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Laser Shock Peening for Suppression of Hydrogen-Induced Martensitic Transformation in Stress Corrosion Cracking

The combination of a susceptible material, tensile stress, and corrosive environment results in stress corrosion cracking (SCC). Laser shock peening (LSP) has previously been shown to prevent the occurrence of SCC on stainless steel. Compressive residual stresses from LSP are often attributed to the improvement, but this simple explanation does not explain the electrochemical nature of SCC by capturing the effects of microstructural changes from LSP processing and its interaction with the hydrogen atoms on the microscale. As the hydrogen concentration of the material increases, a phase transformation from austenite to martensite occurs. This transformation is a precursor to SCC failure, and its prevention would thus help explain the mitigation capabilities of LSP. In this paper, the role of LSP-induced dislocations counteracting the driving force of the martensitic transformation is explored. Stainless steel samples are LSP processed with a range of incident laser intensities and overlapping. Cathodic charging is then applied to accelerate the rate of hydrogen absorption. Using XRD, martensitic peaks are found after 24 h in samples that have not been LSP treated. But martensite formation does not occur after 24 h in LSP-treated samples. Transmission electron microscopy (TEM) analysis is also used for providing a description of how LSP provides mitigation against hydrogen enhanced localized plasticity (HELP), by causing tangling and prevention of dislocation movement. The formation of dislocation cells is attributed with further mitigation benefits. A finite element model predicting the dislocation density and cell formation is also developed to aid in the description. [DOI: 10.1115/1.4036530]

Keywords: stress corrosion cracking, laser shock peening, corrosion mechanism, martensite, phase transformation

Introduction

Material failure by corrosion can often be prevented because corrosive products, such as rust, indicate that the integrity of the material has been compromised. But a special case of corrosion called SCC behaves quite differently from conventional corrosion. SCC occurs when a susceptible material in a suitable corrosive environment experiences a tensile stress. The required stress can be either externally applied or residual stress from a previous manufacturing process, and levels as low as 20% of the material's yield strength have been shown to cause failure [1]. Of most concern with SCC is that it causes sudden and catastrophic material failure. Additionally, materials generally thought of as being resistant to corrosion are susceptible to SCC failure in certain environments, and furthermore, it is quite difficult to predict when the onset of SCC is going to occur.

Many different industrial applications are prone to experiencing SCC. Considerable attention has been paid to the occurrence of SCC in the boiling water reactors found in nuclear power plants [2], where any failures could result in extremely dangerous situations. Pressure vessels and gas pipelines have been found to be at risk [3,4], as are various types of implantable medical devices [5].

Several physical descriptions exist for explaining the mechanisms of SCC, but they often are related to deleterious effects of hydrogen atoms absorbed from the corrosive environment. In this case, the term hydrogen embrittlement is used. Hydrogen has a high diffusivity in metals, and it is highly reactive with the material's lattice. Processes such as electroplating, pickling, or various types of surface cleaning can further increase the levels of absorbed hydrogen within the lattice. Details on the physical changes to the material's lattice and structure will be provided in Background section.

To prevent material failure by SCC, several different mitigation techniques exist. Coating and plasma nitriding of the material can prevent surface reactions and limit the amount of hydrogen that penetrates into the lattice [6,7], but in harsh environments coatings will eventually degrade, crack, or delaminate, since they are not as tough as the metal, leaving the material vulnerable to SCC. A different approach to mitigation is to actually modify the material itself, by imparting a compressive residual stress on the material's surface. One such technique is laser shock peening (LSP), which uses incident laser pulses to generate shockwaves on a material's surface. While originally developed for increasing the fatigue life of metallic components [8], recent studies have shown that LSP processing helps to prevent the onset of SCC [9,10]. The improvement has mostly been attributed to the compressive stress counteracting the necessary tensile stress for SCC initiation, but this cannot be solely attributable, as evidenced by the fact that LSP processing can decrease the corrosion current of 4140 steel [11], an electrochemical effect. LSP causes many forms of microstructural changes to the material, including the generation of lattice dislocations and subgrain dislocation cell formation [12]. Lattice dislocations act as hydrogen trapping sites and will influence the absorption and diffusion of hydrogen [13], and

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structural changes to the lattice symmetry will further influence SCC occurrence. In this paper, we identify the underlying microstructural changes to stainless steel 304 induced by LSP that allow for it to be a beneficial mitigation process against SCC, particularly regarding two main failure mechanisms: martensitic phase change and hydrogen enhanced localized plasticity.

