Influence of electroplating stages on hydrogen pickup in SAE 1005 steel

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Abstract

Hydrogen embrittlement is a common, dangerous, but poorly understood cause of failure in metals and alloys. In coated samples, coatings act as a barrier to hydrogen damage resulting in a decrease in the corrosion rate and consequently reducing hydrogen embrittlement. In order to obtain an effective barrier against the hydrogen income the layer must be continuous, impermeable and stable in the environment so adequate variable control must be followed. Knowledge about absorption/desorption energies of hydrogen from traps as a function of temperature help to design proper thermal treatments to eliminate it. This paper represents a survey about variables involved at each electroplating stage and hydrogen income into steel wires, analyzed through optical microscopy, scanning electron microscopy and thermal analysis.

Keywords: Hydrogen, electroplating, thermal analysis, trapping sites.

Introduction

Many efforts were made to understand susceptibility to hydrogen embrittlement (HE) and corrosion rate of eutectoid steels and its dependence with hydrogen (H) atoms trapped by defects present in the steel microstructure. Embrittlement caused by the presence of H represents a key challenge not only for the gas and oil industries, but also for those that deal with electroplating processes. Hydrogen atoms diffuse into the lattice and migrate to interstitial sites, network defects (vacancies, dislocations) or it can be anchored at grain boundaries, at carbide/matrix or inclusion/matrix interfaces [**1**]. These are high energy sites that promote nucleation and growth of cracks caused by H blisters, leading to abrupt failures of the material [**2**]. In this sense, some authors [**3**] indicate that H embrittlement can occur although a very small concentration of H has been absorbed it diffuses at the contact surface inside grains or ideally at grain boundaries. Penetration depth in steel can reach 100 µm [**4**]. The most common processes are electrochemical electroplating and acid pickling [**5**], where H can be trapped in defects or lattice imperfections (reversibly or irreversibly), causing impact or mechanical properties. This type of damage is temperature dependent, with threshold temperature of 200°C approximately. In such situations Zn alloys are the most used for their low cost, good mechanical properties and cathodic resistance to corrosion processes. In this context and according to Carlson [**6**], electroplating is one of the sacrificial coating processes which involves depositing zinc layer on the workpiece from a zinc saline solution and where a layer of 99% Zn is formed [**7**]. The prior steps to the electrolytic deposition include degreasing and pickling with acid electrolyte, where atomic hydrogen is generated and then absorbed by the steel, being trapped by lattice imperfections or at grain boundaries promoting embrittlement [**8**]. Many authors [**9**-**10**] suggested that H penetration into the steel depends on coating thickness. In addition, they stated that the risk of HE is proportional to exposition time to H source of the galvanized surface.

On the other hand, Castellote [**11**] suggested that electrolytic processes induced HE as a degradation mechanism that may deform the alloy structure. The galvanized steel undergoes to anodic dissolution simultaneously with the evolution of H, which does not stop until the passivation process is completed.

Another author [**12**] attributed, for an API 5L-X52 steel, the increase of steel surface roughness as a consequence of pickling stage, with a less diffusion of H into the metal. On the other hand, the same author report that in electrogalvanized and hot dip galvanized samples, the coating acts as a barrier to H income reducing the speed and corrosion detrimental effect.

Mahmud et al. [**13**] studied zinc electrodeposition in acid medium and they divided the process into two stages: nucleation, followed by a massive electrodeposition in which occur the growth of Zn crystals with its characteristic form.

Solutions based on $ZnSO_4$ also use soluble anodes and pH index among 2-4 to avoid chemical dissolution of the metallic zinc [**14**]. In contrast to chloride bath, these

solutions produce ductile coatings with excellent distribution and thickness. On the other hand, the electrolyte must also include other solutions such as $(NH_4)_2SO_4$ or NH_4Cl to help conductivity and zinc consumption from the anode.

