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ENGINEERING RESIDUAL COMPRESSIVE STRESS TO AVOID HYDROGEN INDUCED CRACKING IN METALS AND ALLOYS

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ABSTRACT
Benefits of laser-peening surface treatments have been demonstrated for stress-corrosion cracking and extension of fatigue lifetimes. Hydrogen appears to degrade fatigue lifetimes, thus laser peening has potential to greatly influence hydrogen storage and transportation systems. In this study, we investigate the effects of internal hydrogen on the tensile properties of alloy 22, corrosion-resistant a nickel-based alloy. Laser-peening is found to have no significant effect on the solubility of hydrogen in thermally precharged alloy 22, and have tensile ductility slightly reduced compared to base materials with internal hydrogen.

INTRODUCTION
Hydrogen-induced embrittlement (or degradation) in metals occurs in a number of forms but the common features are residual or applied tensile stress and the presence of atomic hydrogen or hydride compounds in the material structure. A specific example is the cracking of weldments or hardened steels when exposed to conditions that allow hydrogen to diffuse into the component. Hydrogen embrittlement phenomena are not completely understood and the detection of hydrogen-induced damage (before sudden catastrophic failure) remains a major technical challenge [1, 2]. Hydrogen-assisted fracture is often described in terms of stress corrosion cracking. Issues of importance to hydrogen users include:

- <u>Permeation:</u> hydrogen has high permeation rates through low alloy pressure vessel and pipeline steels (as much as 10^5 greater than stainless steels)
- <u>Hydrogen-assisted fracture:</u> dissolved hydrogen assists nucleation and propagation of cracks in steels by enhancing plasticity and affecting the strength of interfaces such as grain boundaries.
- <u>Hydrogen attack:</u> in some systems under specific environmental conditions (such as high temperature), dissolved hydrogen can irreversibly react with the microstructure to produce brittle phases or in situ cracks.

Recent experiments have demonstrated that laser peening very effectively converts residual tensile stress in metals to high-magnitude and relatively deep compressive stress [3]. Laser peening virtually eliminates the occurrence of intergranular stress corrosion cracking and crack-growth in Ni-based alloys (Alloy 600) and weldments [4, 5].

Laser peening uses a high peak-power laser (GW/cm^2 range) to generate a plasma on the material surface as seen in Figure 1. This plasma is inertially confined to the material surface by a thin layer of water. The resulting shock wave (several GPa) is forced into the material surface, leaving a high magnitude of residual compressive stress (MPa range) on the surface. A sacrificial ablative layer is used to generate the plasma to prevent thermal effects from melting the metal surface.

In this report, we describe the effects of laser peening and internal hydrogen on the tensile properties of alloy 22. In particular, we focus on degradation of ductility due to thermal precharging with hydrogen from the gas phase. We also explore the effects of the compressive residual stresses imparted by laser peening on the solubility of hydrogen.

EXPERIMENTAL PROCEDURES

The composition of the alloy 22 plate that was used in this study is provided in Table 1. Alloy 22 (UNS N06022) is a nickel-base alloy for use in chemical processing due to its excellent resistance to environmental effects.

ASTM E8 subsized rectilinear tensile bars were machined from the plate stock. The specimens had a square cross section of 6.4 x 6.4 mm. The laser peened tensile bars were treated at 10 GW/cm^2 with an 18ns pulse width. The rectangular beam size used is 2.8 mm x 3.1mm with the laser energy set to 16.2 J/pulse. Each laser shot was offset by 3% with respect to its adjacent neighbor. Each surface was laser peened three separate times to insure uniform coverage and an ablative coating was used during each layer of laser peening treatment.

The effects of laser peening on the strength of the material were probed with Vicker's microhardness. Hardness was measured on polished cross sections of tensile specimens at 0.1 mm steps with a load of 100 grams. The gripping surfaces of the tensile bars were avoided since deformation on these surfaces due to gripping was found to substantially increase the hardness to a depth of 0.5 to 1 mm.

A knife-edged extensometer with a gauge length of 12.7 mm (0.5 inch) was used for strain measurements during tensile testing. Testing was performed at a constant displacement rate corresponding to strain rate of approximately ~1.8x10^{-3} s^{-1} (in the plastic regime prior to necking). The yield strength (0.2% offset, S_y) and tensile strength (maximum engineering stress, S_u) are reported as well as the uniform elongation (engineering strain at maximum load, El_u) and total elongation (engineering strain at failure, El_t). Two or three specimens were tested for all conditions.

