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Influence of baking time on hydrogen embrittlement in alkaline nickel-zinc electroplated steel fasteners

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The hydrogen embrittlement (HE) phenomena pose a considerable risk, especially in the application of high-strength steel fasteners. If HE in fasteners is not eliminated, it is a phenomenon that has catastrophic consequences such as crack growth in matter, fracture initiation, and finally instant failure. Hydrogen gas produced during side reactions in the electroplating process of steel fasteners is known to be riskier compared to atmospheric hydrogen exposure. In this study, Ni-Zn electroplated 12.9 bolts have been baked in 200°C for 4, 8 and 12 h to observe its effect on the prevention of HE. The elongation values of the samples have been examined with a slow strain rate test (SSRT), and the best recovery condition of the ductility of the materials was determined. The effects of different baking times on the microstructure are observed by an optical microscope. The morphological structure of the coating is investigated by SEM. An electromagnetic acoustic spectroscopy technique was performed to know the effect of different bake times executed at constant temperature and the effect upon dislocation mobility. The results show that eight hours of baking is sufficient for HE elimination, and therefore twelve hours would be unnecessary in terms of energy saving. Furthermore, the non-destructive testing technique known as acoustic resonance may be used to detect HE.

Keywords: Baking time, Electroplating, Fasteners, Hydrogen embrittlement, Steel, Manufacturing defect

Introduction

Hydrogen embrittlement (HE) is a phenomenon that occurs when atomic hydrogen is introduced into a metal's microstructure, causing a loss of ductility and strength, and leading to sudden and catastrophic failures. This can happen during the manufacturing, processing, or usage of metals and alloys, and it is a significant concern for industries such as aerospace, automotive, and energy. The mechanism of HE involves the diffusion of atomic hydrogen into the metal lattice, where it can form hydrogen gas bubbles or react with other elements to form hydrides. These trapped hydrogen atoms or molecules create local areas of high stress concentration, which can initiate cracks and lead to brittle fractures. Moreover, hydrogen can also increase the local plasticity of the metal by promoting dislocation mobility. This can cause localized plastic deformation, which can result in crack initiation and propagation, ultimately leading to catastrophic failure. In order to prevent or mitigate HE, various techniques are used, such as selecting hydrogen-resistant materials, controlling the hydrogen content during manufacturing or processing, and applying surface coatings to prevent hydrogen absorption. Furthermore, stress relief, heat treatment, and hydrogen removal techniques such as vacuum drying and thermal desorption can also be used to mitigate the effects of hydrogen embrittlement[1-4].

Hydrogen embrittlement is categorized into two categories based on the hydrogen source and the effect on the lattice structure such as (a) internal hydrogen embrittlement (IHE) and (b) environmental hydrogen embrittlement (EHE). IHE occurs when atomic hydrogen is already present in the metal's microstructure due to its manufacturing, processing, or service history. IHE can be caused by a variety of sources, including pickling, or electroplating in acid baths, cathodic protection, and exposure to hydrogen gas during welding or other high-temperature processes. The trapped hydrogen atoms or molecules can create internal stresses and defects, which can lead to crack initiation and propagation, leading to brittle fracture[5,6]. On the other hand, environmental hydrogen embrittlement (EHE) occurs when hydrogen enters the metal's microstructure from an external source, such as exposure to hydrogen gas, hydrogencontaining liquids or solutions, or hydrogen gas generated in situ by corrosion reactions. EHE can cause hydrogen to diffuse into the metal lattice and react with other elements, leading to the formation of hydrides and creating local areas of high stress concentration. This can result in crack initiation and propagation, leading to sudden and catastrophic failures[6-8]. Particularly in high-strength metals and alloys, the effects of such phenomenon are known to be more severe. Materials such as Mn-steel, aluminum alloys, titanium, magnesium alloys, as well as steels with a strength higher than 1000 MPa are also susceptible to hydrogen embrittlement[9].

