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Corrosion Reactivity of Laser-Peened Steel Surfaces

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Laser-shock processing or laser peening (LP) is a novel process used to reinforce surfaces by generating compressive residual stresses that has been investigated to change the surface mechanical state and modify the electrochemical properties of three commercial steels. The first part of this paper relates to experiments where LP has been applied to G10380 and G41400 steels for corrosion testing in an acid $HKSO_4$-0.3 M solution. Only in the case of G41400 martensitic steel is a reduction of the corrosion current observed, depending on the degree of work hardening and the amplitude of compressive stresses. This indicates a small mechanochemical effect of LP, which seems to be restricted to martensitic structure. Second, the effect of LP on stress corrosion cracking (SCC) of AISI 316L stainless steel is demonstrated by static tests in $MgCl_2$ 44% −153 °C solution. The results confirm the applicability of LP to suppress cracks on all the areas processed without occurrence of any problems in the treated-nontreated transitions zones.

Keywords corrosion, laser, residual stresses, shock waves, steels

1. Introduction

Since the early developments of LP,[1] its potential to harden surfaces and improve fatigue properties by laser-driven shock waves has been related several times on steels, titanium, and aluminum alloys.[2,3,4] The principle is as follows. When a focused laser pulse reaches a metal with a sufficiently high intensity (more than 10^{13} W/m^2), a high pressure plasma forms on the metal surface. With the use of a tap water confinement (Fig. 1), the expansion of the plasma is trapped and the pressure increases by a factor of 5 to 10, depending on the pulse duration. This configuration, termed the confined regime, allows the generation of up to 5 GPa pressure levels with 10 ns pulse durations and, most of all, permits a deep plasticization of all metallic materials. Laser peening has also proven to be a possible tool to improve the stress corrosion cracking of AISI 304 steel welded joints in high-temperature water,[5] or the pitting corrosion behavior of AISI 316L steel in NaCl 0.5 M.[6] More widely, questions remain about the influence of mechanical surface states on corrosion properties. For instance, surface preparations such as brushing can modify uniform corrosion rates of ferritic steels[7] by the combined effect of work hardening and residual stresses. In previous studies[8] on the corrosion of cobalt in H_3PO_4 solutions, a simple polishing of the surface modifies the corrosion current densities I_{cor} (the more severe the polishing, the more active the dissolution). All these results tend to indicate a mechanochemical effect, which has been investigated widely theoretically and experimentally by Gutman *et al.*[9]

In this paper, we relate experiments where LP is used to modify the uniform corrosion and SCC properties of three commercial steels. Two applications are envisaged: (1) the uniform corrosion of G10380 and G41400 steels (UNS) in acid ($HKSO_4$-0.3 M) solutions and (2) the SCC of AISI 316L austenitic steel in $MgCl_2$ 44% at 152 °C. We aim first to analyze the surface modifications (153 °C, roughness, and residual stresses) induced by LP, and second to investigate the influence on corrosion properties.

2. Materials and Laser-Peening Procedure

2.1 Materials

Three steels having different crystalline structures (austenitic for AISI 316L steel, ferritic for G10380, and tempered martensitic for G41400) have been treated by LP. Their chemical composition, measured by glow discharge optical spectroscopy (GDOS), is presented in Table 1. As LP can be considered as a dynamic (10^6 s^{-1}) compression of the surface generating less than 5% plastic deformation,[4,6] mechanical properties have been identified by the use of compressive tests at 10^{-2} s^{-1}

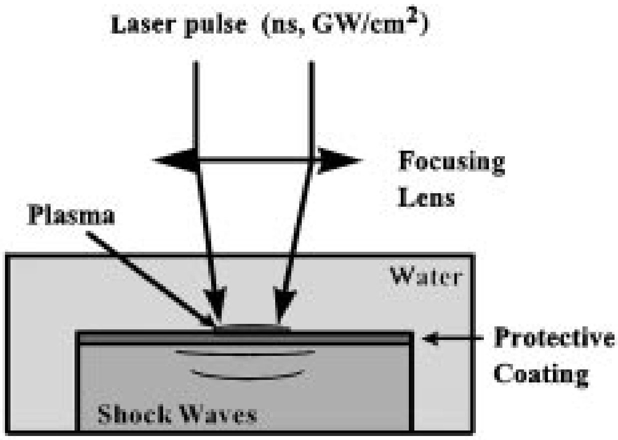

Fig. 1 Basic principle of laser peening in water-confined regime

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Table 1 Chemical composition of the steels (wt.%)

Steel	C	Si	Mn	Cr	Ni	Mo	Cu	Ti	S	Fe
G10380	0.4	0.5	1	0.3	⋯	0.08	0.3	⋯	0.04	Bal
G41400	0.42	⋯	⋯	1.05	⋯	0.3	⋯	⋯	⋯	Bal
AISI 316L	0.019	0.35	1.68	17.1	11.95	2.05	0.14	0.05	0.007	Bal

