Effects of Laser Shock Peening on SCC Behavior of Alloy 600 in Tetrathionate Solution

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ABSTRACT

In this study, the effects of laser shock peening (LSP) on stress corrosion cracking (SCC) behavior of nickel based Alloy 600 in tetrathionate solution were investigated. The LSP induced compressive residual stresses and changes in the near surface microstructure, hardness were characterized. The effects of LSP on SCC susceptibility of Alloy 600 in tetrathionate solution were evaluated by slow strain rate tests and constant load tests. The results indicate a significantly longer time to failure and decreased susceptibility to SCC. These improvements were attributed to LSP induced compressive residual stresses, increased yield strength and hardening caused by near-surface microstructural changes.

Keywords: *A. nickel; B. X-ray diffraction; B. TEM; C. intergranular corrosion; C. stress corrosion*

1. INTRODUCTION

Alloy 600 has been known to be susceptible to stress corrosion cracking (SCC) at room temperature in polythionic acid environments [1,2] which can be attributed to a combination of susceptible microstructure (sensitization), aggressive species (thiosulfate and tetrathionate) and tensile stresses (applied or residual stresses). Detailed studies on the effect of sensitization treatment, pH, solution concentration, temperature have been used to elucidate the mechanism of intergranular stress corrosion cracking (IGSCC) in polythionic acid environments[3–6]. In general, IGSCC can be mitigated by stabilization heat treatment to modify the microstructure, by changing the environment (pH, reducing the concentration of aggressive species) and by modifying the nature of stresses.

Laser Shock Peening (LSP) is an advanced mechanical surface treatment technique that has been widely used in the aerospace industry to improve component fatigue performance. LSP typically uses a Q-switched Nd:Glass or Nd:YAG ($\lambda = 1064\text{nm}$) laser of high energy (1-8 J) and short pulse duration (6-20 ns) that passes through a transparent confining medium (water or glass) to ablate a sacrificial thin coating (tape or opaque medium) on the material surface (Figure 1). As the laser beam passes through the water or glass, it is absorbed by the opaque overlay and only a thin layer (few μm) of this sacrificial layer is ablated creating plasma. Thermal effects on the material surface are suppressed [7]. As the generated plasma continues to absorb the rest of the laser energy, it is readily heated and expands between the material and the confining medium, thus generating a shock wave that propagates through the material. The volume affected by the shock wave is plastically deformed during its propagation to a depth beyond which the peak pressure does not exceed the Hugoniot Elastic limit of the material. The surrounding material in the sub-surface region

is opposed to the lateral straining resulting in biaxial compressive stresses near and under the surface of the material. Physics of LSP technique have been reported elsewhere [7,8].

Recent interest in life extension of nuclear power plants has contributed to a drive towards mitigation strategies that counter materials degradation challenges in these harsh environments. Fatigue damage from mechanical and/or environmental factors, environmentally assisted cracking (including primary water stress corrosion cracking, intergranular stress corrosion cracking and low temperature crack propagation), and weld residual stresses leading to SCC have been cited as causes of failure in metallic components in service [9]. Surface treatments including laser shock peening, shot peening, water jet peening, low plasticity burnishing have proven to significantly increasing the fatigue resistance of aero alloys, SCC resistance [10] introducing deep compressive residual stresses in the material [11–13]. In theory, the presence of compressive residual stresses should mitigate or perhaps prevent stress corrosion cracking. Shot peening has been generally used to introduce compressive residual stresses to improve fatigue performance and also mitigate stress corrosion cracking [14,15].

In this paper, we present the effects of LSP on the SCC behavior of Alloy 600 in polythionic acids. We first quantified the degree of sensitization using double loop EPR tests and performed detailed characterization of residual stresses, hardness and microstructure after LSP on Alloy 600. Furthermore, slow strain rate tests and constant load tests were used to evaluate the effects of LSP on the IGSCC resistance. The results obtained are described and discussed in detail.

2. EXPERIMENTAL

2.1 Material and Laser Shock Peening

Alloy 600 plate with 2 mm thickness (Goodfellow Corporation, USA) with chemical composition as listed in Table 1 was used in this study. Heat treatments, LSP parameters and their respective designations are as listed in Table 2.

To characterize the cross section microstructure, mounted samples were ground progressively to 1200 grit, followed by fine polishing with 0.05 μm colloidal silica suspension to achieve a mirror finish and etched with 10% oxalic acid solution (3V, 15s). Microstructure after sensitization and LSP treatments were characterized using a Keyence VH 600 digital optical microscope.

