An Investigation on Hydrogen Embrittlement of the Cr-Si Spring Steel Using Slow Strain Rate Test and Weibull Model

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Abstract: In this paper, the hydrogen embrittlement of the high strength Cr-Si spring steel with Zn-12%Ni after electroplating, have been evaluated. Slow strain rate test with 3.34×10^{-6} sec^{-1} strain rate was performed, and the hydrogen embrittlement index of the different samples was calculated. The effect of shot peening before plating and the baking after plating and also the effect of applying a nickel interlayer by electroless method, is examined by using the weibull statistical model. The results showed that alloying Zn with nickel considerably reduce the diffusion of hydrogen on the substrate steel structure. So that it increases the average failure time of samples from 4.9 hours for pure Zn to 8.7 hours for Zn- Ni. By applying nickel interlayer, the failure time increased to 11.15 hour. Also by shot peening process before electroplating, the average failure time increased to 12.7 hours which showed the least amount of hydrogen embrittlement among the studied samples. Baking after the electroplating of Zn-Ni samples without interlayer, leaded to an increase in the failure time to 10.15 hours. While baking in samples containing nickel interlayer, showed the opposite effect, reducing the failure time to 8.15 hours.

Keywords: Cr-Si Spring Steel, Hydrogen Embrittlement, Slow Strain Rate Test, Weibull Model

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1 INTRODUCTION

The Cr-Si spring steel with high strength is highly sensitive to hydrogen embrittlement. Electroplating processes expose this steel to the diffusion of hydrogen gas which is released from the cathodic reaction. This causes early failure when the steel is subjected to tensile stresses in working conditions. Furthermore, the electrochemical processes in addition to the release of hydrogen reaction, cause reduction of fatigue life of components under dynamic loading due to the possibility of creating the residual tensile stresses in the steel and also the high density of the microcracks from electroplating [1-2]. In situations where there is a risk of hydrogen embrittlement, one of the useful methods can be dehydrogenation by baking [3]. According to the BS 1706-1990 and ASTM B850-98 standards, steel parts after electroplating, would be heated to 190-220°C, which the time duration of this operation is dependent on the tensile strength of the substrate steel. Therefore, in the case of high strength Cr-Si spring steel, this time should be 24 hours.

Zn-Ni alloy electroplating is increasingly being used to prevent corrosion of steel parts. Zn alloying with 10-12% nickel can remarkably improve the corrosion rate control of the alloy deposits [4-11]. Zn-Ni coatings are formed through an anomalous mechanism, so that participation of the more noble metal, the nickel, on the contrary is less on forming coatings and at the end, it result in the deposition of alloys with high Zn and low nickel [12-14]. If high strength steels be covered by the Zn-Ni electrochemical coatings with a nickel percentage of 10 to 14 percent, they show little tend to hydrogen embrittlement and also better response to dehydrogenation through baking [15-16].

Several reports have demonstrated that the application of a nickel interlayer by electroless, can improve the fatigue life of the electroplated steels [1-2], [17-19]. Naturally, improvement in fatigue life of the substrate steel by the electroless nickel interlayer is possible when the nickel interlayer contains less than 4% or between 10 to 12% of the phosphorus. Since in this range of chemical composition, the interlayer produces compressive residual stresses and increases fatigue resistance of the substrate steel. While in the range of 4 to 9% of phosphorus, the nickel interlayer produces tensile residual stresses and has an adverse effect on the fatigue life [17].

Shot peening as a way to improve the fatigue life of the spring steels are commonly used. This process by creating compressive residual stresses, results in improvement of steel springs fatigue performance in working conditions [20].

In this paper, the hydrogen embrittlement intensity of the high strength Cr-Si spring steel, after Zn-Ni electroplating by using slow strain rate test and calculating the emrittlement index, is evaluated. Furthermore the effect of shot peening before electroplating and baking after electroplating are studied. To have an accurate study, the effect of electroless nickel interlayer is also evaluated and at all stages, the results are compared with the results of the samples coated with pure Zn.