The electrochemical deposition process is accepted to pose an elevated risk of HE, respectively, for materials such as ISO 898-1 grade 10.9 or higher mechanical strength[9-10]. Due to the nature of electroplating processes, hydrogen gas is produced at the cathode as a by-product. The cathode, which is also the product being plated, is exposed to hydrogen gas more intensely than atmospheric hydrogen. Although an acid cleaning pretreatment, which is used to detach unwanted surface impurities or activate the surfaces for plating, also causes the production of hydrogen gas. Therefore, in electroplating, it is important to remove the hydrogen with an additional process to prevent HE[11].

Accordingly, one of the most cost-efficient and commonly used methods in industry is the baking process. Baking is the process of removing HE by applying heat to the material. As the temperature rises, the trapped hydrogen in the crystal lattice gains enough energy to become mobile and can freely diffuse out from the metal surface. The rate of hydrogen diffusion increases in proportion to the applied temperature. Therefore, it is common process that the amount of hydrogen in the component is minimized by baking after electroplating[12,13]. The baking process ought to take several hours due to the fact that the electroplated coating layer acts as a barrier to hydrogen escape. A minimum of 4 h of treatment is required, yet the optimum baking parameters hinge on the coating material, permeability and thickness, mechanical behavior of the metal being coated, and other elements that affect hydrogen diffusion[14]. ISO 19598 is a standard that is an instruction for pretreatment for metallic and inorganic coatings of iron or steel to reduce the risk of HE. According to the guideline, as the strength of the material increases, the recommended baking time increases.

This study aims to investigate the effects of baking time on the mechanical properties of Ni-Zn electroplated 12.9 bolts, which can be correlated to the HE phenomena. Secondly, the acoustic resonance non-destructive testing technique is used to observe the potential of its use in the detection of hydrogen present in these fasteners.

Experimental Section

Materials and method

According to ISO 19598, 12.9 grade steel (1080 MPa minimum yield strength and 1200 MPa tensile strength) is likely to exhibit HE when electroplated. Therefore, in this study, a 12.9 grade, 8.0 x 1.25 mm 41Cr4 quality high strength steel bolt was selected as a proper candidate for the investigation of hydrogen embrittlement after electroplating. The chemical composition of 41Cr4 medium carbon steel was shown in Table 1.

The samples were pretreated with degreasing baths before the electroplating process. After being degreased, samples were activated in an acidic solution bath to improve the adhesion of the surface coating. Samples were Zn-Ni electroplated in an alkaline medium in a coating bath. The bath temperature was set to 22-28°C.The chemical content of the bath solution is shown in Table 2.

After the coating process, the samples were taken into the oven to remove HE. The bolt samples were treated at 200 °C for 4, 8, and 12 h, respectively. To observe the effect of the baking process on the HE, a few of the Zn-Ni-coated samples were not taken into the furnace as reference samples.

Table 1 — Chemical composition of alloy 41Cr4

Element	Content (wt. %)
Fe	97-98,1
Mn	0.6-0.9
C	0.38-0.45
Si	0-0.4
P	0-0.035
S	0-0.035
Cr	0.9-1.2

Table 2 — Electroplating bath chemical content

Chemical	Content
Zn (s)	8- 12 g/L
Ni (s)	0,8-1,8 g/L
NaOH (s)	120-140 g/L
Na_2CO_3 (s)	Max 80 g/L

Characterization

Optical microscopy

Mechanically polished and etched samples were examined by optical microscopy. Cross-section areas that are close to the coating regions were chosen to be examined. The number of the grains, size of the grains, and phase area ratios (ferrite/pearlite) were analyzed by ImageJ, which is an open-access Java-based image processing software[16,17].