Specimens were tested in the as-machined and laser-peened conditions. The effect of internal hydrogen was studied by precharging both as-machined and laser-peened materials in 138 MPa hydrogen gas at 573 K. In addition, witness specimens (25 mm long cylinders with a diameter of 6.4 mm) of both as-machined and laser-peened materials were precharged simultaneously with the tensile specimens. Precharging was conducted for 34 days to ensure uniform hydrogen saturation through the thickness of the specimens. Details of the thermal precharging procedures are given elsewhere [6].

Upon removal from the thermal precharging apparatus, specimens were stored in a freezer at about 253 K until testing, less than 3 days. Specimens were warmed to room temperature before testing. Broken specimens were also stored at 253 K to prevent hydrogen off-gassing prior to hydrogen analysis. The witness samples, as well as approximately 6 mm thick pieces cut from the grip sections of the tensile specimens, were sent to a commercial testing laboratory for hydrogen analysis by hydrogen extraction (LECO-type analysis).

RESULTS

An optical micrograph of the hardness indents is shown in Figure 2. The hardness profiles from as-machined and laser-peened specimens are plotted in Figure 3; the individual hardness values are an average determined from two indentations at approximately the same depth relative to the surface. A significant surface effect was observed for both conditions; however, the hardness was fairly uniform in the as-machined specimen for depths from 0.2 mm to the center of the specimen (~3 mm depth). The laser-peened material shows a linear decrease in hardness from a depth of 0.2 mm to a depth of almost 2 mm. In the center of the laser-peened material, the nominal hardness is slightly lower than in the as-machined material: 232 VHN versus 243 VHN.

The hydrogen content after thermal precharging was found to be the same for as-machined and laser-peened specimens: 110 wtppm (0.7 at%). The solubility of hydrogen in alloy 22 is estimated to be 32 mol H_2 m^{-3} MPa$^{-1/2}$ (using hydrogen fugacity of 217 MPa; (see Ref. [7]) for discussion of solubility and the use of fugacity in place of pressure for high-pressure hydrogen). It should be emphasized that this is an upper bound of solubility, since concentration measurements generally include both the hydrogen in equilibrium with the gas (often called lattice hydrogen) and hydrogen trapped in the microstructure, while solubility by definition represents only the lattice hydrogen [7].

Tensile properties are summarized in Table 2; note the values are averages of two or three measurements. It is common to normalize environmental properties by the value of the property measured in air, thus normalized values greater than 1 indicate a increase in the property when measured in the specific environmental condition, while values less than 1 indicate a reduction in that property. The normalized properties are denoted by an "R" before the variable that represents the property, such as RS_y, RS_u, REl_u, REl_t and RRA, and are given in Table 3. Plots of the stress-strain curves are provided in Figure 4; note that data for all the tests are plotted, closed symbols marking the tests without hydrogen and open symbols marking the tests with internal hydrogen.

DISCUSSION

The increase in microhardness in the laser peened material is expected as published by [**ref**]. The residual compressive stress on the surface acts to increase the apparent hardness of the material. Likewise, the center regions of the coupon with a lower hardness than the base material are due to the residual tensile stress imparted by the laser peening process [**ref**].

The hydrogen content of the laser peened and non-peened samples with hydrogen precharging was the same in both specimens at 110 wtppm (0.7 at%). This hydrogen content is similar to that expected of austenitic stainless steel [7, 8], but significantly greater than observed for ferritic steels [9]. This value is also consistent with hydrogen concentrations reported for other nickel-based alloys, if the higher pressure and lower temperature used here are taken into consideration [10]. Thus the residual compressive stresses imparted by laser peening did not act as a barrier to hydrogen transport or substantially change the solubility of hydrogen in the material. If the residual compression substantially changed hydrogen transport, a change in the measured hydrogen concentration should have been apparent, since hydrogen saturation would have taken substantially longer than our estimates of about 30 days [11, 12]. Thus, it appears that hydrogen transport was largely unaffected, although permeation/diffusion experiments are needed to confirm this hypothesis.