Background

Hydrogen-Induced Martensitic Transformation. Of particular concern for SCC in stainless steels is the formation of martensite, a phase that is brittle and susceptible to fracture and corrosion [14]. The fracture surfaces of initially austenitic stainless steel that has failed by SCC show that brittle failure has occurred, which is most often accompanied by the presence of martensite on the fracture surface [15,16]. Even materials that initially are fully austenitic can form martensite through various environmental processes, thereby embrittling the material [17]. Martensite is characterized as a phase that forms via a diffusionless transformation, in that long-range movement of atoms does not occur, and the materials composition remains constant. In the case of stainless steel, the initially FCC austenite transforms into martensite which can be of either BCC or HCP crystal systems. Fewer slip systems and a more complex crystal structure result in the martensite being a quite brittle phase. In carbon steel systems, this transformation occurs upon rapid cooling from elevated temperatures. This does not allow time for carbon to diffuse, and the remaining carbon atoms sit in interstitial lattice sites, causing distortions and subsequently the phase change. In corrosive environments, the same type of lattice transformation from austenite to martensite occurs, except that it is now hydrogen atoms causing the lattice distortions and internal stress. During exposure to the corrosive environment, once this transformation has occurred, even locally, the likelihood of brittle failure is greatly enhanced. Therefore, prevention of the martensitic transformation would be a powerful method for mitigation of SCC failure in austenitic stainless steels.

Olson and Cohen described the initiation sites for martensite as the intersection of shear bands and identified which lattice planes the transformation will occur on Ref. [18]. As hydrogen from the corrosive environment diffuses into austenite, it causes expansion and an internal stress that acts as a driving force for the formation of martensite. This strain energy increases the free energy of the austenite, subsequently making the martensite phase more stable. Plots of the free energy of the respective phases are shown versus temperature in Fig. 1, where ΔG_{ch} is the difference in chemical free energy of the two phases.

In stainless steels, the addition of alloying elements promotes the formation of austenite, so that in Fig. 1 T_0 can be below room temperature. For the stress-induced martensitic transformation to occur, the internal strain energy must be equal to $\Delta G_{\rm crit} - \Delta G_{\rm ch}$.



Fig. 1 Free energy diagram showing the suitable conditions for the formation of deformation-induced martensite [19]

081015-2 / Vol. 139, AUGUST 2017

Martensite becomes the lower energy phase with increasing amounts of absorbed hydrogen because the BCC and HCP lattices provide more interstitial spaces for the hydrogen to reside [20], but this is also accompanied by a volumetric expansion of nearly 4% when the hydrogen to metal atomic ratio approaches 20% [21].

Since the martensitic transformation requires significant levels of hydrogen to reach the required strain energy, accelerated testing by cathodically charging the workpiece is often performed. X-ray diffraction, which measures lattice spacing, is a preferred method for detecting phases present in a metallic sample. Narita et al. have used this method to identify the formation of martensite, as well as relating lattice shifts of the austenite peaks to expansion caused by absorbed hydrogen [22]. Prevention of this phase transformation is therefore crucial to SCC mitigation, and this can be accomplished by generating lattice dislocations, as described in the "Results and Discussion" section.

Hydrogen Enhanced Localized Plasticity. While various explanations have been proposed which describe the process of stress corrosion cracking, one of the leading theories involves hydrogen influencing the behavior of lattice dislocations, and is called HELP. In this, hydrogen can shield the interactions between dislocations, reducing repulsive forces and thereby allowing for increased dislocation motion [23]. In regions of a crack tip, the localized flow stress thus decreases significantly, allowing for small-scale ductile fracture to occur at the propagating crack tip and low stresses, while macroscopically the part retains the appearance of brittle failure. Analyses of fracture surfaces have shown that microscopic ductile failure can occur in SCC, providing evidence of the existence of HELP. Additionally, TEM imaging in hydrogen environments has shown an increase to dislocation mobility, albeit the samples have been restricted to low densities of dislocations [24].

Numerical analyses have also been developed to describe the process of hydrogen influencing dislocation mobility, based on elasticity [25], finite element crack propagation [26], and atomistic approaches [27]. While the previous approaches found increases to hydrogen's mobility in the lattice in the presence of hydrogen, other researchers have concluded that hydrogen does not have an influence on dislocation mobility [28]. But in order for HELP to occur, ease of dislocation interactions must be provided. As such, prohibiting the mobility of dislocations will result in mitigation against HELP and SCC material failure, and the Laser Shock Peening and Lattice Changes section will describe how lattice changes resulting from shockwave processing can provide this beneficial effect. Dislocations can be of different form, and the discrepancy of whether hydrogen increases mobility may be dependent on the type of dislocation [29]. Additionally, the shielding effects have been described for dislocations with similar orientations, so that when large dislocation densities occur, as is the case for laser shock peening, the shielding effects may disappear.