Table 2 LP conditions

Steel	Intensity ($\times 10^{13}$ W/m^2)	Impact diameter (mm)	Number of local impacts	Estimated pressure (GPa)	Thermal protection
G10380	6	7	2–8	5	Al adhesive
G41400	6	7	1–4	5	Al adhesive
316L	8	7	4	7	Al adhesive

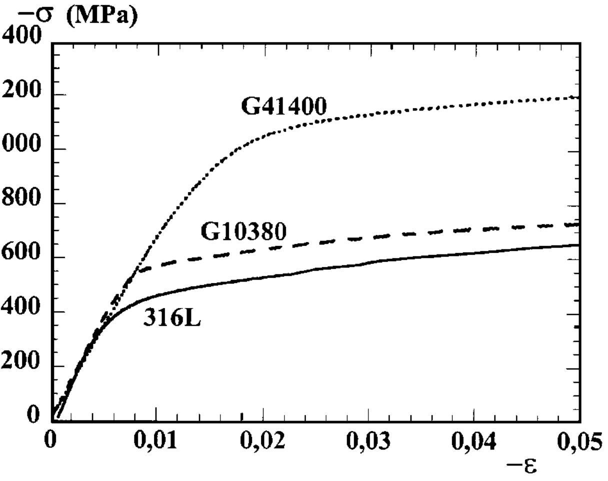


Fig. 2 Compression stress-strain curves at 10^{-2} s^{-1}

strain rate. Corresponding stress-strain curves are presented in Fig. 2. Yield strengths at 0.2% elongation $Rp_{0.2}$ vary between −350 MPa (316L), −550 MPa (G10380), and −1000 MPa (G41400). One can notice that the elastic-plastic transition seems to be more distinct for G10380 than for the two others.

2.2 Laser Peening Conditions

Shock experiments have been carried out with a Nd:YAG laser operating at 1.06 μm wavelength and delivering 30 J maximum output energy in 10 to 20 ns Gaussian pulses, with a frequency of one shot every minute. The laser beam, initially 50 mm in diameter, is focused on the part to be treated with a 600 mm focus lens, to reach 6 to 7 mm focus spots.

Samples submitted to uniform corrosion are 14 mm diameter and 8 mm high disks. They have been treated by LP in a water confined regime (Fig. 1) and protected from thermal effects by 0.1 mm aluminium-base coatings. The resulting effect is a high-pressure (5 to 7 GPa) plasma generation and a uniaxial plastic deformation that persists during nearly 0.1 μs at the surface of the metals. Shock conditions for all three metals are summarized in Table 2. According to previous investigations,[6] laser intensities have been limited to $8 \cdot 10^{13}$ W/m^2 to avoid breakdown phenomena in water above 10^{14} W/m^2, which are limiting factors for the pressure rise of the plasma. With such LP conditions, secondary ion mass spectroscopy did not evidence any chemical modification of the surface composition after LP. Therefore, possible effects on the corrosion properties will be due only to mechanical or morphological changes of the surface.

2.3 Surface Characterization and Electrochemical Testing

Surfaces have been characterized by: (1) their residual stress (RS) level (x-ray diffraction (XRD) measurements), (2) their work-hardening level (hardness, x-ray peak broadening), and (3) their topography (roughness parameters *Ra* and *Rt*) measured by a one-dimensional profilometer. As mentioned in Section 2.2., surface chemistry was confirmed to be unchanged by GDOS spectroscopy.

The XRD tests have been performed using the $2\theta = f(\sin^2\psi)$ relation.[10] The XRD conditions for body-centered cubic (bcc) steels (G10380 and G41400) and face-centered cubic (fcc) steels (316L) are summarized in Table 3.

Electrochemical tests have been carried out in $HKSO_4$−0.3 M acid (pH = 0.8) aerated medium to estimate the influence of LP. This medium was chosen because it allows us to avoid differential aeration and, in turn, ensures a good stability of rest potentials.[7]

The first test, which consists of rest potential recordings $E_{rest} = f(time)$ during 45 min immersion time, gives information on the degree of ennoblement or disnoblement of the surface. The second one consists of potentiodynamic tests $I = f(E)$ at 0.2 and 0.5 mV/s scan rates to estimate the corrosion current I_{cor}. A classical three-electrode device (platinum as counterelectrode, CE; Hg/Hg_2Cl_2 as a reference electrode, RE; and metal surface surface as work electrode, WE) controlled by a potentiostat (Solartron SI1287 electrochemical interface, SOLARTRON Group, Ltd., England) was used for corrosion testing.

