# Role of shot-peening on hydrogen embrittlement of a low-carbon steel and a 304 stainless steel

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Shot-peening surface treatments were performed on a low-carbon steel and a 304 stainless steel. The influence of residual stresses on hydrogen permeation and distribution was investigated. The results were correlated with the tensile properties measured in air after cathodic charging and in a NACE medium under slow load-rate straining. The role of shot-peening on the hydrogen embrittlement of the low-carbon steel is strongly dependent on the severity of the hydrogen environment and testing conditions. The detrimental effect of shot-peening on the hydrogen embrittlement of the stainless steel is related to phase transformations induced by cold work.

## 1. Introduction

The reduction of hydrogen entry in metals and the design of steels with microstructural features (trapping sites) which may play a beneficial role [1, 2] when hydrogen penetration cannot be avoided, are of major interest in the prevention of hydrogen embrittlement (HE) of engineering materials. Surface treatments can lead to superficial changes in the structure at the atomic scale (amorphization), the microstructure, the local chemistry, the stress state, etc. [3–5]. These modifications may provide an improvement in the mechanical behaviour as well as an increased resistance of the materials surface to wear and corrosion [6]; they may also help to delay the penetration of hydrogen in metallic structures when HE can occur.

Surface treatments such as superficial melting with laser beams [7], implantation of nitrogen [8] or shotpeening, are already used industrially to improve the surface properties of steels. Shot-peening is assumed to reduce the permeability of ferritic steels to hydrogen due to the creation of compressive stresses on the surface [9] but few details are available to account for this beneficial effect.

Because HE and stress corrosion cracking are important problems in fcc and bcc steels, the improvement and the risks brought by these surface treatments have to be assessed. This paper presents some results on the influence of shot-peening on the HE sensibility of a low-carbon steel and a 304 stainless steel. The effect of this surface treatment on the materials microstructure and on hydrogen permeation and distribution was investigated and correlated to the tensile properties measured in the presence of different hydrogen environments.

## 2. Experimental procedure

2.1. Materials and shot-peening conditions The chemistry of the low-carbon steel and the 304 stainless steel is reported in Table I, together with the heat treatments given to the 1 mm thick sheets. The corresponding microstructures are characteristic of a  $30 \,\mu\text{m}$  grain size austenitic structure, and a ferritic structure with the same grain size and a small amount of globular perlite.

Shot-peening was conducted with ceramic microballs on one face of 1 mm thick sheets for hydrogen permeation studies and on each side of flat tensile specimens for the testing of the mechanical properties.

The different treatments (1 and 2) were performed by changing the speed of the projectiles and thus the thickness of the cold-worked metal. The main features of these shot-peening treatments are listed in Table II.

## 2.2. Techniques

The thickness of the cold-worked layer formed on the peened surface of the samples was determined by microhardness measurements on the cross-section of the samples, by X-ray diffraction (XRD), and by optical microscopy when a phase transformation was observed.

The residual stresses induced by the shot-peening treatments were measured by XRD [10]. A sub-

Material and heat treatment	Wt%			p.p.m. (wt)						
	Cr	Ni	Mo	Mn	С	Р	Si	S	Al	Cu
Low-C steel 920 °C, 1 h air $-q$ . + 700 °C, 24 h	0.029	0.027	_	0.20	530	110	110	80	450	140
304 stainless steel 1050 °C, 5 mn, air – q.	18.0	9.4	0.04	1.4	640	210	6300	40	_	-

TABLE I Chemistry and heat treatments

TABLE II Shot-peening conditions.

Treatment 1	Treatment 2
425	425
3–4	8-10
125	125
	425 3–4

sequent annealing at 320 °C for 1 h was given to some samples presenting the largest cold-worked zone, in order to study the effect associated with the relief of superficial stresses [11]. The corresponding change in residual stress was characterized by XRD.

Tensile tests allowed a study of both the role of shot-peening on the mechanical properties of the steel and the effect of hydrogen on specimens with and without a surface treatment. The tensile tests were performed on small tensile samples (gauge length 16 mm × 2 mm × 1 mm) under constant strain rate ( $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ ) at room temperature in air, or under slow load-rate conditions (16.9 ± 0.2 N min<sup>-1</sup>), in the NACE solution composed of 5% sodium chloride and 0.5% acetic acid saturated with H<sub>2</sub>S gas at 1 atm [12].

