metals

Article

Decrease in Hydrogen Embrittlement Susceptibility of 10B21 Screws by Bake Aging

Kuan-Jen Chen [1], Fei-Yi Hung [2,*], Truan-Sheng Lui [2] and Chien-Hao Tseng [2]

1 Instrument Center, National Cheng Kung University, Tainan 70101, Taiwan; kjchen1982@gmail.com
2 Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan; luits@mail.ncku.edu.tw (T.-S.L.); kevin601032002@gmail.com (C.-H.T.)
* Correspondence: fyhung@mail.ncku.edu.tw; Tel.: +886-6-275-7575 (ext. 62950)

Academic Editor: Hugo F. Lopez
Received: 11 July 2016; Accepted: 26 August 2016; Published: 31 August 2016

Abstract: The effects of baking on the mechanical properties and fracture characteristics of low-carbon boron (10B21) steel screws were investigated. Fracture torque tests and hydrogen content analysis were performed on baked screws to evaluate hydrogen embrittlement (HE) susceptibility. The diffusible hydrogen content within 10B21 steel dominated the fracture behavior of the screws. The fracture torque of 10B21 screws baked for a long duration was affected by released hydrogen. Secondary ion mass spectroscopy (SIMS) result showed that hydrogen content decreased with increasing baking duration, and thus the HE susceptibility of 10B21 screws improved. Diffusible hydrogen promoted crack propagation in high-stress region. The HE of 10B21 screws can be prevented by long-duration baking.

Keywords: low-carbon boron steel; hydrogen embrittlement; baking; secondary ion mass spectroscopy

1. Introduction

Hydrogen can be introduced into low-carbon steel screws during production processes such as acid pickling and electroplating. Screws are susceptible to hydrogen embrittlement (HE). HE has been observed in structural beams, vehicle axles and fasteners that would cause a serious damage for life and property [1,2]. Reducing HE susceptibility to prevent brittle fractures is an important issue.

Various methods have been proposed for preventing HE in screws, such as processing improvements [3], thermal treatments [4,5], and material modification [6]. In industry, quenching and tempering heat treatment is commonly used to prevent HE in low-carbon steel screws [5]. When quenched steel is heated below the austenite transformation temperature, martensite transforms into cementite and ferrite, enhancing steel toughness. The hydrogen atoms in a metal can be divided into diffusible hydrogen and non-diffusible hydrogen [2]. Non-diffusible hydrogen is usually located at interphase boundaries or in dislocations and is not easily removed. This type of hydrogen atom can form hydrogen traps that limit the movement of hydrogen atoms, enhancing HE resistance [7]. In contrast, diffusible hydrogen can freely move, and easily accumulates to form hydrogen molecules which damage the host material. Some reports have indicated that hydrogen atoms within a material can be released by long-duration baking, reducing HE susceptibility [8,9]. Hwang et al. reported that adding particular elements to low-carbon steel can enhance the hardenability of steel [10].

The present study uses low-carbon boron (10B21) steel screws to investigate the baking effects on the HE susceptibility. Tempering and baking treatments are used to serve as improvement plans for the HE of 10B21 screws. Secondary ion mass spectroscopy (SIMS) is used for detecting hydrogen within the material [11]. The advantage of SIMS is that hydrogen and the various isotopes of elements can be detected. However, the study for hydrogen detecting of high-strength low-carbon steel by SIMS has never been reported. The hydrogen concentrations in 10B21 screws are detected to investigate the relation between baking effect and HE susceptibility.

2. Materials and Methods

2.1. Material Preparation

Commercial 10B21 steel was used in the present study. The chemical composition of the steel is summarized in Table 1. The steel was extruded to form a wire rod (Φ = 5.5 mm) after spheroidizing annealing. Self-drilling screws were then formed via cold forging. The screws were austenitized at 950 °C for 30 min in an air furnace, and quenched in water. Then, the quenched screws were tempered at 260 °C for 30 min in a salt bath. The heat-treated screws were acid-pickled, and then electroplated with zinc (Figure 1a). The screws were then baked at 215 °C for various durations (0–16 h) in an oven to estimate HE susceptibility.

Table 1. Chemical composition of 10B21 steel (wt. %).