In an interesting article about the rupture of washers [**15**], this phenomenon was attributed to hydrogen embrittlement mechanism associated with H uptake during acid pickling operation. They explained that for samples subjected to dehydrogenation treatment at 220°C for 4-8 hours, the behavior of washers changed to a ductile type, and the failure mechanism was transformed from intergranular to ductile with coalescence of microvoids. However, the heating process of the parts until to a complete removal of hydrogen requires a long time and involves high energy costs when operate at 250°C which would have to be considered for the complete removal of H from the steel. On the other hand, Haglund et al. [**16**] studied the influence of heat treatment at 200°C for 4 days, on high-strength steels samples to avoid deleterious effects of H showing that its concentrations drop was noticeable. It is known that, thermal analysis can provide energy measurements about endothermic or exothermic changes associated with different H trapping sites in steels [**17**], so they can be used as a key to design adequate thermal treatments. This paper represents a survey about the variables involved at each electroplating stage, with specially emphasis in its influence on H income into the steel. The H presence was analyzed through optical microscopy, scanning electron microscopy and thermal analysis.

Experimental

Steel wires (SAE 1005) of 2.64 mm in diameter and 10 mm long were used for this study. Chemical composition is: 0, 06% C, 0, 25/0, 5% Mn, <0, 03% P, <0, 035% S, <0, 14 % Si. Metallographic studies were carried out using an Olympus GX51 light microscope with an image analyzer system Leco IA 32. The microstructure consists of ferrite and perlite grains with marked deformation in the drawing direction. The coating process was developed according to: degreasing, pickling and galvanizing.

Initially the samples were placed with isopropyl alcohol for 15 minutes in a TESTLAB TB010 ultrasonic washer. To proceed with the degreasing, a solution of HCl (10% W/V) was used at room temperature (20°C), for about 2 minutes under gases extraction bell. Then samples were removed from the solution and dried in hot air (70°C) for about 2 minutes. After that, samples were pickled in acidic solution of H_2SO_4 (37% W/V). In the case of sulphate-based electroplating, pickling with H_2SO_4 is required to have a sulphated surface and thus to allow a suitable coating grip. Main electrolytic variables considered were: time, temperature and current density. Further, a solution of $ZnSO_4$ (37.4% W/V) and $(NH_4)_2SO_4$ (1.1% W/V) for the electroplating tests was used, sample as the cathode and Zn - 99.99% purity were employed. At any time, heating plate with magnetic stirring was used to have solutions temperature uniformity. Microstructural analyses were performed in picked and electrogalvanized samples as well using Olympus SZ61 and Olympus GX51 microscopes. In order to analyze the quality and adhesion between the base steel and the coating, a winding test was carried out, according to the reference standard UNE 7425 [**18**] which consists of winding a wire over another of equal diameter using a maximum speed of 15 turns/ minute and forming closed turns. In this way, a good coating should not be cracked during the test and the material is considered suitable when rubbing the surface of the wire does not release particles of zinc. Subsequently, H desorption behavior thermal analysis were performed with a Shimadzu differential scanning calorimeter DSC-60, from room temperature to 500°C. For each sample, it was employed a heating rate of 2°C/min, [**19**]. A special microprint technique developed from Schober and Dieker [**20**] was used to reveal hydrogen presence and distribution, which consists of a special attack with a solution of Ag salt. Because of hydrogen interaction with the salt, metallic Ag particles are reduced and when metallographic samples are observed with Scanning Electron Microscope (SEM) those bright irregular particles of Ag reveal where hydrogen was occluded.

Results and discussion

During pickling stage, the scope is in roughness increment associated with larger contact surface for coating anchoring. As consequences of a meticulous process, the pickling variables were studied, **Table 1**, in order to obtain the best combination, i.e. best coating: current (0,1A), pickling time (3 minutes) and bath temperature (40°C).