2 MATERIALS AND METHODS

2.1. Substrate

The Cr-Si Spring steel 55SiCr6 with tensile strength of 1920 MPa and hardness of 56 RC was used as substrate. The chemical composition of this steel is shown in Table 1.

Table 1 Chemical composition (%) of Cr-Si spring steel 55SiCr6

C	Mn	Cr	Si	P	S
0.55	0.68	0.64	1.44	0.009	0.007

2.2. Zn-Ni electroplating

In this study, an alkaline bath was used for producing Zn-Ni alloy coating with a chemical composition shown in Table 2. Electroplating at 25°C and pH=13 with 3A/dm^2 current density is done to achieve Zn-12%Ni glossy deposition with thickness of 10 μm. After several attempts, the optimal duration of 30 minutes was selected to achieve this thickness.

2.3. Pure Zn electroplating

A standard cyanide bath with chemical composition and characteristics given in Table 3 was used for pure Zn electroplating. To achieve the coating thickness of 10μm, after several attempts, plating time of 20 minutes was selected.

Table 2 Chemical composition and characteristics of the Zn-Ni electroplating bath

characteristics	Composition of electrolyte (g/lit)					pH	temperature (°C)	current density (A/dm^2)
	$ZnCl_2$	$NiCl_2$	NaOH	Na_2CO_3	brightener			
amount	10	1	130	60	4	13	25	3

Table 3 Chemical composition and characteristics of the pure Zn electroplating bath

characteristics	Composition of electrolyte (g/lit)					pH	temperature (°C)	current density (A/dm^2)
	NaCN	ZnCN	NaOH	Na_2CO_3	brightener			
amount	47	61	79	15	4	12.3	25	3

2.4. Electroless nickel interlayer application

In this study, application of an electroless nickel interlayer between the substrate steel and Zn-Ni deposit, was investigated. So in order to achieve nickel interlayer with less than 3% of phosphorus, an electroless plating alkaline bath with chemical composition and properties as shown in Table 4 was used. After several attempts, the deposit with a thickness of 5 μm was formed in 30 minutes. It should be noted that before the process of electroless nickel, the samples were rinsed in 10% nitric acid to active their surfaces and due to the wettability improvement, make them ready to absorb the nickel electroless deposition.

Table 4 Chemical composition and characteristics of the Ni electroless plating bath

characteristics	Ni electroless solution composition (g/lit)					pH	temperature (°C)
	$NiCl_2.7H_2O$	NaH_2PO_2	NH_4Cl	NH_4OH	$Na_3C_6H_5O_7.5H_2O$		
amount	30	20	50	9	80	9.5	80

2.5. Slow strain rate test

For slow strain rate test, based on the EN10002-1 standard, wire samples of Cr-Si spring steel without machining were used. So wire form samples with 10.2mm diameter and 200mm length were provided, where 50mm of this length was used as the gauge length and the rest of sample was engaged in the machine grips. Slow strain rate test was done in a tensile machine at a 0.01mm/min traction speed and a strain rate of $3.34\times10^{-6}sec^{-1}$ and failure time of each sample was recorded. In each of the conditions, 10 samples were tested by slow strain rate test.

Some of the samples were shot peened before electroplating. Shot peening was done by using shots with 0.6mm diameter and 58RC hardness, for 30 minutes on a machine with 90m/sec shot injection velocity. Some of the samples were subjected to baking at 200°C for 24 hours after electroplating. In accordance with ASTM B850 standard, baking treatment was performed with time delay less than 3 hours after the electroplating.

3 RESULTS

In this study, the weibull statistical model was used for the description of the variables effects. The likelihood of results confusion resulted from the slow strain rate tests that can be attributed to the performance mechanism of hydrogen atoms in the metal lattice and also features variety of microstructural defects in the substrate steel, is the reason of selecting this model. Hillier and Robinson successfully used this model to describe the performance of Zn-Co alloy coating [21]. In this model, the probability of a sample without failure, P_s, may be expressed by equation (1).

$$P_s=1-P_f=\exp[-x(t-t_i)] \tag{1}$$

Where P_f is probability of failure, t is failure time and x is the shape parameter which is concerned to the weibull curve slope. As well t_i is the minimum time that the sample fails. In other words, ti is the time that the probability of no failure is one, so be $t=t_i$. Table 5 shows the results of slow strain rate test and mean time of different samples failure. More details about drawing weibull diagram, such as for unplated specimens, would be described.

