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# Material Influence on Mitigation of Stress Corrosion Cracking Via Laser Shock Peening

Stress corrosion cracking is a phenomenon that can lead to sudden failure of metallic components. Here, we use laser shock peening (LSP) as a surface treatment for mitigation of stress corrosion cracking (SCC), and explore how the material differences of 304 stainless steel, 4140 high strength steel, and 260 brass affect their mitigation. Cathodic charging of the samples in 1 M sulfuric acid was performed to accelerate hydrogen uptake. Nontreated stainless steel samples underwent hardness increases of 28%, but LSP treated samples only increased in the range of 0–8%, indicative that LSP keeps hydrogen from permeating into the metal. Similarly for the high strength steel, LSP treating limited the hardness changes from hydrogen to less than 5%. Mechanical U-bends subjected to Mattsson's solution, NaCl, and MgCl<sub>2</sub> environments are analyzed, to determine changes in fracture morphology. LSP treating increased the time to failure by 65% for the stainless steel, and by 40% for the high strength steel. LSP treating of the brass showed no improvement in U-bend tests. Surface chemical effects are addressed via Kelvin Probe Force Microscopy, and a finite element model comparing induced stresses is developed. Detection of any deformation induced martensite phases, which may be detrimental, is performed using X-ray diffraction. We find LSP to be beneficial for stainless and high strength steels but does not improve brass's SCC resistance. With our analysis methods, we provide a description accounting for differences between the materials, and subsequently highlight important processing considerations for implementation of the process. [DOI: 10.1115/1.4034283]

Keywords: laser shock peening, stress corrosion cracking, microstructure, fracture analysis

## Introduction

When choosing which materials to implement into engineering designs what may often go overlooked is how mechanical stress influences corrosion behavior. Stress corrosion cracking (SCC) is a phenomenon where a corrosive environment effectively lowers the fracture strength of a material. Rather than traditional failure by corrosion, which is evident by a slow dissolution of the material, SCC occurs without warning. This lack of visual clues is what makes SCC of concern; its sudden cracking can lead to unpredictable, catastrophic failure of integral parts. The biggest problem from a design perspective is that stress corrosion cracking is difficult to make conclusive predictions of when and where it will occur. It is highly dependent on the specific material/environment pair, where a material that is resistant in one environment may become dangerously susceptible to SCC in other environments.

The stress required for SCC can either be externally applied or be a residual stress from previous manufacturing processes. Some situations where this occurs are pipe taps and fittings, nuclear reactors, pressure vessels, or high strength pipeline steels. Brass is machinable and generally considered as corrosion resistant, but it is still susceptible to SCC, and when this does occur it can cause excessive damage. Small concentrations of ammonia are found to be the main cause for brass's failure by SCC, where even the low concentrations found in drinking water can be problematic [1]. Residual stresses caused during installation—such as tightening of threaded components—can cause material failure. Other residual stresses, most prominently those caused by welding, can make a material susceptible to SCC. Many of the pipelines found in chemical processing plants are at risk, as are pipelines for distribution of gases. Recently, a natural gas pipeline rupture was attributed to SCC, where a combination of the internal pressure and corrosive gas as well as the external soil moisture and movement combined to cause failure [2]. Another critical example of SCC's concern is in nuclear reactors, where susceptibility and cracking has been extensively documented [3]. Additionally, the elevated temperatures and exposure to radiation compound the concern for premature failure of reactors.

With the identification of SCC's potentially catastrophic effects, the question arises as how to prevent this phenomenon from occurring. While proper selection of materials does help, sometimes further enhancement of a material's SCC resistance must be provided by surface processing treatments. Shot peening has been identified as potentially beneficial, attributed to imparting a compressive residual stress upon the surface of the material [4]. But the macroscopic morphological changes caused by this process may be undesirable, and the precision unsuitable for small parts. Another method is heat treating the final piece to relieve residual stresses, but this is not always practical, especially on large parts such as nuclear reactor cores. Furthermore, the additional effects of heat treating (grain refinement, oxide or precipitate formation) may be undesirable.