3. Experimental Results

3.1. Surface Modifications Induced by Laser Peening

Before LP treatment, G10380 had a ground surface and G41400 had a mechanically polished surface (SiC grade 1000). Figure 3(a) and (b) show RS evolution with LP conditions (mainly the number of passes). For the G10380 specimens, RS measurements indicate a nearly −450 MPa isotropic maximum level, whereas on G41400 alloy, LP modifies the surface only to a very small extent compared to the initial RS amplitude (−100 MPa maximum difference after LP). The integral widths

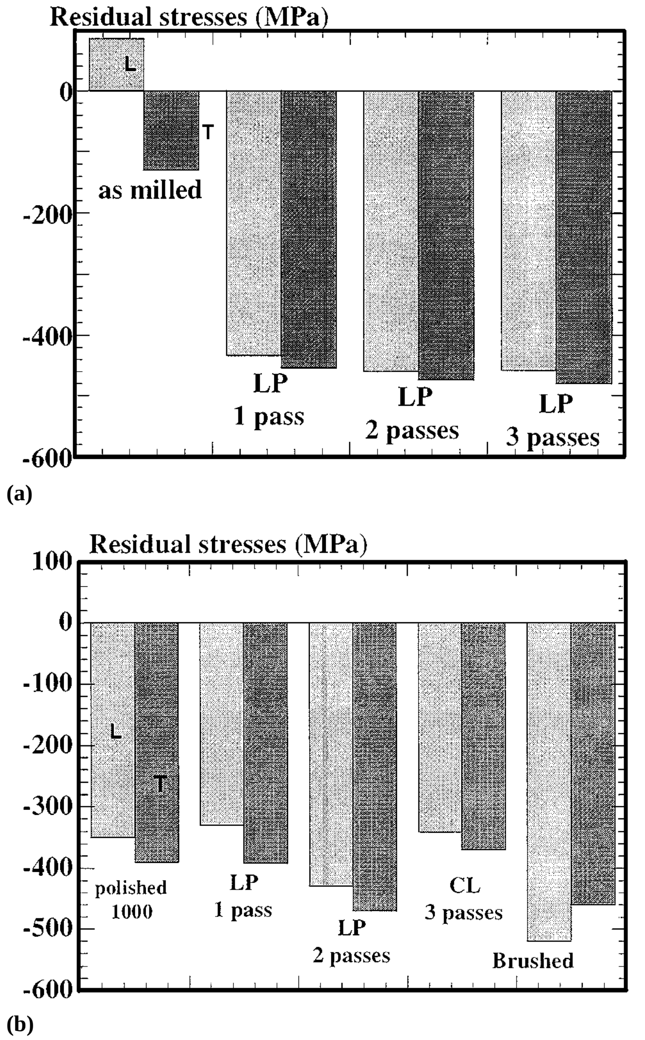


Fig. 3 Residual surface stresses induced by LP on G10380 and G41400 steels. (**a**) G10380 and (**b**) G41400. Influence of operating conditions (L = longitudinal = parallel to the milling streaks and T = transverse). Error bars on RS values = ±40 MPa

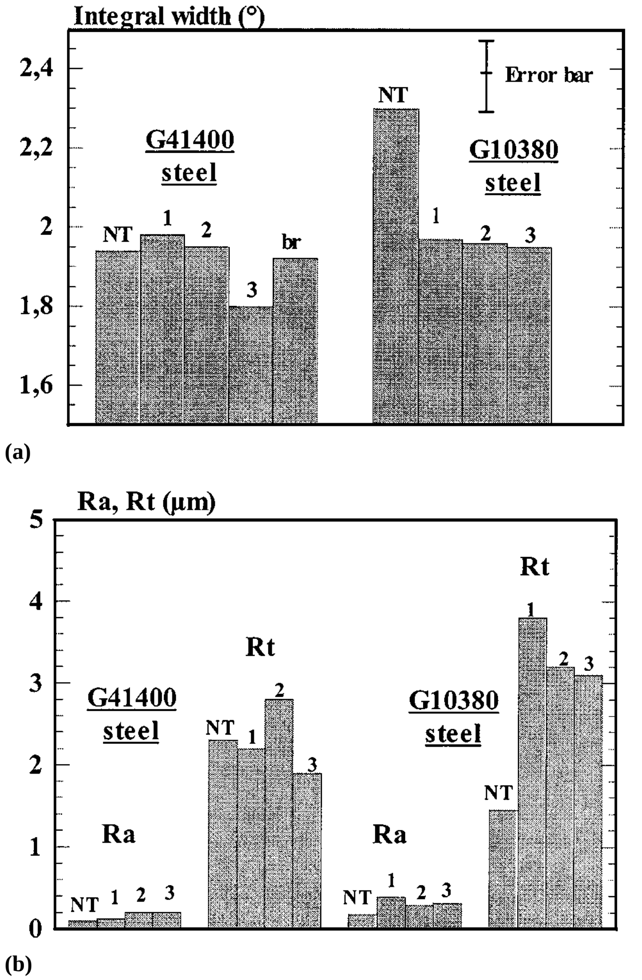


Fig. 4 (**a**) Characterization of the work-hardening level: integral widths of x-ray peaks before and after treatment and influence of operating conditions (NT = nontreated, and br = brushed, 1, 2, and 3 passes). Error bars on integral widths values = ±0.1°. (**b**) Surface morphology: average and maximal roughness values. Error bars on *Ra* and *Rt* = ±15%