To assess the role of internal hydrogen on the mechanical properties of the steels, hydrogen was introduced in the tensile specimens by cathodic charging using a conventional potentiostatic technique. The charging procedures were: 1N H<sub>2</sub>SO<sub>4</sub>, 20 °C, 3 h, V = -600 mV/SCE for the low-carbon steel; molten salts, 150 °C, 5 h,  $V = -800 \text{ mV/Ag-Ag}^+$  [13] for the stainless steel. The tensile test was performed immediately after charging to avoid any hydrogen desorption. The role of the high fugacity of the external hydrogen is evinced by the slow load-rate tests in the NACE medium.

Potentiostatic permeation tests were performed on 1 mm thick membrane of low carbon steel in a 0.1 N NaOH solution at -1.35 V/SCE using a procedure previously described [8].

The tritium autoradiography technique [14] allowed a comparison of the tritium distribution and trapping on the steels surfaces with and without shotpeening after cathodic charging under the same conditions as for the tensile specimens.

# 3. Characteristics of the cold-worked layer after shot-peening

## 3.1. Low-carbon steel

During shot-peening, various changes occur on the surface: the roughness of the surface increases as shown in Fig. 1a. Small holes and cracks are produced



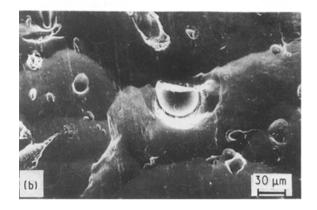


Figure 1 Microgeometrical aspect of a peened surface on a low-carbon steel.

under the projectiles' impacts and some microballs remain wedged in the metal (Fig. 1b). Furthermore, the density of dislocations is increased [15]. For both shot-peening conditions, the microhardness measurements (p = 25 g) indicate the same enhancement of the surface hardness (230 H<sub>v</sub>) when compared to the microhardness of the matrix (140 H<sub>v</sub>). No phase transformation is to be expected in the low-carbon steel; this point was checked by optical microscopy.

The results of thickness measurements are shown in Table III. The differences in the absolute values can be explained by the scatter in the microhardness data and by the destructive procedure used for the measurement of the surface stress by the XRD technique [10].

After annealing for 1 h at 320 °C, the surface stress decreases, whereas the extent of the peened layer remains quasi constant. In this case the magnitude of the compressive stress is constant over the entire section of the metal affected by the surface treatment (Fig. 2), instead of the decreasing profile observed on the non-annealed samples.

The extent of the cold-worked layer is larger for the more severe shot-peening condition. The magnitude of

TABLE III Thickness of the cold worked layer after shot-peening.

Steel	Shot-peening treatment	Thickness of the affected zone (μm)		
	110.	X-rays	microhardness	
Low-C steel	1	60-70	100-150	
	2	120-150 (150-180) <sup>a</sup>	150-200	
Stainless steel	1	150-180	50-70	
	2	200-250	100-150	

<sup>a</sup> The thickness of the cold-worked layer after annealing at  $320 \,^{\circ}\text{C}$  for 1 h.

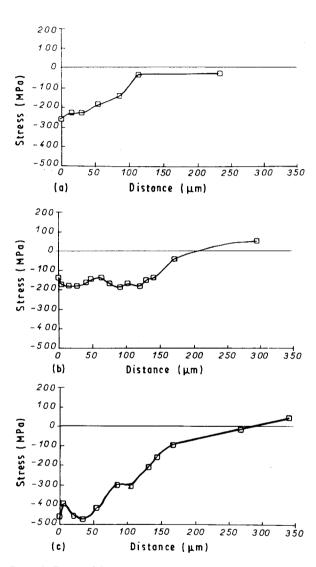


Figure 2. Extent of the compressive stress on the surface of (a, b) the low-carbon steel after shot-peening: (a) treatment 2, (b) treatment 2 + annealing, and (c) 304 stainless steel, after treatment 2.

the compressive stresses induced by the shot-peening treatment is reported in Table IV. The curves representing the stress gradient in the cold-worked layer are plotted in Fig 2.