A schematic of the LSP process is shown in Figure 1. LSP was performed using a Q-switched Nd:YAG laser (Continuum Powerlite Plus) with infrared wavelength (1064 nm) and a frequency of 1 Hz. The target (Alloy 600 sample) was moved using a XY table to create a pattern with 50% overlay. Flowing water was used as confining medium and vinyl tape was used as the sacrificial ablative coating. Based on a series of experiments involving variations in the LSP parameters and counterpart measurements of the surface residual stress, the conditions of pulse energy of 3J, spot size of 2 mm diameter and pulse width of 20 ns was used for treatment of all the coupons prior to SCC testing and other characterization. The laser power density for each pulse based on these parameters was $\sim 5.6 \text{ GW/cm}^2$.

2.2 Transmission Electron Microscopy

Characterization of the near-surface regions of the LSP-treated samples is important for understanding the fundamental microstructural changes introduced by these types of surface treatments. Enormous care was given to the preparation of thin foils for Transmission Electron Microscopy (TEM) for observations of the near-surface microstructure of the LSP-treated samples, for which conventional twin-jet electro-polishing is not suitable. Consequently, thin foils from the specimens (sensitized, LSP-treated, etc.) for TEM observations of these microstructural changes were prepared by normal dimpling and ion

milling procedures. To obtain foils from close to the LSP treated surface, a thin section was sliced off parallel to peened surface, polished to a thickness of $\sim 100\text{ }\mu\text{m}$, dimpled using a Fischione Instruments Model 150 dimpler from the side opposite to the peened surface to obtain a one-sided web of thickness of $\sim 20\text{ }\mu\text{m}$ near the center, leaving the peened surface untouched and intact. The foil was then ion milled using a Fischione Instruments Model 1010 Ion Milling System only from one side using a shallow incidence angle (12°) and low energy (4 keV, 45° stage rotation) to ensure that there is no damage induced by ion beam. This enables one to obtain thin areas which are very close to surface. The near surface samples are important as they help in understanding the fundamental microstructural changes introduced by these surface treatments. The same technique was utilized to prepare thin foils of all samples, including those in the non-LSP treated sensitized conditions.

TEM thin foils were observed with a Phillips/FEI CM-20 TEM operated at 200 kV and photographs from relevant regions were recorded under bright field (BF), dark field (DF), weak-beam dark field (WBDF) and selected area diffraction (SAD) modes. Energy dispersive X-ray (EDS) spectroscopy in TEM was conducted at several points at and across grain boundaries to obtain chromium concentration. X ray intensities were collected at each position for 40 s by stepping the electron beam (spot size of 15 nm diameter) in increments of 50-100 nm across grain boundaries in the sensitized (S1 and S2) samples. Standardless analysis was used to quantify the concentration of Cr and the other elements from the x-ray intensity data.

2.3 Double Loop Electrochemical Potentiokinetic Reactivation (DLEPR) tests

Electrochemical potentiokinetic reactivation (EPR) tests have been used previously to quantify degree of susceptibility to IGA/IGSCC in Ni-based Alloy 600 [16,17]. The double loop electrochemical potentiokinetic (DLEPR) test is a fast, reproducible and quantitative method to determine degree of sensitization (DOS). The DOS after heat treatments was

quantified as the ratio of maximum current in the reactivation loop to maximum current in the activation loop. DLEPR tests were performed in accordance with ASTM G108-94 in a solution composed of 0.01 M H₂SO₄ + 20 ppm KSCN using a Gamry Potentiostat (Reference 600) [16]. The scan rate was set at 0.5 mV/s for activation and reactivation loop and the sample size was 1 cm². Each heat treated coupon was mechanically ground to 1200 grit, wet polished with 1 μm diamond suspension and finished with 0.05 μm colloidal silica suspension. Freshly prepared solution was de-aerated with high purity Ar gas before and during each test. All tests were performed at room temperature. Samples were kept immersed in the test solution for 1 hour at open circuit potential before the start of each test. The extent of intergranular attack after DLEPR tests was observed using a FEI XL-30 Scanning Electron Microscope (SEM).

2.4 Residual Stress and Hardness Characterization

In the sin²ψ method, a number of XRD measurements are made at different psi (ψ) tilts where ψ is the angle between the normal of the sample and the normal of the diffracting plane. Presence of strain causes peak shift (2-theta peak position) and inter-planar spacing (d) can be measured at each ψ tilt. The stress was then calculated by fitting the data in the d versus sin²ψ plot and knowledge of the plane-specific x-ray diffraction elastic constants (S1 and S2) of the material[18].