The solubility and thus concentration of hydrogen in the material can also be changed by residual stresses. The concentration of hydrogen in an elastic stress field can be expressed as [1, 10]

$$c = c_o \exp\left(\sigma V_H / RT\right) \tag{1}$$

where c and c_o are the equilibrium hydrogen in an elastic stress field and the without stress respectively, σ is the hydrostatic stress, V_H is the partial molar volume of hydrogen (which is equal to about 2 cm^3 mol^{-1} for steels), R is the the universal gas constant and T is temperature in Kelvin. Assuming an upper bound residual stress of about 500 MPa, as observed elsewhere for laser peened alloy 22 [3], and the hardness profile from Figure 3, we estimate a decrease in hydrogen concentration of less than 10%. This is roughly the expected uncertainty in the hydrogen concentration measurement, thus it is not surprising that a significant difference in hydrogen concentration was not observed.

The laser peening process increased the yield strength of these alloy 22 tensile specimens by almost 25%, while the ductility was slightly decreased, approximately a 15% reduction in uniform elongation, although virtually no change in reduction of area. Ductility in metals typically scales inversely with yield strength when that strength is achieved by thermomechanical processing (laser peening could be described as a thermomechanical process), thus the reduction in ductility due to laser peening is expected. We should note that the change in apparent properties due to laser peening will be a function of specimen size (and laser peening parameters). A larger tensile specimen, for example, will show a smaller increase in yield strength (and less ductility loss) for the same laser peening parameters, because the volume of material subjected to compressive residual stress will be less since the depth and magnitude of the compressive stresses will be relatively unaffected.

An increase in strength due to precharging with hydrogen was also observed for both the as-machined and laser-peened specimens. The observed 10% increase in the yield strength of alloy 22 is similar to the increase observed in an independent study for austenitic stainless steel precharged with hydrogen at nominally the same conditions [6]. Austenitic stainless steels are generally considered to have good resistance to hydrogen-assisted fracture, thus we use this broad class of materials as a baseline for comparison. Compared to a nickel-based superalloy, X-750 [10], alloy 22 appears to be somewhat more resistant to hydrogen, possibly due to the lower nominal strength of alloy 22. The slightly greater increase in yield observed for the stainless steel in Ref. [6] can be attributed to the significantly greater solubility for hydrogen in the stainless steel, in which case the hydrogen appears to act as a solid-solution strengthener. It is interesting to note, however, that the ultimate strength is slightly reduced, while increased in stainless steels [6], which may be an indication of greater susceptibility to internal hydrogen in alloy 22 compared with austenitic stainless steels. Indeed, this is born out in the ductility, which is significantly reduced for alloy 22 with internal hydrogen,

The as-machined alloy 22 shows about 10% reduction in uniform elongation when precharged with internal hydrogen. The RA displays a significantly greater reduction due to internal hydrogen: RRA is 0.57 corresponding with greater than 40% reduction of RA. This loss of ductility is greater than typically observed for stable austenitic stainless steels [6], but not as great as observed for X-750 [10].

The ductility of the laser-peened specimens, in comparison, is more degraded by internal hydrogen: RRA is 0.42 for the laser-peened specimens. It is generally accepted that susceptibility to hydrogen-assisted fracture increases as the yield strength increases [1], thus it might be expected that the laser-peened specimens, having greater yield strength, would be more susceptible to hydrogen. With respect to tensile ductility, however, relatively small changes in yield strength, as those reported here due to laser peening, do not necessarily translate to significant changes in ductility as measured by RRA (at least for stainless steels [6]). It may be that the residual stresses imparted by laser peening change the local distribution of hydrogen (although as discussed above the average hydrogen concentration is nominally unchanged, at least for these specimens dimensions), thus affecting deformation and fracture. Further work is necessary to determine if there is an intrinsic effect on hydrogen susceptibility due to the residual stress state developed as a consequence of laser peening.

In closing, it is important to consider absolute measures of ductility as well. The laser-peened specimens with internal hydrogen had the lowest RA in this testing with a value of about 30%. An RA of 30% is still ductile compared to other classes of structural alloys such as aluminum alloys and may not preclude this alloy from some applications.

CONCLUSION

Laser peening does not reduce the solubility of hydrogen in alloy 22, nor does it improve the resistance to hydrogen-assisted fracture in tensile testing of specimens precharged with hydrogen. However, this is not a complete description of the material behavior: laser peening substantially improves fatigue lifetimes in particular, while the limited available data seems to indicate that hydrogen enhances degradation in fatigue. We believe that significant improvements may be realized by laser peening materials that are subject to a hydrogen environment.