The data of Tables III and IV for the low-carbon steel show that there is no significant increase in the magnitude of the surface stress after shot-peening condition 2, but only an increase in the extent of the zone in compression.

## 3.2. 304 stainless steel

The superficial microhardness of the peened stainless steel was found to depend slightly on the shot-peening conditions. The measured values are, as expected, larger than the values found in the case of the low-carbon steel (400 and 350  $H_V$  compared to 200  $H_V$  in the matrix).

TABLE IV Magnitude of the compressive stress on the surface after shot-peening

Steel	Shot-peening treatment no.	Maximum surface stress (MPa)
Low-C steel	1	- 280
	2	-250
	2 + 1 h, 320 °C	-180
Stainless steel	1	- 300
	2	- 450

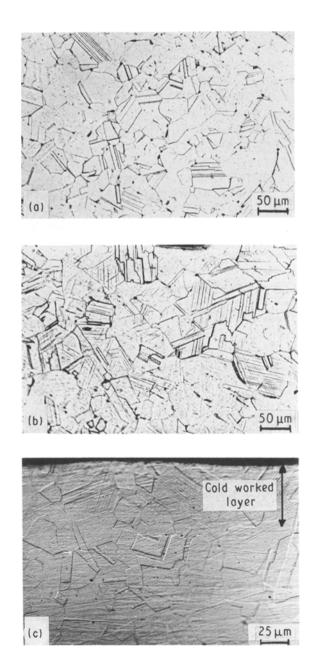


Figure 3 Microstructural transformations induced by shot-peening in the near surface of a 304 stainless steel: (a) untreated, (b) treatment 2, (c) treatment 2 cross-section.

After both shot-peening treatments the magnitude of the stresses in compression increases with the speed of the projectiles (Table IV). By comparison with the low-carbon steel, the magnitude of the stresses induced by shot-peening is larger on the 304 stainless steel due to the larger tenacity of the austenitic structure. The formation of martensite associated with the cold work induced by shot-peening was evinced by optical microscopy (Fig. 3). The volumic fraction of martensite on the peened surface is of the order of a few per cent.

## 4. Hydrogen effect on the mechanical behaviour after shot-peening

#### 4.1. Low-carbon steel

The influence of shot-peening and preliminary cathodic charging on the tensile properties in air of the lowcarbon steel, is illustrated in Table V. The main effect of the surface treatment is a significant decrease in the elongation (46% for treatment 1 and 48% after treatment 2) of uncharged samples. Hydrogen charging of peened specimens has no measurable effect on the mechanical characteristics unless an annealing treatment is given after shot-peening treatment 2; in this case the elongation capacity is slightly decreased.

The beneficial effect of shot-peening on H.E. of the low-carbon steel depends on the testing conditions: slow load-rate experiments performed in the  $H_2S$ containing environment indicate a larger susceptibility to HE after shot-peening, as shown by the results of Table VI. The slight improvement in the mechanical properties after annealing (smaller embrittlement index) may, in this case, be related to a decrease in the number of potential sites for the formation of microcracks under large hydrogen fugacities; this would be the result of triaxial stress relief at critical trapping sites.

The fracture surfaces of the low-carbon steel with and without a surface treatment evince a fully ductile fracture mode after straining in air (Fig. 4a and b). Very little change is observed on the hydrogenated specimens except for a few decohesions on the surface of the untreated samples. This mode turns to transgranular with decohesion areas related to precipitates or inclusions when the samples are strained and broken in the  $H_2S$  environment (see Fig. 4c and d). Cracks are found on the external surfaces of the samples, due to the severity of the charging conditions

TABLE VI Tensile properties of peened low-carbon steel in the presence of external hydrogen ( $H_2S$  environment)

Shot-peening treatments and charging condition	σ <sub>UTS</sub> (MPa) ns	Reduction of area (%)	F (%) <sup>a</sup>
Untreated:	326	84	
uncharged (air)			26
H <sub>2</sub> S	345	62	
1: uncharged	344	88	33
$H_2S$	345	59	33
2: uncharged	350 (350) <sup>b</sup>	88 (88) <sup>b</sup>	40 (40)h
H <sub>2</sub> S	360 (353) <sup>b</sup>	45 (51) <sup>b</sup>	49 (42) <sup>b</sup>

<sup>a</sup>  $F^* = (RA_0 - RA_H)$ . 100/RA<sub>0</sub> where RA<sub>0</sub> is the reduction of area (%) measured on uncharged samples, and RA<sub>H</sub> is the reduction of area (%) measured on samples strained in the H<sub>2</sub>S medium. <sup>b</sup> The mechanical properties of the peened samples given an annealing treatment of 1 h at 320 °C.

during straining and to the presence of a cold-worked external layer.