Laser Shock Peening and Lattice Changes. Generating shockwaves on the surface of a metallic sample causes plastic deformation and a residual compressive stress. While this can be performed with processes such as mechanical shot peening, a more effective method which provides effects deeper into the surface is LSP. In LSP, the workpiece is coated with an ablative layer and then a confining medium transparent to the laser is placed on top. Upon laser irradiation, the ablative layer is ionized and a plasma cloud forms. This tries to expand, but the confining medium restricts the expansion and thus a shockwave is generated that propagates down into the material, resulting in a residual compressive stress within the material. Since the laser is completely absorbed in the ablative layer, no thermal effects are caused in the workpiece, which is especially important for SCC considerations because any heat-affected zone (HAZ) in the material could negatively affect its corrosion resistance. Rastering

the laser beam across the workpiece allows large areas to be processed.

Upon LSP processing, many lattice changes are induced within the workpiece, altering the behavior and effect of absorbed hydrogen within the lattice, and can be responsible for the SCC mitigation performance of LSP. Plastic deformation is accompanied with the generation of lattice dislocations, where LSP has been shown to cause large increases in dislocation density. Hydrogen diffusing through a crystal lattice gets stuck in the dislocations, known as hydrogen trapping. This effectively reduces the diffusivity of hydrogen within the material while also increasing its solubility by providing low energy places for the hydrogen to reside.

A unique feature of dislocations is the way that they will interact and tangle with each other. With increasing amounts of deformation, this tangling will result in the formation of dislocation cells [30]. Elastic energy is minimized via the cell configuration, and as such acts as the driving force of formation. The periodic dislocation cell structure has walls of high dislocation density and interiors of lower densities, and these cells are present within individual grains of the polycrystals. The nonhomogeneous dislocation density results in cell walls that have larger flow stresses than the cell interiors, resulting in alternating strain states. Dislocation cell formation has been experimentally detected using micro-XRD measurements that provide micron-level spatial resolution [12], as well as TEM imaging showing the cellular structure [31].

LSP processing introduces additional considerations for the theory of dislocation generation, because it causes incredibly high strain rates. Since dislocation multiplication is often considered as the result of tangling dislocations (such as Frank–Read sources), it cannot account for the whole phenomenon of LSP dislocation generation because it would require dislocations within the lattice to be traveling at speeds higher than physically possible in order to keep up with the wave front. To rectify this, Meyers and Murr proposed [32] a mechanism of homogenous dislocation generation which does not require dislocation motion to keep up with the wave front for generation. When the shear stress from the shock wave reaches sufficient value in a cubic lattice, dislocations are homogenously generated, as expressed in the empirical relationship of the below equation

$$\tau_h = 0.054G \tag{1}$$

where τ_h is the shear stress required for homogeneous generation, and *G* is the material's shear modulus. At the wave front, high shear stresses do form, and by this equation it is indicated that this additional mechanism for dislocation generation will result in high dislocation densities from LSP, restricting hydrogen-induced martensite formation as well as causing dislocation tangling to restrict their mobility.

Numerical Modeling. Using finite element methods (FEM), a numerical model was implemented for obtaining the dislocation density, homogenous generation, and cell size induced by various levels of LSP processing. The high strain rates in LSP require that the material be analyzed with hydrodynamic considerations [33]. Rather than the usual Hooke's law governing deformation, the Mie–Gruneisen equation of state has been implemented, relating energy to internal pressure as

$$p - p_H = \Gamma_o \rho_o (E_m - E_H) \tag{2}$$

where p is pressure, p_H is the Hugoniot pressure, E_H is the Hugoniot energy, ρ_o is the reference density, and Γ_o is a material constant. Combining this with the Hugoniot jump conditions results in [34]

$$p = \frac{\rho_o c_o^2 \eta}{\left(1 - s\eta\right)^2} \left(1 - \frac{\Gamma_o \eta}{2}\right) + \Gamma_o \rho_o E_m \tag{3}$$