The line intercept method was used to figure out the average grain size for each specimen, using Eq. (1)[18]. Average particle number analysis was also performed on polarized magnitude images to obtain quantitative data.

$$\text{Average Grain Size} = \left(\frac{\text{Line Length}}{\text{Number of Grains}}\right) \quad \ldots (1)$$

Slow strain rate testing

The tensile test for bolts samples also known as "slow strain rate test" has been conducted in accordance with ISO 898-Part 1 standard, which is suitable for bolts, screws, and studs with specified property classes[10]. Crack formation may not occur because of too low or too high strain rates; therefore, SSRT is a common method used in the examination of stress corrosion cracking as well as for HE evaluation[19]. The selected strain rate is usually between 10^{-8} and 10^{-3} s^{-1}. In order to understand the effect of different baking time on recovering ductility, slow strain rate tests were carried out at a constant strain rate of 1.0 x 10^{-6}/s.

Electromagnetic acoustic spectroscopy

Electromagnetic acoustic spectroscopy is a non-destructive method that instantaneously determines the state of free hydrogen trapped in the substrate material by observing dislocation mobility. The method applied is a narrowband continuous wave excitation system. Here, a signal generator sweeps a narrow frequency determined by either calculation or by empirically finding a proper frequency and performing comparative measurements. Driving a specially tuned bulk shear wave EMAT, the complimentary receiving transducer simultaneously receives the resonant acoustic signal, which is then demodulated and digitized. The signal is then computer-analyzed for attenuation characteristics[20,21].

Results and Discussion

Coating characteristics

After electroplating zinc-nickel on the 41Cr4 steel bolts, the surface was analyzed by scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy (EDX) was also performed to obtain a quantitative interpretation of plating elements. Fig. 1 shows the SEM/EDX images of the Zn-Ni coated steel sample (cross section of (a) the head region and (b) the thread region).

Accordingly, on surfaces such as the thread region that have sharp edges, the coating thickness showed a regionally heterogeneous distribution compared to the head region. That is due to the edge effect, where the non-uniform current density on the sharp corners

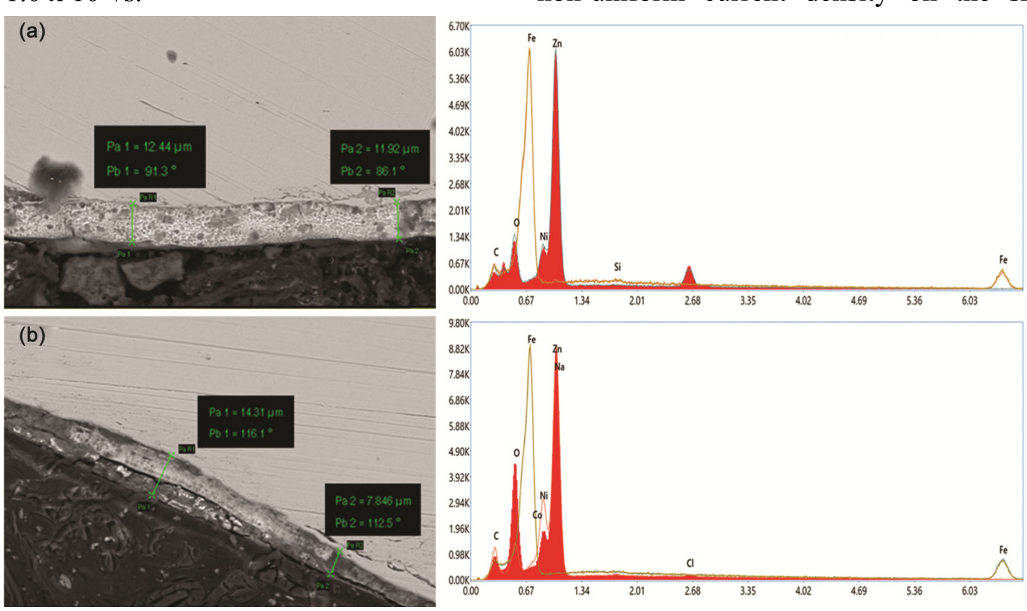

Fig. 1 — SEM images of the coating surface and EDX composition analysis of the particles present in (a) cross section of head region and (b) cross section of head region (magnification 2000X)

is transferred to non-uniform deposition layers. Especially when electroplating the thread region, such an event causes a thicker coating on the crest wherever the root remains thinner[22]. Conversely, for the bolt head section, a uniformly thick coating was obtained. Based on the SEM images, the average coating thickness was found to be 13 µm which complies with the ISO 4042 standards essentials[23].