Laser shock peening (LSP) is a surface treatment process that has the potential for helping to mitigate the effects of SCC without damaging other characteristics of the material. While originally developed for increasing the fatigue life of materials, LSP uses laser generated shock waves to impart compressive residual stresses onto the surface [5], with affected regions as deep as 1 mm into the metal, much deeper than traditional shot peening. Another benefit of LSP over other processes is that it maintains minimal changes on overall feature morphology and metallurgy, thus avoiding the requirement of modifications to the design. The capability of LSP to prevent SCC has previously been investigated

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by several researchers. For example, LSP treatment of stainless steel has been found to increase the time-to-failure in boiling MgCl<sub>2</sub> solutions of U-bend specimens, where the improved behavior was attributed to the residual compressive stress counteracting the applied load [6]. While this is a simple explanation of beneficial effects, it does not capture the overall phenomenon, namely, the electrochemical effects are not taken into consideration. Even though LSP does not impart any thermal effects on the surface, it still causes significant changes to the surface chemistry and microstructure. As proof, multiple researchers have shown that LSP treatment increases the rest potential of metals during polarization testing [7]. Increased rest potentials are indicative of more inert surfaces, but in most cases, it was found that over time the rest potential decayed back towards the initial, untreated level.

Across these previous investigations, it is clear that LSP has the potential to effectively reduce the effects of stress corrosion cracking. But the mechanism driving the SCC resistance improvement has yet to be fully understood, where achieving this understanding could lead to identification of scenarios that would benefit the most as well as optimization of the process. In this paper, we work to provide a further description of the mitigation effects imparted by LSP, not just including stress analysis but also by providing a discussion of the microstructural and electrochemical changes that make LSP a valuable tool for SCC mitigation, as well as differences caused by material characteristics.

#### Background

Mechanisms of Stress Corrosion Cracking. Several different failure mechanisms have been proposed to explain the occurrence of SCC, but no definitive consensus has been reached. This may be a result of different mechanisms dominating under different circumstances. Some of these theories are hydride formation, hydrogen enhanced decohesion, hydrogen enhanced localized plasticity, and adsorption-induced dislocation emission [8]. In many cases, the most preeminent factor and common theme are the effect of hydrogen. Hydrogen present in the corrosive environment can have negative effects by penetrating into the microstructure of the metal, known as hydrogen embrittlement. When a material is stressed in tension, and the crystal lattice is elongated, hydrogen's diffusivity becomes even more exaggerated. The additional hydrogen atoms within the already stressed lattice may push the material over its threshold by weakening the atomic bonding, and result in failure. But developing a simple relationship between applied stress and SCC occurrence cannot be achieved [9], illustrating the unpredictable nature of the phenomenon.

Once it has penetrated the metallic surface, the distribution and location of hydrogen throughout the lattice are important. Grain boundaries act as high diffusivity paths, allowing for deep penetration of hydrogen [10]. Cold working generates dislocations within the lattice structure, and these dislocations act as hydrogen trapping sites. It is most likely that the hydrogen atoms will be found in the trapping sites rather than interstitial locations [11], and as a result, the solubility of hydrogen raises with increasing dislocation density. With excessive amounts of hydrogen present, a material's lattice becomes stressed and subsequently, its hardness is increased [12]. This enables measuring hardness increases in materials exposed to hydrogen containing environments to be used as an indicator of the amount of hydrogen that has penetrated into the lattice.

Laser Shock Peening. The physical configuration for LSP processing consists of an ablative layer placed in between a target surface and a confining layer [13]. Since the confining layer is transparent to the laser's wavelength, upon irradiation the laser beam passes through this layer and is absorbed into the ablative layer. Using a sufficiently intense laser beam instantly vaporizes the ablative layer causing it to expand. But the confining layer

restricts the expansion, and thus, a shock wave is generated and travels into the material resulting in a compressive residual stress [14]. The metallic surface does not undergo any thermal effects, as all of the laser energy is absorbed by the ablative layer.

An important characteristic of materials' corrosion responses is the formation of a surface oxide layer. This layer can help to passivate the material, preventing the occurrence of further corrosion. Stainless steel, for example, achieves its corrosion resistance from the formation of a chromium oxide layer, which encases and protects the iron. Thickness and uniformity of such oxide layers are very important, and therefore, any surface processing treatment has the potential to negatively impact the oxide layer. Additionally, the stress state on the surface influences the formation of oxide layers as well [15]. Surface roughness also plays an important role in the initiation of stress corrosion cracking. Within crevices on a material's surface, hydrolysis may acidify the electrolyte so that the pH within the crevices does not match the pH of the bulk solution. This causes an increase in the surface's anodic reactions. In this case, the applied stress works to open up and expose more surface crevices.