Journal of Manufacturing Science and Engineering

for c_o and s the Hugoniot parameters and $\eta = 1 - \rho_o/\rho$. The incident laser pulse was simulated as a spatio-temporal pressure on the top surface, with the value calculated by [8]

$$P = A \left(\frac{\alpha}{2\alpha + 3}\right)^{1/2} \sqrt{Z * I}$$
(4)

where *P* is the exerted pressure from the shock wave, *A* is a constant, $\alpha \approx 0.1$, *Z* is the shock impedance, and *I* is the laser intensity. As discussed in Laser Shock Peening and Lattice Changes section, during deformation the generation of dislocations and their subsequent arrangement into cellular structures will influence the behavior of hydrogen within the lattice. Tofh et al. derived equations for the rate of dislocation generation with deformation as [35]

$$\frac{d\rho_w}{dt} = \frac{6\beta^* \dot{\gamma}_c (1-f)^{2/3}}{bdf} + \frac{\sqrt{3}\beta^* \dot{\gamma}_c (1-f)\sqrt{\rho_w}}{fb}$$
$$- k_o \dot{\gamma}_w \rho_w \left(\frac{\dot{\gamma}_w}{\dot{\gamma}_o}\right)^{-1/n} \tag{5}$$

$$\frac{d\rho_c}{dt} = \alpha^* \frac{\dot{\gamma}_w \sqrt{\rho_w}}{b\sqrt{3}} - \beta^* \frac{6\dot{\gamma}_c}{bd(1-f)^{1/3}} - k_o \dot{\gamma}_c \rho_c \left(\frac{\dot{\gamma}_c}{\dot{\gamma}_o}\right)^{-1/n}$$
(6)

where ρ is the dislocation density with subscript *w* for cell walls and *c* for cell interior, α^* and β^* are constants, *f* is the volume fraction of the cell walls versus cell interior, *b* is the magnitude of the Burgers vector, *d* is the lattice spacing, and $\dot{\gamma}$ is the shear strain rate. These equations are incrementally solved using the Euler method during shock wave propagation and relaxation to determine the distribution and density of dislocations and cells, and the relationship $\rho = f \rho_w + (1 - f) \rho_c$ is used to determine the total dislocation density.

Experimental Setup

AISI 304 stainless steel samples were used as the workpieces. A Continuum NY61 pulsed Nd:YAG laser with a wavelength of 1064 nm, pulse energies ranging from 125 to $300 \,\mu$ J, spot size of 1 mm, and pulse lengths of 17 ns was used for the LSP processing. In the experimental configuration, the ablative layer was black electrical tape and the confining medium of clear acrylic was clamped on top. For the TEM imaging, a FEI Talos F200X S/TEM was used. Specimen preparation for the TEM was performed on a FEI Helios NanoLab 660 scanning electron microscopy (SEM)/FIB using the lift-out technique. Cathodic charging of the samples in 1 M sulfuric acid at a current density of 50 mA/cm² for up to 48 h was also performed, and lattice spacing and phase detection were carried out in a PANAlytical XPert3 Powder XRD. The finite element analysis was implemented in ABAQUS.

Results and Discussion

Detection of Martensite Formation. Characterization of the microstructural changes induced by absorbed hydrogen within the lattice has been performed by making XRD measurements on stainless steel samples that underwent cathodic charging. The bottom line of Fig. 2 shows a selected portion of the XRD spectrum of the AISI 304 prior to any cathodic charging and is thus our reference state. The two peaks present at 43.45 deg and 50.68 deg are both austenitic and correspond to the (111) and (200) orientations, respectively [36]. Full spectrum scans for 2θ values up to 110 deg were performed to ensure that the material is fully austenitic, but only the selected spectrum of 42-53 deg is presented in the figures because this is the region where most of the induced changes are found to occur. After 24 h of cathodic charging, distinct microstructural changes occurred in the sample, as seen in Fig. 2. A

AUGUST 2017, Vol. 139 / 081015-3



Fig. 2 XRD measurements of lattice changes from cathodic charging a specimen without LSP treatment. Prior to cathodic charging, the material is fully austenitic (a). After 24 h (b), the absorbed hydrogen has caused the formation of a martensite peak, (c) with further increases after 48 h.

new peak at 45.98 deg is present, which corresponds to (110) α '-martensite. As no thermal or mechanical processes have been used, this phase transformation is strictly a result of the cathodic charging and subsequent hydrogen absorption. Once this transformation has occurred, the stainless steel's susceptibility to premature failure by SCC is greatly increased. Hydrogen diffusion is also higher in martensite than it is in austenite, so the SCC mechanisms that are dependent on hydrogen will be exaggerated upon martensitic formation as well. The top line of Fig. 2 shows the same sample after 48 h of total cathodic charging time, and the martensite peak has become even more prominent. This increasing amount of martensite within the lattice simply further increases the material's SCC susceptibility.