#### 4.2. Stainless steel

The tensile properties in air indicate that, beside a slight increase in yield strength and ultimate tensile strength (UTS) due to the superficial cold work, the surface treatment has no significant effect on the deformation ability of uncharged 304 specimens. The effect of internal hydrogen (Table VII) on untreated samples is less pronounced than was previously measured on a similar alloy for the same charging conditions [16]; this is presumably a consequence of the strong HE dependence on the grain size (30 µm instead of 100  $\mu$ m as previously) in these  $\gamma$  structures [17]. Peened samples exhibit a different behaviour depending on the shot-peening conditions. No detrimental effect of the treatment is observed for the less severe conditions (treatment 1). The elongation loss is much more important when the surface treatment 2 favours a highly cold-worked surface layer with a larger amount of martensite on the surface. This is in agreement with the high HE sensitivity of coldworked 304 containing  $\alpha'$  martensite, whereas the presence of  $\varepsilon$  martensite associated with a low cold work level was shown to be beneficial [16].

The effect of external hydrogen (Table VIII) on UTS and reduction in area (RA) is more important; in this case, peened samples are always more embrittled, the

TABLE V Tensile properties of peened low-carbon steel in the presence of internal hydrogen

Shot-peening treatment and charging conditions	E <sub>0.2%</sub> (MPa)	$\sigma_{\text{UTS}}$ (MPa)	E <sub>h</sub> (%)
Untreated: uncharged (air)	248	325	33.7
charged $H_2$ , 20 °C, 3 h	236	333	27.6
1: uncharged	253	328	18
charged $H_2$ , 20 °C, 3 h	260	333	20.2
2: uncharged	250	337	17.4
	(260) <sup>a</sup>	(329) <sup>a</sup>	(16.9) <sup>a</sup>
charged H <sub>2</sub> , 20 °C, 3 h	252	336	17.3
Margod 112, 20 0, 0 1	(260) <sup>a</sup>	(327) <sup>a</sup>	(14.2) <sup>a</sup>

<sup>a</sup> The mechanical properties of the peened samples given as annealing treatment of 1 h at 320 °C.

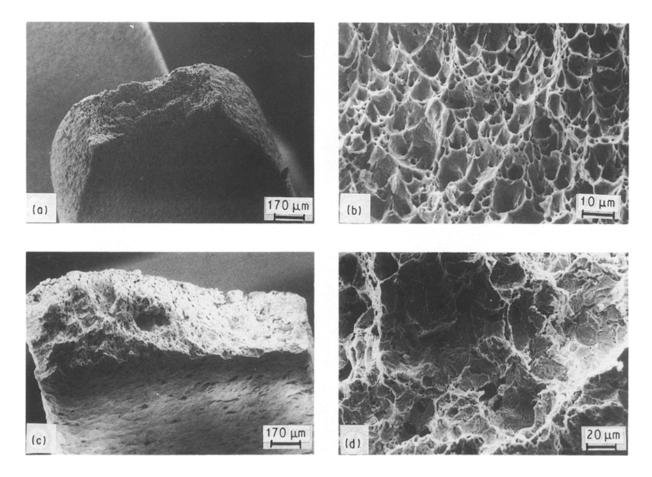


Figure 4 Role of shot-peening and slow load-rate testing in  $H_2S$  environment on the fracture surface of a low-carbon steel. (a, b) Tested in air, (c, d) tested in  $H_2S$ .