3.1. Weibull diagram for unplated samples

Table 6 shows the slow strain rate test results for unplated samples. Since in this research, the number of tested samples in each of conditions is 10, the values of $Ln(p_s)$ would be as it is shown in Table 6. For example, the probability of no failure up to 12.7 hours is 100%, because no sample in less than this time has failed. Another example: the probability of no failure up to 13.1 hours is 60%, because only 40% of the samples prior to this time have failed. Figure 1 shows the Weibull diagram which is obtained based on the results of Table 5. It is clear that the samples in the range of 12.7 to 14 hours have failed at a mean time of 13.25 hours. To determine the value of x, the shape parameter of Weibull curve, it is sufficient to determine the slope of trendline which passes the diagram. So the weibull equation for the failure time of unplated samples is $Ln(P_S)=-1.56(t-12.7)$.

Table 5 Results of slow strain rate test for failure time of different samples (In each case, the failure time of samples has sorted from low to high).

samples conditions	time to failure in slow strain rate test (hour)										
	1	2	3	4	5	6	7	8	9	10	mean
pure Zn	4.1	4.2	4.5	4.75	4.8	4.9	5.2	5.3	5.5	5.75	4.9
Ni/ pure Zn	6.85	6.9	7.1	7.55	7.75	7.9	7.9	7.95	8.3	8.9	7.7
Zn-Ni	7.8	8.15	8.35	8.4	8.65	8.75	9	9.2	9.25	9.65	8.7
Ni/ Zn-Ni	10.35	10.5	10.55	10.9	10.9	11.15	11.5	11.6	11.7	12.2	11.15
shot/ Zn-Ni	8.9	9.3	9.65	9.75	9.8	9.85	9.9	10.3	10.3	10.5	9.8
shot/ Ni/ Zn-Ni	12.1	12.25	12.3	12.5	12.6	12.7	12.85	13	13.1	13.45	12.7
Zn-Ni/ baking	9.4	9.6	9.7	9.75	9.8	10.15	10.55	10.6	10.9	11.1	10.15
Ni/ Zn-Ni/ baking	7.1	7.2	7.35	7.5	8.25	8.3	8.4	8.6	9.1	9.7	8.15
unplated	12.7	12.75	12.9	12.9	13.1	13.25	13.5	13.6	13.8	14	13.25

Table 6 Results of slow strain rate test for unplated samples based on the calculations of weibull model

t (hour)	P_s	$Ln(P_s)$	x
12.7	1	0	∞
12.75	0.9	-0.11	2.11
12.9	0.8	-0.22	1.11
12.9	0.7	-0.36	1.78
13.1	0.6	-0.51	1.28
13.25	0.5	-0.69	1.26
13.5	0.4	-0.92	1.15
13.6	0.3	-1.2	1.34
13.8	0.2	-1.61	1.46
14	0.1	-2.3	1.77

3.2 Effect of Zn-Ni electroplating

According to Figure 2, Zn-Ni alloy electroplating shows less hydrogen embrittlement than pure Zn. Mean failure time for Zn-Ni samples is 8.7 hours while for pure Zn samples, it reaches to 4.9 hours. Although both of which result in considerable hydrogen embrittlement. So that, the mean failure time for unplated samples is 13.25 hours. In other words, in the presence of nickel, alloy coatings are useful to reduce the severity of hydrogen embrittlement, but mechanical properties are still affected by hydrogen diffusion adversely effect.

