



Effect of laser surface hardening on the hydrogen embrittlement of AISI 420: Martensitic stainless steel

B. Mahmoudi^{a,*}, M.J. Torkamany^b, A.R. Sabour Aghdam^a, J. Sabbaghzadeh^b

^a Department of Materials Engineering, Tarbiat Modares University, Tehran, Iran

^b Iranian National Centre for Laser Science and Technology, PO Box 14665-576, Tehran, Iran

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ABSTRACT

The susceptibility of stress corrosion cracking (SCC) of AISI 420 which was surface transformed hardened by a pulsed Nd:YAG laser, was investigated in 5% sodium chloride + 0.5% acetic acid solution by the U-Bend method, in the range of pH value from 3.5 to 6, in the absence and presence of 1 ppm thiosulphate ion, at 25 and 60 °C. The results showed that the laser-treated areas are more susceptible to SCC than the base metal. Hydrogen embrittlement (HE) is the main cause of crack propagating, mostly effective on the grain boundaries and the interface between carbide particles and second phases; tempered martensite or ferrite.

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1. Introduction

Cavitation erosion is a common cause of failure in machineries such as hydro-turbines, ship propellers, pumps, valves and diesel engines [1,2]. The local pressure variations within the liquid lead to the nucleation of cavities and their subsequent collapse generates high-pressure shock waves and microjets which cause erosion of the material. Martensitic stainless steels offer excellent cavitation erosion resistance followed by austenitic and ferritic stainless steels [3]. However, the occurrence of severe erosion has increased in recent years due to higher operational pressures and speeds of hydraulic systems required to cope with increasing energy requirements. The results of previous studies proved that laser-based transformation hardening was an effective and feasible method to increase cavitation erosion resistance in these kind of conditions [4–6]. In some cases like hydro-turbine blades, the local laser-treated areas are under high-tension pressure which originates from high rotating speed or pumps which operate in diverse environments in different pH values and tension stresses. After laser surface hardening, the two different phases, the ferrite and the martensite, with different thermal and mechanical properties, are produced adjacent to each other. Considering high-tension stress at the treated area, the SCC would occur especially in the boundary between treated and untreated regions.

There have been various studies until now in which the SCC mechanism of martensitic stainless steels has been investigated. Adsorption-induced cleavages, atomic surface mobility, film ruptures, stress-accelerated dissolutions, film-induced cleavages, and

tunnel pitting are prominent mechanisms which have been proposed up to now [7]. However, scientists mostly believe that hydrogen induces cracks by concentrating in carbide precipitations, reducing plasticity and consequently embrittling them [7]. Under the action of an electrolyte, pits appear on a metal surface, at the apices, of which the nucleation of corrosion cracks is facilitated due to the production of stress concentration. Besides the increase in the stress concentration at the apex of a pit, an essential role in the nucleation of cracks is played by the hydration and embrittlement of the metal in the zone adjacent to the apex. Therefore, the resistance of substrate against the embrittling action of hydrogen may affect the mechanism of the pit-to-crack transition and crack growth markedly [8].

HE of diverse materials or different microstructures of a metal can be compared with the term of hydrogen permeability. The hydrogen permeability is the combination of diffusivity and solubility of hydrogen into the materials [9]. The metallurgical structure and composition influence the solubility and diffusivity of hydrogen into the steels. For instance, a ferritic base-centered cubic (bcc) structure enables a high diffusion rate and a low solubility due to its open lattice structure. In contrast, the austenitic face-centered cubic (fcc) structure gives a lower diffusion rate and a higher solubility due to its close-packed lattice. At room temperature, D in austenitic stainless steel is about 10^{-10} cm²/s compared to 10^{-5} cm²/s for pure iron [9]. On the other hand, the solubility in the austenitic structure is much greater than in the ferritic. As a consequence, regarding the effect of both solubility and diffusivity factors, austenitic structure has less permeability compared to ferritic one. Solubility, diffusivity and permeability are strong functions of temperature and follow empirical Arrhenius type equation and by increasing the temperature the absorption

* Corresponding author. Tel./fax: +98 711 6281392.

E-mail address: b.mahmoudi@modares.ac.ir (B. Mahmoudi).

kinetics increases [9]. In general, it is difficult to assess the solubility without taking into account the diffusivity. Permeability is the quantity which is usually determined experimentally. In addition, permeability has a relationship with pH and some additional agents like hydrogen sulphides and chlorides ions. At the corrosion potential, the hydrogen entry kinetics increases with the acidity of solution. Thus, the lower the pH is, the higher the entry rate will be. However, the category and microstructure of the steels play a significant role in stopping hydrogen entering.