Table 3 X-ray diffraction conditions

Material	Structure	Diffracting planes	Anticathode/ filter	Bragg angle (°)	Number of ψ angles
G10380 and G41400	bcc	{211}	Cr/V	156°	13
316L	fcc	{311}	Mn/Cr	152.3°	13

of x-ray peaks, which provide an estimation of the work-hardening level,[10] *i.e.*, on the density of defects and the local yield strength, are presented in Fig. 4(a). Mostly, a decrease of peak widths is evidenced after LP, especially on G10380. This phenomenon is believed to be due to relaxation mechanisms occurring during LP. Indeed, the very surfaces of strongly ground ferritic surfaces (G10380) or polished martensite structures (G41400) supersaturated with carbon in interstitial positions are initially saturated with defects, thus being able to relieve under shock-wave loading. However, no distinct hardness modification could be pointed out after LP on both steels (nearly constant at 180 to 190 HV_{50} value). This indicates that dislocation density has been modified to a very small extent, only detectable with x-ray peak narrowing.

Surface profilometry results for laser-peened specimens indicate small modifications of the roughness parameters (Fig. 4b). Modifications are smaller on G41400 because of its higher mechanical properties (+20% *Rt* on G41400 versus +120%

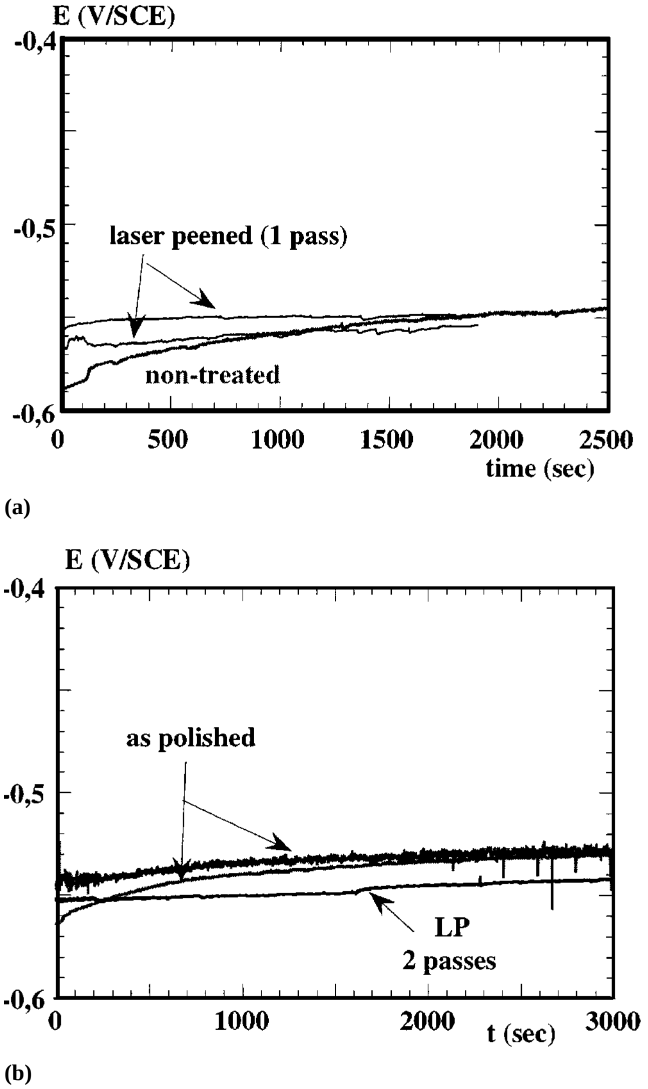


Fig. 5 Rest potential recordings in HKSO$_4$-0.3 M. (**a**) G10380 treated with one pass. (**b**) G41400 treated with a two-pass LP

on G10380). Above a number of LP passes, one can observe a smoothing effect on the surface, especially on grinding streaks, which results in a reduction of *Rt* parameter (after two impacts for G10380 and three for G41400, which is more resistant to plastic flow; Section 2.2).

3.2 Electrochemical Results

Rest potential measurements $E = f(t)$ recorded on the two steels increase with time in acid medium (Fig. 5a and b), without really reaching a stabilized step. This is due to the continuous dissolution with time in acid medium (no passivity or oxide layer remains on the surface). On G10380 steel (Fig. 5a), LP creates a small positive shift of E_{rest} at the beginning of the tests (+0.03 to 0.04 V) that tends toward the base material value (−0.54 to −0.55 V/SCE) after 1000 s. On G41400 steel, E_{rest} values are nearly constant during the test (Fig. 5b) and LP seems to have no effect on the equilibrium potentials.

