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Crack Initiation by Cathodic Hydrogen Charging in Nickel Single Crystal

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It has been reported that cracks grow along {100} independent of the tensile direction in hydrogen embittement in nickel single crystal. Behavior of crack initiation by cathodic hydrogen charging was investigated in the present work to clarify the mechanism of hydrogen embrittlement. Hydrogen was charged on (100) or (111) surface of specimens during 180 hours at 100 A/m^2 cathodic current density. Nickel α phase was transformed into the hydride by hydrogen. A lot of cracks were observed in the nickel-hydride layer without external stress. They were along {100} independent of the plane charged hydrogen, though the distribution of the cracks on the surface depends on it. Therefore, {100} cracking is preferred in nickel hydride. It corresponds to the morphology of the fracture surface in hydrogen embrittlement in nickel single crystal.

KEY WORDS: hydrogen embrittlement; nickel-hydride; Ni (100) and (111) surfaces.

1. Introduction

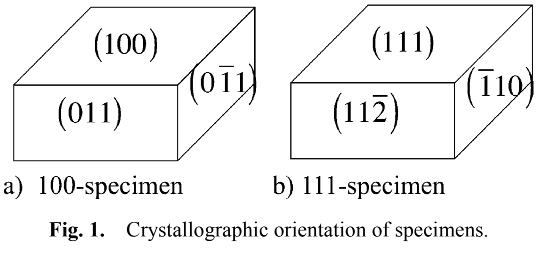
It is well known that nickel is embrittled in hydrogen atmosphere, though it has great ductility in air. Latanision and Opperhauser[1)] reported that the grain boundary fracture is occurred by the hydrogen-assisted slip at the vicinity of the grain boundary. It has been also presented that hydrogen mainly causes the transgranular fracture, on which surface slip lines, striation-like pattern and Y-shaped hillocks have been observed, in nickel.[2,3)] These patterns have been also observed in nickel single crystal.[4,5)] They are composed of slips along {111} and local brittle fracture along {100}. The local slips are well explained by the hydrogen assisted slip mechanism, but it is not explained how hydrogen contribute to the brittle fracture.

On the other side, Hinotani *et al.*[6)] reported that nickel-hydride is responsible for the intergranular fracture. Nickel-hydride is formed with high pressure H_2 atmosphere about 600 MPa at room temperature or cathodic charging.[7)] It has the same fcc crystal structure as pure nickel, but its lattice parameter is about 6% larger than of pure nickel[8)] because of a high concentration of interstitial hydrogen atoms. Then, the hydride formation causes tensile stress field. Pielaszek[9)] reported that the decomposition of nickel-hydride induces a few micro cracks along {100} without external stress. Then, it is considered that hydrogen embrittlement is caused by both the hydrogen assisted slip and the local brittle fracture along {100}.

The authors proposed that a crack grows along {100} independently of tensile direction in nickel single crystal with charging hydrogen.[5)] That implies that cracks develop along {100} independent of external stress. In the present work, it is proposed that the cracks develop only along {100} independent of the crystallographic plane charged hydrogen.

2. Experimental Method

Nickel single crystal was made of nickel chips (99.9% pure) in the vertical Bridgeman furnace. It was cut into specimens (10 mm square and 6 mm thickness), which base was (100) or (111) plane (hereafter called 100-specimen and 111-specimen). Their crystallographic orientations are shown in **Fig. 1**. They were chemically polished with 20 mass% HNO_3 after mechanical polished with 0.05 μm alumina powder. Five surfaces except a base on the parallelepiped specimen was covered by silicone resin as shown **Fig. 2**. Hydrogen was charged in 50 mol/m^3 H_2SO_4 electrolytic solution with 1.4 kg/m^3 thiourea as a recombination poison using electrochemical cathodic charging method at room temperature. The current density was 100 A/m^2. The charging time was 180 hours. After the hydride was measured using X-ray diffraction (tube: Cr-Ka, 40 kV, 40 mA),



a) 100-specimen b) 111-specimen

Fig. 1. Crystallographic orientation of specimens.

hydrogen in the specimen was evolved in glycerin at 318 K during 180 hours. The surface was observed by a scanning electron microscope (SEM).