Spectroscopy results showed that the cathodic-protecting barrier contains an average of 86% Zn and 14% Ni in the structure. Conforming to Table 2, the Zn content in the bath is 6 to 10 times higher than the Ni content; therefore, this result is compatible with EDX. In a vacuum environment, oxygen was also found (6%), which may be a sign that oxidation has started in the coating or that oxygen was trapped in cracks that formed on the coating surface by the mechanical sanding and polishing process.

Microstructure analysis

To assess the effect of the baking process on microstructure and mechanical behaviours, overview optical microscope images were collected for each tested specimen. Metallographic examination of the longitudinal sections from the head and the shank showed the typical microstructure of medium carbon steel, which consists of perlite and ferrite phases.

As shown in Fig. 2 (bright phases) ferrite and (dark phases) pearlite phases present in the microstructure. The ratio of ferrite and pearlite regions depends on the carbon (C%) content of the steel. In the literature, the carbon content of medium-carbon steel is considered to be in the range of 0.3 to 0.6 [Ref. 24,25].

The ratios of different phase areas were calculated for each specimen using images with various magnifications. Binary analyses showed that for all specimens, the mean values of the ratios of dark and bright regions were between 37.8 and 42.1%. This result indicated the carbon content in the steel was 0.3-0.4% by weight, which showed that this result was consistent with the chemical composition presented in Table 1.

The total number of ferrite and pearlite grains and the mean size of the grains were also determined on 500x images for each sample. As presented in Table 3, no dissimilarity was observed between microstructures. Hence the results are relatively close; it was seen that the heat treatment had little to no effect on the microstructure.

Slow strain rate test

Slow strain rate tests were performed to understand the mechanical behaviour appropriately. Mechanical properties such as yield, tensile stresses, and strain on the zinc-nickel electroplated specimens baked at

