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Effect of Nitrate via CVD Coating on Hydrogen Embrittlement in High Strength Steel Treated with Zinc PVD Coating

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Abstract

High strength low alloy steel (HSLAS) is quite sensitive to hydrogen embrittlement due to its different phases. This study investigated the hydrogen embrittlement (HE) behavior of uncoated, physically vapor deposition (PVD) coated, and chemically vapor deposition (CVD) coated HSLAS. The XRD indicates the formation of ZnO, $Zn(N_3)_2$, γN and C_3N_4 phases at the outer coating layer. The results show that combination of surface nitriding and zinc deposition are efficient method against hydrogen embrittlement. This could be attributed to the reduction of hydrogen that is generated by the reaction of surface $Zn(N_3)_2$ phase and the low rate of hydrogen transport through the γN phase. The coatings were tested by immersing the tensile samples in a diluted H_2SO_4 solution with water for 24 hours. Additionally, the result shows that combined coating resulting in higher tensile strength, yield stress, and tensile elongation compared to uncoated samples. Hardness results indicate that the combined coatings (PVD + CVD) has the higher value of about 258 HV, followed by the uncoated sample of about 218 HV, while the PVD only coated sample have the lower hardness value of about 175 HV.

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1. Introduction

High-strength low-alloy steel is alloy steel with higher mechanical characteristics and corrosion resistance than carbon steel [1]. To maintain formability and weldability, they contain a carbon concentration of 0.05–0.25 percent [2, 3]. The primary components for low wt.% combinations are niobium, vanadium, or titanium [4]. The micro-alloy steels used a limited number of micro-alloy elements for single and multi-elements from 0.10% to 0.15% wt. [5]. The most important problem that can occur in HSLAS is hydrogen embrittlement (HE) [6, 7]. Subcritical crack development, fracture initiation, and catastrophic failure are all caused by HE [8]. This has resulted in a loss of mechanical characteristics such as ductility, toughness, and strength [9]. One of the most effective procedures in the commercial process used to preserve steel components exposed to corrosive conditions is the production of zinc coats on steel [10, 11]. However, because of new uses in the automotive and construction industries, many studies have been done recently on all aspects of new forms of Zn coatings and how they relate to actual applications of Zn [12, 13]. Zinc primers are commonly utilized because of their excellent corrosion resistance [14]. It also provides cheap costs, simplicity of production and application, and product availability [15-17].

Similar studies on high-strength steels investigate the coating and nitriding process on hydrogen embrittlement. Kyoung et al. indicated that aluminized layer deposited on high-strength pressed steel reduces the hydrogen transfer to base substrate significantly at higher temperature, whereas galvanized layer helps hinder hydrogen diffusion into steel substrate at room temperature [18]. Particular attention should be considered; a recent study demonstrates that baking the steel would eliminate the residual amount of hydrogen present. However, this would not eliminate the hydrogen completely. Protective coating proved to be more reliable in preventing hydrogen attack [19]. This work aims to use a gas-phase method to deposit Zn nanostructure-coatings on a high-strength steel substrate surface to increase hydrogen embrittlement resistance and minimize hydrogen penetration to the metal surface. Mechanical testing was done to illustrate the adhesion of Zn coating. Comparison of non-coated and combined (nitriding + coating) was studied and analyzed.

2. Experimental Procedure

HSLAS specimens with the following dimensions (2×10×10 mm) for hardness testing and scanning electron microscope (SEM) analysis were utilized in this study. The samples for the hydrogen embrittlement and tensile tests were prepared with the following dimensions of (2×10×50 mm) for the thickness, width, and length, respectively. The material composition in weight percent was analyzed by using spark technology at Central Refineries Company in Baghdad, Iraq. The compositions of HSLA steel are listed in Table 1 as follows:

Table 1: Composition of low alloy steel.