Fe	C	Mn	P	S	Si	Al	B
Bal.	0.18	0.78	0.015	0.005	0.06	0.044	0.002

2.2. Twist-Off Strength and Hydrogen Embrittlement Testing

For the twist-off strength test, a torque spanner (KING TONY, Taichung, Taiwan) was sed as the testing tool. A high-carbon steel sleeve (Figure 1b) (Self-Made, Tainan, Taiwan) was used to ensure that the screws were maintained in a vertical orientation and simultaneously received a tensile stress when the screws were fractured. The screws with the high-carbon steel sleeves were fastened to a steel plate, indicating that the screw was received a torque force and tensile force in the meantime (Figure 1c). The torque force was increased with increments of 0.5 N·m until the screws fractured, and acquired the fracture torque (mechanical properties). To examine the effect of hydrogen on HE susceptibility of screws, HE testing was performed in accordance with ANSI/ASME B 18.6.4. Screws with pre-stress of 60% or 80% (16 or 22 N·m) of the maximum twist-off strength were fastened to a steel plate, and held for 24 h. After that, the screws were loosened and checked for HE. Finally, the twist-off strength testing was carried out on non-fractured screws.

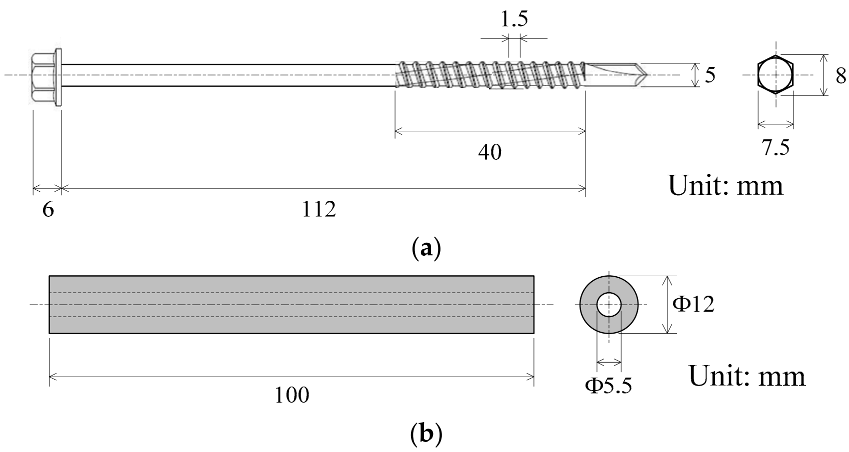
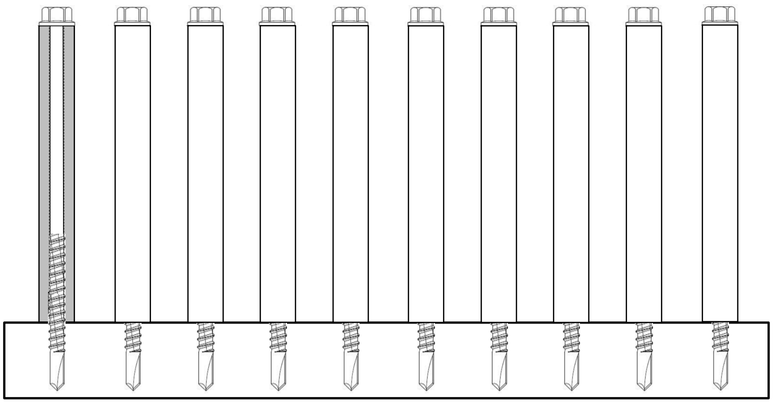


Figure 1. *Cont.*



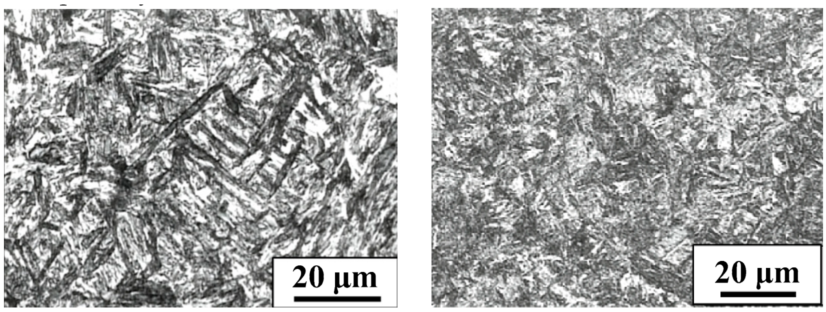
(**c**)

Figure 1. Schematic diagram of (**a**) self-drilling screw, (**b**) sleeve, and (**c**) twist-off strength and HE testing.

