreated control specimens did not crack. Therefore, laser melting resulted in increased susceptibility to SCC.

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Figure 29. Residual stresses. Residual stresses in a conduction melted 304 stainless steel test coupon after exposure to boiling magnesium chloride (154 Celsius for 27 and 72 hours. *Reported measurement made on a similarly processed laser-melted test coupon.

<table>
<thead>
<tr>
<th>Point</th>
<th>Exposure Time</th>
<th>$\sigma_y$</th>
<th>$\sigma_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>no exposure*</td>
<td>+ 61.0 ksi</td>
<td>+ 70.5 ksi</td>
</tr>
<tr>
<td>A</td>
<td>27 hours</td>
<td>+ 9.6 ksi</td>
<td>+ 15.4 ksi</td>
</tr>
<tr>
<td>A</td>
<td>72 hours</td>
<td>+ 6.8 ksi</td>
<td>+ 5.7 ksi</td>
</tr>
</tbody>
</table>
Figure 30. Residual stresses. Residual stresses in a keyhole melted 304 stainless steel test coupon after exposure to boiling magnesium chloride (154 Celsius for 27 and 72 hours. *Reported measurement made on a similarly processed laser-melted test coupon.

<table>
<thead>
<tr>
<th>Point</th>
<th>Exposure Time</th>
<th>$\sigma_x$ (ksi)</th>
<th>$\sigma_y$ (ksi)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>no exposure*</td>
<td>+33.0</td>
<td>+57.0</td>
</tr>
<tr>
<td>A</td>
<td>27 hours</td>
<td>+17.6</td>
<td>+4.8</td>
</tr>
<tr>
<td>A</td>
<td>72 hours</td>
<td>-8.0</td>
<td>+3.6</td>
</tr>
</tbody>
</table>

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Figure 31. Cross-sections. Cross-sections of four point bend samples after exposure to boiling magnesium chloride (154 Celsius) for 18 hours. a) Laser melted sample. Two major cracks are present, but outside of the region of maximum external loading. b) Control sample. One major crack is present. The crack is located in the region of maximum external loading.
Crack penetration in both the laser-treated and untreated four point bend samples was approximately the same after 18 hours exposure to boiling magnesium chloride. However, because of the magnitude of the residual stresses in the laser-melted region, the actual level of stress in the laser-melted four-point bend sample was much higher than the untreated four-point bend sample because of the additive effect of the residual stresses. It is, therefore, possible that a residual stress free laser-melted material would be more resistant to SCC than untreated material.
Chapter 5

SUMMARY AND CONCLUSIONS

The present work indicates that laser surface melting of 304 stainless steel introduces high tensile residual stresses in the surface of the melted regions which renders the material susceptible to chloride SCC. However, laser-melted microstructures may be more resistant than untreated material under identical conditions of stress. Unless measures can be found to eliminate or reverse the residual stress, laser melting does not appear to be a viable technique to mitigate chloride SCC in these alloys.
Chapter 6

SUGGESTIONS FOR FURTHER WORK

Several authors have shown that laser surface melting of 304 stainless steels improves such properties as oxidation resistance, intergranular stress corrosion cracking resistance, and electrochemical behavior (elevated pitting potentials) [91-94]. However, the SCC susceptibility of laser-melted 304 stainless steel in chloride containing environments resulting from the introduction of residual stress severely limits practical applications. It is, therefore, necessary to develop techniques to reduce or eliminate the residual stresses.

The effects of laser parameters and workpiece constraint on the generation of residual stresses must be quantified. It may be possible to limit the magnitude of the residual stress to acceptable levels for some applications by correct selection of parameters. The effectiveness of conventional stress relief techniques for laser-melted material should also be examined. Treatments such as annealing or post-weld stress conversion treatments (post weld cooling, heat sink welding, etc.) are effective for some conventional welding applications and may be applicable to laser-melted material.

A phase change accompanied by a volume expansion is one way to induce compressive residual stress. Proper alloying of the laser melt pool may result in this type of phase change. One might consider the formation of a martensitic surface layer on an austenitic bulk material. For such a
treatment, it will also be necessary to fully characterize the altered surface to insure that the material is still suitable for its intended application.

An important effect of laser surface melting is the redistribution of alloying elements. It was observed both in this work and elsewhere that laser melting may normalize sensitized structures [95]. A possible application of the process may be to mitigate intergranular stress corrosion cracking (IGSCC). Laser melting clearly renders sensitized structure resistance to IGSCC. If the service environment did not include environmental factors that promote other forms of SCC, the residual stress introduced by the process might not be detrimental from a corrosion standpoint.
Chapter 7

FOOTNOTES


Vita

Michael Brady was born on June 19, 1964. He graduated from C.H.S. (Cohasset, Ma.) in 1982. He chose to attend Virginia Tech to study engineering and play collegiate tennis. Health problems almost eliminated the former and prevented the latter. He graduated in 1986 with a B.S. in Materials Engineering and defended his Masters thesis on July 26, 1988. He officially graduated with his M.S. in Materials Engineering a short time later (on a geological time scale that is). Along the way he rebuilt his legs, assisted with the woman's tennis team, and encountered the finest group of friends and professors anyone could ever ask for. He is currently pursuing his Ph.D. in Materials Engineering at the University of Florida under Dr. Ellis Verink.

Michael P. Brady