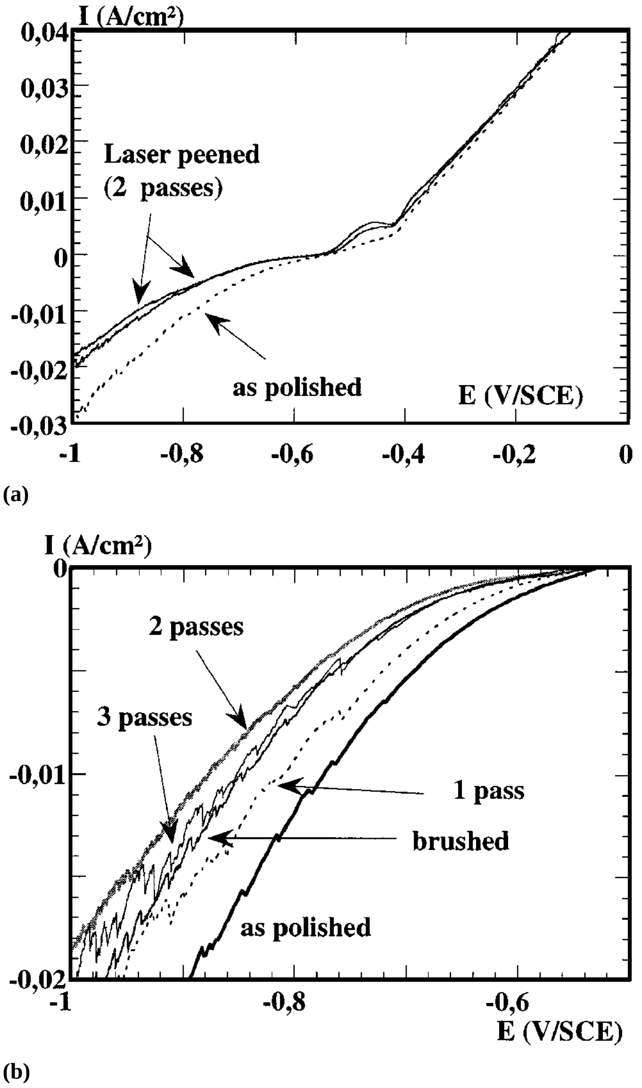


Fig. 6 Polarization curves of G41400 in HKSO$_4$-0.3 M after LP. (**a**) Influence of a two-pass LP treatment. (**b**) Cathodic part of the curves: comparison of LP and brushing treatments

Potentiodynamic tests $I = f(E)$ carried out in acid medium do not reveal any detectable influence of LP on G10380 treated with two local impacts. Besides, on G41400 martensitic steel, a reduction of current amplitudes is clearly evidenced in the cathodic parts of the polarization curves, in a very reproducible manner from one test to another one (Fig. 6a). This effect is maximum for a two-pass laser peening and even more severe than after a surface brushing (Fig. 6b). This result agrees with previous studies on electrochemical reactivity after surface preparation.[7]

From these polarization curves on G41400, and with the use of Tafel's formulations (Ln $I = f(E)$), we can deduce the corrosion current values for two scan rates (Fig. 7). After an LP, a factor of 3 decrease is evidenced at 0.5 mV/s (0.035 to 0.01 A/cm^2) and a 30% decrease at 0.2 mV/s (0.085 to 0.058 A/cm^2). All the experimental curves (including brushing conditions performed with the same experimental conditions as in Ref 7) confirm a reduction of the corrosion rate with surface

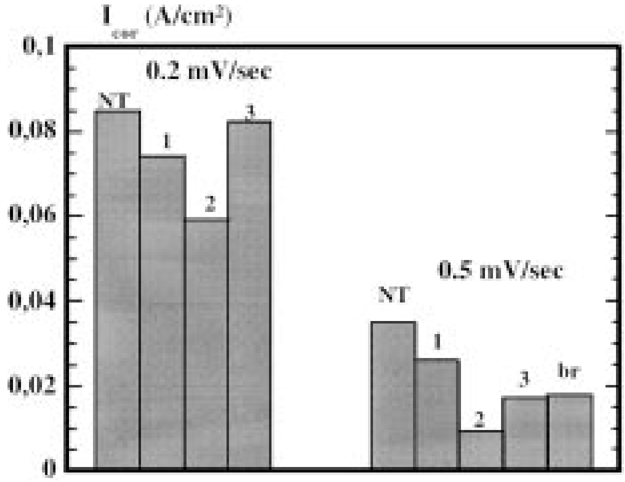


Fig. 7 Corrosion current values determined with the Tafel method (G41400 in HKSO$_4$-0.3 M) at 0.5 m/s and 0.2 mV/s scan speeds

treatment. This reduction, which is maximum after two passes of LP, occurs only in the cathodic part of the curves, which corresponds in acid medium (pH 0.8 in our case) to the reduction of hydrogen through the following reactions:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$
$$2H^+ + 2e^- \rightarrow H_2. \qquad \text{(Eq 1)}$$

Between the second and third passes, a corrosion current increase seems to occur (Fig. 7). This phenomenon will be discussed in Section 5.