The microstructures of the screw specimens were observed using optical microscopy (OLYMPUS, Tokyo, Japan). The microhardness profile was measured through different cross-section along the screws using a Rockwell-C hardness machine (MITUTOYO, Kanagawa, Japan). To investigate the effects of baking on dehydrogenation, the hydrogen content in the screws was measured with SIMS using a CAMECA IMS-6f analyzer (CAMECA, Genevilliers, France) with a Cs^+ primary beam. The liquid nitrogen was used in sample chamber to minimize the hydrogen background. After twist-off strength testing, the fracture surfaces of the screws were examined using high-resolution scanning electron microscopy (HR-SEM) (HITACHI, Tokyo, Japan).

3. Results

The microstructure of a quenched screw specimen is shown in Figure 2a, where the grey black regions are martensite (α') and the white regions are ferrite (α). Lath martensite only appears in low-carbon steel matrix, and grows in the orientation of the austenite grain [12]. After tempering for 30 min, the entire screw consisted of uniform tempered martensite with scattered recrystallized ferrite (Figure 2b). Notably, the microstructure of the screw did not significantly change even after long-duration tempering. Figure 3 shows the microhardness profile of the screw specimen, with point measured at 15-mm intervals. The average hardness was approximately 43 HRC (Rockwellhardness), higher than that of general heated low-carbon steel [13]. The HE was highly sensitive to high hardness characteristic [14]. The screws were baked for various durations to determine HE susceptibility.



(**a**) (**b**)

Figure 2. Microstructure metallograph of screw specimen after (**a**) quenching and (**b**) quenching and tempering.

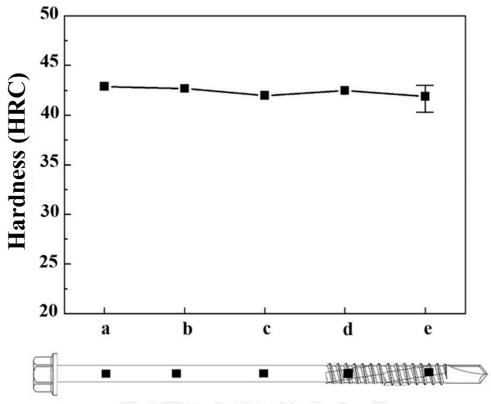
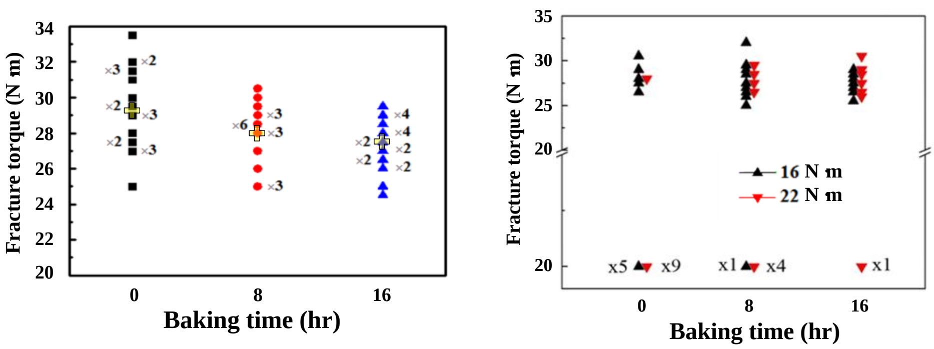


Figure 3. Microhardness profile of 10B21 screw (points at 15-mm intervals) (**a**–**e** indicated different cross-section positions along the screw).