Table 1. Experimental conditions of pickling

Sample	Pickling parameters	Roughness index (%)
1D	0,10 A - 180 s - 20°C	3
2D	0,41 A - 180 s - 20°C	4
3D	0,10 A - 60 s - 40°C	5
4D	0,10 A - 180 s - 40°C	6
5D	0,90 A - 180 s - 40°C	5

Roughness profile was determined by contour segments measurements, following the irregularities caused by pickling, using a LECO IA 32 image analyzer attached to an Olympus GX51 microscope, **Fig. 1**. A non-galvanized commercial wire sample was taken as reference. In this context, the perimeter increment is associated to a Roughness index. Under these conditions, samples 4D has shown 6% increase in roughness with respect to as received or pickled at room temperature [**21-22**].

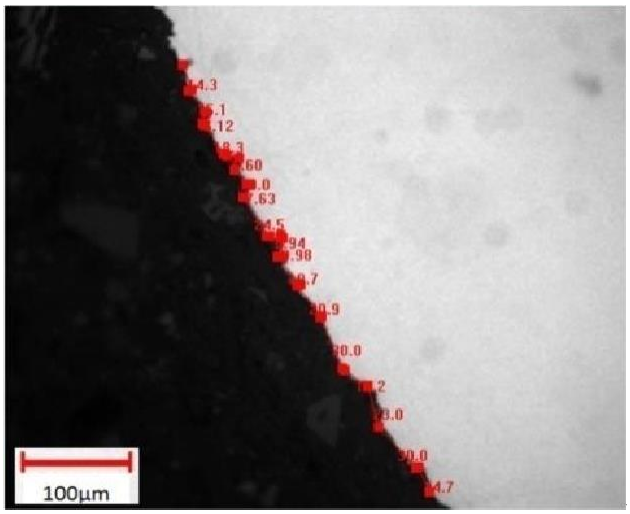

Fig. 1. Sample profile measurements (500X).

As mentioned by some authors [**11**], less rough surfaces favor H absorption into the material, although there is less atomic H adsorbed on the metal surface. In this way, the conditions of maximum roughness achieved in the pickling stage were used to evaluate its influence on the electroplating. Thus, to avoid the possible H pick up during pickling, the rougher samples were galvanized at 1A, 25°C for 160s.

Electroplated surfaces samples were observed by the Olympus SZ61 TSView Magnifier. In order to evaluate coating regularity/continuity, transverse wire measurements were made. The procedure consisted of to measure 20 segments per micrograph of the transverse wire section and then to compare those measurements with theoretical values [**23**].

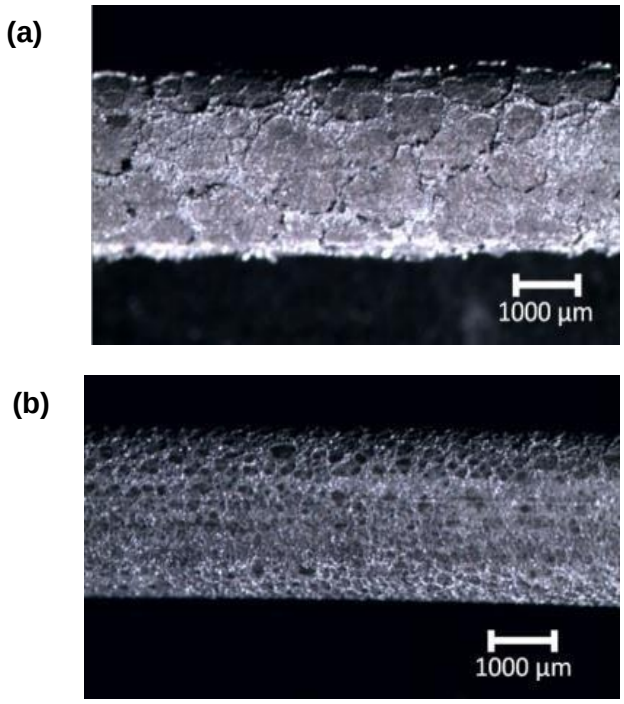

Fig. 2. (a) Electrogalvanized wires at room temperature, (b) at 40°C (1,2X).