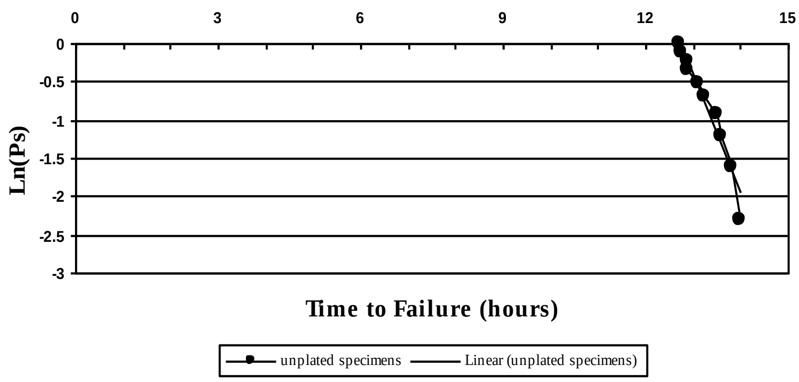

Fig. 1 Weibull diagram for failure time of unplated samples in slow strain rate test

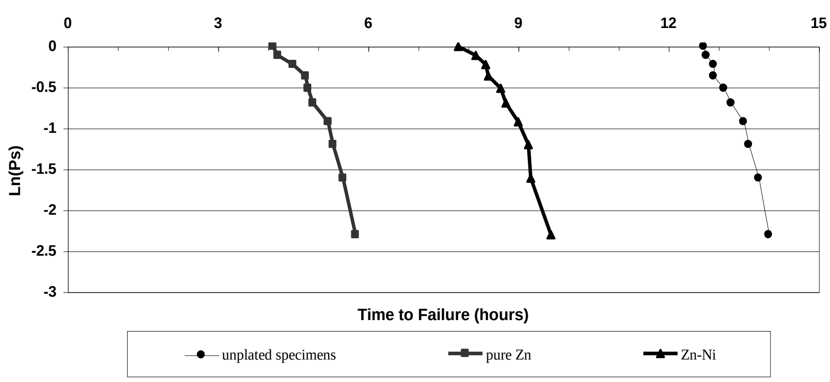

Fig. 2 Weibull diagram for failure time of samples in slow strain rate test for comparison of pure Zn and Zn-Ni

3.3. Effect of electroless nickel interlayer

As Figure 3 shows, with a 5μm nickel interlayer by electroless, the average failure time increases from 4.9 to 7.7 hours for pure Zn samples. Also in the case of Zn-Ni alloy coatings, the mean failure time increases from 8.7 to 11.15 hours. As it is shown, the presences of electroless nickel interlayer shows considerable effect on reducing hydrogen embrittlement. This proves the beneficial effect of nickel as a barrier against the diffusion of atomic hydrogen. However, according to the mean failure time of unplated samples, such a conclusion would be that nickel interlayer cannot completely prevent the occurrence of hydrogen embrittlement.

3.4. Effect of shot peening before electroplating

Slow strain rate test results of the shot peened samples are shown in Figure 4. The shot peening on substrate surface prior to Zn-Ni electroplating, increases the mean failure time of samples from 8.7 to 9.8 hours. The interesting point is that by application of an electroless nickel interlayer, shot peening is more effective in reducing the diffusion of hydrogen. Hence by using samples with Zn-Ni coating, which have been shot peened first and then a nickel interlayer is deposited, the mean failure time of samples reaches to 12.7 hours. In other words, shot peening along with nickel interlayer, makes the failure condition same as unplated samples due to hydrogen embrittlement.

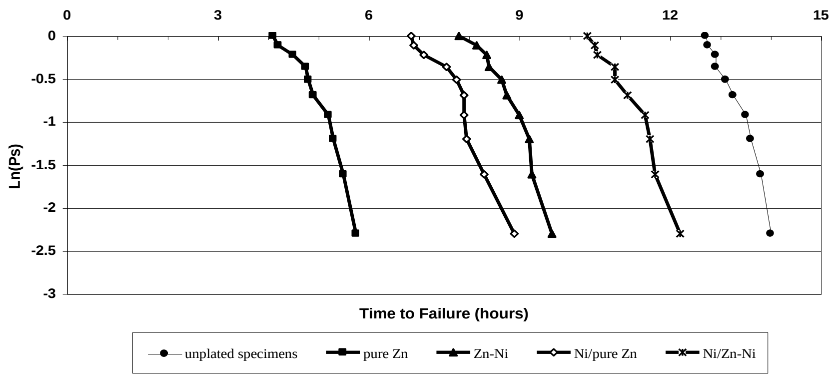

Fig. 3 Weibull diagram for failure time of samples in slow strain rate test for assessment of electroless nickel interlayer