To investigate the effects of baking and pre-stress on the HE susceptibility of the screws, the twist-off strengths of the screws were determined (Figure 4). Figure 4a shows the torque strength of the screws with different baking durations. The fracture torque of the screws gradually decreased with increasing baking duration, and there was a tendency towards the average torque strength (hollow cross). Hydrogen was absorbed within the metal lattice and tended to accumulate in high-stress areas, which led to solid solution strengthening, enhancing the tensile strength [15]. The hydrogen effused during the baking process, which reduced mechanical strength [16]. In addition, there was a slight tempering effect on the mechanical strength due to the baking treatment temperature (215 °C) being close to the low tempering temperature (260 °C). Although the torque strength of screws slightly deteriorated after baking, the HE susceptibility may improve. For HE testing, the fracture torque of the screws with pre-stress (16 or 22 N·m) for 24 h as a function of baking duration are shown in Figure 4b. The results show that the screws without baking treatment (0 h) had serious brittle fractures. This fracture behavior can be attributed to the HE of steel. The hydrogen was easily adsorbed on the material surface during the screw manufacturing process (acid pickling, galvanization), and diffused into the material. The hydrogen migrated to high-stress regions was caused by a continuous tensile stress and resulted in the formation of a crack [17]. After baking for 8 h, the HE of the screws slightly decreased. For the screws with lower pre-stress (16 N·m), HE did not occur after baking for 16 h. This result confirms that hydrogen can be effectively released by baking treatment to reduce HE susceptibility [4]. The effects of hydrogen content in screws on HE susceptibility need further clarification. Therefore, the SIMS is used to detected hydrogen content in screws.



(**a**) (**b**)

Figure 4. (**a**) Twist-off strength (cross symbol: average fracture torque; ×2: 2 screws; ×3: 3 screws, the rest by analogy) and (**b**) HE testing results of 10B21 screws baked for various durations (×5: 2 screws; ×9: 9 brittle fracture screws, the rest by analogy).

Figure 5 shows the depth profiles of hydrogen in the 10B21 screws specimens subjected to baking for various durations. The SIMS depth profile was measured through cross-section of the screws to avoid the effects of Zn-electroplated layer. The surface peak is present from the start sputtering, which attributed to the surface effects [18]. For the SIMS depth profile, the area under the curve corresponds to the element concentration. In this case, the number of hydrogen atoms in the 10B21 screws significantly decreases after baking treatment. This result is consistent with the HE testing (Figure 4b), confirming that long baking duration can effectively prevent the occurrence of HE.

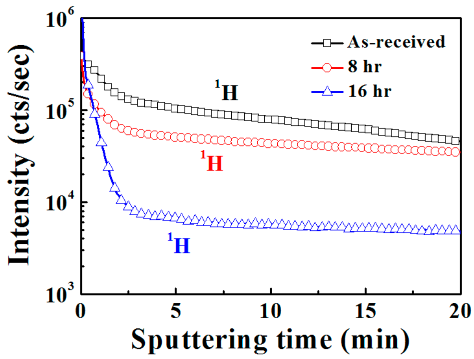


Figure 5. A depth profile of Hydrogen content in 10B21 steel after baking at 215 °C for different durations.

The macrostructure characteristics and fracture surfaces for a ductile screw and a brittle screw are shown in Figure 6. The screw baked for 16 h fractured at the thread of stress concentration and its fracture surface was flat (Figure 6a). The microstructure of the fracture surface shows many small holes, which is a typical ductile material characteristic. The fracture of the unbaked screw occurred at the threaded rod (Figure 6b). Note that HE in the screws was an unpredictable fracture mode. Hydrogen atoms were diffused into interior steel and accumulated at the grains boundaries or defects, resulting in a stress concentration that randomly fractured the screws. The position of the fractures may not occur at the treaded zone. In this case, HE effect was greater than the stress concentration factor. In addition, the directions of maximum shearing stress (τ_{max}) on the screw surface was parallel and perpendicular when a torque (T) was applied to the screw (Figure 6c). At which time, the direction of the maximum tensile stress (σ_{max}) was at an angle of 45°. The brittle material had lower resistance for this tensile stress (σ_{45°) and caused a 45° spiral fracture plane. This tensile stress perpendicular to a torque is $\sigma_{max} \times \cos45^\circ$. The microstructure of the fracture surface was a typical intergranular fracture. This can be mainly attributed to hydrogen molecules accumulating at the grain boundaries or defects, resulting in a stress concentration that reduced intergranular strength (Figure 6d). Baking promotes the release of diffusible hydrogen within the material, which decreases the HE susceptibility of 10B21 screws.