Additional testing has been initiated to investigate potential benefits on the fatigue life of materials with high concentrations of internal hydrogen.

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TABLES AND FIGURES

Table 1.
Nominal composition (wt%) of alloy 22† used in this study.

	Ni	Co	Cr	Mo	W	Fe	Si	Mn	C	V
Alloy 22 plate (UNS N06022)	Bal	0.5	21.8	13.0	3.0	3.8	0.08	0.34	0.002	0.18

† Alloy 22 plate material was supplied in conformance to ASTM B-575-97.

Table 2.
Tensile properties† of alloy 22 as-machined and laser-peened, with and without internal hydrogen (thermally precharged 34 days in 138 MPa H_2 gas at 573K: 110 wtppm H).

Material	Condition	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)
As-machined	uncharged	383	810	58.5	89.0	71.5
	precharged	426	793	52.0	56.5	40.8
Laser-peened	uncharged	473	822	50.1	78.3	70.3
	precharged	508	779	32.3	33.7	29.3

† All testing was performed at room temperature in air with a constant displacement rate corresponding to a strain rate of ~1.8×10^{-3} s^{-1} (in the plastic regime prior to necking).

Table 3.
Normalized tensile properties of alloy 22 as-machined and laser-peened, with and without internal hydrogen (thermally precharged 34 days in 138 MPa H_2 gas at 573K: 110 wtppm H); absolute properties from Table 2.

Material	RS_y	RS_u	REl_u	REl_t	RRA
As-machined	1.11	0.98	0.89	0.63	0.57
Laser-peened	1.07	0.95	0.64	0.43	0.42