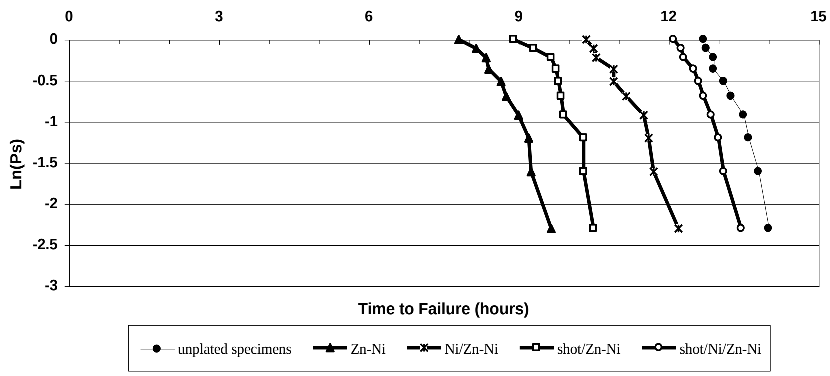

Fig. 4 Weibull diagram for failure time of samples in slow strain rate test for assessment of shot peening effect

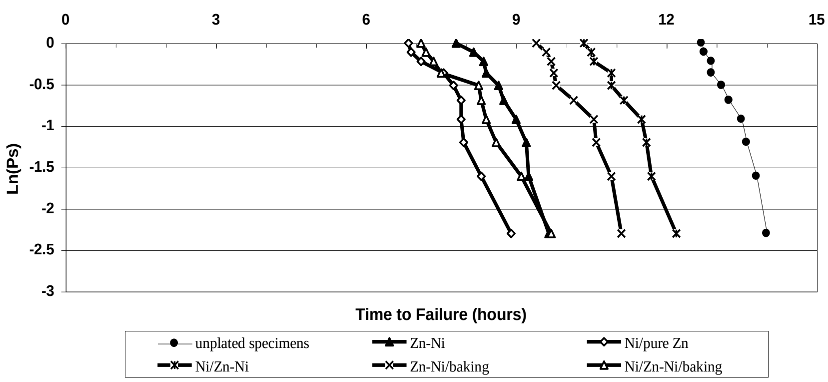

Fig. 5 Weibull diagram for failure time of samples in slow strain rate test for assessment of baking effect

3.5. Effect of baking after electroplating

The results concerning the effect of baking, is shown in Figure 5. As it is shown, baking increase the average failure time of Zn-Ni samples from 8.7 to 10.15 hours. However, in the presence of the nickel layer, baking has an opposite effect. So that baking reduces the mean failure time of Zn-Ni samples containing nickel interlayer, from 11.15 to 8.15 hours. Weibull curves in Figure 5 show that the failure time of Zn-Ni samples contained interlayer by baking after plating, drop to pure Zn samples containing interlayer. Reverse effect of baking process in the presence of the nickel interlayer, will be discussed.

3.6. Calculation of embrittlement index

One of the methods to calculate the hydrogen embrittlement index, based on the failure time of the samples in the slow strain rate test is defined as follows [21]:

$$EI=1-(tp/tc) \qquad (2)$$

Where tp and tc, are failure time of plated and unplated samples, respectively. Average indexes of hydrogen embrittlement, based on the mean failure time of samples in the slow strain rate test are shown as diagram in Figure 6.

4 DISCUSSION

4.1. Effect of Zn alloying with nickel

Generally results of slow strain rate test data for the failure time of plated samples indicate that the electroplating of Cr-Si spring steel with Zn and Zn-Ni alloy, strongly cause the risk of hydrogen embrittlement. The intensity of hydrogen embrittlement caused by Zn-Ni electroplating significantly is less than pure Zn. So that the mean failure time of the samples in terms of pure Zn, only reaches to 56% of the time failure samples in Zn-Ni terms (Figure 2). Furthermore embrittlement index of deposit drops from 0.63 for pure Zn coating to 0.343 for the Zn-Ni. This favorable effect of alloying Zn by nickel is attributed to the deposition mechanism during electroplating.