**Dislocation Generation.** During LSP processing, the material experiences extremely high strain rates as the shock wave propagates through it, reaching levels as high as  $10^6 \text{ s}^{-1}$ . This causes plastic deformation [16] as well as the formation of many lattice dislocations. As stated above, dislocations act as trapping sites for hydrogen, whereby LSP can be used to alter the hydrogen behavior and distribution within the lattice. Hydrogen's solubility increases with dislocation density and, subsequently, its diffusivity decreases as described by the following equation [17]:

$$D = D_L \frac{C_L}{C_L + C_x (1 - \theta_x)} \tag{1}$$

where *D* is the effective diffusivity,  $D_L$  is the normal (defect free) diffusivity,  $C_L$  and  $C_x$  are the concentrations in the lattice and trapping sites, and  $\theta$  is the population fraction of available trapping sites.

Upon plastic deformation, the rate at which dislocation density increases will vary for different materials. Dislocation generation by plasticity has three stages: easy glide, dislocation multiplication by tangling, and dynamic recovery. Each one of these stages can be numerically described in terms of the rate of change of dislocation density  $\rho$  versus shear strain  $\gamma$ , as derived in Malygin et al. [18]. For easy glide

$$\left(\frac{d\varrho}{d\gamma}\right)_m = \chi_m = \left(b\lambda_m\right)^{-1} = \delta_m b^{-1} \tag{2}$$

where *b* is the Burgers vector and  $\lambda$  is the average distance between dislocations and obstacles such as grain boundaries. The second stage is described by

$$\left(\frac{d\varrho}{d\gamma}\right)_f = \chi_f \varrho_f^{1/2} \quad \chi_f \approx 10^{-2}b \tag{3}$$

The third and final stage, dynamic recovery is when dislocation annihilation occurs, by dislocations of opposite signs coming into contact or by grain refinement

$$\left(\frac{d\varrho}{d\gamma}\right)_a = -\chi_a \varrho \quad \chi_a = \frac{\omega_s^{5/2} \mu}{24\pi^2 \alpha \tau_c} = b^{-1} \delta_a \quad \omega_s \approx 0.5 \tag{4}$$

where  $\mu$  is the shear modulus,  $\alpha$  is a dislocation interaction constant, and  $\tau_c$  is the critical resolved shear stress. Summation of the combined effects and rearrangement of variables yields

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$$\frac{d\varrho}{d\gamma} \sim (\sigma - \sigma_s)\theta$$
$$= \frac{1}{2}m^3(\alpha\mu b)^2 \left[\chi_m + \chi_f \left(\frac{\sigma - \sigma_s}{m\alpha\mu b}\right) - \chi_a \left(\frac{\sigma - \sigma_s}{m\alpha\mu b}\right)^2\right] \quad (5)$$

where  $\theta$  is the work hardening coefficient,  $\sigma$  is stress, and  $\sigma_s$  is the yield stress. Thus, by use of Eq. (5), the rate of change of dislocation density versus strain (deformation) can be estimated based on material characteristics.

Work Function and Corrosion Potential. It is evident that the corrosive response of metals is dependent on surface characteristics, which leads one to desire ways to characterize the surface's electrochemical behavior as it may lead to additional insights regarding SCC behavior. One such characterization is to analyze the work function. By definition, the work function is the amount of energy required to remove an electron from the surface, as expressed by the equation

$$W = -e \not O - E_f \tag{6}$$

where *e* is the elementary charge,  $\emptyset$  is the vacuum electrostatic potential, and  $E_f$  is the Fermi Level. Oftentimes, the work function is discussed regarding photoelectric devices, but it can also be applied to corrosion analyses, particularly as related to the open circuit potential during polarization testing. A linear relationship between increasing work functions and increasing rest potentials has been reported, thus providing an empirical basis [19,20]. Examinations of the validity of this relationship have been made on iron surfaces exposed to humid environments, where it has been concluded that work function analysis is an effective method for corrosion characterization [21].

Multiple factors can affect the work function, particularly stress, both applied and residual. The Fermi level depends upon electron density, leading some researchers to develop relationships between elastic stress and work function changes. Based on density functional theory, Wang et al. have modeled the distribution of atoms in Cu (100) and how applied loads affect their density and thus work function [22]. They found that tensile strains decrease work function, while compressive strains cause work function increases. While this provides a good basis, the plastic deformation caused by LSP further complicates the discussion. Dislocations are lattice imperfections, regions where electrons may be more easily ejected from the surface. Increasing the amount of plastic strain in copper samples results in both decreased work function and decreased corrosion potential [23]. The competing effects elastic and plastic strain have on work function is a trade-off that must be understood in order to fully maximize the benefits LSP has on SCC.