4. Influence of Laser Peening on AISI 316L Stress Corrosion Cracking

Laser peening as a compressive stress generator is expected to improve the SCC behavior of stainless steels in chloride ion media just like shot peening (SP) does.[11] This has been demonstrated already on 304 welded steel for nuclear plants.[5]

In this subsection, we wish to analyze the influence of LP on 316L milled surfaces having a large amplitude of tensile stresses.

4.1 Residual Stress Modifications Induced by Laser Peening on 316L

Laser peening was carried out with a 50% overlapping ensuring four local impacts on all the irradiated surfaces, with the conditions presented in Table 2. Deformation bands appear after LP (Fig. 9). Their density increases with the number of impacts.[6]

In-depth RS measured by XRD (conditions for γ austenite in Table 3) indicate that compressive stresses rapidly decrease within the first 200 μm as the shock wave propagates into the metal. However, nearly 1 mm plasticized depth can be generated with a -400 MPa maximum level close to the surface (Fig. 8a). This stress amplitude is smaller compared to usual SP treatments, mainly due to the larger number of impacts (cyclic hardening behavior of 316L steel) and to the possible γ austenite $\rightarrow \alpha'$ martensite phase transformation occurring during an SP treatment,[6] but the affected depth is three times greater. Moreover, the surface work hardening detected by x-ray peak broadening (Fig. 8b) is smaller after LP.[6,11]

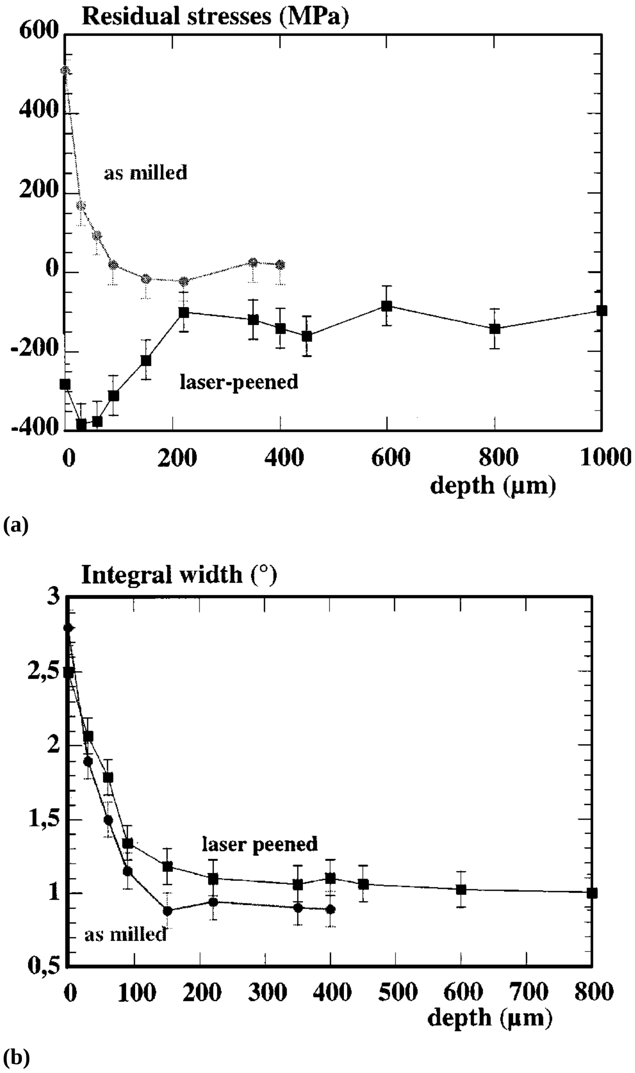


Fig. 8 (**a**) In-depth residual stresses induced by LP on 316L milled steel. (**b**) Integral widths of x-ray peaks

4.2 Stress Corrosion Cracking Tests

The SCC tests only consist of an immersion of the treated samples 24 h in MgCl$_2$ 44% boiling solution at 153 °C, and metallographic observations of the treated areas and the transition zones. As shown in Fig. 10(a) and (b) (surface) and 11(a) and (b) (in-depth), LP completely inhibits SCC and prevents macrocracking, except on very local zones where small surface cracks develop (Fig. 11b). On nontreated areas, cracks begin and develop perpendicular to the machining streaks. This observation is consistent with the RS amplitude, which is maximum