Residual stresses induced in the material after LSP treatment were measured using the sin²ψ technique with a Proto LXRd instrument (single axis goniometer using Ω geometry) with parameters as listed in Table 3. Calibration of the system was checked by collecting a diffraction pattern from a strain free standard polycrystalline SS316 powder prior to conducting the experiment in accordance with ASTM E915-10 (“Verifying the Alignment of X-ray Diffraction Instrumentation for Residual Stress Measurement”) [19].

To measure residual stress through depth, samples were electro-polished to remove 10 - 50 μ m layers using 87.5:12.5 vol.% CH₃OH:H₂SO₄ solution. Thickness of layer removed was calculated by measuring the thickness of the sample with a precise micrometer before and after electro-polishing. Strain and layer removal corrections were applied to the residual stress values using established procedures included in the software.

The relaxation of LSP induced residual stresses due to applied stress was observed by measuring residual stresses on the gage section of the same sample before and after constant load SCC tests. Before testing, residual stresses were measured at least 2 times along and perpendicular to the loading direction on each sample. After constant load tests, residual stresses were measured twice on the gage section of samples that did not fail in 500 hours. The average values of surface residual stresses on the gage section along the loading direction have been reported in this study.

Hardness measurements were performed using a CSM Instruments Nano-Micro Indentation system with a Berkovich indenter, a load of 100 mN with loading/unloading rate of 200 mN/min and a pause of 5 seconds at the peak load. At least 3 hardness values were recorded at each depth on polished cross-sectioned LSP treated samples.

2.5 SCC tests

a. Slow Strain Rate Test (SSRT)

Flat samples with the dimensions as shown in Figure 2 were machined using wire EDM from sensitized sheets of Alloy 600, polished to 1200 grit, degreased with acetone, dried and immersed in the test solution for 1 hour prior to straining. Samples were strained at rates of 2×10^{-6} /s and 10^{-6} /s for S1 and S2 sensitization conditions respectively. LSP was performed using vinyl tape as the ablative layer and water as the confining medium with the parameters described earlier. Samples were LSP treated on 2 opposite sides of the gage section as shown in Figure 2. Slow strain rate tests (SSRT) were performed at room

temperature with a mechanical testing system (Cortest Inc. Willoughby, Ohio) driven by a servo motor and fitted with a custom built environmental chamber. Load and displacement values were recorded periodically using calibrated load cells and 2 LVDT's respectively and samples were tested to failure. Strain was calculated from the average displacement measured by the 2 LVDT's. Solutions with concentration 0.001 M or 0.005 M were prepared using reagent grade $\text{Na}_2\text{S}_4\text{O}_6$ sodium tetrathionate (Sigma-Aldrich) and distilled water. For certain SSRT tests, the solution pH was adjusted to 3 with the appropriate amount of dilute H_2SO_4 .

b. Constant Load Tests

Constant load tests were performed by loading the samples (dimensions as shown in Figure 2) using calibrated Proof rings (Cortest Inc. Willoughby, Ohio) to the predetermined loads/stresses and the time to failure was recorded using a timer switch. The test solutions were prepared according to the same procedure described earlier. Fracture surfaces of failed samples from SSRT and constant load SCC tests were observed in an FEI XL-30 SEM to ascertain the mode of failure.

3. RESULTS

In this section, we first present the effects of LSP on the microstructure, residual stresses and hardness. Next, SCC test results including SSRT and constant load tests in tetrathionate solution are described.

3.1 Microstructure

The cross-section optical micrographs recorded in Figure 3(a,b) from the untreated (S1) and LSP-treated (LSP1) samples respectively show no changes in the grain size following the LSP treatment. Figure 3(c) shows the microstructure of the sensitized sample in which a small area was LSP treated. No significant difference in grain size can be observed between the untreated and LSP-treated regions in the micrograph. Other studies on effects of

LSP on microstructure have reported no significant changes in grain size due to the relatively lower plastic strain induced during the treatment [20].