Coating thickness was measured for galvanized samples under conditions described in **Table 2**. Concerning with sample in **Fig. 2(a)**, the large amount of Zn agglutinated they probably indicates that they were caused to H bubbles were adhered to the surface, forcing Zn depositing on the free spaces between them. On the other hand, sample 4G has similar thickness to that of the commercial one but discontinuous. Whereas for samples pickled at 40°C, coatings present greater adhesion to the wire and less quantity of Zn deposited, **Fig. 2(b)**. Besides, the relationship between roughness and coating average thickness show that sample 4D has higher roughness and, although the coating thickness is lower, it turned out to be uniform. However, sample 1D, presents a smaller roughness, a greater coating thickness but not uniform (presence of agglutinated Zn). It is known that, the grip and the uniformity of the coating are function of the roughness achieved in the pickling stage, which contributes to a lower H diffusion. According to reference [**11-12**] the pickling is a potential source of H income. As described, the greater the roughness, the greater the grip of the coating on the base metal and lower is the probability of H income into the structure. Then, under experimental conditions, it is inferred that sample 1D (less rough) will present greater susceptibility to H damage since it offers a smaller surface for the H_2 recombination process, as studied by Pérez Escobar et al. [**24**]. The results obtained up to now; show that temperature and time during pickling have the highest impact on surface roughness which directly influences coating adhesion and its relation with possible H absorption. Summarizing, the best variables combination used during electrolytic pickling that allowed to obtain suitable roughness conditions and a good adherence **[21-22]** to the base metal were: temperature (40°C), voltage (1.5V) and pickling time (180s), i.e. sample 4D. In the same direction, during electroplating different currents, times and temperatures were used in order to determine the influence of each of them on the quality of the final coating in **Table 2.**

Table 2. Electroplating variables at constant time and main characteristics of the coatings obtained.

Sample (electrogalvanized variables)	Thickness (µm)	Characterization
1G (1A - 30°C)	26	Lack of grip, discontinuous.
3G (1A - 50°C)	50	Good grip, discontinuous.
4G (2A - 40°C)	35	Lack of grip, discontinuous, uniform thickness
5G (3A - 40°C)	18	Good grip, continuous, uniform thickness
6G (5A - 40°C)	42	Lack of grip, discontinuous, non-uniform thickness

It was found that in those samples exposed to electroplating times greater than 160s presented coating continuity foul and coalesced Zn zones; therefore it was

decided to discard these samples from the analysis. From these results, sample 5G present clearly an optimum coating with respect to grip, uniformity and continuity, besides average thickness of 18 μm. And so the latter is the most suitable since the recommended coating thickness usually vary between 5 to 25 μm depending on the use of the products [**22**].

With the purpose to evaluate the influence of the electrodeposition current on coating quality, the masses deposited of Zn were measured in each sample, from the difference of weights before and after electrodeposition and comparing with theoretical mass obtained by simple electrochemistry calculations. Best experimental conditions to achieve great coatings were: 40°C and 3A and 160s, corresponding to sample 5G.

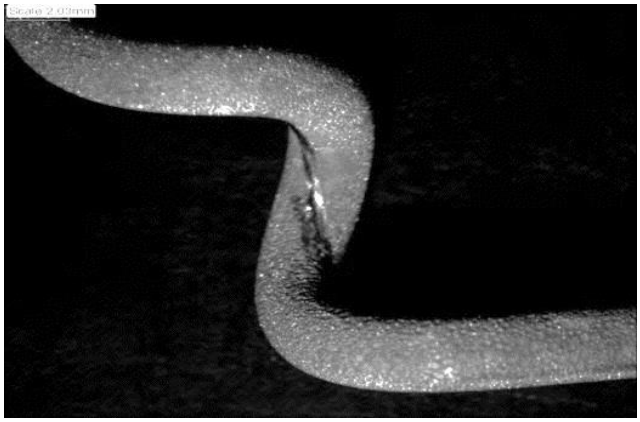

Fig. 3. Sample 5G winding test (0,67X)