TABLE VII Tensile properties of peened 304 stainless steel in the presence of internal hydrogen

Shot peening treatments	E <sub>0.2%</sub>	$\sigma_{\text{UTS}}$	$E_{\mathbf{h}}$	$F = \frac{E_{\text{unch.}} - E_{\text{ch.}}}{E_{\text{unch.}}}$
and charging conditions	(MPa)	(MPa)	(%)	(%)
untreated: uncharged (air)	243 ± 7	659 ± 4	58.4 ± 3.9	
charged $H_2$ , 150 °C, 5 h	$258 \pm 15$	$640 \pm 18$	49.4 <u>+</u> 2.9	15.4
1: uncharged	284	674	61.9	
charged H <sub>2</sub> , 150 °C, 5 h	299	648	53.7	13.2
2: uncharged	308	679	59.0	
charged H <sub>2</sub> , 150 °C, 5 h	405	615	28.0	52.5

TABLE VIII Tensile properties of peened 304 stainless steel in the presence of external hydrogen (H<sub>2</sub>S environment)

Shot-peening treatments	$E_{0.2\%}$ $\sigma_{\rm UTS}$ $E_{\rm h}$		$E_{ m h}$	Σ	$F = \frac{\Sigma_{\rm unch.} - \Sigma_{\rm ch.}}{\Sigma_{\rm unch.}}$
and charging conditions	(MPa)	(MPa)	(%)	(%)	(%)
Untreated uncharged (air)	262	646	67	71.5	
H <sub>2</sub> S	316	632	41	55	23
1: uncharged	290	646	61	72.6	
H <sub>2</sub> S	322	546	31.3	48.7	33
2: uncharged	406	666	53.5	70.5	
H <sub>2</sub> S	424	548	29.5	40	43

RA loss increasing with the severity of shot-peening conditions. This can be easily explained by the fact that, for these testing conditions, the material encountered a plastic deformation during hydrogen charging; this means that an increasing amount of martensite is formed on the surface exposed to cathodic hydrogen. The  $\alpha'$  martensite pre-existing on the peened surface or formed during the deformation favours the hydrogen entry into the bulk of the specimen because the time required for a test (2-4 h) is sufficient for a significant diffusion of hydrogen into the martensitic phase. Additional transport by dislocations could

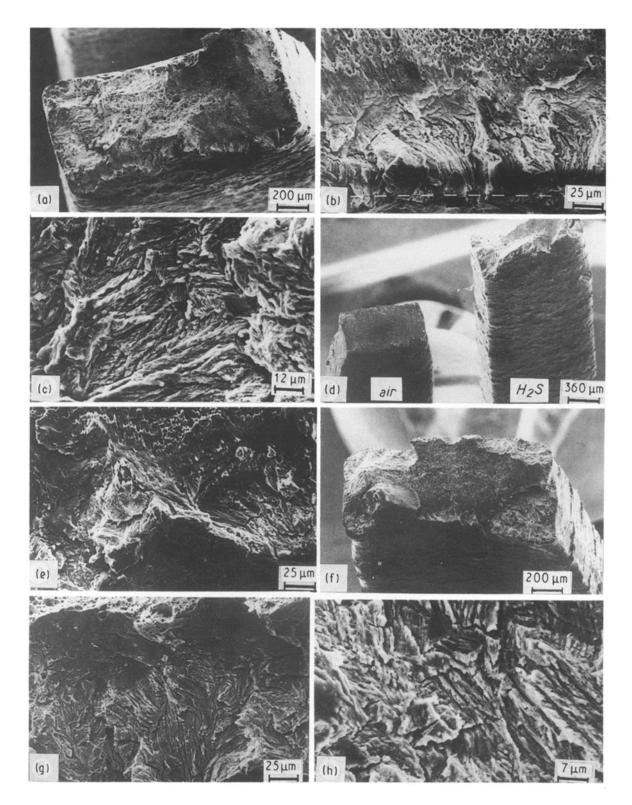


Figure 5 Role of shot-peening and slow load-rate testing in  $H_2S$  environment on the fracture surface of a 304 stainless steel: (a-c) untreated, (d, e) treatment 1, (f-h) treatment 2.

favour the hydrogen entry into the specimen. Furthermore, the  $\alpha'$  martensitic phase is more easily embrittled by hydrogen discharged on the surface. This explains the main features of the fracture surfaces (Fig. 5): a very limited extent of cracking and the existence of an external brittle zone for the untreated specimen (Fig. 5a-c); and a large number of superficial cracks in the peened layer while the bulk of the sample remains ductile (Fig. 5d, f). The external brittle zone is typical of an  $\alpha'$  martensite-rich phase (Fig. 5 h); its extent increases with the severity of the shot-peening treatment (Fig. 5e, g).