Heat treatment conditions were chosen such that Alloy 600 was sensitized to induce IGSCC susceptibility in tetrathionate solutions at room temperature. TEM micrographs from the sensitized samples (S1 and S2) showing in carbide precipitation along grain boundaries can be observed in Figure 4(a, b) respectively. Carbides (M_7C_3 , $M_{23}C_6$) along the grain boundaries usually results along the grain boundaries usually results in depletion of Cr from the surrounding regions, the extent of which depends on the sensitization treatment. Chromium concentration profiles across grain boundaries in sensitized samples (S1 and S2) are shown in Figure 4(c). Cr concentration was as low as 9.4 wt.% and 13.4 wt.% at the grain boundary in S1 and S2 respectively. This suggests that precipitation of carbides during both sensitization treatments led to Cr depletion.

LSP being a mechanical surface treatment technique influences the microstructure and TEM micrographs from the near surface region after LSP treatment have been presented in Figure 5(a-f). The pressure pulse/shock wave generated during the LSP treatment causes plastic deformation, which results in the formation of a high dislocation density and misoriented sub-grains/crystallites that have sizes in the range of 30-200 nm in the near-surface regions, which can be clearly seen in the BF micrographs in Figure 5(a-c). In addition, narrow twins were observed occasionally as seen in the BF micrograph in Figure 5(d) and confirmed by the extra twin reflections at the expected positions for FCC crystals in the [011] SAD pattern in Figure 5(e) from the encircled area surrounding the twins and revealed more clearly in the DF micrograph in Figure 5(f) recorded from a twin reflection. This is in accordance with other studies that have reported a high dislocation density and twinning after shot peening and LSP treatments [7,11, 21].

3.2 Residual stresses, FWHM and hardness

Residual stresses versus distance from the peened surface, measured using the $\sin^2\psi$ method in two orthogonal directions (X and Y), are shown in Figure 6. The residual stresses were of the order of about -500 MPa at the surface and the depth of the compressive residual stress layer was about 0.4 mm (in a 2 mm thick sample). The surface residual stresses have been significantly modified from tensile (100 MPa) before LSP to compressive (-500 MPa) after LSP.

X-ray diffraction peak broadening characterized by full widths at half maximum (FWHM) values, which are a qualitative indication of the level of plastic strain introduced in a material were also recorded during residual stress measurements and have been plotted in Figure 7. In LSP treated Alloy 600, the level of plastic strain is higher at the surface (FWHM of ~ 3.5) but drops rapidly in the first 100 μm and decreases gradually through depth to a more or less constant value after $\sim 400 \mu\text{m}$.

Indentation hardness at the surface after LSP was about 4.99 GPa and drops gradually to 3.75 GPa at 600 μm below the surface. The indentation hardness before LSP was about 3.28 GPa and the increase in hardness can be attributed to the repeated impacts during the LSP process. Pressure pulse generated during LSP process have short pulse duration and attenuates as it travels through the material. This explains the gradient nature of residual stresses, plastic deformation and hardness.

3.3 Double Loop Electrochemical Potentiokinetic Reactivation Tests

The DOS values obtained from DLEPR for solution annealed and sensitized samples are shown in Table 4. The sensitization treatment at 650°C resulted in increased DOS from 0.56 for AR to 0.78 and 2.04 for S2 and S1 conditions respectively.

A higher degree of sensitization indicates a deeper Cr depletion zone and greater the susceptibility to intergranular stress corrosion cracking. SEM micrographs of the surface after DLEPR tests for AR, S1 and S2 samples are shown in Figure 8(a-c) respectively. The

increased attack on the grain boundaries can be clearly seen in microstructure of the sensitized samples and is indicative of the amount of Cr depletion due to the sensitization treatment, which is also consistent with the Cr concentration profiles in Figure 4 determined using EDS.

3.4 Slow Strain Rate Tests (SSRT)

SSRTs were used to quantify the susceptibility of sensitized Alloy 600 to IGSCC in tetrathionate solution at room temperature and particularly to understand the effects of LSP on the SCC susceptibility. Figure 9 shows the effect of sensitization treatments (different DOS), solution concentration and LSP on the SCC susceptibility in tetrathionate solution. Strain to failure, maximum stress and mode of failure from SSR tests conducted in this study are tabulated in Table 5. For comparison, sets of untreated (S1) and LSP treated (LSP1) Alloy 600 (same sensitization condition) were strained at the same rate in the same environment. Both S1 and S2 sensitization conditions were observed to be susceptible to IGSCC in the 0.001 M tetrathionate solution. Maximum elongations were 31% and ~23% for S1 and S2 respectively in the tetrathionate solution (0.001 M) as compared to ~60% in air (neutral environment). DLEPR test results (Table 4) and Cr depletion profiles (Figure 4) indicated that S2 was less sensitized as compared to S1 and hence a lower strain rate was used for SSR tests. This ensured that the mode of failure was intergranular SCC. Once the baseline conditions (DOS, strain rate and environment) were established, LSP treated samples were tested under the same conditions. Since the LSP treatment was done after sensitization treatment, any changes can be attributed to the effects of LSP. The stress-strain curves shown in Figure 9 indicate higher yield stress (YS) and ultimate tensile strength (UTS) for LSP treated Alloy 600 compared with the untreated condition. This effect was seen in all LSP treated samples irrespective of the sensitization condition or environment. For example, YS

was ~40% higher after LSP for the same sensitization condition. The strain to failure was also higher for LSP treated samples compared with untreated samples.