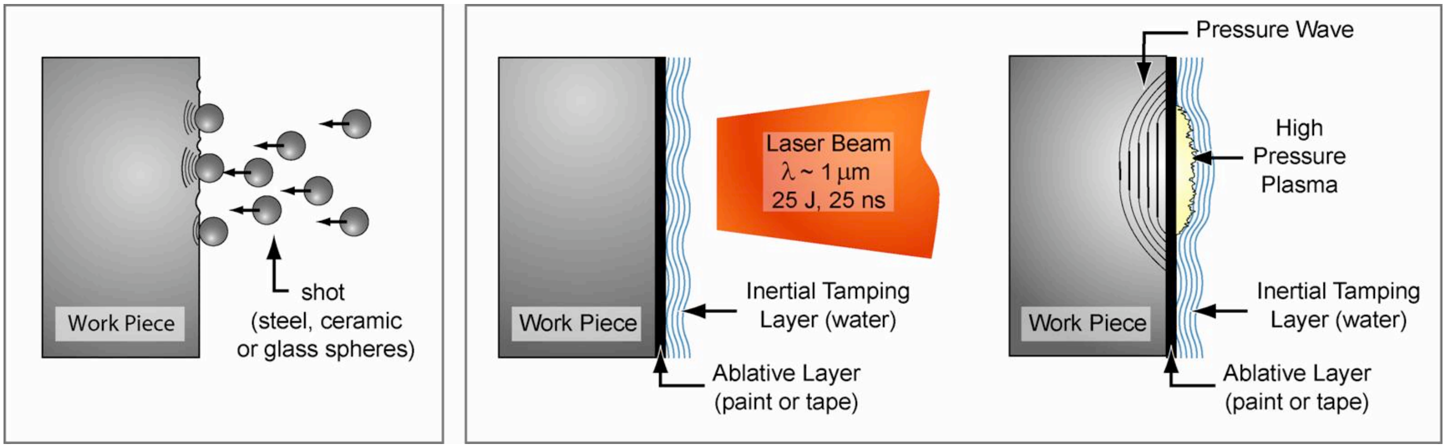


Figure 1.
Laser Peening Concept

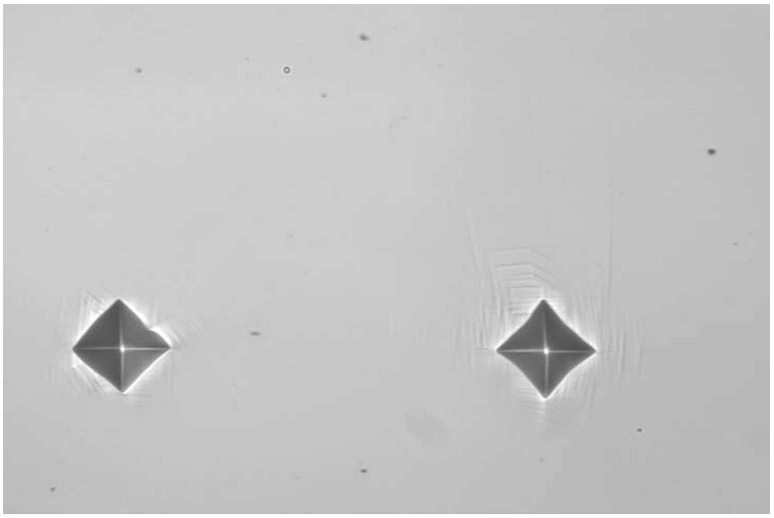


Figure 2.
Optical micrograph of indents near the surface of as-machined alloy 22 tensile specimen.