C%	Si%	Mn%	P%	S%	Cr%	Mo%
0.05-0.15	0.50	0.3-0.6	0.025	0.025	1.9-2.6	0.78-1.13

All specimens were mechanically grinding on emery paper in sequence of 220, 320, 400, 600, 800, and 1200 grit, washed up using distilled water, and dried with a clean tissue. The prepared specimens are polished with a suspension gel, which is a very fine abrasive until a mirror-like finish is obtained. Then it is kept in a desiccator over the silica gel layer until the time of use. Zinc (Zn) target made by Sermatech International Inc., UK, and with a purity of 99.9%, was used to produce the basic component of Zn coatings. The zinc sputtering parameters on steel substrate were 18mA for current density, the vacuum pressure of 10^{-1} Torr, and the argon gas flow rate of 2 sccm (standard cubic centimetre per minute). Ammonia (NH_3) gas was used to provide the atomic nitrogen for the reactant gases, and nitrogen gas was used as a carrier gas to accomplish the nitriding process. The breaking down temperature of NH_3 gas is between 500 °C and 900 °C. A temperature of 500 °C was chosen to avoid the residual stresses as much as possible. Before charging the steel specimens with hydrogen, the shoulders of the specimens were covered with an insulating liquor to protect them from hydrogen attack, and only the rest of the specimens, length will be attacked. The steel specimens were charged with hydrogen gas only along the gauge length, i.e., 50 mm. Hydrogen charging of tensile test specimens was carried out using an electrolytic cell comprised of stainless-steel plate acts as an anode, and HSLA steel specimen acts as a cathode.

The electrolyte solution was diluted sulfuric acid solution (0.4M H_2SO_4 solution). The current was provided from a PL 320 power supply. The electric characteristics of the cell were 0.9V and a current density of 0.4A. Tensile testing was done using WDW- 200 E III tensile testing machine with 200 KN capacities. The microstructure and morphology analysis of Zn deposited surface coatings layer on steel substrate was carried out using Tescan VEGA 3SB scanning electron microscope with accelerating voltage of 200V to 30kV and magnification power from 233X to 5000X. Digital Micro Vickers Hardness Tester, model-TH715 (Bei jing Time High Technology) was used to test the hardness with a load of 0.98N. Hardness was measured before coating and after the Zn deposition and nitriding process. The crystal structures of the materials were determined using Shimadzu XRD-6000 X-ray diffractometer (XRD) with an incident angle of 0.154nm and Cu-Kα radiation with a wavelength of 1.506Å.

3. Results and Discussion

3.1. Crystalline Structure Analysis

Figure 1 shows the XRD pattern of the HSLAS with different surface treatments. In this figure, the Zn coated substrate can show the presence of Fe phase at 2θ angle (44.71), (64.94) at (101) and (200) [ICDD card no. 00-006-0696] respectively. The only phase that was observed in the XRD patterns along with the Fe phase was the

ZnO phase, where this phase show existence at 2θ angle of (29.6), (34.2), and (39.7) with (002), (001), (100) respectively [20]. The nitride samples exhibit significant differences in the phases present and the microstructure than the former Zn coated samples, which consequently can have a strong effect on the mechanical and tribological properties of the surface. The XRD pattern for the nitride sample shows the existence of the C_3N_4 phase at 2θ angles (28.39), (37.13), and (72.43) with (100), (110), (112) indices [ICDD card no. 00-053-0671], respectively. This can be evidence for the intermixing between the substrate and the nitriding layer as the nitriding process was carried out at a temperature of 500℃ for one hour. Also, γN phase at 2θ angles (37.4), (43.1), and (53.6) with (101), (111), (200) indices can be indicated in this pattern [21, 22]. The XRD phase analysis of HSLA steel samples with two layers (nitride + Zn) is also shown in Fig.1.The XRD pattern for the combined layer shows the existence of both the Zn coated and nitride layers, wherein this pattern ZnO phase, C_3N_4, and γN phase can be observed. The XRD test for this sample also detected new phases, a clear peak for $Zn(N_3)_2$ at (24.65), (33.42), (47.36) with indices of (200), (210), (123) [ICDD card no. 00-023-0740] could be referred to in this pattern.