Processing Concerns. With many different factors contributing to LSP's influence on corrosion response, it is of concern that focusing on improving one aspect could actually result in harming another one. This leads to concerns that overprocessing of the metallic samples will start to undo any beneficial effects that had been imparted. For example, while initially austenitic, stainless steel can experience martensite formation upon excessive deformation. The corrosion response of martensitic phases differs from austenitic ones, thereby destroying the material's homogeneity and thus decreasing the corrosion resistance. Increased strain rates also cause more martensitic formation [24], making this a particular concern for LSP. Cold working of metals may result in grain refinement. While grain refinement is sometimes desirable for strengthening a material, from a corrosion standpoint it can be harmful. Grain boundaries have lower work functions than the grain interiors, so increased amounts of grain boundaries by grain refinement may therefore be detrimental. Conversely, grain refinement could act as a barrier to crack propagation and have a beneficial effect on the SCC response. These concerns illustrate that in

order to optimize the LSP process for SCC resistance, all of the underlying effects must be understood, where simply continuing to impact the surface with as many laser impulses as possible will not be the most effective approach.

#### **Experimental Procedure**

Three different materials were investigated: stainless steel 304, AISI 4140, and 260 cartridge brass. The stainless steel had a brushed satin finish and a thickness of 1.22 mm, the 4140 high strength steel was 2.4 mm thick, while the brass was 1.6 mm thick. The confining layer for LSP was 6.35 mm thick acrylic, and black electrical tape was used as the ablative layer. A Continuum NY61 Nd:YAG laser, operating at 1064 nm provided 17 ns laser pulses at a repetition rate of 20 Hz. Laser spot sizes ranged from 0.9-1.1 mm in diameter while pulse energies ranged from 125 mJ to 300 mJ. Topography measurements were made with a Zygo Optical Profilometer. For the U-bend testing, two-stage bending was performed as specified in ASTM G30, with a radius of curvature of 4.05 mm for the stainless steel and brass, and 8.5 mm for the 4140 steel. A 25 mm long region was LSP treated in the center of the samples before bending. The stainless steel samples were exposed to a boiling magnesium chloride solution at 155 °C, the brass to Mattsson's Solution at room temperature, and the 4140 steel to 3% NaCl at 80°C. A PANalytical Xpert3 Powder X-ray diffraction (XRD) was used for microstructure analysis and martensite detection, and a Hitachi S-4700 scanning electron microscope (SEM) was used for imaging. Cathodic charging was performed in 1 M sulfuric acid at a current density of 800 mA/cm<sup>2</sup> for 30 min. Work function measurements were made on a Bruker Dimension FastScan AFM operating in Peak Force Kelvin probe force microscopy (KPFM) mode and using PFQNE-AL probes. The finite element method (FEM) model was implemented in ABAQUS.

# **Results and Discussion**

Surface Morphology. Characterization of the surface morphology is first performed to understand the impact the LSP treating had on the surfaces. Figures 1 and 2 show optical profilometer measurements across LSP indentations, where the two lines are measured in perpendicular directions. Figure 1 is a stainless steel sample irradiated at 250 mJ showing indentation depth of slightly over 3  $\mu$ m. As compared to the stainless steel sample, a brass sample processed with the same parameters has a similar depth, but it is clear that the roughness within the indentation is much higher on the brass. Much more surface deformation has occurred, such as the emergence of large slip bands, and this result could be potentially harmful to the brass. Increased surface roughness provides the corrosive environment more cracks and crevices to penetrate into, and as such, smoother surfaces are generally more corrosion resistant. But it is important to keep in mind the scale of this roughening. The indentations on the stainless are large and smooth enough that they should not cause any detrimental effects such as crevice corrosion or local acidification of the electrolyte. As the laser scans across the surface, it creates a uniform array of



Fig. 1 LSP indentation profile of a stainless steel sample irradiated at 250 mJ with a spot size of 0.9 mm. The two lines are traces across perpendicular directions.

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Fig. 2 Indentation profile of brass LSP processed at 250 mJ. More surface roughening effects are visible than on the stainless steel sample.

indentations, of which a 3D topographical map is shown in Fig. 3 for a brass sample. This pattern is for 0% overlapping between adjacent pulses, and good uniformity of the surface indentations is seen across the samples.