The results obtained in SAE 1005 steel wires show that the bath temperature exerts influence on the coating grip to the base steel meanwhile electrodeposition current influences on its uniformity. Industrially a way of testing coating grip quality is by means of winding test, depicted in **Fig. 3** for sample 5G. Scarce coating cracking in compression zones were observed but coating stay intact at tension ones putting the coating suitable for subsequent uses. Evidence collected up to now allows determining that critical stages of hydrogen income are pickling and electroplating. Also that the main electrochemical parameters are current and electrolytic solution temperature, playing an important role at each stage and must be carefully observed.

Differential scanning calorimetry tests were performed on sample 5G with the aim of analyzing hydrogen absorption during pickling and electroplating processes, **Fig. 4.** Tests were conducted in a Shimadzu model DSC-60 differential calorimeter, from room temperature to 400ºC at a heating rate of 2°C/min. This technique allows classifying hydrogen traps into strong and weak in connection with absorption /desorption energy peaks obtained. To clarify understanding of activation energies analysis, the temperature range was divided into: zone 1 from 100°C to 200°C; zone 2 from 200°C to 300°C; and zone 3 from 300º to 400ºC and only the higher energy desorption peaks per zone were considered.

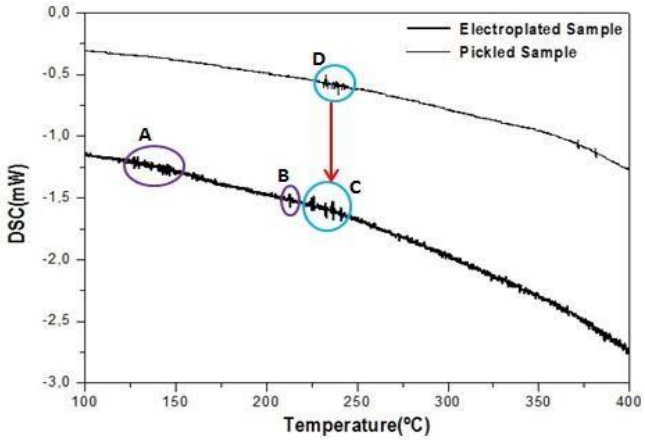

Fig. 4. Released energies vs. temperature obtained in DSC tests.

Note that from the absorbed/desorbed energies curves, the one corresponding to the pickled sample (upper curve), is developed for greater energy values of than that corresponding to the galvanized sample (lower curve It can also clearly seen in galvanized sample, there are peaks of absorption/desorption energy (peaks B and C) in coincidence with those in the pickling curve (peak D). It can also clearly seen in galvanized sample, there are peaks of absorption/desorption energy (peaks B and C) in coincidence with those in the pickling curve (peak D), indicating that galvanizing can avoid H exit introduced in pickling operations. As it is described by author [**25**], who using TDA for dual-phase steels indicate that zinc hinders the escape of H from the steel and that the desorption peaks are close to 250°C. In present case, hydrogenation occurs between 200°C and 250°C due to H trapped in the pickling stage. In this temperature range, greater amount of higher intensity peaks for the galvanized sample are manifested, from which it is inferred that H entered during pickling was reinforced by H trapped in electroplating stage, i.e., that the hydrogen is occluded by the coating [**25-26**]. On the other hand, the pickling stage produce H income in the range already mentioned as zone 2 between 200°C to 300°C. The knowledge of the specific sites where the H was trapped was obtained through the application of a specific metallographic technique [**20**]. Scanning electron micrographs reveals Ag (white) particles precipitated silicoaluminate, hint of H presence associated with them. Besides, less rough sample also presented silver particles at grain boundaries. This result, verify the close relationship between roughness and the H income during pickling. In this case, it was evidenced a significant amount of silver particles, mainly related to the inclusions and grains boundaries and consistent with several studies [**12,21,27]** where the pickling variables are related to winding tests which represent a measure of the coating´s adhesion.