Zn-Ni alloy deposits forms through an anomalous mechanism that on the contrary, the amount of more noble metal, nickel, is much smaller than the more active metal, Zn. Based on deterrence hydroxide model [22-23], unusual behavior of Zn-Ni alloy deposition can be justified by a layer of more active metal hydroxide, Zn $(OH)_2$, in the cathodic surface of substrate, which act as a barrier against the reduction of nickel. On the other hand, hydrogen reduction at the cathode surface, leads to higher local pH in the substrate surface adjacent solution and thereby attracting more zinc hydroxide.

It would also promote the prevention of Ni2+ discharge in the substrate cathode surface. It seems that the accumulation of discharged Ni2+ ions, in the vicinity of the cathode surface cause desorption of H+ ions and reduces the diffusion of hydrogen on the surface of the steel substrate. On the other hand, reports demonstrate that first, a thin layer enriched with nickel, is formed in the interface of coating/ substrate which acts as a physical barrier against the diffusion of hydrogen into the steel substrate [3,21,24]. This layer enriched with nickel is formed in a normal mechanism at the start of Zn-Ni electroplating process. By continuing process and increasing the pH due to the hydrogen reduction at the vicinity of the cathode surface, the normal mechanism changes to anomalous and the Zn content increases in deposit.

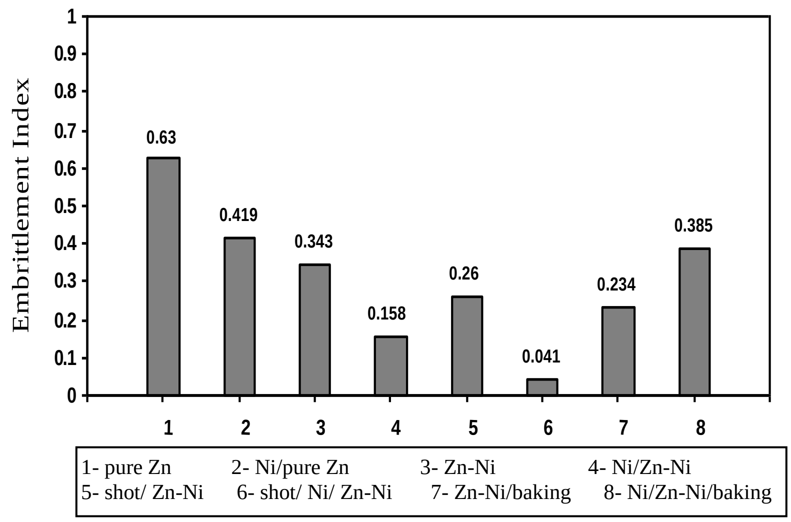

Fig. 6 Average indexe of hydrogen embrittlement calculated for each of plating conditions

4.2. Effect of nickel interlayer

Figure 3 shows that the creation of a nickel interlayer has a desired effect on reducing the amount of hydrogen embrittlement of Cr-Si steel spring. So that the failure time of the samples coated with pure Zn, in the presence of the nickel interlayer, increase from 4.9 to 7.7 hours. The failure time of the samples coated with Zn-Ni alloy, in the presence of the nickel interlayer, increases from 8.7 to 11.15 hours. However, with respect to the mean failure time of unplated samples, it is clear that nickel interlayer cannot completely prevent the occurrence of hydrogen embrittlement, although it has reduced the average index of hydrogen embrittlement dramatically.

The nickel interlayer effect that can be justified by the interlayer created by the alkaline bath of the nickel electroless, has compressive residual stresses [25]. While the Zn-Ni deposit created by electroplating, has tensile residual stress [26]. Hence, although a rich layer of nickel can act as a physical barrier against diffusion of hydrogen, but because of the lack of balance between the compressive residual stresses of interlayer with the tensile residual stresses of alloy deposit, the interface between the interlayer and above layer would become disequilibrium and finally its high energy level provide the proper driving force for hydrogen atoms to move from upper layer to the interface.