Martensitic stainless steels have shown a high resistance against SCC in different environments. They have a high resistance in carbonate and chloride solutions. It is noticeable that H₂S environments can cause SCC in the martensitic stainless steels [10], since a number of species have the effect of increasing the kinetics of the hydrogen entry into iron, steel, and ferritic alloys. The significant feature is that, in many cases, very small additions of these substances bring about a substantial increase in the hydrogen entry kinetics. The generic terms “cathode poison” or “cathodic promoter” are applied to these species because they are said to poison the evolution reaction and therefore promote hydrogen absorption. H₂S and Cl are the prominent ones. Several authors have used thiosulphate ion (TIO) instead of H₂S [11] because H₂S is a pernicious and toxic gas.

After 1993, several researches have been performed to identify the influence of TIO on the SCC of corrosion resistant alloys and common steels in the solutions containing high amounts of chloride concentration. Thiosulphate solutions can be considered as an alternative environment for HE tests.

The SCC of sensitized AISI 304, nickel alloys and Carbon Steel in acidic solutions containing TIO has been the subject of many investigations [11–15].

Rocha Pinto and co-workers [16] chose 5% sodium chloride + 0.5% acetic acid and 10⁻³ M TIO solution and the Slow Strain Rate Test (SSRT) method. They evaluated the HE of two C/Mn steels. The authors concluded that these tests indicated the HE of the regarded steels.

Zucchi et al. [17] studied the resistance to SCC of 13Cr; UNS S42000 martensitic stainless steel (M) and UNS S41125 super martensitic steels (SM) by means of SSRT method. It was evaluated in 5% sodium chloride solution, buffered with acetic acid and sodium acetate in the pH range between 2.7 and 6.0, as a function of TIO concentration. The authors concluded that the SCC resistance of SM steels was higher than that of M ones because the quality of surface protective layer of SM is better than M.

The aim of this study is comparing the SCC resistance of the laser treated lines (LTL) with the base metal in different pH values (3.5, 4.5, 5.0 and 6.0 ± 0.1) and finding the critical condition of the solution in which no cracks could be observed in the LTL regions. Therefore, U-Bend method was chosen, because it is suitable for testing the alloys which contain different phases in the same environment. The time of immersion was 1440 h. The effect of the presence of 1 ppm TIO on the resistance of treated areas against SCC is evaluated and discussed. The mechanism of crack growth is considered and discussed in further sections. The results showed that LTLs are suffered from HE and it is the main cause of crack propagation and growth. There was not any fully broken sample after 1440 h (60 days) and the cracks depth was measured as a comparison criterion and the length of the deepest crack was 600 μm in the most aggressive solution with pH value 3.5 and 1 ppm additional TIO.

2. Experimental details

2.1. Sample preparing

A sheet of AISI 420 steel with 2.5 mm thickness was cut to the 2 × 12 cm narrow strips. The U-Bend specimens were formed by

bending the flat strips into the U-shape specimens (with curvature radius of $R = 2.5$ cm) using a hydraulic press and maintaining them in the same shape by means of bolts and nuts. When U-Bend sample is stressed, the material in the outer fibers of the bend is strained into the plastic region. The total strain “ ε ” on the outside of the bend is given by the following equation:

$$\varepsilon = T/2R \quad \text{When } \ll R \quad (1)$$

If T is the specimen thickness and R refers to the radius of the bend, the value of the outer fiber stress can be obtained by the stress–strain curve of the test material by using the value of strain as determined by the above equation. In these tests, an applied stress was corresponding to 80% of the material's room-temperature which yields strength value, irrespective of the test solution. To avoid the galvanic corrosion, specific rubber washers were used between the specimen and the bolt or nut. The actual product is shown in Fig. 1. After bending, to obtain a smooth and fine surface, samples were polished by 400 grit SiC paper. The chemical composition of samples is shown in Table 1.

2.2. Laser surface treatment

The average power of laser in all experiments was set on 220 W; the pulse parameters were 20 ms pulse width, with 14 Hz frequency. The distance between the laser focal plane and the sample surface was fixed at 12 mm and the process scan speed was 1 mm/s. The output beam of the long pulsed Nd:YAG laser source used in the experiments is mainly composed of TEM00 and TEM01 spatial modes that TEM01 mode has more contribution. These parameters led to 210 μm maximum depth of hardened layer. Two single LTLs with 4 cm length and a distance of 1 cm between them were treated in a peripheral direction (Fig. 2). During laser processing stages, the temperature was measured by means of a Thermal imager. This camera is made in Flir Company and its model is A40M Thermovision.

2.3. Solution preparing

The solution with composition of 5% NaCl + 0.5% CH₃COOH was employed for the tests. The 5% NaCl solutions were buffered by 0.5% acetic acid to reach the required pH values (3.5, 4.5, 5.0 and 6.0 ± 0.1) in the presence and absence of 1 ppm TIO, at 25 and 60 °C in electric water bath. Each specimen was put into specific glassware, and the head of the glassware was closed to prevent the air flow. Eight different solutions in four categories were



Fig. 1. Actual product SCC sample.

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