As the austenite phases absorb hydrogen, they undergo volume expansion, and this expansion is detected as peak shifts in the XRD spectrum, as seen in Fig. 3. The change in lattice parameter can be expressed as [37]

$$a_H = a_o + K \cdot C(x, t) \tag{7}$$

where a_H is the lattice parameter after hydrogen absorption, a_o is the initial lattice parameter, K is a constant, and C(x,t) is the



Fig. 3 Hydrogen-induced lattice expansion for 24 and 48 h of cathodic charging

081015-4 / Vol. 139, AUGUST 2017



Fig. 4 XRD measurements of a selected region of the spectrum for samples after LSP processing (a) and then subjected to 24 h (b) and 48 h (c) of cathodic charging. The initially austenitic peaks experience broadening after 24 h, but no martensite formation occurs, illustrating the effectiveness of LSP processing as a mitigation tool. Some martensite does eventually form after 48 h.

concentration of hydrogen. With consideration of Bragg's Law, increases in lattice parameters correspond to decreases in 2θ values. After 24 h of cathodic charging, the (111) peak has shifted to 43.41 deg, and it has shifted to 43.28 deg after 48 h. The steady expansion for the untreated sample in Fig. 3 indicates the continued absorption of hydrogen.

For analysis of the mechanism whereby SCC and hydrogen embrittlement can be mitigated, LSP-treated samples were exposed to the same amount of cathodic charging, as presented in Fig. 4. While it is possible for plastic deformation from the LSP processing to induce martensite, Fig. 4 confirms that this transformation has not occurred during our processing. In order to generate deformation-induced martensite in LSP, a threshold of induced pressure from the plasma must be reached, which for stainless steel has been reported to be around 5 GPa [38]. Using Eq. (4), the induced pressure in our configuration is 2.25 GPa. Although the samples were processed three times, keeping the induced pressure below the martensite formation threshold has prevented its formation. After 24 h of cathodic charging, shown in the middle line of Fig. 4, the austenite peaks have slightly broadened (a result of distortions to the lattice), but no martensite peak has formed. This is in direct contrast to Fig. 2 and demonstrates that LSP processing suppresses martensite formation and thereby limits the stainless steel from SCC susceptibility. But, from Fig. 3, the (111) peak has undergone greater expansion compared to the untreated sample after 24 h. This is because no martensite is available in the LSP-treated sample to accommodate hydrogen. The microstructural changes from LSP that provide this mitigation will be discussed in Mechanism of SCC Mitigation section. After continued cathodic charging for 48 h of the LSP-treated sample, martensite eventually does begin to form, as shown in the top line of Fig. 4. But this figure is similar to the shape of the untreated sample charged for 24 h in Fig. 2. So even once martensite does begin to form in the LSP-treated sample, the amount is still less than that of an untreated sample and therefore also less likely to suffer premature failure. In Fig. 3 the lattice expansion of (111) has now significantly decreased from the value at 24 h, indicative of how the deformed austenite no longer needs to retain as large of amounts of hydrogen and can thus relax.

The rearrangement of the lattice during martensite formation enables the visual detection of its presence. Polished samples after cathodic charging are imaged using differential interface contrast (DIC) optical microscopy and presented in Fig. 5, with the sample of (a) being untreated and (b) being LSP treated prior to the hydrogen exposure.







(b)

Fig. 5 (a) Untreated stainless steel sample after cathodic charging 24 h showing large amounts of martensite formation, seen as the grains with platelet like structure and (b) samples which were subject to LSP prior to cathodic charging have considerably fewer martensitic grains

The large majority of Fig. 5(a) is indicative of martensite, while only a few martensitic grains are found in Fig. 5(b). Since no etchant was used to obtain these images, and the samples were initially polished to a mirror like finish, the surface deformation is the sole result of hydrogen effects. But to detect the structure of the grain interiors, SEM imaging was also performed on the same samples after etching, and is shown in Fig. 6. Martensite structure is clearly seen throughout the entirety of the grain from the untreated sample in Fig. 6(a). In contrast, the grain of the LSPtreated sample in Fig. 6(b) has a small region of martensite formation, indicated by the arrow, but the phase transformation has been prevented from propagating throughout the entirety of the grain. This is the result of the increased dislocation density from the LSP processing resisting the transformation, confirming the results of the numerical model and Eq. (8) below.