Therefore, although the hydrogen diffusion coefficient in the nickel interlayer is down, a few hydrogens diffuse into the substrate. So the nickel interlayer cannot prevent the hydrogen diffusion completely and eliminate the hydrogen embrittlement. So that the mean failure time of samples coated with Zn-Ni and containing Ni interlayer, only reaches 84% of the unplated samples.

4.3. Effect of shot peening before electroplating

As Fig. 4 shows, shot peening of steel substrate surface, increases the mean failure time of the samples coated with Zn-Ni from 8.7 to 9.8 hours. It is clear that application of a nickel interlayer makes the previous shot peening more effective on the increasing the average failure time. So that the mean failure time of the Zn-Ni samples containing nickel interlayer with early shot peening reaches to 12.7 hours, which is very close to the unplated samples. In this state, the embrittlement index is at lowest level (0.041) among the different studied conditions.

It seems that the most important point about the positive effect of substrate shot peening process, in reducing the amount of hydrogen embrittlement, is creating a thin layer containing of compressive residual stresses on the substrate surface. On the one hand the thin layer due to reducing the lattice parameter of steel and empty available spaces, decreases the hydrogen permeability and on the other hand it causes a considerable time delay in hydrogen diffusion. There is a report which can prove that shot peening can produce up to 400% time delay in the hydrogen diffusion [20]. In addition, the positive effect of shot peening can be attributed to a decrease in the growth rate of micro cracks caused by the tensile stresses in terms of services. Propagation velocity of the cracks becomes considerably slow when the tip of the crack reaches the region which contains compressive residual stresses. In addition, several changes of the crack path can also increase the toughness. Figure 7 shows schematic of crack growth in shot peened steel substrate with the multilayer coating system which is under this study. These factors, along with better mechanical lock between coating and substrate, justify excellent effect of shot peening process at increasing the failure time of samples and reducing the hydrogen embrittlement index.

4.4. Effect of baking treatment after electroplating

Figure 5 shows that the baking has a desired effect at increasing the mean failure time of the Zn-Ni samples. So that the failure time of these samples, after the baking, reaches to 77% of the failure time of unplated samples. The embrittlement index of these samples drop from 0.343 to 0.234 in baked terms, which is a considerable reduction. Due to the fact that the baking is done at 200°C and no structural changes occurred in this temperature [27-29], the positive effect of baking is attributed to the creating proper thermodynamic conditions for the removal of diffusive hydrogen. There are several reports that prove a dense network of microcracks at the interface of Zn-Ni alloy coating and steel substrate [10,11,26,30]. However, the existence of these microcracks is due to the residual stresses at non epitaxial interface of coating/ interlayer. Due to the baking, extreme difference in thermal expansion coefficient of the Zn-Ni alloy with Cr-Si steel, leads to worsening the microcrack network. Hence, hydrogen diffusion through this dense network is more quick and this leads to more hydrogen atoms output and increase the average failure time of samples in the slow strain rate test.

On the other hand, Fig. 5 shows that the baking in the presence of nickel interlayer has a reverse effect. In other words, the mean failure time of Zn-Ni samples containing nickel interlayer, significantly reduces after baking. Beside, amount of embrittlement index increases dramatically from 0.158 to 0.385, which represents an increase in substrate sensitivity to hydrogen embrittlement. As previously mentioned, the layer of Zn-Ni alloy has tensile residual stresses and nickel interlayer has compressive residual stresses. So when the surface microcrack network expands to the overall thickness of Zn-Ni alloy coating, it reaches to the interface of Zn-Ni with nickel interlayer. Since the hardness of nickel interlayer due to compressive residual stresses, is more than Zn-Ni layer, the entry of crack tip plastic zone in to the interlayer faces difficulty, (Figures 7 (c) and (d)) . These conditions result in reduction of crack growth and even stop it at the interface of Zn-Ni/ Ni. Therefore, due to the inhibition of nickel interlayer, the dense network of microcracks does not expand along the interlayer to steel substrate. While these interconnected networks provide an appropriate route for the exit of diffusive hydrogen to the free surface. So the access of hydrogen atoms which has diffused into the Cr-Si steel, to the free surface is reduced and the amount of hydrogen remaining in the steel substrate increases more than samples without nickel interlayer. As a result, Zn-Ni samples containing nickel interlayer, show more brittleness conditions after baking than not baked samples.