The occurrence of any phase transformations was investigated with XRD. Stainless steel samples were processed at 250 mJ, and then in attempts to induce excessive deformation, the samples were reprocessed one and two more times. This gave three samples with either one pass, two passes, or three passes, where retreating the LSP sample compounds the shockwave's effects. Austenitic stainless steel has large  $2\theta$  diffraction peaks at 43.58 deg, 50.79 deg, 74.70 deg, and 90.69 deg. The presence of martensite would cause the emergence of new diffraction peaks, because of the different lattice spacing of the martensite phase. Although other researchers have found deformation induced martensite in LSP treated stainless steel samples, we detected no martensite phases in any of our samples. In terms of corrosion, this is a positive result, as martensite's presence would be detrimental to the corrosion resistance.

**Cathodic Charging and Hardness Increases.** While LSP is known to increase the surface hardness of metallic samples, the absorption of hydrogen also can cause increases in hardness levels near the surface [25]. Cathodic charging is thus an effective way for performing accelerated testing of hydrogen uptake in metallic samples. The excess electrons provided by the power supply react with the acidity of the corrosive environment to produce hydrogen molecules. As the hydrogen permeates into the metal, it locally stresses the lattice, resulting in the measured hardness increase. Thus, the hardness changes are an indicator of the amount of hydrogen influence that each sample has experienced.



Fig. 3 Morphology of a patterned brass sample after LSP processing. Individual indentations are still visible because of the 0% overlap condition.

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Hardness increases induced by cathodic charging of stainless steel samples and 4140 high strength steel are plotted in Figs. 4 and 5, respectively. Vickers hardness (HV) is determined by the equation

$$HV = 0.0018544 \times L/d^2$$
(7)

where L is the applied indenter load in grams, and d is the observed diagonal length. Based on this relationship, and using our applied load of 100 gf, we can estimate that for HV = 300 the indentation reached about 5  $\mu$ m into the sample, indicating that by using the low indenter load we are measuring in the near-surface regions that would experience the LSP effect. Five different processing conditions are shown where the hardness for each respective treatment level is plotted before and after cathodic charging. With increasing amounts of laser processing, there is a clear decrease in the amount of hardness increase by cathodic charging. For untreated stainless steel samples, cathodic charging caused nearly 30% hardness increases, while all of the LSP treated samples underwent less than 10% increases, with the increase becoming statistically insignificant for the samples processed at 20% and two passes. The high strength steel shown in Fig. 5 underwent lower percent increases from both LSP and cathodic charging, but show the same trend as for stainless steel. As this material is much less ductile than stainless steel, the 10% hardness increase in the untreated sample could still have significant detrimental effects.

LSP processing can influence the hydrogen behavior in various ways. First, it may act to prevent the initial entry of hydrogen into the surface. But once the hydrogen has entered the lattice, the dislocations generated from LSP will further prevent the hydrogen from diffusing deeper into the metal, where dislocations act as trapping sites for hydrogen. If there is insufficient energy to remove hydrogen from trapping sites, diffusion will be prevented, causing the hydrogen to remain near the surface. While a hydrogen enriched region is of some concern, the potential it has for decreasing the total amount of hydrogen that gets into the metal could be a strength of LSP for preventing SCC.

U-Bend SCC Testing. The U-bend tests provide the most definitive proof for the effectiveness of LSP processing on



Fig. 4 Hardness increases after cathodic charging on stainless steel samples, caused by increased hydrogen absorption into the lattice. The values on the abscissa correspond to the amount of overlapping between adjacent LSP pulses, and 2X indicates that the surface was treated with two passes. As the level of LSP processing increases, the amount of hardness changes via hydrogen decreases.



Fig. 5 Hardness increases of AISI 4140 steel after cathodic charging. The level of LSP processing causes the hydrogen effects to be lessened, indicating mitigation to hydrogen embrittlement. The percent increases are lesser than for the stainless steel show.

preventing stress corrosion cracking, as summarized in Table 1. Stainless steel samples with no LSP processing fractured after  $97 \pm 22$  min, while samples LSP treated at 250 mJ and three surface passes fractured after  $160 \pm 7$  min. Failure time was defined as when crack propagation was observed which penetrated completely across the outer face of the sample. This significant increase in fracture time is the result of several beneficial factors imparted on the stainless steel via LSP treating, as will be discussed. For all of the samples, no evidence of general corrosion was visible. That is, aside from close inspection to detect the cracks, the samples appeared as if they were not suffering at all from corrosion. It is this aspect of SCC which makes it of great interest: its ability to cause catastrophic failure on apparently noncorroded parts.