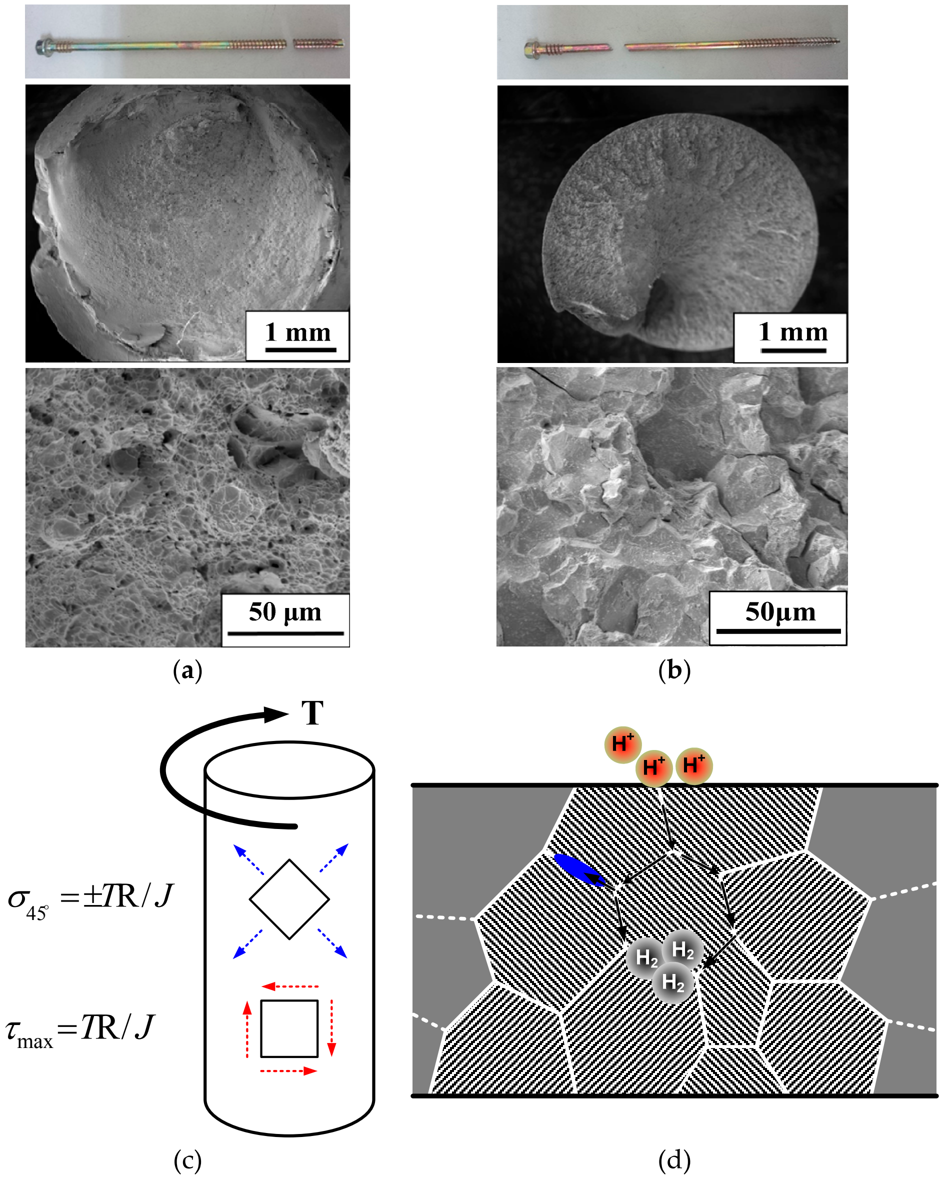


Figure 6. Macrostructure characteristics and fracture surfaces of (**a**) ductile screw and (**b**) brittle screw; (**c**) Force diagram for screw; (**d**) Diagram of HE mechanism.

4. Conclusions

This study investigated the effects of heat treatment on the HE susceptibility of 10B21 screws. After quenching and tempering treatment, 10B21 screws maintained their high hardness, and thus had high HE susceptibility. Baking treatment promoted the effusion of hydrogen within the material, which decreased the fracture torque of the 10B21 screws. When a continuous pre-stress was applied to the 10B21 screws, hydrogen-induced brittle fracture was the most serious for unbaked screws. Excess hydrogen caused the screws to lose the plastic deformation. For baked screws, the diffusible hydrogen was released, decreasing HE susceptibility. SIMS results confirmed that hydrogen concentration in the screw material decreased after baking treatment. 10B21 screws baked for a sufficient duration had a ductile fracture surface and low HE susceptibility.

Acknowledgments: The authors are grateful to Ministry of Science and Technology (MOST) Instrument Center at National Cheng Kung University (NCKU) and MOST, Taiwan for financially supporting this study under Grant No. MOST 104-2221-E-006-027.