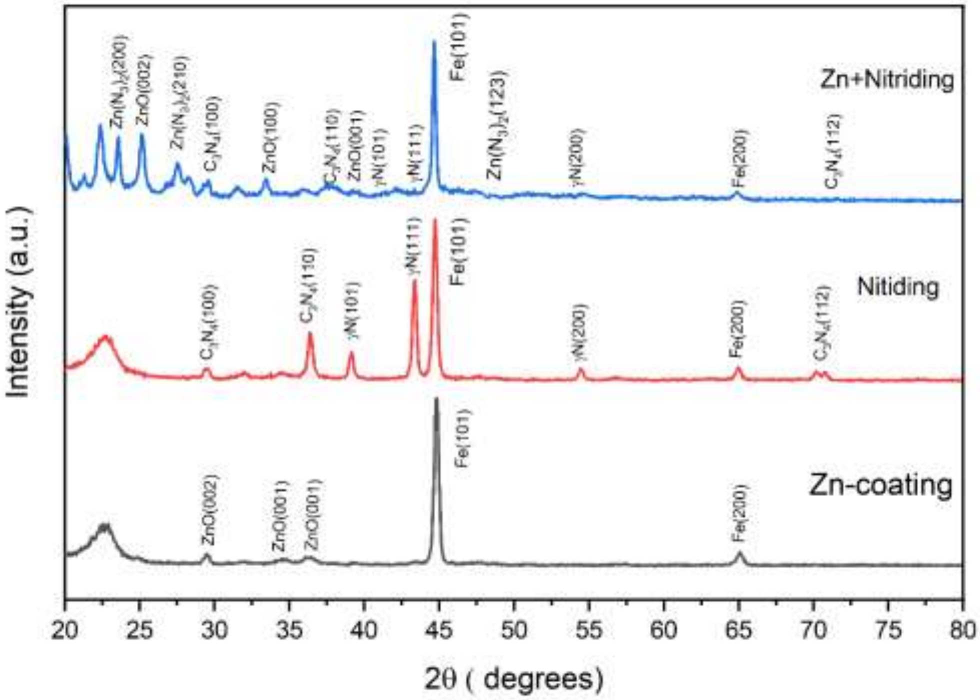

Figure 1: The XRD pattern of an HSLA steel substrate with various surface coatings.

3.2. Microstructure Analysis

Figure 2 shows the surface morphology for the Zn coated HSLAS samples. In this figure, many irregular pores can be detected in the matrix. According to XRD analyses, this sample contains only two surface phases; the ZnO phase and the Fe phase. In addition to non-uniformities and abnormalities in terms of structure and size, the ZnO phase exhibits a higher degree of clustering as it can be detecting from the dispersion of ZnO phase in SEM images with low and high magnifications.

Figure 3 show the SEM images for the nitrided and Zn coated HSLAS samples. The surface layer appears to have two regions: the first has a needle-like morphology, and the second has a shell region with zinc crystals randomly protruding from the surface. According to the XRD test, three phases $Zn(N_3)_2$ phase, γN phase, and Fe phase was detected in these samples. Due to the nitriding process, the substrates were expected to have higher average particles size after temperature 500 ◦C, and it indicated that the nitriding exhibited a dense microstructure characterized by a dense matrix which will lead to increasing the pores volume and size distribution as small particles that represents the third phase were precipitated. Figure 4 show the cross-section SEM images for coated HSLAS samples. The resulting thickness for the Zn coating was found to be about 38 μm. This is considered as a large thickness which was achieved due to the presence of zinc coating layer, while the thickness for the nitriding and zinc coating layer was found to be of about 40.3 μm.

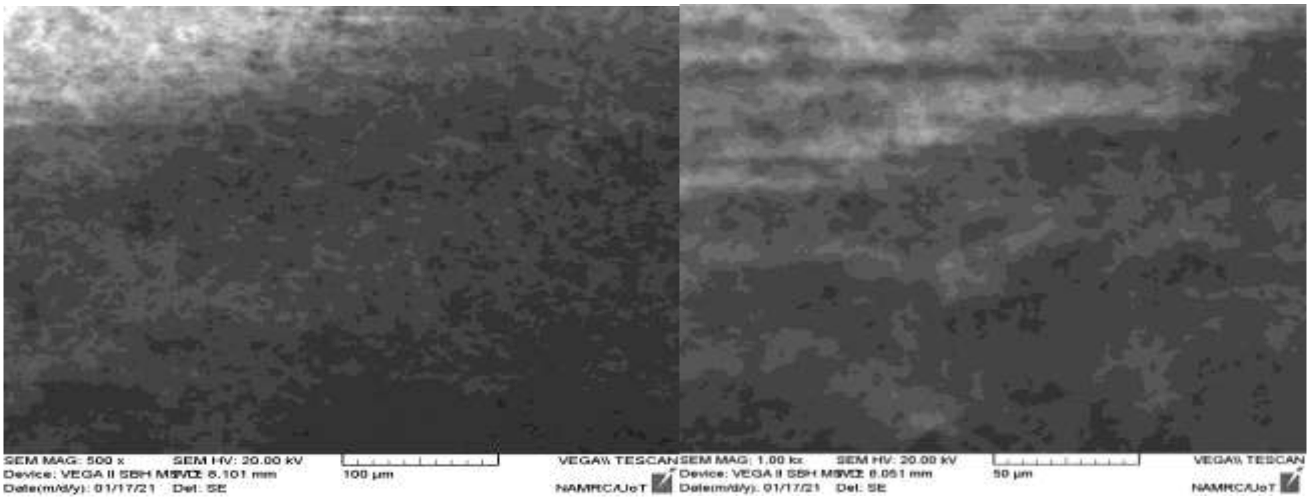

Figure 2: SEM topography of HSLA steel with Zn coating at different magnifications.