While SSRTs can be used to provide information about the susceptibility of an alloy in the given environment, constant/cyclic load tests are more representative of the stress state. Also, the residual stresses induced by LSP are likely to relax on straining beyond the yield stress of the material. The increase in yield stress and ultimate tensile strength after LSP would possibly increase the threshold applied stress for IGSCC in a given environment. A single crack that propagated through the cross-section of the sample was observed in all samples that were tested in 0.001 M $\text{Na}_2\text{S}_4\text{O}_6$ solution. This may be attributed to a combination of less sensitization, less aggressive environment and strain rate. Secondary cracks were observed in samples that were tested in the acidified (pH 3) 0.001 M $\text{Na}_2\text{S}_4\text{O}_6$ solution thereby indicating that the acidified solution was more aggressive towards sensitized Alloy 600. Low magnification SEM micrographs of fracture surfaces of failed samples after SSRTs have been shown in Figure 10 (a, c, e and g) whereas the higher magnification images in Figures 10 (b, d, f and h) show inter granular cracks in more detail. The mode of failure was (partial) IGSCC for sensitized and LSP treated samples.

3.5 Constant Load Tests

Constant load tests were used to evaluate the effects of LSP on Alloy 600 under static loading conditions in different solution concentrations. Figure 11 summarizes the effects of LSP on SCC resistance in terms of applied stress and time to failure. For the untreated samples, the time to failure decreased with increase in applied stress in 0.001M tetrathionate solution. The applied loads were chosen such that they were between 80-140% of the YS load for sensitized Alloy 600. In general, LSP treated samples tested at same loads had much longer time to failure or did not fail in 500 hours after which the tests were terminated. Sensitized samples failed in shorter time compared with the LSP treated samples for all loads and solution concentrations/pH tested.

The increase in time to failure after LSP can be attributed to the beneficial compressive residual stresses (Figure 6) induced by LSP which were as high as -550 MPa at the surface at the start of test, as well as near-surface hardening (Figure 7) caused by the increased dislocation density and formation of misoriented, 30-100 nm-size sub-grains/crystallites, whose boundaries act as obstacles to dislocation glide (Figure 5). Cracks were not observed in sensitized Alloy 600 (S1) after 500 hours in 0.001M tetrathionate solution at a load of 300 MPa which suggests a stress threshold for IGSCC. SEM micrographs of the fracture surfaces from constant load tests for sensitized (S1) and LSP treated (LSP1) are shown in Figure 12(a, b) respectively, and intergranular cracking was observed in both cases.

The effects of LSP on resistance to IGSCC in acidified tetrathionate solution (0.001 M $\text{Na}_2\text{S}_4\text{O}_6$ pH 3) were also investigated. The time to failures dramatically decreased for sensitized samples (S1) from 176 hours in 0.001M tetrathionate to 30 hours when the pH was reduced to 3. In this test, the LSP treated sample showed multiple cracks in the gage section after 423 hours (applied stress = 350MPa). At a lower applied stress (300 MPa), the LSP treated sample did not show cracking even after 500 hours, whereas the untreated sample failed in about 45 hours in the acidified tetrathionate solution.

4. DISCUSSION

The SSRT and constant load test results suggest that LSP has a significant effect on improving the IGSCC resistance of Alloy 600. In this section, SSRT data were used to calculate the SCC susceptibility index and quantify the effect of LSP induced residual stresses. In addition, we discuss the effects of LSP under different applied load, solution concentration and DOS conditions, with attention to mechanistic aspects.