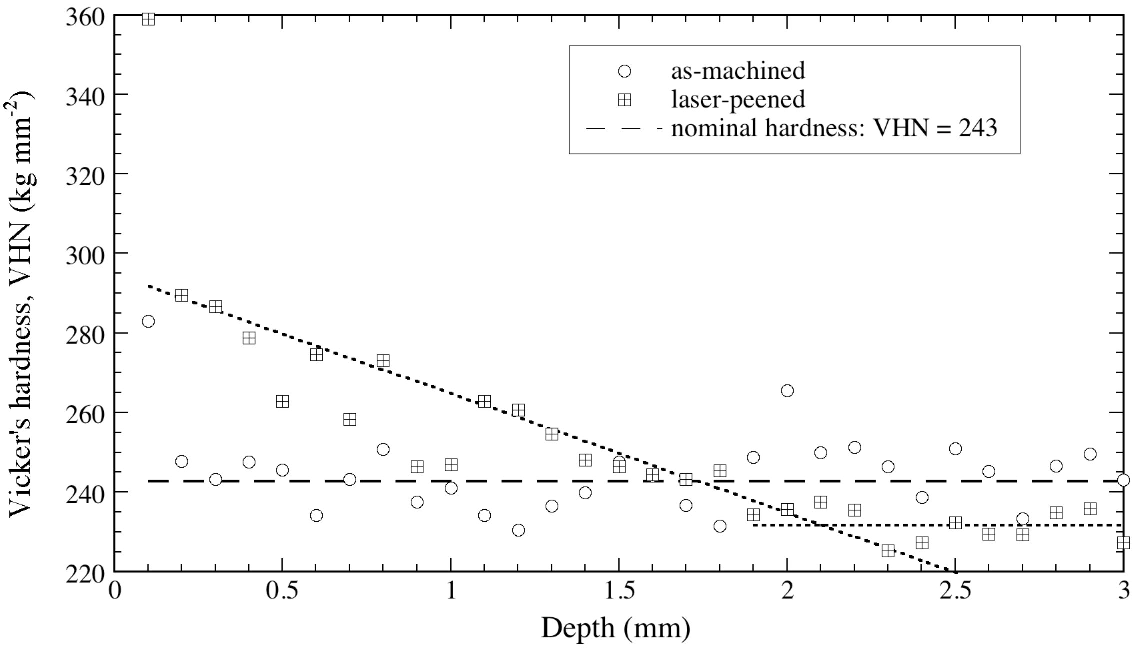
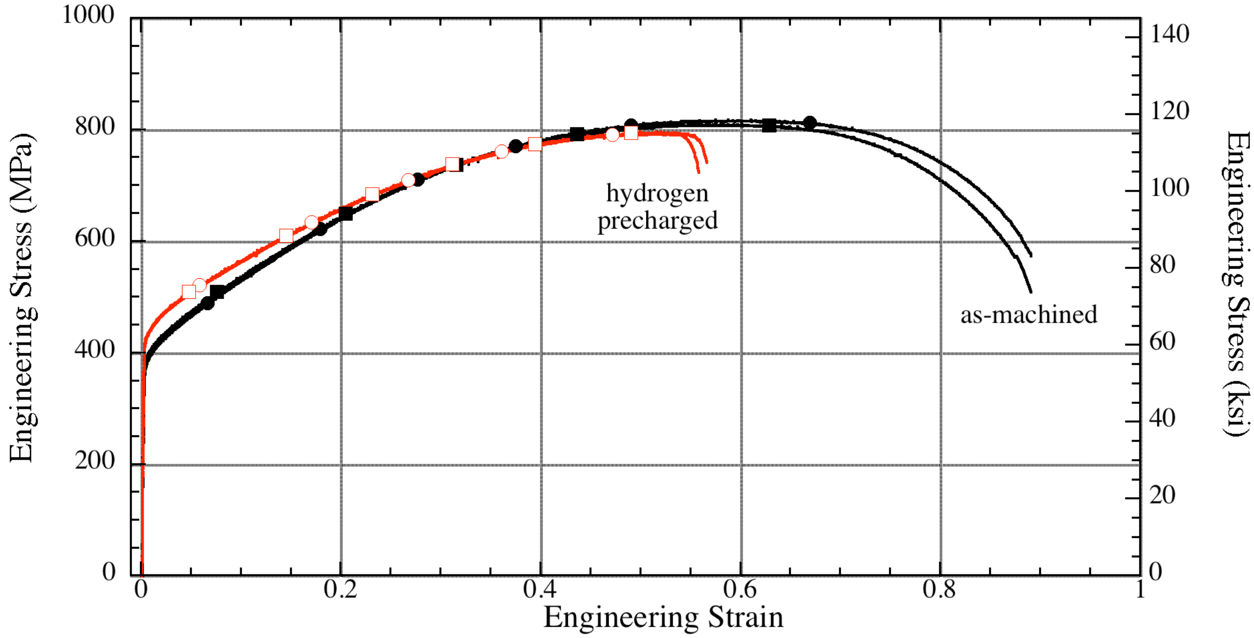
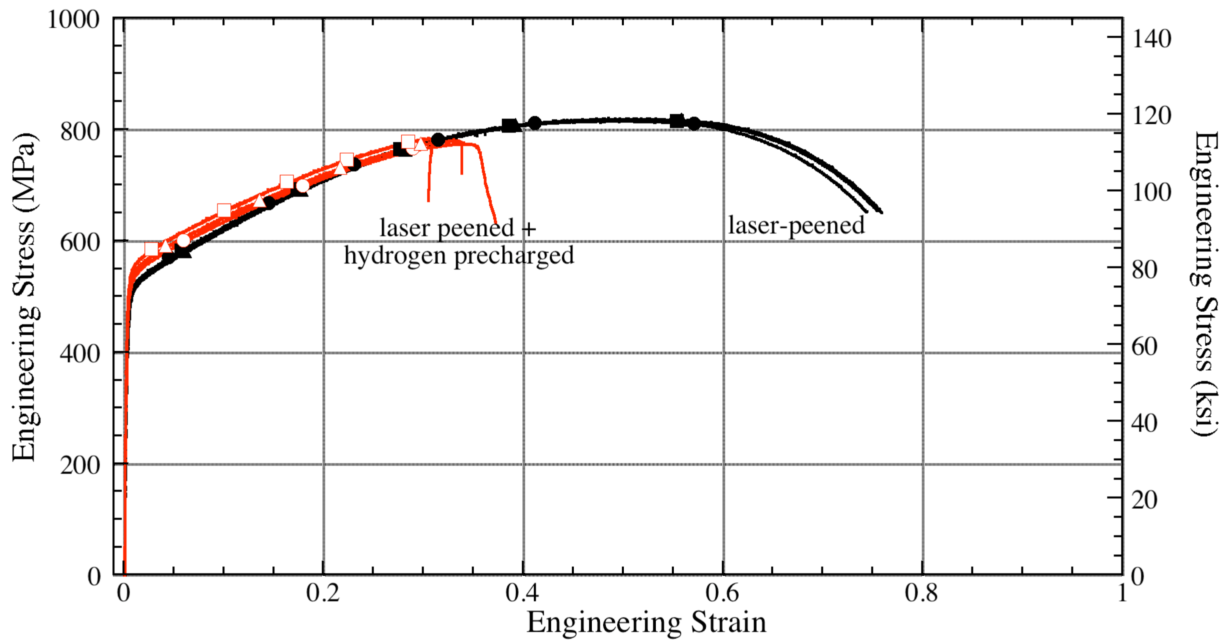


Figure 3.
Vicker's microhardness (100 gram load) as a function of depth for the as-machined and the laser-peened alloy 22.



(a)



(b)

Figure 4.
Stress-strain curves of uncharged and hydrogen precharged alloy 22 (a) as-machined, and (b) laser-peened.