An image of the fractured surface of an untreated stainless steel sample is shown in Fig. 6. In this, the samples were exposed to a boiling magnesium chloride solution for precisely 1 h, and then removed regardless of observing failure or not. In this way, comparisons can be made showing the benefits of LSP at a snapshot in time. A dominant large crack can be seen in the center of Fig. 6, nearly propagating through the entire thickness. Two other minor cracks are also evident. The large cracking did not occur on LSP treated samples after the 1 h MgCl<sub>2</sub> exposure, but some smaller crack initiation was found. While the sides of the specimens were not LSP treated, the cracking appears to initiate on the outer surface (bottom edge of images) which is the side that LSP processing was executed and also where the highest levels of tensile stress occur. At the edge of the sample, if the crack begins propagating across the outer surface, catastrophic failure will be inevitable.

On the untreated sample in Fig. 7(a), it is clear the propagation does occur in both directions, as this figure is taken at an angle showing both the side and the outer face of the sample. In the treated samples, as seen in Fig. 7(b), the crack is prevented from



Fig. 6 SEM micrograph of the side of an untreated stainless steel U-bend specimens after 1 h of exposure to boiling magnesium chloride

propagating down the front, LSP treated surface. This effect of preventing existing cracks from propagating onto the LSP treated surface is most likely the result of the compressive stress induced by the processing. Even though these samples are in tension because of the U-bending, having an initial compressive stress lowers the amount of tensile stress found in the final form [6]. Furthermore, not only does LSP treating prevent crack propagation, but it also prevents the formation of cracking, as illustrated in Fig. 8. This image is of the outer surface of an untreated sample, showing that after 1 h of magnesium chloride exposure cracks begin to form. Conversely, no initiation was found on the LSP treated samples. While the mechanical compressive stress definitely plays a role, other factors to be discussed later become nearly as significant.

Etching the fractured surface enables examination of the failure type differences between the untreated and treated samples, which can be seen in Fig. 9. The untreated samples have both large intergranular cracking and many smaller branches with transgranular failure characteristics. Conversely, the treated samples showed only intergranular failure without the occurrence of branching. The differences in fracture mode should be considered while remembering that hardness increases suggest the presence of more hydrogen in the untreated samples than the treated ones. Hydrogen's presence within the grains may effectively reduce their fracture toughness, via hydrogen enhanced decohesion, allowing cracks to propagate directly through these weakened grains. Processing by LSP has also been shown to increase the grain size uniformity [26]. Since nonuniformity will result in the stress not being evenly distributed across grains, certain grains in non-LSP treated samples may be at increased risk to failure, and thus suffer from transgranular failure.

LSP processing was also found to increase the time to failure of AISI 4140 high strength steel in U-bends exposed to 3% NaCl at 80 °C, simulating conditions found in certain marine environments. Untreated samples experienced failure after  $114 \pm 33$  h, while LSP treated samples lasted  $160 \pm 15$  h. The LSP samples were treated with three passes at 300 mJ pulse energies with a 1 mm spot size and zero overlap of adjacent pulses. As opposed to

Table 1 Summary of U-bend stress corrosion testing. The corrosive environments have been to chosen to provide the most susceptibility to SCC for each material.

Material	Corrosive environment	Time to failure (untreated) hours	Time to failure (with LSP treatment)	Percent increase
Stainless steel 304	155 °C Magnesium chloride	$1.62 \pm 0.37$	$\begin{array}{c} 2.67 \pm 0.12 \\ 160 \pm 15 \\ 20 \end{array}$	65%
High strength steel AISI 4140	80 °C 3% NaCl	$114 \pm 33$		40%
260 Brass	20 °C Mattssons solution	20		0%

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Fig. 7 Untreated (a) and LSP treated (b) images showing the edge of stainless steel U-bend samples, where the bottom part of these images is the outer surface. LSP prevents cracks from propagating onto the outer surface in (b).



Fig. 8 Outer U-bent face for untreated stainless steel samples. Indicated by the arrow, cracking has occurred for the untreated sample, but was been prevented from occurring on the LSP treated sample.



Fig. 9 Optical micrographs of etched stainless steel samples exposed to 1 h of boiling magnesium chloride. (*a*) has not been LSP treated, and shows a combination of transgranular and intergranular fracture. (*b*) has been LSP treated, where the fracture mechanism is now dominated by intergranular fracture. The effects of increased hydrogen penetrating the lattice in (*a*) may cause the transgranular failure.

the stainless steel failing by a single catastrophic crack propagating, many adjacent cracks formed simultaneously in the high strength steel samples, as seen in Fig. 10. The different SCC mechanisms can be attributed with this variation. Passive layer breakdown is often cited as a cause of SCC failure in stainless steel. Once a particular location fails in the stainless steel, it is reasonable that sudden, localized failure will occur in the region, particularly if the underlying lattice has been weakened by hydrogen absorption. Conversely, the high strength steel does not have the protective oxide layer, which is why simultaneous failure may occur across larger regions.