4.1 SCC Susceptibility Index

To quantify the effect of LSP on the susceptibility to IGSCC in tetrathionate solutions, the following equation (Equation 1) proposed by Abe et al. [21] was used to calculate the SCC susceptibility index (I_{SCC}),

$$I_{SCC} = \left[\frac{1+e_n}{1+e_n^{SCC}} \right] \times \left[\frac{P_n}{P_n^{SCC}} - 1 \right] \quad (1)$$

where e_n and e_n^{SCC} are strains at the maximum load for load-elongation plot in air and environment respectively. P_n and P_n^{SCC} are the maximum loads for load-elongation plot in air and environment respectively. I_{SCC} is used to quantify the degree of susceptibility to SCC in a particular solution with respect to a neutral environment at the same strain rate. Table 6 summarizes the I_{SCC} for the tests as per SCC susceptibility proposed by Abe et al.[22].

SCC susceptibility of LSP treated sensitized Alloy 600 was lower than that of counterpart untreated sensitized Alloy 600. Increasing the solution concentration from 0.001M to 0.005M $Na_2S_4O_6$ did not increase the I_{SCC} appreciably but decreasing the pH to 3 had a more significant effect. S2 was strained at a slower rate than S1 which explains the relatively higher susceptibility to SCC in the same solution despite having lower DOS. The higher yield stress and UTS contributed to the reduced SCC susceptibility for LSP samples. I_{SCC} was lower even in more aggressive environment where the pH was 3. SSRT tests involve straining the samples continuously and residual stresses relax as the applied stress exceeds the yield stress [18]. Hence, residual stresses are likely to be ineffective in mitigating SCC if the samples are plastically deformed to large strains.

As noted earlier, the mode of failure was IGSCC even for the LSP treated samples which have lower I_{SCC} . It is important to note that the LSP treated samples show a much higher yield stress as compared with the untreated samples. This increase in yield stress is a result of LSP induced deep compressive residual stresses and near surface hardening from the increased dislocation density and refined sub-grains/crystallites, whose boundaries act as obstacles to dislocation glide. I_{SCC} proposed by Abe et al. takes into account the strain, load at

the maximum load and is better suited to quantify the effects of residual stresses on SCC susceptibility. The higher yield stress for LSP1 vs S1 and LSP2 vs S2 contribute to reduced susceptibility.

4.2 Effect of Applied Load and Solution Concentration

Constant load test results presented in Figure 11 suggest that lower degree of sensitization increased the time to failure in the same solution under similar applied loads. Residual stresses of ~ -150 MPa were measured after the constant load test (applied stress = 400MPa) in cases where samples did not fail in 500 hours. This is lower than the initial surface residual stresses of ~ -550 MPa before testing. This indicates that a part of the residual stresses relaxed during loading. It is known that residual stresses will redistribute and relax as cyclic/static load is applied especially if it exceeds the yield stress of the material [23]. This was confirmed by measuring residual stresses on the gage section constant load SCC tests and the results have been summarized in Table 7. Also, residual stresses were close ~ 10 MPa on LSP treated samples that had failed before 500 hours. This indicates that compressive residual stresses induced by LSP had a significant effect in the mitigating SCC. Moreover, this effect was seen in cases where the solution is more acidic (pH 3). The presence of compressive residual stresses (albeit lower than those in the as LSP treated condition) after constant load tests (500 hours) suggests that threshold stress was higher.

Constant stress tests on the sensitized, but non-LSP treated samples were conducted at stress levels both below and above the yield stress. At applied stresses below the yield stress, for example 300 MPa, failure due to SCC was not observed in the normal pH solution but occurred at short times in the more aggressive environment (pH 3). The applied stress was close to or above the yield stress of the sensitized samples but below the yield stress of LSP treated samples. It must be noted that this increase in threshold stress may be lower or higher in more or less aggressive solution/sensitization conditions respectively.

Tests at stresses above the yield stress of the LSP-treated samples were not conducted because plastic yielding would cause relaxation of the compressive residual stresses and little or no improvement in SCC life would be expected. Nevertheless, the important conclusion to be drawn is that LSP considerably increases the threshold stress and life for failure from SCC. The better resistance of LSP treated samples to SCC under constant load in tetrathionate solutions may be attributed to the higher yield stress (from the hardening associated with the increased dislocation density and refined sub-grains/crystallites whose boundaries serve as obstacles to slip).