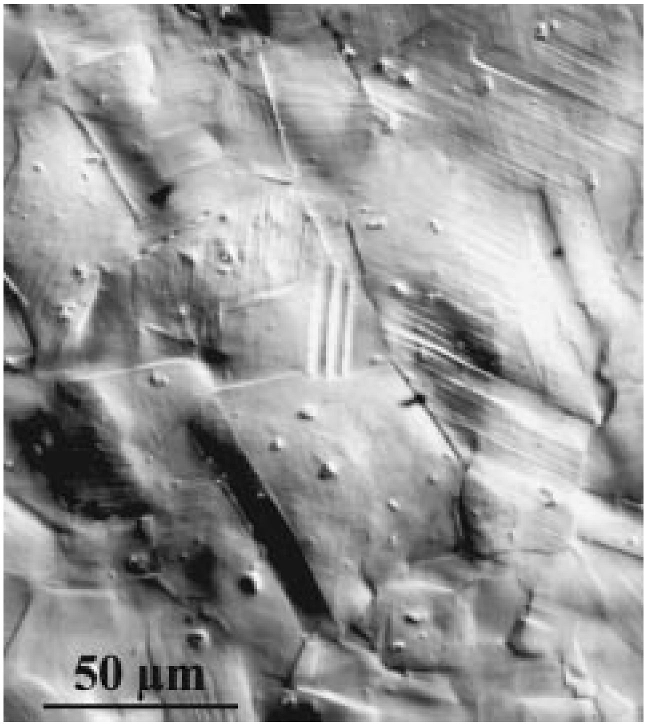


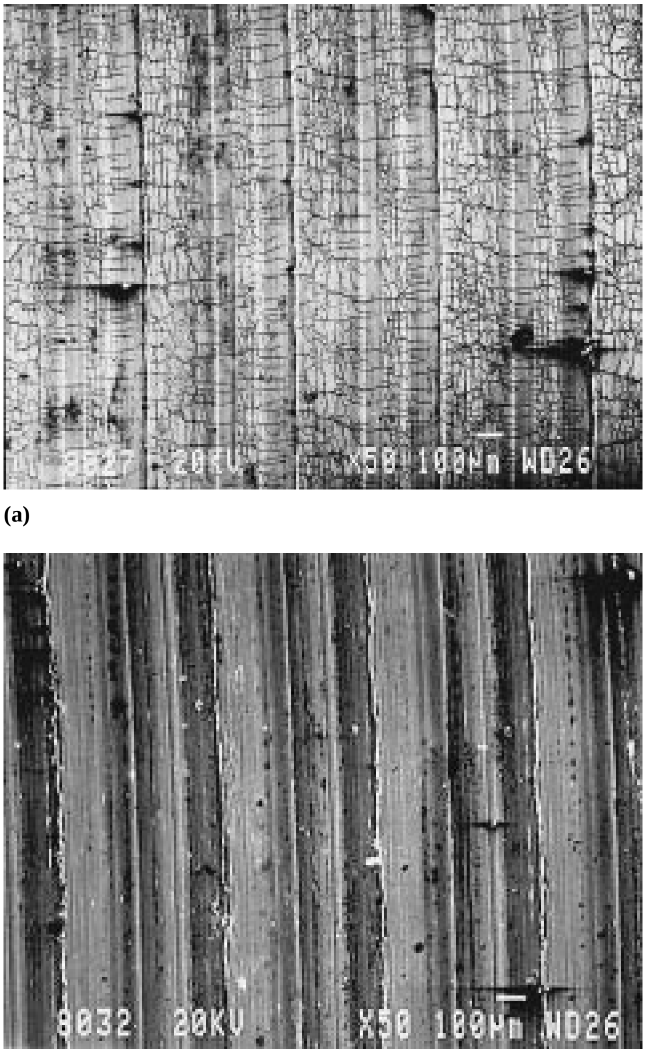
Fig. 9 Deformation bands in γ grains of 316L steel after LP 8 · 10^{13}W/m^2

in the longitudinal direction (+750 MPa in longitudinal and +400 MPa in transverse). These results confirm others obtained on 304 steel for nuclear plants, where LP was shown to suppress SCC in a boiling-water environment.[5]

5. Discussion

We have investigated the influence of LP and, more widely, of mechanical surface treatments on the corrosion behavior of three steels: two non passivable steels submitted to uniform corrosion in acid medium and an 316L stainless steel submitted to SCC in hot chloride medium. First, it has been shown that LP could increase the amplitude of compressive stresses at the surface of the three metals, with rather low modifications of their surface roughness.

Second, uniform corrosion results on G10380 and G41400 steels have evidenced very small modifications of rest potentials after LP. After a stabilization step, all rest potential values fluctuate around −0.55 V/SCE and no effect of LP can be evidenced (Fig. 5a and b). Consequently, G10380 and G41400 surfaces submitted to anodic dissolution in acid medium do not undergo any detectable mechanochemical effect without polarization. This indicates that future fatigue-corrosion tests should not be influenced by the electrochemical effects of LP in the absence of polarization. This result disagrees with Gutman's[9] theory about the modification of rest potentials with internal stresses, due to a modification of the Gibbs function *G* being independent of the sign of the stresses.