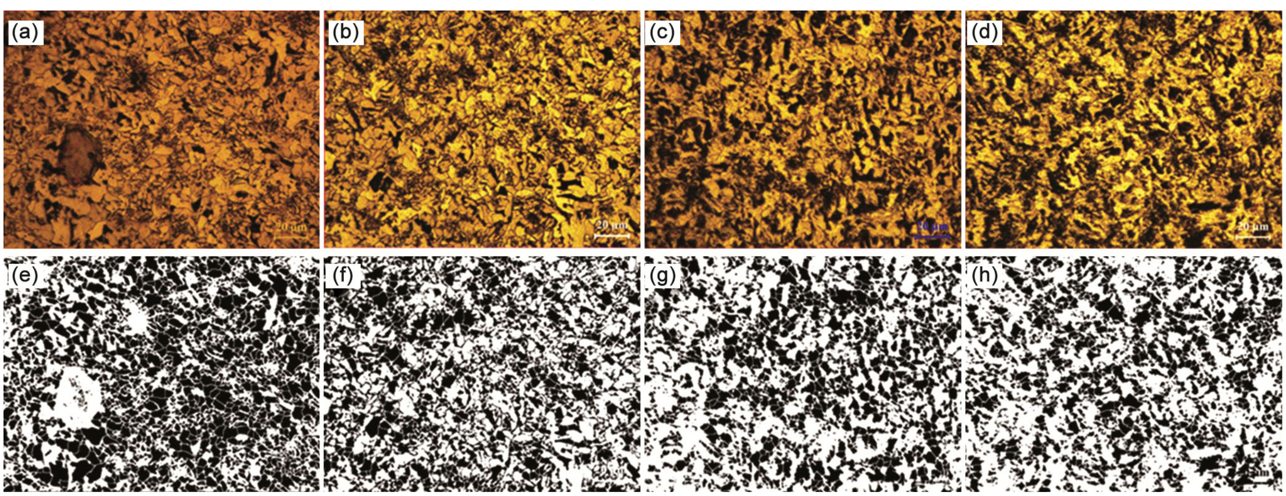

Fig. 2 — Optical microscope images of; (a-e) reference sample, (b-f) 4h-baked sample, (c-g) 8h-baked sample, and (d-h) 12h-baked sample (right-side are the binary images)

Table 3 — Slow strain test results of electroplated 12.9 bolt samples

Sample Name	Average Yield Strength (MPa)	Average Tensile Strength (MPa)	Average Elongation(%)	HDR
Reference	1200.1	1295.4	13.9	-
4h-baked	1217.5	1296.1	14.9	7.19
8h-baked	1214.8	1305.1	15.4	11.4
12h-baked	1213.2	1313.7	15.5	11.5

various times were examined[26]. The effect of the time the samples spent in the HE furnaces on the ductility values of the materials were observed with the amount of elongation[27].

The stress-strain diagram and elongation values obtained from slow strain rate tests were shown in Fig. 3 and Table 4. As a result, the difference in tensile and yield strengths between each sample was found to be significantly low. The maximum difference between the strength values did not exceed 1%. However, a clear distinction in strain rates was observed. A linear regression was observed between elongation and heat treatment time in samples fired at different times[28]. To better understand, the elongation values were also used to determine the hydrogen ductility recovery (HDR) by using Eq. 2.

$$\mathrm{HDR},\% = \left(\frac{\varepsilon_0-\varepsilon_H}{\varepsilon_0}\right)\cdot 100 \quad \text{... (2)}$$

Here, ε_0 and ε_H are the strains of the reference sample and the baked samples, treated for 4, 8, and 12 h, respectively. A higher HDR implies that the bolts have a higher elimination of hydrogen-induced embrittlement and carry a lower risk of HE compared to the reference sample. The HDR of a 4 h baked bolt was 7.1% higher than that of a not-baked reference sample. In the cases of 8 and 12 h of baked HDR, it was 11.3% and 11.5%, respectively. This result indicates that, compared to the reference specimen, ductility was recovered for all baked samples[30,31].

Due to the differences in the HDR results, it was determined that 4 h of baking did not provide sufficient conditions for a total recovery of ductility; however, in the case of 8 and 12 h baked samples, given enough time, the hydrogen diffuses out from the metal grain boundaries until the residual hydrogen is removed.

Dislocation Mobility

The research of a potential technique to ascertain the impact of various bake periods carried out at a constant temperature and the impact on dislocation mobility assessed using electromagnetic acoustic spectroscopy was presented[32].

Dislocation mobility is assessed primarily through the attenuation behavior by measuring the rise and fall times of the resonance and anti-resonance peaks of low frequency (~10 MHz) resonances. The obtained data indicated that the dislocation mobility is reduced, or the hydrogen is moved to trapping zones or released with increased bake times[33].

According to Fig. 4, as the baking times were increased, the pulse width decreased, which was also interpreted as a reduction in dislocation mobility[34]. It was observed that the pulse width decreased as the firing times increased, and this decrease was thought to be a reason for the decrease in dislocation mobility. The highest dislocation mobility was obtained in the unbaked samples, and it was observed that it decreased as the baking time increased. However, no

