Reducing hydrogen permeation in 304 stainless steel by compound layers of Al, Zr and Ti oxides films

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Abstract. A single and double layer formed by thin films coatings of aluminium oxide, zirconium oxide and titanium oxide were deposited over 304 stainless steel surface by ultrasonic spray pyrolysis technique. The steel samples were conformed for tensile tests. The purpose of these layers is to reduce hydrogen embrittlement effect in steel. An electrochemical cell was used in hydrogen charged, where a low concentration of sulfuric acid is utilized like electrolytic solution. Tension trials show the change the fracture type in samples with or without coating after hydrogen charged. The embrittlement percent factor and SEM micrographs indicate a reduction of hydrogen permeation for coated samples with double layer.

1. Introduction
In many cases the metals and alloys are in environments with extensive possibilities to generate hydrogen by the electrolytic natural phenomena, by example the different steels used in pipelines of the petrochemical industries or like structural materials in different devices and vehicles [1]. In these conditions hydrogen can adhere to the surface metal and diffuse into, this process is possible to ambient temperature [2, 3]. Then to occur the formation in the metal of hydrogen-rich zones, which will is accumulating more and more thereby causing cracking and embrittlement of the metal [4-6]. This can lead to catastrophic consequences. Is necessary to protect metals in rich ambient of hydrogen because can occur embrittlement [7, 8]. To prevent or reduce hydrogen diffusion it been proposed ceramic coatings like barriers [9].

J. P. Hirht [3], propose a parameter to evaluate the hydrogen embrittlement effect (%HE) in terms of the area reduction percent for samples without (%ARsH) and with (%ARcH) hydrogen charged after tensile test,

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%HE = \frac{%AR_{cH} - %AR_{sH}}{%AR_{sH}} \times 100
\]  

(1)
In this work, single and double layers formed by aluminium (Al), zirconium (Zr) and titanium (Ti) oxides thin films are used to reduce the hydrogen diffusion in the 304 stainless steel. The charged of hydrogen is realized with an electrochemical cell.

2. Experimental details
Fig. 1 has the drawing and photograph of the tensile test piece of commercial purity 304 stainless steel. The steel has the nominal composition (weight %): 0.08 C (max.), 1.00 Si (max.), 2.00 Mn (max), 18.00-20.00 Cr, 8.00-12.00 Ni, Fe (balance). The steel pieces were stress relieved treatment at 650°C by 60 min and sensitized by 30 hr at 1050°C.

Coated films over tensile samples were deposited by ultrasonic spray pyrolysis technique from a solutions of Al, Zr and Ti acetyl-acetonates dissolved in N,N-dimethylformamide, with the respective concentrations; 0.32M, 0.38M and 0.10M. In only test piece one-side films were deposited. The deposit of a single layer was performed in the following order; first, the Al oxide film at 550°C by 50s, after the Zr oxide film at 550°C by 50s and finally the Ti oxide film at 500°C by 50s (Fig.2). The second layer is obtained in the same form. The coated morphology is analysed with optical (OM) and electronic (SEM) microscopies.

The charged of hydrogen was realized with an electrochemical cell, a 0.5M concentration of acid sulfuric was used like solutions media and 0.45 mA/cm² current density applied during 96 hours.

The tensile test was doing with the mechanical essay universal machine, (Instron, mod. 5500R). Test was to 0.16mm/s mobile head velocity. Mechanical parameters; yield stress, tensile strength, elongation % and reduction area % are evaluated from the stress vs. strain curve and SEM micrographs. The parameters values between specimen with and without coated are compared. And the fracture surface morphology was evaluated with OM and SEM.

Figure 1. a Tensile test piece drawn and b sample picture.
3. Results and discussion

OM and SEM micrographs show a smooth and uniform coating with 3μm for single-layer and 5.4μm of double-layer of thickness average (Fig. 3b). The Fig. 3a show grains in form of twins and many precipitates in the grains limit in the sensitized steel surface. Initially in hydrogen charged process a transitory stage the hydrogen diffusion process begins with the accumulation of hydrogen in the surface and proper diffusion follows.

The Fig. 4 shows the characteristics stress-strain curves for tensile testing until fracture for the specimens in different conditions: testing (1 curve), single layer coating and hydrogen charged (3 curve), with double-layer and hydrogen charged (2 curve) and only hydrogen charged (4 curve). The curves present a similar form. The maximum elongation occurs for the testing samples and minimum in the sample only with charged. The yield stress, elongation %, tensile strength and area reduction % are shown in the Table 1. The control sample and the sample charged double layer and hydrogen have similar mechanical properties, it appears to have no effect of the presence of ceramic films.

It is remarkable the difference in value of the maximum stress or tensile steel hydrogen only charged relative to the other samples and lower % elongation. This behaviour is associated with greater hydrogen diffusion and therefore steel hardening. The mechanical behaviour of sample with double layer is nearing to testing sample, which is indicative of lower hydrogen diffusion; the layer acts as a barrier for hydrogen movement to the metal interior.

The embrittlement percent factor (% HE) is evaluated in the fracture surfaces of tension test. Minor % HE values obtained for the samples with ceramic layer, 6.2 and 8.4, with respect to the sample only hydrogen charged of 17.2, indicate a reduction in the hydrogen permeation. That is, ceramic layers decrease the intensity of hydrogen diffusion in the steel.
Figure 4. Stress-strain curves; 1 testing, 2 double-layer coating, 3 single-layer and hydrogen charged and 4 only charged.

The comparison of the morphologies of fracture surfaces shows different fracture surface (Fig. 5). The testing sample has a typical morphology of ductile fracture; neck formation and void coalescence (Figs. 4 and 5). The sample only hydrogen charged (control piece) and samples with coating and hydrogen charged don’t form neck, this result indicates that a brittle fracture. However, the fracture mechanism is different, in the first case samples show a quasi-cleavage fracture type and in the other case the surface shows big voids, similar morphology to a ductile material. Brittle fracture is related to hardening of the material associated with the presence of hydrogen-rich zones and fractures.

Table 1. Tensile test parameters and embrittlement factor of characteristics samples.

| Sample          | Yield Stress | Tensile strength | Elongation | Area reduction | Embrittlement factor |
|-----------------|--------------|------------------|------------|----------------|---------------------|
| 1(testing)      | 258.4 MPa    | 633.3 MPa        | 58.1 %     | 53.6 %         | ----                |
| 2(double-layer) | 249.1 MPa    | 624.9 MPa        | 60.0 %     | 50.3 %         | 6.2 %               |
| 3(single-layer) | 282.4 MPa    | 637.2 MPa        | 52.3 %     | 49.1 %         | 8.4 %               |
| 4(only charged) | 270.5 MPa    | 698.1 MPa        | 40.7 %     | 44.4 %         | 17.2%               |
4. Conclusions
Uniform coating of one and two layers of aluminium, zirconium and titanium oxides films were deposited on 304 stainless steel by the ultrasonic spray pyrolysis technique. The results of the mechanical tests for charged and uncharged samples with hydrogen have the effect on the steel mechanical properties. Embrittlement factor (% HE) resulted largest for the sample with double layer, this suggests that the layer is reducing diffusion of hydrogen. Also, the fracture surface micrograph shows big voids, morphology characteristics of ductile material.

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