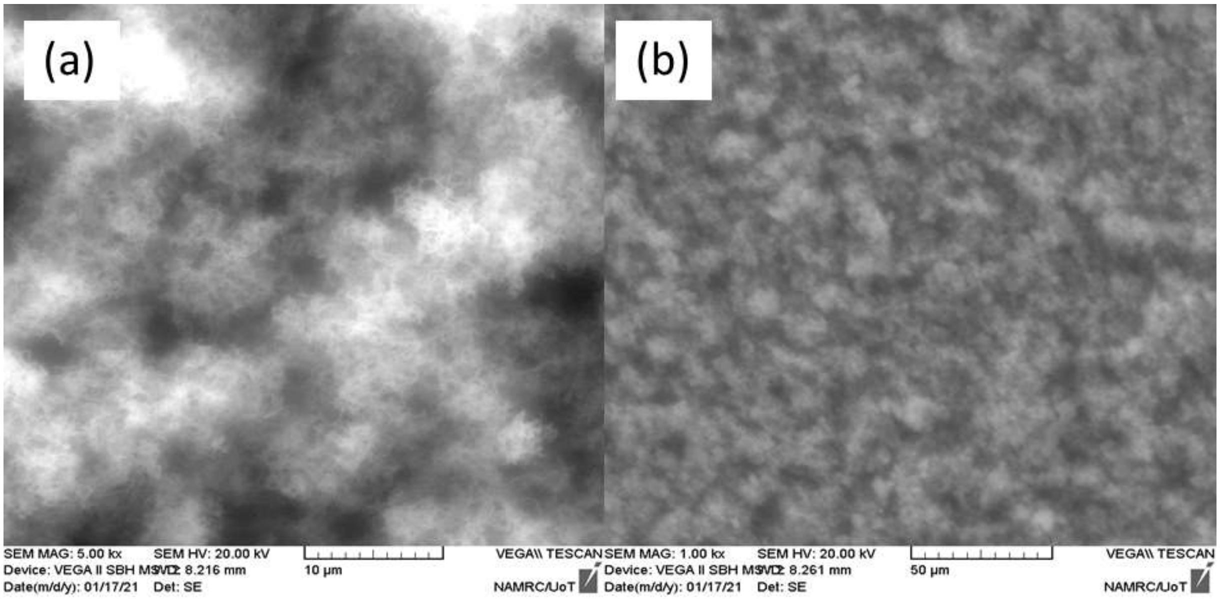

Figure 3: SEM topography of HSLA steel nitride and Zn coated at different magnifications.