Mechanism of SCC Mitigation. LSP processing causes numerous changes to the microstructure of the material, but perhaps most importantly to the mitigation of SCC is increases of dislocation density. Figure 7 shows the dislocation density as a function of depth below the surface after one, two, and three LSP impacts as determined by the finite element model. Increases of nearly four times are induced by the first pulse, with decreasing







Fig. 6 Magnified images after etching the samples of Fig. 5, for an untreated sample (*a*) and LSP treated (*b*) both after cathodic charging



Fig. 7 Increases to the dislocation density after LSP processing at 1.6 GPa, which act as an impediment to hydrogeninduced martensite formation. The largest increase is seen upon the initial incident pulse.

Journal of Manufacturing Science and Engineering

amounts of gains for the following pulses. The increase decays with depth into the sample, with the extent of the effects reaching nearly 1 mm, for which the scale is similar to the other reports of the depths of plastic zones in LSP. Mitigation benefits are provided by dislocations because when they tangle they will restrict motion within the lattice, particularly the coordinated lattice movement required for the martensitic transformation to occur. Interruptions to the lattice therefore prevent propagation of the martensite transformation, as was seen in Fig. 6(b). When martensite begins to form in a region within a grain, the lattice dislocations prevent further propagation, resulting in the rest of the grain remaining in the austenite phase. Chatterjee et al. developed a theory describing this stabilization of the austenite phase, expressed as [39]

$$\Delta G = \frac{1}{8\pi(1-\nu)} \mu b \sqrt{\rho} \sqrt{\frac{\varepsilon}{L}} + \tau_s \tag{8}$$

where ΔG is the magnitude of the driving force required for transformation, ρ is the dislocation density, μ is the shear modulus, *b* is Burgers vector, ε is strain, *L* is the mean distance moved by the dislocations, and τ_s is shear stress from solution hardening. By increasing the density of dislocations, a larger driving force is required, which in the case of SCC means that larger amounts of hydrogen within the lattice are required for the detrimental phase transformation to occur.

A second effect caused by the increase of dislocation density is a result of dislocations behaving as hydrogen trapping sites, altering both the diffusivity and solubility of hydrogen within the material's lattice. Decreasing the diffusivity will result in the hydrogen not being able to penetrate deep into the material and restrict any hydrogen-induced changes to the near surface level. Additionally, hydrogen residing in trapping sites will cause less internal stress within the lattice and therefore be less likely to cause brittle failure. The influence of dislocation density on the hydrogen diffusion coefficient is expressed as

$$\frac{D}{D_o} = \left[1 + \frac{N_x N_L K}{\left(N_L + K c_L\right)^2}\right]^{-1} \tag{9}$$

where *D* is the material's hydrogen diffusion coefficient after LSP, D_L is the initial hydrogen diffusion coefficient, N_x is the number of trapping sites (determined by dislocation density), N_L is the number of interstitial lattice sites, *K* the equilibrium constant of the reaction defined as $K = \exp(-\Delta E_x/RT)$, ΔE_x is the





Fig. 8 Decrease in the diffusion coefficient after various levels of incident pressure from LSP processing. The dotted line of dislocation density shows its inverse relationship to the diffusion coefficient.

081015-6 / Vol. 139, AUGUST 2017



Fig. 9 Distribution of dislocation cell size after three LSP impacts. Symmetry is used along the boundary at the left side.

energy difference between the lattice site and trapping site, and C_L is the hydrogen concentration. Implementation of Eq. (9) into the dislocation density results of the FEM model provide the percentage decrease in hydrogen diffusion coefficient, as shown in Fig. 8. Different types of trapping sites can form, with varying strengths of trapping, and this is represented by larger values of ΔE_x and subsequently larger K values. The decrease of diffusivity is much more dramatic for stronger trapping sites.

The formation of dislocation cells by LSP processing can provide further restrictions to martensitic formation. Figure 9 shows a 2D cross section of the dislocation cell size after three incident LSP pulses, with symmetry being used along the left hand boundary. An initial distribution of a cellular arrangement is required for the model, but this is set to 1.8 μ m, which is large enough that it can nearly be considered to be the grain size. Again since the hydrogen-induced martensitic transformation requires coordinated lattice movement, microstructural disruptions can prevent the transformation. The martensitic transformation will not propagate across grain boundaries, and in the same way dislocation cells may prevent propagation as well. Along grain boundaries, misorientation creates high diffusivity paths for hydrogen to penetrate, but dislocation cells are not associated with misorientation, and therefore dislocation cells may be further advantageous over grain boundaries.