Author Contributions: Fei-Yi Hung and Truan-Sheng Lui conceived and designed the experiments; Chien-Hao Tseng performed the experiments; Fei-Yi Hung, Truan-Sheng Lui and Chien-Hao Tseng analyzed the data; Fei-Yi Hung, Truan-Sheng Lui and Kuan-Jen Chen contributed reagents/materials/analysis tools; Kuan-Jen Chen wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

10B21	low-carbon boron steel
HE	hydrogen embrittlement
SIMS	secondary ion mass spectroscopy
OM	optical microscope
HR-SEM	high-resolution scanning electron microscopy

References

1. Woodtli, J.; Kieselbach, R. Damage due to hydrogen embrittlement and stress cracking. *Eng. Fail. Anal.* **2000**, *7*, 427–450. [CrossRef]
2. Rebak, R.B.; Muchjin, L.; Szklarska-Smialowska, Z. Hydrogen diffusion and accumulation in automotive fasteners. *Corrosion* **1997**, *33*, 481–488. [CrossRef]
3. Uhlig, H.H.; Revie, R.W. *Corrosion and Corrosion Control*, 3rd ed.; Wiley: New York, NY, USA, 1985; p. 274.
4. Knott, J.K. Some new aspects of hydrogen-assisted crack growth in steels. *J. Chin. Corros. Eng.* **1995**, *9*, 215–224.
5. Curry, D.A.; Knott, J.F. Effect of microstructure on cleavage fracture toughness of quenched and tempered steels. *Met. Sci.* **1979**, *13*, 341–345. [CrossRef]
6. Yu, X.; Wen, S. Hydrogen-induced delayed failure of TWIP steel with vanadium addition. *Shanghai Met.* **2014**, *36*, 18–22.
7. Bhadeshia, H.K.D.H. Prevention of hydrogen embrittlement in steels. *ISIJ Int.* **2016**, *56*, 24–36. [CrossRef]
8. Kuruvilla, A.K.; Stoloff, N.S. Hydrogen embrittlement of Ni_3Al+B. *Scr. Metall.* **1985**, *19*, 83–87. [CrossRef]
9. Murakami, Y.; Kanezaki, T.; Mine, Y.; Matsuoka, S. Hydrogen embrittlement mechanism in fatigue of austenitic stainless steels. *Metall. Mater. Trans. A* **2008**, *39*, 1327–1339. [CrossRef]
10. Hwang, B.; Suh, D.W.; Kim, S.J. Austenitizing temperature and hardenability of low-carbon boron steels. *Scr. Mater.* **2011**, *64*, 1118–1120. [CrossRef]
11. Wittmaack, K. Background formation in SIMS analysis of hydrogen, carbon, nitrogen and oxygen in silicon. *Nucl. Instrum. Methods* **1983**, *218*, 327–332. [CrossRef]
12. Morito, S.; Saito, H.; Owawa, T.; Furuhara, T.; Maki, T. Effect of austenite grain size on the morphology and crystallography of lath martensite in low carbon steels. *ISIJ Int.* **2005**, *45*, 91–94. [CrossRef]
13. Fukuda, Y.; Oh-ishi, K.; Horita, Z.; Langdon, T.G. Processing of a low-carbon steel by equal-channel angular pressing. *Acta Mater.* **2002**, *50*, 1359–1368. [CrossRef]
14. Hardie, D.; Charles, E.A.; Lopez, A.H. Hydrogen embrittlement of high strength pipeline steels. *Corros. Sci.* **2006**, *48*, 4378–4385. [CrossRef]
15. Eastman, J.; Heubaum, F.; Matsumoto, T.; Birnbaum, H.K. The effect of hydrogen on the solid solution strengthening and softening of nickel. *Acta Metall.* **1982**, *30*, 1579–1986. [CrossRef]
16. Hillier, E.M.K.; Robinson, M.J. Hydrogen embrittlement of high strength steel electroplated with zinc–cobalt alloys. *Corros. Sci.* **2004**, *46*, 715–727. [CrossRef]
17. McMahon, C.J., Jr. Hydrogen-induced intergranular fracture of steels. *Eng. Fract. Mech.* **2001**, *68*, 773–788. [CrossRef]
18. Wittmaack, K. Pre-equilibrium variation of the secondary ion yield. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 39–50. [CrossRef]