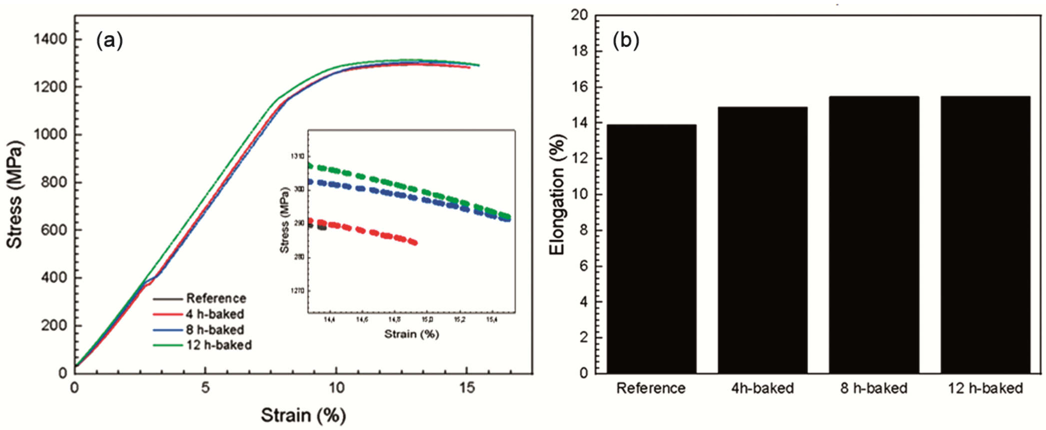

Fig. 3 — Slow strain rate test results: (a) Stress-strain curves and (b) Elongation

Table 4 — Slow strain test results of electroplated 12.9 bolt samples

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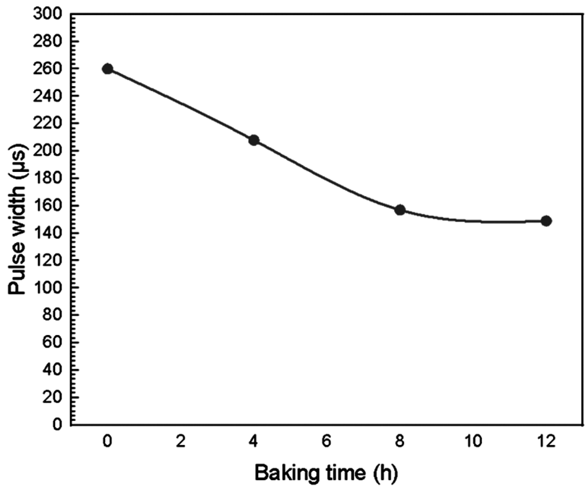

Fig. 4 — Electromagnetic acoustic spectroscopy test results

appreciable difference in dislocation mobility was observed between 8 and 12 h baked sample.

Conclusion

Theoretically, we would expect hydrogen trapped in the metal to increase the brittleness of the material. So, the sample that has not been treated in the hydrogen embrittlement furnace supposed to show lower elongation values compared to the samples that heat treated, since it is not free of hydrogen in its content. SSRT results confirmed that baking process is a healthy method for ductility recovery by removing hydrogen in the structure.

The mechanical test results showed that the yield and tensile strength of baked samples did not change, however the elongation values were linearly increased with the increased baking time. Specifically for Zn-Ni electroplated bolts, 12 h of baking has little to no significant effect on ductility and can be considered as a waste of energy compared to 8 hours of baking process. Due to HDR results, the best baking parameters were obtained by 8 h baking process.

It has been seen that the number of grains and sizes through microstructural analysis of each specimen are quite similar. It was figured out that the furnace temperature (200 °C) and the time spent in the process did not cause a notable change in the microstructure and phase metallurgy. Therefore, the differences in the results of the SSRT were naturally assumed to be due to hydrogen related.

There is a substantial amount of research work writing down that the presence of hydrogen alters dislocation behaviour and the increase in dislocation mobility is caused by hydrogen shielding of the dislocation sites[32]. This phenomenon is seen across both edge and screw dislocations in the microstructure of FCC, BCC and HCP ordered and disordered materials.

Electromagnetic acoustic spectroscopy results proved that it is a highly reliable method for assessing the efficiency of hydrogen release bake. Because HE and dislocation mobility correlation, consistent results were obtained with the SSRT results.

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