Figure 10 presents the dislocation cell size at various depths below the surface for increasing numbers of LSP impacts. Shock pressure governs the size of the dislocation cells formed, while



Fig. 10 Dislocation cell size for increasing number of incident LSP pulses at four depths



Fig. 11 Asymptotic increase of the ratio of dislocation density in cell walls to cell interior

the pulse duration determines the definition between walls and cell interiors [32]. Similar to the dislocation density, the greatest change in cell size is caused by the first laser pulse, especially near the surface. But at $450 \,\mu\text{m}$ deep, the cell size continues to decrease after the second and third pulses. This suggests that further increases to the number of incident pulses will help to cause deeper effects of cell formation, but a minimum cell size will be eventually attained.

The induced pressure from the LSP impact will significantly influence the formation and structure of the dislocation cells. In Fig. 11, the ratio of the dislocation densities of cell walls to the cell interiors are plotted as a function of increasing incident pressure for a single impact. Below 1 GPa insufficient deformation occurred to plastically deform the material. But as the pressure increased, the ratio asymptotically increases as well, approaching a ratio of 8 as the pressure nears 5 GPa. As previously mentioned, stainless steel will experience deformation-induced martensite from the shockwave at pressures above 5 GPa. Therefore, significant microstructural changes are occurring, which were not captured on the basis for this numerical model and therefore place an upper limit on our modeled pressure range. But since martensite is to be avoided for providing SCC mitigation, the higher incident pulse pressures should be avoided regardless.

Imaging Analysis. TEM imaging of the stainless steel samples at various magnifications in order to analyze and interpret microstructural changes induced by LSP, and also to relate these microstructures to SCC mitigation, was performed. Figure 12(a) shows the structure of an untreated sample, in the as-received condition. Even before LSP treating, low concentrations of dislocations are present in the samples with a loosely aligned structure corresponding to the assumption of an initial concentration that was used for defining the FEM model. Annealing of the samples would provide further reductions in the initial dislocation density if desired. Little restriction to the motion of hydrogen and dislocations is provided, since long free paths are present without the effects of tangling. Hydrogen can freely diffuse through this structure, and upon the initiation of a hydrogen-induced martensitic transformation, large regions of coordinated lattice shifting will occur without obstruction, spreading the amount of martensite and increasing the material's SCC susceptibility.

After LSP processing, a significant increase in the dislocation concentration is detected as shown in Fig. 12(b) at the same magnification as was presented in Fig. 12(a). This sample has been processed with three LSP pulses, where the dark line running through the center of the image is a grain boundary. The darker



(a)



Fig. 12 (a) Untreated sample showing lower densities of dislocations and (b) increase of dislocation density after three LSP impacts at $2.5 \,\text{GW} \,\text{cm}^{-2}$

regions of the image correspond to dense dislocation tangling, and some regions with low dislocation densities are found on the right hand side. Tangling of dislocations is much more apparent than in the untreated sample, which will prevent long-range dislocation diffusion from occurring. Stainless steel has a low stacking fault energy (SFE), resulting in screw dislocations often decomposing into partial dislocations, as well as the formation of twinning.

Dislocation behavior between neighboring grains may be significantly different because the dislocations will not diffuse across the grain boundary and since the grains have different rotational orientation to the direction of loading, the slip systems that have become activated will not be the same. Dislocations in Fig. 13 can clearly be seen accumulating near the grain boundary, with discontinuities in density across the boundary. Behavior at the grain boundary is important to SCC, since the misorientation along grain boundaries can act as high diffusivity regions for the hydrogen. Regions with twinning formation are also found along the top portion of the image, indicated with the arrow, where the mirror-like appearance of adjacent diffraction spots in the TEM image indicates this as well. Twinning can be an intermediate step in the formation of deformation-induced martensite, but the low

Journal of Manufacturing Science and Engineering



Fig. 13 Pile ups of dislocations at the grain boundary. Regions of twinning, indicated by the arrow and letter "T" are also found, with the inset a diffraction image indicative of lattice twinning.

amounts formed from this LSP processing appear to not have detrimental effects.