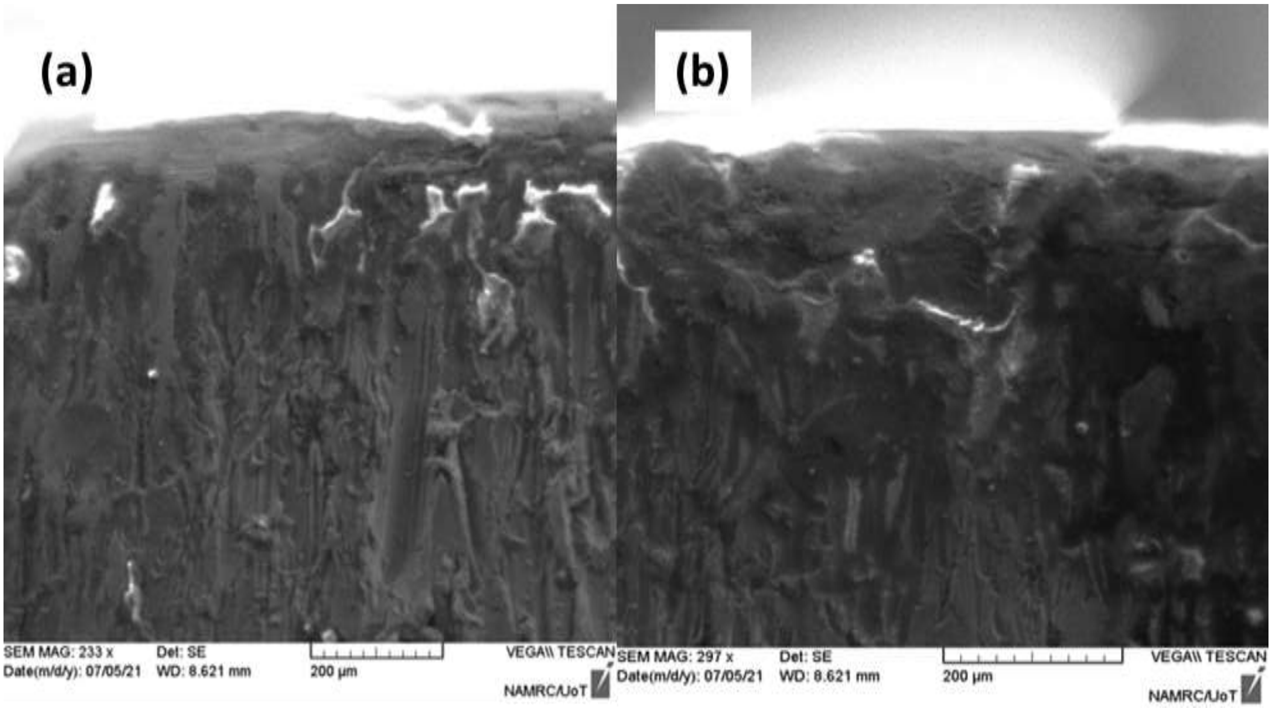

Figure 4: SEM cross- section image for HSLA steel coated with Zn layer in (a) and nitrided + Zn coated in (b).

3.3. Tensile Test

Three groups of HSLAS material specimens with various coatings and nitriding-coating conditions are evaluated according to ASTM E8. This was done to determine ultimate tensile strength, yield strength, and total elongation, as indicated in Table 2. The effect of hydrogen embrittlement on the mechanical properties for the HSLAS can be seen clearly for sample that was exposed to the hydrogen embrittlement test (sample no. 1) in table 2 and figure 5. Where in these samples the elongation ratio was 14 % for the sample that was exposure to the hydrogen embrittlement process, while a higher Tensile strength was need before the fracture occurred for the original HSLAS sample (sample no.2) that was not exposure to the hydrogen embrittlement process. The ultimate tensile strength (UTS) and yield strength of the coated and nitriding specimens come out to be highest than that of the Zn coated specimen, where elongation (%) in the coated and nitriding specimen was approximately 30%(sample no.4), while elongation(%) for the uncoated specimen comes out to be 23% (sample no.2) and elongation in the sample with Zn coating was 20%(sample no.3). This indicates the brittleness that was induced by HE when using only zinc coating process for the HSLAS samples as the ductility is sharply reduced as illustrated in Figure 5 for these samples [22]. On the other hand, the nitrided surfaces that was coated with Zn nanostructured (sample 4) film shows a promising result for a protection layer against hydrogen embrittlement of HSLAS, where these samples have tensile strength of 430Mpa with elongation rate of 30%. These results can be attributed to the presence of multi layers treatment, as the Zn coating film strongly decreases the absorption of hydrogen and its transport to HSLA steel through the modified layer, where the combination of surface treatments (Zn coating and nitriding) improve the mechanical properties of bulk and surface for HSLA steel [23, 24].

Table 2: Tensile test results for HSLAS with different surfaces treatments.

Sample no.	Tensile strength, MPa	Yield strength, MPa	Elongation %
1	144	78	14 %
2	265	172	23 %
3	235	169	20%
4	430	275	30 %