Tsai et al. [14] had observed increased resistance of shot peened sensitized Alloy 600 to SCC in thiosulfate solutions and the beneficial effect was attributed to the presence of compressive residual stresses though the residual stresses were not quantified. Sano et al. [8] also observed increased resistance to crack initiation after LSP treatment on SS304 in high temperature pure water. They observed that LSP (without coating) prevented SCC even if the residual stresses introduced after LSP were as low as -100 MPa. In addition, LSP had prevented crack initiation and mitigated crack propagation. Peyre et al. [24] reported that LSP acted like a tensile stress inhibitor which contributed to the improved SCC resistance in boiling MgCl_2 solution in SS316L. Recently, Lu et al. [25] attributed the increase in SCC resistance of ANSI 304 austenitic stainless steel in boiling MgCl_2 solution to modified grain refinement and residual stresses due to LSP treatment. Lu and colleagues also observed relaxation of residual stresses after LSP treated AISI 304 SS samples were bent to form U-bend specimen [26]. Additionally, these samples failed by SCC in boiling MgCl_2 solution as compared with samples that were LSP treated after being bent into U-bend specimens that did not fail. This indicates that LSP induced compressive residual stresses significantly reduce the susceptibility of austenitic stainless steels to SCC. Results from this study suggest

that compressive residual stresses and near surface hardening induced by LSP treatment substantially increased the resistance of alloy 600 to SCC in tetrathionate solution.

5. CONCLUSIONS

The findings of this study have led to the following conclusions.

1. DLEPR tests were used to quantify the DOS for sensitized Alloy 600. Sensitized Alloy 600 was susceptible to IGSCC in sodium tetrathionate solution at room temperature. A higher DOS corresponded to greater susceptibility of sensitized Alloy 600 to SCC in tetrathionate solution.
2. Deep compressive residual stresses were introduced and a substantial increase in hardness and strength was observed after LSP in Alloy 600. Near-surface microstructure of LSP treated Alloy 600 shows deformation bands, high dislocation densities, misoriented subgrains of 30-200 nm size and occasionally narrow twins.
3. Slow strain rate tests used to evaluate IGSCC susceptibility of sensitized Alloy 600 in tetrathionate solution revealed that LSP substantially reduced the susceptibility of sensitized Alloy 600 to IGSCC for conditions with different DOS, solution concentration and pH.
4. LSP treatment led to a significant improvement in resistance to SCC indicated by longer time to failure or no failure at same applied stress in sensitized alloy 600 as shown by constant load tests for different DOS and pH in tetrathionate solutions.
5. The improvements in SCC resistance by LSP treatment are attributed to a combination of deep compressive residual stresses, near-surface microstructural changes and the associated hardening and increased yield strength of the alloy.

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C	Mn	Si	S	Cr	Fe	Co	Cd	Ti	Cu	P	Al	Ni
0.08	0.16	0.18	0.001 max.	14.99	8.05	0.18	0.01	0.18	0.1	0.001 max.	0.08	Bal.

Table 1. Chemical composition of the Inconel Alloy 600 used in this study.

Designation	Sensitization and LSP treatments
AR	As Received (annealed)
S1	AR + 650 °C, 5h, air cooled
S2	AR + 650 °C, 2h, air cooled
LSP1	S1 + LSP 5.6 GW/cm ²
LSP2	S2 + LSP 5.6 GW/cm ²

Table 2. Designation for sensitization and LSP treatments considered in this study.

Item	Description
Detector	Position sensitive scintillation detector(PSSD) 20° 2θ
Radiation	MnKα ₁ (λ = 2.10314 Å)
Tilt angles	0, ± 2.58, ± 9.07, ± 12.45, ± 18.8, ± 23.0
Aperture size	1 mm diameter
Plane(Bragg's angle)	{311}, 156°
X-ray elastic constant	S2/2: 5.66 x 10 ⁻⁶ MPa ⁻¹

Table 3. XRD parameters used for residual stress measurement

Designation	DOS, %	Sensitization time at 650°C, h
AR	0.56 ± 0.06	0
S1	2.04 ± 0.09	5
S2	0.78 ± 0.08	2

Table 4. Degree of sensitization for the test conditions considered in this study.

Specimen/Environment	YS, MPa	UTS, MPa	Elongation, %	Test variable	Mode of Failure
S1_0.001M	280	514	31.27	Baseline	IGSCC
LSP1_0.001M	528	731	31.14	LSP	IGSCC
S1_0.005M	310	514	33.82	Solution concentration	IGSCC
LSP1_0.005M	554	725	41.83	LSP, Solution concentration	IGSCC

S2_0.001M	296	441	23.10	%DOS, strain rate	IGSCC
LSP2_0.001M	520	787	42.50	%DOS, strain rate, LSP	IGSCC
S1_0.001M_pH3	312	496	18.89	Solution pH	IGSCC
LSP1_0.001M_pH3	563	808	29.08	Solution pH, LSP	IGSCC
S1_Air	330	864	66.78	Neutral environment	Ductile
S2_Air	326	753	61.47	Neutral environment	Ductile