In other regions of the sample, periodic structure formation can be found, as presented in Fig. 14(a). These dislocation cells effectively partition the inner regions of the grain, helping to prevent the propagation of any martensitic transformation. Once martensite formation has begun to occur in a region, in order for it to propagate coordinated lattice motion is required. But the cell walls disrupt this transformation, limiting the amount of hydrogeninduced martensite, which in turn results in less susceptibility to material failure by SCC. Dislocation cells can also provide for effective mitigation against the HELP mechanism. Mobile dislocations will become tangled at the walls [40,41], and by preventing their motion localized decreases to flow stress will be avoided. Figure 14(b) also shows the formation of dislocation cells, where it is clear that they are subgrain structures. Although grain boundaries would also provide barriers to dislocation movement, it is important to note that dislocation cells occur within individual grains, because the high levels of misorientation occurring at the grain boundaries actually can allow for increased amounts of hydrogen diffusion. At high levels of deformation, it is possible for LSP to induce grain refinement, where the increased grain boundaries with high amounts of misorientation will provide high diffusivity paths for the hydrogen to deeply penetrate the lattice. The inset of Fig. 14(a) shows a TEM diffraction pattern obtained in the region of apparent cell formation. For polycrystalline regions, the diffraction pattern would show concentric rings indicative of the various orientations of each lattice structure [31]. But the singular alignment of the diffraction pattern indicates that there is not any misalignment across the boundaries, thereby ensuring that high hydrogen diffusivity paths are not formed.

Performing high-resolution TEM enables the direct observation of the material's lattice, albeit sacrificing the size of area covered. In Fig. 15, obtained at $1 \text{ M} \times$, lattice orientations at various angles are seen. Stainless steel has low SFE. A region containing a stacking fault has been identified in the figure. Stacking fault energy is an important parameter that determines the behavior of the material on a microstructural level during deformation. Cell formation occurs more readily in high SFE materials, but cell formation still occurs in low SFE materials. When SFE is low, rather than cross-



(a)



(b)

Fig. 14 (a) Dislocation cell formation, with the inset diffraction image indicating no grain misorientation and (b) dislocation subgrain structure, where the formation of within individual grains ends at the grain boundaries

slipping, screw dislocations dissociate into partial dislocations. Point defects from shock processing promote cross-slip [31] and thus enhance the occurrence of dislocation cells.

The results from these TEM images are consistent with the previous analysis from both the phase detection and finite element analyses. Significant increases in dislocation density, as determined in Fig. 7, are found and this increase helps to restrict the driving force for the martensitic transformation. But since dislocation generation will occur during conventional types of plastic deformation, distinctions with the shockwave deformation of LSP must be highlighted. The high strain rates and pressures encountered during LSP processing result in the homogeneous generation

081015-8 / Vol. 139, AUGUST 2017



Fig. 15 High-magnification TEM showing resolved lattice structure

of dislocations, so that the overall dislocation density is significantly increased. This allows for more dislocation tangling and pinning to occur at lower amounts of macroscopic deformation than would be required in a conventional cold working process of the material. Furthermore, by performing LSP at conditions below the threshold for deformation-induced martensite and grain refinement, as done in our experiments, increased amounts of beneficial effects toward mitigation of SCC can be provided.

Conclusion

The microstructural effects of how LSP provides mitigation for stainless steel against stress corrosion cracking has been explored with regard to two of the SCC failure mechanisms: hydrogeninduced phase changes and hydrogen enhanced localized plasticity. As hydrogen from a corrosive environment penetrates into the lattice of stainless steel, it can induce a phase change of the material from austenite to martensite, resulting in increases to the material's susceptibility to failure by SCC. We have shown that laser shock peening is an effective process for preventing this transformation and thus improving stainless steel's resistance to SCC. Cathodic charging induced martensite in untreated samples within 24 h, while 48 h were required to detect martensite in samples that had undergone LSP. The increases to dislocation density and cell formation induced by LSP processing restrict the driving force of the transformation, so that larger amounts of hydrogen are required to cause the detrimental phase change. TEM imaging confirmed the dislocation increase and arrangement. Likewise, these microstructural changes also promote tangling of mobile dislocations, which in turn helps prevent premature failure from HELP. As HELP is prevalent in regions of low dislocation density, increasing the density reduces the ability of hydrogen to shield the elastic interactions between dislocations. SCC mitigation by delaying the onset of material failure can thus be achieved, but complete resistance to SCC cannot, since even after LSP treating martensite does eventually form.

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Journal of Manufacturing Science and Engineering

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