U-bend testing of the brass samples found significantly different results than for stainless and high strength steel samples. Namely, no increase of time to failure was observed on the brass samples that were LSP treated. All of the tested specimens ranging from untreated to four different laser processing

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Fig. 10 Multiple cracks found in an AISI 4140 U-bend sample LSP three times at 300 mJ. Unlike the stainless steel, the high strength steel fails by many parallel cracks rather than one major failure.

parameters—fractured at nearly the same time after approximately 20 h exposure to Mattsson's Solution. Stress corrosion cracking can occur via different mechanisms, and this suggests that the mechanism present in stainless steel differs from that of the brass. Also, material factors may further influence the cracking behavior, as discussed regarding work function changes in the following section, "Kelvin Probe Force Microscopy."

A finite element model was used for estimating the levels of stress in each of the U-bend samples. Even though the bend geometry is the same for the stainless steel and brass (4 mm radius of curvature), their yield strengths and strain hardening result in differences. Figure 11 shows a 3D representation of the final geometry of a bent specimen overlaid with Mises stress, where it can be seen that the highest stress magnitudes occur at the bottom and along the sides. Tensile stress causes SCC, and a plot showing the tension on a path along the center of the outside (bottom) face is shown in Fig. 12. The peak stress experienced by the brass samples is nearly 100 MPa higher than that of the stainless steels, owing to the higher ductility of the stainless steel, and subsequently more plasticity occurring in the brass. Since both of these levels are above the material's yield strengths, dislocation generation from forming the U-bend does occur, potentially interacting with LSP's effects and increasing the total amount of dislocations available for hydrogen trapping. This suggests that U-bend samples with lower induced stress would see even larger relative mitigation improvement from LSP processing.

Kelvin Probe Force Microscopy. For each of the three materials tested, the effect on work function from LSP processing is shown in Fig. 13, where the x-axis plots the radial distance outward from the center of a single incident laser pulse. The incident laser has a radius of about 500  $\mu$ m, where beyond this the material is considered as untreated. Since increases in work function are associated with increases in corrosion rest potentials, ideally there would be increased work functions in the processed areas. But upon initial inspection of the figure, it is clear that each of the materials behave differently. High strength steel does show an increase in work function, suggesting improved corrosion resistance, which corresponds to the improvement found in the U-bend testing. But brass actually decreases in the laser processed area while the stainless steel shows essentially no change in work function. These different responses can be explained by exploring fundamental differences of the three materials.

While dislocations have beneficial effects in terms of hydrogen trapping, they can simultaneously have detrimental effects by

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Fig. 11 Mises stress in Pascals overlaid on the final deformed shape of a U-bend specimen from FEM simulation

reducing the work function, and subsequently the corrosion resistance. By modeling the work function as a summation of individual coulomb forces acting on an electron from each positive atomic nuclei in the lattice, it can be shown that the electrons will reside in potential wells that exist between the lattice sites [23]. Since the work function is the energy required to remove an electron, it is analogous to the depth of these potential wells and can be expressed as

$$\phi \approx \sum_{n} \frac{ze^2}{4\pi\varepsilon_0 |x_i - x_{e_n}|} \tag{8}$$



Fig. 12 Tension on a path along the long direction in the center of the U-bend samples. The peak stress is higher for the brass.



Fig. 13 Work function measurements for brass, stainless steel, and high strength steel. The center of the LSP pulse is at 0  $\mu$ m, and each material changes differently in response to the incident shockwave. Brass experiences work function decreases from LSP, while the high strength steel experiences an increased work function. The scale on the high strength steel figure covers a wider range than the other two, indicating an increased response to the shockwave processing.

where  $\phi$  is the work function, z is the effective nuclear charge of the lattice atoms, e is the elementary charge, and  $|x_i - x_{en}|$  is the distance from the equilibrium position (bottom of the well) to each lattice site. Below an edge dislocation, where the lattice experiences tension, the distance to the lattice atoms increases, and the summation indicates that this causes the work function to decrease. Above the dislocation the lattice experiences compression, and this causes an increase in the potential depth. But this does not have an increase on the work function because the work function simply corresponds to the energy required to remove an electron from the shallowest well. With dislocations having the effect of decreased work function, it must be reconciled as to how LSP processing-which increases the number of dislocationscan increase the work function of some materials. This comes down to a competing effect between the compressive residual stress and the dislocation density of the processed material.