Table 5. Summary of all results from SSR tests on sensitized Alloy 600

Specimen/Environment	Maximum load, N	Strain at maximum	
		load, %	I _{SCC}
S1_0.001M	359	16.58	0.88
LSP1_0.001M	510	15.02	0.24
S1_0.005M	359	17.82	0.87
LSP1_0.005M	506	12.82	0.26
S2_0.001M	308	10.58	1.31
LSP2_0.001M	549	29.93	0.11
S1_0.001M_pH3	346	12.33	1.00
LSP1_0.001M_pH3	564	22.61	0.09
S1-Air	603	50.90	-

Table 6. Comparison of SCC susceptibility index using strain and maximum load relationship for sensitized and LSP treated Alloy 600.

Sample Designation, Environment	Applied stress for 500 hours, MPa	Residual stress before test, MPa	Residual stress after test, MPa
LSP1, 0.001 M	350	-550 ± 15	-156 ± 14
LSP2, 0.001 M	400	-550 ± 15	-172 ± 18
LSP1, 0.001 M	500	-550 ± 15	-14 ± 10
LSP1, 0.001M pH 3	300	-550 ± 15	-165 ± 17

Table 7. Average value of surface residual stresses on the gage section along the loading direction after constant load tests in tetrathionate solution.

Figure 1. Schematic of the Laser Shock Peening process

**Figure 2. Schematic of the sample used for slow strain rate tests and constant load tests.
All dimensions in mm.**

Figure 3. Optical micrographs from cross sections of sensitized a) S1, b) LSP1 (LSP treated) condition samples and c) untreated and LSP treated (right) regions from surface of S1.

Figure 4. Bright field TEM micrographs showing the presence of carbides along grain boundaries from (a) S1 and (b) S2 condition samples. Chromium concentration profiles at and with distance into the matrix from grain boundaries in S1 and S2 is shown in (c).

d

Figure 5. TEM Micrographs from LSP1 sample (a, b and c) showing high dislocation density and 30-200 nm size sub-grains/crystallites. (d) Bright field micrograph revealing twins, which are confirmed by the extra reflections at the expected positions for twins in FCC crystals in the [011] SAD pattern in (e) from the encircled region in (d). (f) Dark field micrograph recorded from the twin reflection encircled in red in (e) revealing narrow twins.

Figure 6. Residual stresses through depth in two orthogonal directions in LSP treated Alloy 600.

Figure 7. Nano-indentation hardness and FWHM of diffraction peak through depth in LSP treated Alloy 600

Figure 8. SEM micrographs showing surface microstructure after DLEPR test for a) As received (AR), b) S1 and c) S2 conditions

Figure 9. Stress-strain curves of sensitized and LSP treated Alloy 600 tested in 0.001 M tetrathionate solution at room temperature. Strain rate for S1, LSP1 was 2×10^{-6} /s while strain rate for S2, LSP2 was 10^{-6} /s. For tests designated with pH3, appropriate amount of H_2SO_4 was added to reduce the pH to 3.

b

d

f

Figure 10. SEM micrographs showing fracture surface from a), b) S1; c), d) LSP1; e), f) S1_pH3 and g), h) LSP1_pH3. Environment: 0.001 M $\text{Na}_2\text{S}_4\text{O}_6$, pH3 denotes acidified 0.001 M $\text{Na}_2\text{S}_4\text{O}_6$. Strain rate: $2 \times 10^{-6} \text{ s}^{-1}$. Black boxes in the low magnification SEM micrographs in (a), (c), (e) and (g) highlight the locations for corresponding high magnification micrographs in (b), (d), (f) and (h) and white arrows point to intergranular cracks.

Figure 11. Summary of results of constant load SCC tests on sensitized and LSP treated Alloy 600 samples in 0.001M $\text{Na}_2\text{S}_4\text{O}_6$ (tetrathionate) solution. Open and closed symbols indicate samples that did not fail in 500 hours and those that failed, respectively. pH3 indicates acidified 0.001 M tetrathionate solution and the red line denotes the yield stress for sensitized Alloy 600.

b

Figure 12. SEM micrographs of fracture surface showing intergranular cracking after constant load test (applied stress = 400MPa) in 0.001M tetrathionate solution of a) sensitized (S1) and b) LSP treated (LSP1) Alloy 600 samples.