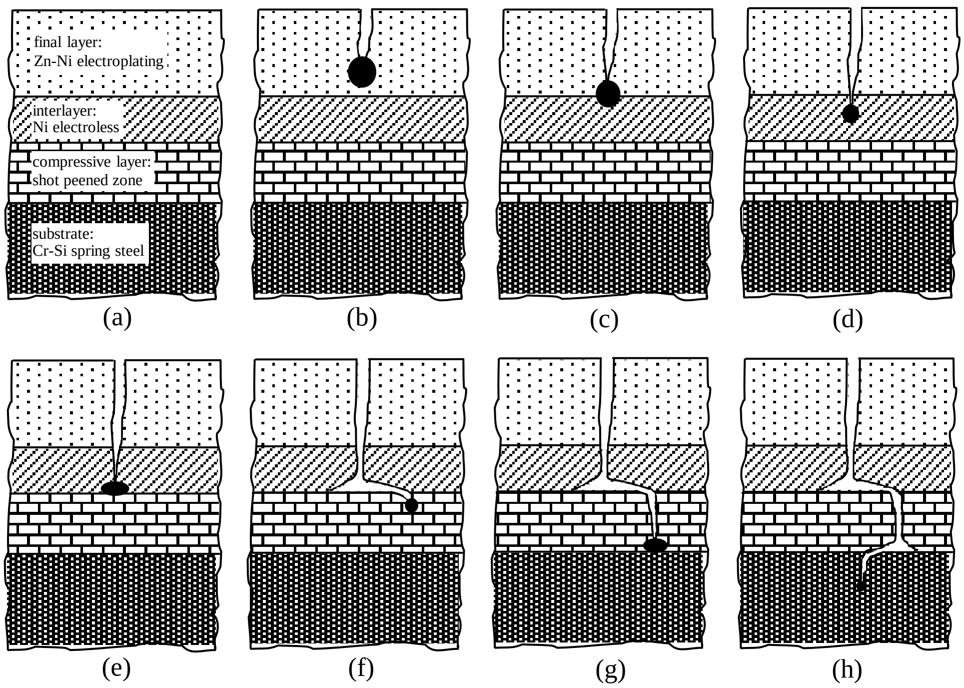

Fig. 7 Schematic of crack propagation in steel substrate in presence of a multilayer coating system containing Zn-Ni alloy and interlayer nickel

5 CONCLUSION

1- Use of Zn-12%Ni alloy coating instead of pure Zn, reduces embrittlement index of Cr-Si spring steel from 0.63 to 0.343.

2- Presence of electroless nickel interlayer acts as a physical barrier against diffusion of hydrogen and reduces the hydrogen embrittlement index of Cr-Si steel with pure Zn coating from 0.63 to 0.419 and with Zn-12%Ni coating from 0.343 to 0.158.

3- Shot peening before electroplating, has a considerable effect in reducing hydrogen embrittlement index. So that shot peening process, decreases the embrittlement index of Cr-Si steel coated with Zn-12%Ni from 0.343 to 0.26.

4- The best behavior of the studied samples belongs to shot peened Cr-Si steel coated with Zn-12%Ni containing nickel interlayer. In this state, the embrittlement index indicates the reduction up to 0.041.

5- Baking treatment after Zn-Ni electroplating, reduces the embrittlement index of Cr-Si spring steel from 0.343 to 0.234.

6- Baking treatment after Zn-Ni electroplating, in the presence of nickel interlayer, has a reverse effect on hydrogen embrittlement index. So that the embrittlement index increases from 0.158 to 0.385.

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