Plotting Eq. (5) for our three materials of interest is shown in Fig. 14. The values on the ordinate axis are proportional to the dislocation density, showing how the two types of steel initially behave similarly and the brass is distinctly different. Upon plastic deformation, the high strength steel develops dislocations at a much faster rate than the brass. But for given deformations, the high strength steel actually will have fewer dislocations because of its much higher yield strength (675 MPa versus 360 MPa). Laser shock peening imparts a compressive residual stress in the materials, and in order for the high strength steel to be capable of having an increased work function, this compressive stress must outweigh the detrimental effects of increased dislocation density. Contrasting this is the brass, where the lower yield stress allows for more plastic deformation, and thus larger increases in



Fig. 14 Rate of change of dislocation density, on the vertical axis for, varying amounts of plastic deformation. The three materials generate dislocations at varying rates. But since the yield strength of high strength steel is the largest, it will have lower dislocation generation for a given amount of deformation.

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dislocation density. Prior heat treatments will also affect the rate at which dislocations are generated in a material. Figure 15 shows the rate of dislocation generation for annealed, normalized, and quenched high strength steel. It can be seen that annealing, resulting in the highest ductility, results in the slowest rate of dislocation generation. For implementing LSP to mitigate SCC, it is thus important to take the thermal history of the target material into account.

The above analysis shows the variation in material parameters and their effect, but does not incorporate strain-rate effects, which can reach very high levels in LSP processing. The plasma formation causes shock waves to propagate through the target material, and the shockwave itself is what can cause dislocation generation. At sufficiently high pressures homogenous generation of perfect dislocations at the wave front can occur if the shear stress reaches sufficient values, as expressed by [27]

$$\tau = 0.054\mu\tag{9}$$

The maximum shear stress at the front of a shockwave of pressure p is

$$\tau_{\max} = \frac{3(1-2\nu)}{2(1+\nu)} * P \tag{10}$$

for Poisson's ratio v, and by substitution, this gives the expression defining the required pressure for dislocation generation

$$P_{\min} = \frac{0.036(1+\nu)}{(1-2\nu)}\mu$$
(11)

For brass 260, this gives a minimum necessary pressure of 6.5 GPa, stainless steel 304 is 10.1 GPa, while the value for AISI 4140 is 8.9 GPa for generation of perfect dislocations. These numbers are higher than the Hugoniot elastic limits (HEL) for each material, where the HEL of brass is 0.217–0.243 GPa [28] and of SS304 is 0.35 [29], but this is a result of Shockley partial dislocations being accounted for in the HEL. Nevertheless, Eq. (11) provides a clear relationship of the increasing pressure requirements



Fig. 15 Rate of change of dislocation density for high strength steel with three different types of heat treatments. As such, the downward slope of the annealed sample above 350 MPa does not indicate decreasing dislocation density but rather that dislocations are being generated at a slower rate.

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as being dependent on the shear modulus. The results from KPFM analysis, of decreasing work function for the brass, may thus be an effect of it experiencing much more plastic deformation than the other materials because of its lower threshold for dislocation generation.

Even though the dislocation generation in stainless steel is expected to be similar to the high strength steel, Fig. 12(b) shows no change in the work function as a result of LSP. As for the brass, the activation of slip systems and dislocation generation that occurs for the stainless also occurs, but the major factor contributing to stainless that is absent from the brass is the presence of a thick surface oxide layer. Stainless's chromium oxide layer greatly impacts the work function, so any of the reduced work function regions in the bulk of the material may be concealed by the oxide layer. Compressive stresses also promote oxide layer growth, another benefit of the LSP process. In this way, LSP processing of the stainless steel may exhibit only the beneficial effects because the oxide layer works to suppress any detrimental material imperfections.

#### Conclusion

Our results have helped to identify the mechanism by which LSP processing of metallic samples is capable of improving their corrosion resistance, and how it varies for different materials. While the compressive residual stress is beneficial, microstructural effects within the crystal lattice also play large roles. It has been highlighted that this process cannot be arbitrarily applied; each situation must be fully understood to ensure that negative effects do not occur. Additional analysis, particularly regarding dislocation generation and the role it plays in hydrogen trapping and diffusion, will help lead to developing the process further.

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