## 5. Influence of shot-peening on the hydrogen permeation in the low-carbon steel

Typical permeation curves obtained with the peened side of the sample facing the cathodic compartment of the cell are plotted on Fig. 6. The values of usual

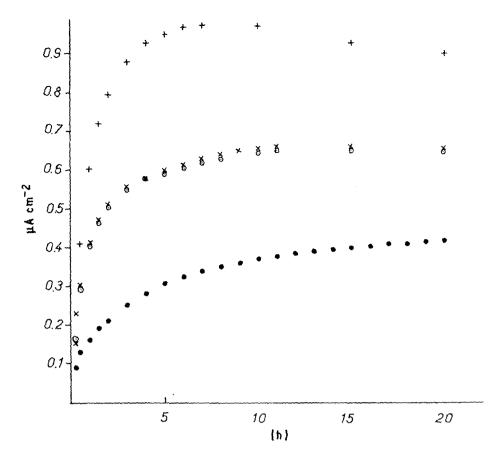


Figure 6 Role of shot-peening on hydrogen permeation in a low-carbon steel. (+) Untreated steel, (x) treatment 1,  $(\bigcirc)$  treatment 2,  $(\bullet)$  treatment 2 + annealing.

TABLE IX Permeation data obtained on the low-carbon steel as a function of the shot-peening severity and the location of the peened face in the permeation cell

Shot-peening	Permeation data				
treatment; location of the permeation cell	$P_{\infty}(10^9 \text{ cm}^{-2} \text{ s}^{-1})$	$D_{t,1}(10^7 \text{ cm}^2 \text{ s}^{-1})$	$D_{b,t}(10^6 \text{ cm}^2 \text{ s}^{-1})$		
1: Cathodic compartment	6.7	3.6	1.1		
2: Cathodic compartment	6.9	3.9	1.4		
Detection compartment	7.6	0.8	0.45		
Untreated steel	8.2	3.3	1.3		
2, +1 h, 320 °C: Cathodic compartment	4.7	1.5	2.4		

characteristic times used for the apparent diffusion coefficient  $(D_{app})$  computation (when Fick's laws solutions are valid), the corresponding diffusion coefficients and the steady-state permeability coefficients are reported in Table IX. When compared to the untreated material, the hydrogen flow through peened specimens is slightly reduced but no difference between the two shot-peening treatments could be found. This indicates that the permeability of peened samples to hydrogen is not dependent on the thickness of the cold-worked layer. Furthermore, compressive stresses on the surface do not impede significantly the hydrogen diffusion in the steel, in the case of "soft" charging conditions.

Although Fick's laws may not be valid for the determination of apparent diffusion coefficients, the data of Table IX show that shot-peening does not induce any change in the diffusivity, because the break-through time (b.t.) and the time-lag (t.l.) values are very similar with or without the surface treatment. The same conclusion can be drawn from the degassing transients which illustrate only a slight decrease of the degassing kinetics of hydrogen in the case of the peened samples.

When permeation tests are conducted on samples with the peened side facing the detection compartment of the cell, the main influence of the cold-worked layer is to induce a large decrease of the hydrogen diffusivity, as shown by the increase in the breakthrough time and the time-lag values. In this case, the permeability coefficient is practically unchanged by comparison with the material without surface treatment.

These results seem to account for a dependency of the apparent diffusion coefficient on the concentration of hydrogen present at the interface solution/peened surface or at the interface metal/peened metal. When the peened side is located on the exit face of the permeation membrane, the hydrogen concentration available for the diffusion through the cold-worked metal is small, due to the concentration gradient in the thickness of the specimen; thus, the time needed to fill the great number of traps (dislocations, point defects, etc.) is larger than in the case where the cold-worked surface faces the charging chamber of the cell. In this latter configuration, the hydrogen activity (determined by the electrochemical conditions) is maximum. The decay of the hydrogen flow recorded on the peened side of the sample is also slower, accounting for a smaller hydrogen diffusivity through the coldworked layer.