3. Results

X-ray diffraction patterns are shown in **Fig. 3**. Nickel-hydride was confirmed in both specimens charged hydrogen. The diffraction lines of nickel α phase disappeared after charging hydrogen. Most of the nickel α phase transformed to the hydride in the region where X-ray can reach. Lattice constants of nickel and nickel-hydride are determined as 3.530 and 3.731 nm. Then, the increase of the lattice constant is about 5.7%, that almost agrees with the result by Pielaszek.[9]

Hydrogen evolution curves in glycerin are shown in **Fig. 4**. The amount of hydrogen of the 100-specimen was more than that of the 111-specimen. Moreover, evolution rate was higher in 100-specimen.

Cracks were observed on the surfaces of hydrogen charged specimens. They were not micro cracks, which have been reported already, but large ones. **Figure 5** shows SEM photographs of surface and side of 100-specimen. There were cracks only near the side of the specimen. The cracks on (100) surface were at an angle of 45 degrees with the direction [011]. They could be confirmed with eyes, which length was a few millimeters. They were almost perpendicular to the specimen's surface, as shown in Fig. 5(b), which is side surface of the specimen. Cracks parallel to the surface were also observed in Fig. 5(b).

Cracks were observed over the surface in 111-specimen. **Figure 6** shows SEM photographs of surface and side of 111-specimen. The cracks on (111) surface were at angles of 30 degrees with the direction $[11\bar{2}]$. These were at an angle of 35 degrees with $[11\bar{2}]$ on the side of specimen, which is $(\bar{1}10)$ plane.

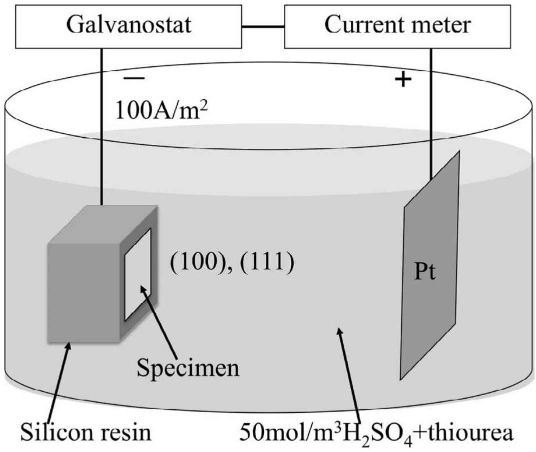


Fig. 2. Schematic illustration of the apparatus for electrochemical cathodic charging method.

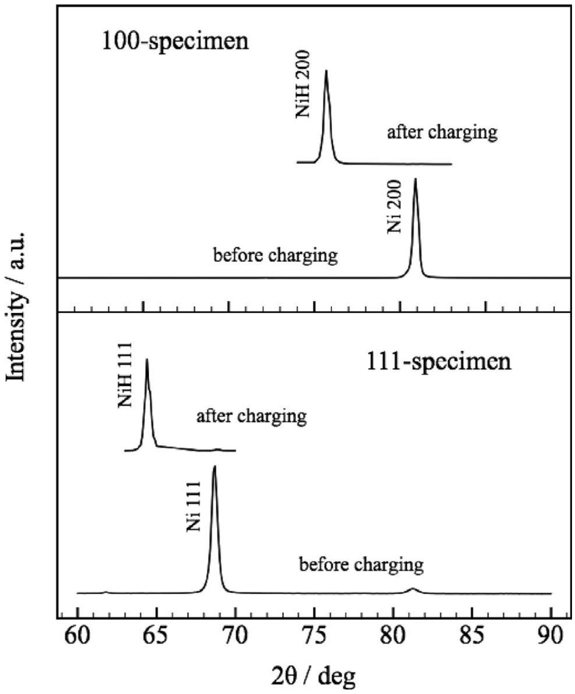


Fig. 3. XRD results for nickel single crystal before/after hydrogen charging.

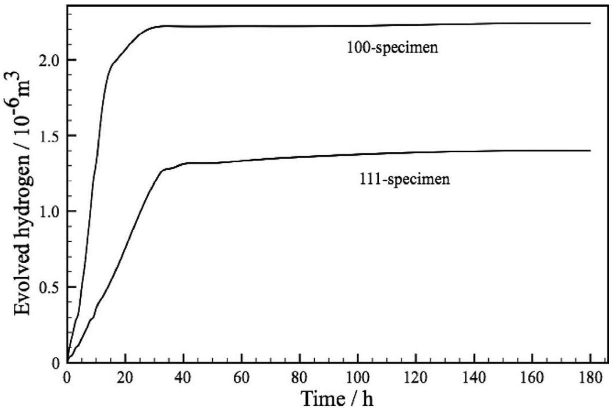


Fig. 4. Transition of the hydrogen evolution from charged nickel single crystal.