In contrast, scarce white particles were detected on less rough samples as expected. As a further matter, on zinc-coated sample shown in **Fig. 5**, silver particles, some them encircled, were detected inside the metal coating also in the wire. This suggest that the coating itself act as a barrier for H desorption that remained trapped at the interface.

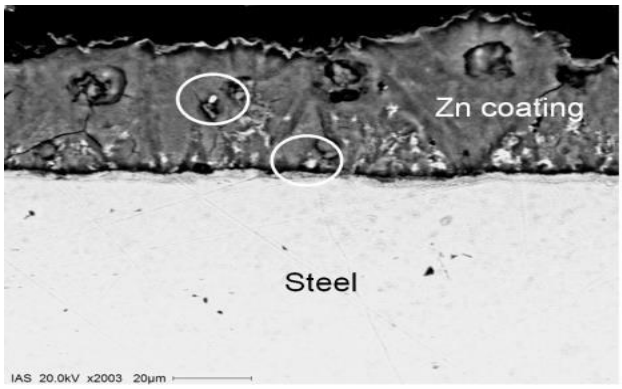

Fig. 5. Scanning electron microscopy where white Ag particles in the Zn coating indicate H occlusion sites.

It is well known that H trapped may produce fails in steels, thus a method of H removal could be valuable. For example, some studies [**28**] have reported a decrease in H concentration for high-strength electrogalvanized steels, as a consequence of a 4h at 200°C treatment. According to calorimetric results, Fig. 4, it was decided to carry out an annealing heat treatment for 8 hours at 250 ºC and cooling in the furnace in order to removed H absorbed during galvanizing procedure.

Besides, to check the effectiveness of thermal treatment, calorimetric tests were developed and outcome compared with corresponding sample of commercial galvanized wire. As expected, desorption of H trapped during galvanizing in laboratory was achieved. Always, commercial galvanized wire was kept as counter-sample and depicted simultaneously in **Fig. 6**. As shown, previously detected energy peaks due to electroplating disappeared, and the sample behaves like commercial ones. Similar result was pointed out by S. Brahimi [**29**], who attributed that hydrogen removed by suitable heat treatment would be which was free as interstitial in the steel network.

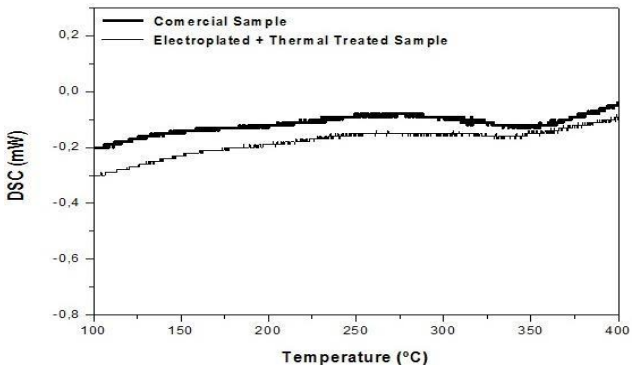

Fig. 6. Released energies vs. temperature after thermal treatments.

Conclusion

The best coating variables set were obtained for proper combination or current and galvanizing solution temperature as in sample 5G (3A - 40ºC).

Besides, although in both stages, i.e. pickling and galvanizing, there is hydrogen income, in the second one it occurs in greater quantity.

Thermal dehydrogenation process developed at 250°C would eliminate hydrogen occluded at the Zn-Steel interface and reduce the corrosion process that could be a risk to hydrogen embrittlement. These results are very useful for their application in the industries of the region.

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