The largest drop in permeability was observed for the peened samples annealed at 320 °C for 1 h. Moreover, when compared to the corresponding peened and non-annealed specimens, the diffusion coefficient is decreased (by a factor of 3). The annealing treatment induces a decrease in the magnitude of the compressive stress; this cannot account for the present permeation data. The smaller permeability coefficient and diffusivity must presumably be related to the creation of dislocation walls and/or to a process of void coalescence during annealing and thus to the creation of defects trapping hydrogen more efficiently than dislocations formed during the shot-peening treatment.

## 6. Influence of shot-peening on hydrogen trapping

After cathodic charging of peened (treatment 2) lowcarbon and 304 stainless steel samples, the macroscopic distribution of tritium was observed on the surface of the specimens by the film technique using Amersham films. The images obtained after the photographic processing of the autoradiographic emulsion show an enhancement of the tritium concentration on that part of the specimen corresponding to the surface cold-worked by shot-peening. This was observed for both steels as shown in Fig. 7. The reason why this trapping phenomena could not be clearly evinced in the low-carbon steel during the permeation tests may probably be related to the activity of hydrogen evolving on the surface of the samples. In the case of cathodic polarization in 0.1 N NaOH, the hydrogen concentration is much smaller than in  $H_2SO_4$ , and the trapping is less efficient. Additional permeation experiments in  $H_2SO_4$  are required to verify this point.

## 7. Discussion

The role of shot-peening on the hydrogen embrittlement of a low-carbon steel is strongly dependent on the severity of the hydrogen environment and testing conditions. When exposed to internal hydrogen introduced without irreversible damage in the material, shot-peening improves the HE resistance of a lowcarbon steel. This beneficial effect is more related to changes in the hydrogen distribution and trapping than to a strong reduction in hydrogen entry in the material. A more homogeneous distribution of hydrogen in the external cold-worked layer decreases its local activity and then increases the critical concentration required for cracking, while the presence of compressive stress has an additional beneficial effect on crack initiation.

When hydrogen entry is not associated with the formation of defects in the material ("mild" charging conditions) shot-peening does not significantly change the kinetics of hydrogen entry. Previous observations of a strong reduction in hydrogen diffusivity in coldworked material [18] are to be related to the formation of blisters during the permeation measurements because of severe charging conditions.

In the present case, the surface treatment slightly decreases the hydrogen stationary flow through the permeation wall. However, no significant relationship was found between the extent of compressive stress on the surface and the reduction in hydrogen flow. The possible reduction by a compressive stress of the amount of diffusible hydrogen [9, 19–22] seems to be balanced in this low-resistant bcc steel by an increase

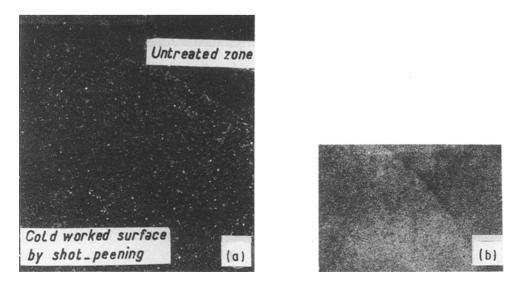


Figure 7 Role of shot-peening on the tritium distribution in (a) a low-carbon steel and (b) a 304 stainless steel: the density of white dots imaging tritium trapping is larger on the peened surface of the samples.

in the amount of reversible traps which favours an increase in the hydrogen stationary flow.

The particular behaviour of the samples given a stress relief treatment at 320 °C for 1 h after shotpeening can be explained by the formation of dislocations cells (and void coalescence) with a larger hydrogen trapping energy which reduce the apparent diffusion coefficient of hydrogen and favour a more heterogeneous distribution of hydrogen in the coldworked zone. The corresponding larger hydrogen concentration could promote a local cracking in the presence of an applied stress (Table V).

The beneficial effect of shot-peening on the blistering of low-carbon steel occurring under severe cathodic charging conditions (in the presence of As<sub>2</sub>O<sub>3</sub> as a "poison" in the present case) is illustrated in Fig. 8. The blisters are readily formed on the untreated part of the sample's surface while no local superficial damage was observed on the peened surface. The blistering is known to be the result of a preferential hydrogen trapping on a limited number of defects (sulphides or carbides) in the annealed material [23]. On the other hand, numerous sites are available for trapping in the cold-worked layer of the peened samples as indicated by the autoradiographic observations of tritium distribution obtained with a large hydrogen fugacity (cathodic charging in  $H_2SO_4$ ); this favours, for a given amount of hydrogen discharged on the surface, a more homogeneous hydrogen distribution in the near surface and reduces the local blistering. However, for long charging times, the cold-worked layer is saturated with hydrogen and/another cracking mode occurs at the interface peened/annealed material where the concentration of trapping sites is too low to accommodate the large hydrogen activity.