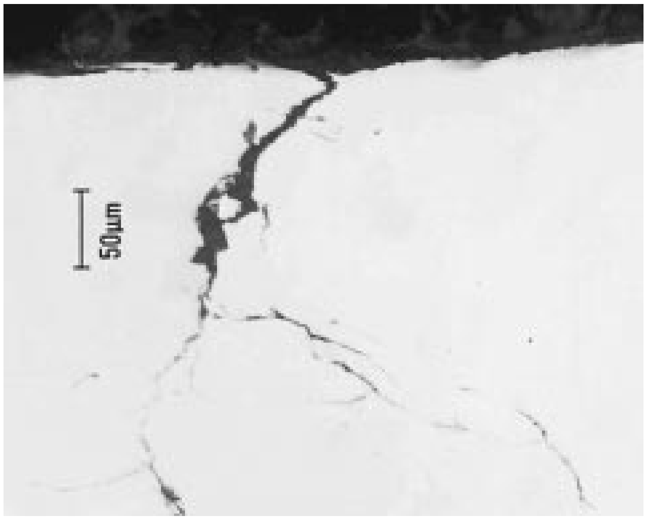


(a)

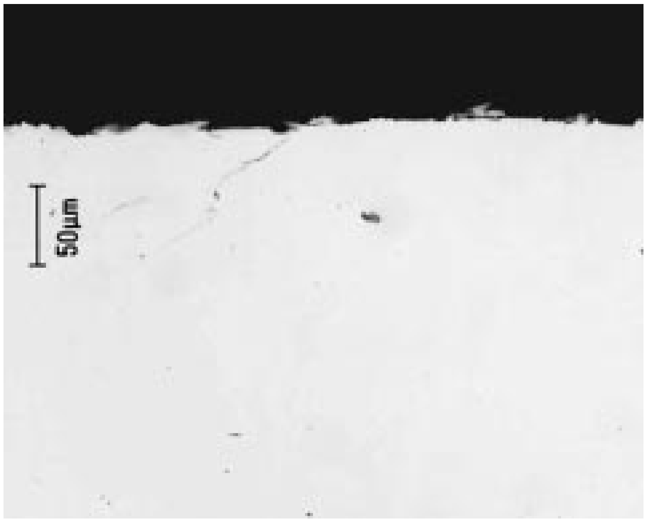
(b)

Fig. 10 Scanning electron microscope observation of surfaces for 316L steels after 24 h immersion in $MgCl_2$ 44%-153 °C: (**a**) nontreated and (**b**) laser peened

An effect of LP on polarization curves in acid medium is only visible in the case of G41400 (Fig. 6b). On G10380 steel, galvanic microcoupling between the α matrix and Fe_3C in the pearlitic structure may screen the influence of LP on the α matrix, as compared with the martensitic structure where carbon is in interstitial position. According to Ref 12, the cathodic discharge of hydrogen happens in two steps: an adsorption step ($H^+ + e^- \rightarrow H_{ads}$) and a recombination step ($2\ H_{ads} \rightarrow H_2$). Therefore,[9] small modifications of I_{cor} may be attributed to some changes in the electron work of exit or to a reduced diffusion of hydrogen in a work-hardened layer. Concerning the residual surface stresses, a relaxation seems to occur for three passes of LP, which is possibly due to a structural evolution of the martensite above a given plastic strain level.[13] This relaxation evidenced on RS amplitude (Fig. 3b) and integral widths (Fig. 4a) seems to influence the increase of surface reactivity evidenced between passes 2 and 3: the evolution of the dissolution rate (the lower I_{cor}) follows very closely the evolution of compressive stresses and work hardening (the higher the compressive and work-hardened state, the lower the



(a)



(b)

Fig. 11 Cross-sectional micrograph of the 316L surfaces after SCC tests in $MgCl_2$. (**a**) Nontreated: stress corrosion cracking. (**b**) LP treatment: microcracks localized at the surface

surface reactivity). Therefore, the electrochemical reactivity of G41400 in the $HKSO_4$-0.3 M acid medium appears to be directly linked to its work hardening and residual stress state.

The SCC tests on 316L (Fig. 10a and b and 11a and b) simply confirm the potential of LP as a tensile stress inhibitor to stop cracking in corrosive environments. If we compare with the usual stress generators such as shot peening, LP affects deeper layers (nearly 1 mm) with a reduced work-hardening level.

6. Conclusion

We have examined for the first time the effects of LP on the uniform corrosion behavior of G10380 and G41400 steels and on the SCC behavior of 316L steel. In both cases, LP resulted in a modification of residual surface stresses and work-hardening levels leading to specific changes in the surface reactivity.

In most of the free corrosion experiments, LP influence has been shown to be rather low, but, under polarization, a 30 to 120% reduction of G41400 corrosion current in acid medium has been evidenced. This seems to reveal a mechanochemical effect possibly due to a modification of the hydrogen-metal interaction. More widely, and beyond the simple effect of LP on steel reactivity, this result indicates that mechanical surface states such as compressive stresses can lead to an inhibiting effect on dissolution rates.

Second, on 316L steel, the heterogeneous plasticization generated by LP allows for suppression of the tensile state due to surface preparation before treatment and for inducement of an isotropic compressive state on a millimetric layer. This allows the prevention of any kind of stress corrosion cracking in boiling chloride medium without occurrence of problems in the transition zones.

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