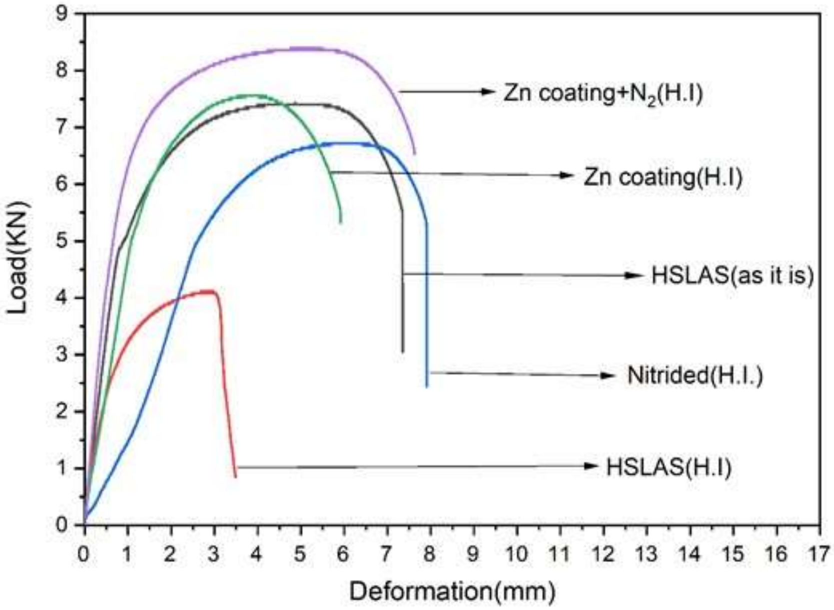

Figure 5: Force-deformation diagram resulted from tensile test for HSLAS with different surfaces treatments.

3.4. Hardness Test

The average microhardness of metal surface and coating layers has been evaluated by using microhardness testing machine. Table 3 shows a very wide variation in the recorded hardness tests that were measured for the HSLAS substrate and both coating and nitriding processes. The very low hardness that was measured for samples coated with Zn (D-1) results from the low mechanical property surface layer of zinc, in which Zn coating leads to the formation of low mechanical property oxides (Zn-oxides) that was already indicated in the XRD results in Figure1,where in this sample (D-1), the most drastic reduction of hardness is caused by the formation of ZnO on the coated surface. The role of oxygen is immensely detrimental, highly dependent on deposition process parameters. Thus, to increase the new surface layer hardness, a second hard surface film should be added to this coating system to improve the mechanical properties of this coating film. For the samples that was coated with Zn film after the nitriding process (D-2), the recorded hardness was higher than the hardness of base metal (218.6 HV) as a hardness of 258.3 HV was achieved. This was caused by the new nitrided thin-film performed by a CVD process. Such coatings belong to the group of phases modulated hard layers where two or more surface layers work together as one system to enhance the base metal chemical and mechanical properties. Using such a system (Deposition of Zn coating by PVD and using CVD for nitriding process) causes the surface layer hardness to increase, reaching from 175 HV to 258.3 HV, which is a significant increase in the Zn-coating hardness. Using of the phases modulated hard layers has aattracting attention to a number of coating systems, whereby using this method it is possible to develop new systems with higher specifications than the original systems, one example of such new systems is the using of nitriding with titanium alloy that showed significantly improve to the alloy's mechanical properties and wear resistance. In addition, nitriding will enhance the compressive residual stresses and surface hardness to significantly higher values leading to improve the surface strength [25]. Also using of two surface layers techniques can end in a crucial deposition ratio and intensive coatings that may be promptly gained because of its flexibility that will permits several alterations in composition throughout deposition. Thus, in resent studies the combination of both nitriding and other surface coating layer can be beneficial on mechanical properties and significantly promotes the adhesion of the performed coating on the used substrate [26, 27].

Table 3: The hardness of samples under various conditions.

Sample no.	Hardness (HV) of fixed Points on sample surfaces	Average of Hardness (HV)
D -0(HSLA) No coating	226.8, 206.3, 222.9	218.6
D- 1(HSLA) with Zn coating	195.8, 206.2, 185.3	195.7
D-2(HSLA) nitriding-Zn coating	270.4, 248.7, 255.9	258.3

4. Conclusions

The deposition of Zn-base coating and surface nitriding using NH_3 gas was successfully implemented on the surface of HSLA steel. XRD indicates the formation of ZnO, $Zn(N_3)_2$, γN and C_3N_4 phases at the outer coating layer. The Coated samples generally showed higher tensile strength, yield stress, and tensile elongation than uncoated samples. The combined CVD and PVD coating process increase the tensile elongation to about 30%. The thickness of outside Zn coated layer analyzed by SEM is reached to approximately 40µm. This is considered an excellent thickness that act as a barrier against hydrogen attacks. The nitriding process carried out at 500°C was very important for mechanical properties improvement and also provide a rough surface for the successive coating of Zn layer. However, the hardness of PVD coating is less than the uncoated sample, while the hardness of combined (PVD + CVD) was higher than the uncoated samples. Furthermore, vacuum evaporation remains a possible method for precipitating a hydrogen-free layer on the steel.

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Conflict of interest

The authors have declared no conflict of interest.

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