The hydrogen saturated cold-worked layer also becomes more sensitive to HE as does any hydrogenated cold-worked steel submitted to tensile stress [11]. This explains the behaviour observed in slow loadrate experiments in  $H_2S$ : the combined effect of severe charging conditions and of a continuous charging during the long period (2-4 h) required for plastic deformation, makes the embrittlement of the superficial cold-worked zone easier, and explains the larger HE susceptibility of peened samples and the corresponding fracture surfaces (Fig. 4). Moreover, tensile stresses which are known to favour HE are present in the bulk of the peened samples and can play an additional role; this could explain the beneficial effect brought about by the stress relief treatment on HE sensitivity (Table VI) because the magnitude of the tensile stresses is supposed to be smaller after annealing.

The detrimental effect of shot-peening on the HE of 304 stainless steel is related to the phase transformation induced by cold work. The  $\alpha'$  martensite is known to enhance both hydrogen entry and HE in austenitic stainless steels [17]. The HE susceptibility of peened samples must be mainly related to the amount and distribution of this phase in the samples. The effect of the testing conditions on the extent of the embrittlement is a consequence of differences in the amount of hydrogen in the specimens.

For the internal hydrogen case, the precharging of the samples at 150 °C favours a large hydrogen permeability in the material in which the amount of  $\alpha'$ martensite is only controlled by the surface treatment. In slow load-rate experiments performed at room temperature, the hydrogen diffusivity is lower but the hydrogen fugacity on the surface is larger (H<sub>2</sub>S "poison" effect) and the amount of  $\alpha'$  martensite increases during the whole experiment, allowing a significant hydrogen entry by diffusion, as the time of the tests is quite long. This explains the larger HE susceptibility measured under these conditions on samples containing initially no (untreated) or a little (treatment 1) amount of  $\alpha'$  martensite (Tables VII and VIII).

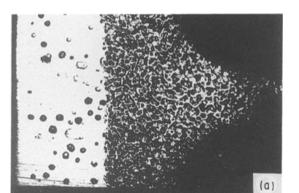
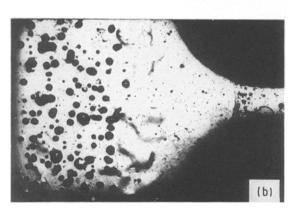
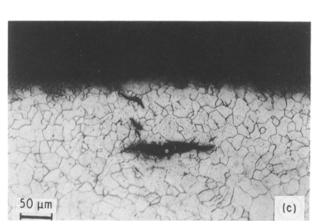


Figure 8 Role of shot-peening on hydrogen blistering of a lowcarbon steel (cathodic charging in 1N H<sub>2</sub>SO<sub>4</sub> + As<sub>2</sub>O<sub>3</sub> 50 mg l<sup>-1</sup>, V = -600 mV/ECS): (a) as-peened surface,  $\times 8$ , (b) repolished surface,  $\times 8$ , (c) cross-section in the untreated part of the specimen.





## 8. Conclusion

The role of shot-peening on the hydrogen embrittlement is dependent on the material and on the hydrogen environment. In the present conditions where the peened volume is small compared to the volume of the untreated metal shot-peening reduces the HE susceptibility of low-carbon steel when the hydrogen activity is small. This is a consequence of the more homogeneous distribution of hydrogen in the coldworked superficial layer and of the beneficial effect of compressive stress on crack initiation. In a severe hydrogen environment ( $H_2S$ ), shot-peening is detrimental.

The effect of shot-peening on the HE susceptibility of unstable 304 stainless steel is always detrimental; it is related to the presence of  $\alpha'$  martensite in the coldworked layer. The dependence of the embrittlement on the testing conditions is attributed to the influence of this phase on hydrogen entry and distribution in the material.

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