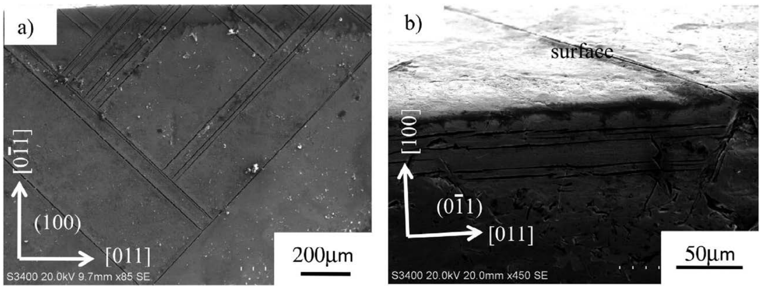


Fig. 5. SEM photographs of the surface a) and the side b) in hydrogen charged 100-specimen.

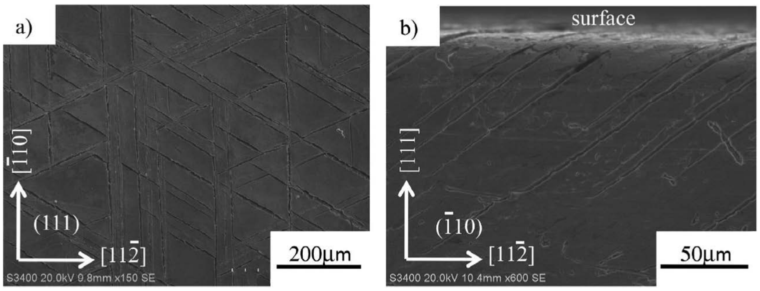


Fig. 6. SEM photographs of the surface a) and the side b) in hydrogen charged 111-specimen.

4. Discussion

The results of X-ray diffraction show that all of the α phase transformed to the hydride in the region where X-ray can reach. Its depth is suggested to be tens of micrometers. The authors have been presented that the nickel-hydride was formed from the surface to the depth of tens of micrometers under the same charging condition.[10] The depths of hydride formation in 100 and 111-specimen were about 40 μm and 60 μm in that work. These correspond to the depths of cracks as shown in the side photographs (Figs. 5(b) and 6(b)). These results indicate that the cracks were formed in the hydride layer without external stress. The cause of the crack formation is considered to be internal stress by hydride formation and decomposition, as presented by Pielaszek.[9] The cracks observed in the present work are comparatively large because of long charge time and high hydrogen fugacity.

Figure 4 shows that the 100-spceimen absorbs more hydrogen than the 111-specimen. It is noted that the evolution curves were not obtained for specimens in which hydrogen was charged until the equilibrium state and evolved hydrogen originated not only in hydride but also in dissolved hydrogen in nickel α phase. Hydrogen evolution is influenced by hydrogen solubility, hydrogen diffusivity, adsorption rate and decomposition rate of hydride. Both solubility and diffusivity are considered to be same between 100 and 111-spceimens, because they are macroscopic bulk properties. The adsorption rate, however, depends probably on the surface. Fassaert *et al.*[11] proposed that the stability of hydrogen adsorption of (100) is higher than that of (111) in nickel using the LCAO calculation, though Christman *et al.*[12] estimated experimentally that the heat of adsorption is almost equal between (100) and (111). It is considered that the equilibrium hydrogen concentration at the surface is different between 100 and 111-spceimens. Moreover, Tomov[13] reported the anisotropy on formation of nickel hydride and hydrogen permeation. These considerations are related to the possibility of the anisotropy on hydrogen absorption. Pielaszek[14] reported the anisotropy on the decomposition of nickel hydride. In the present experiment, the measurement of hydrogen evolution was carried out after X-ray diffraction. The anisotropy on the decomposition probably causes a difference of the amount of hydrogen during X-ray diffraction. A more detailed research is necessary to clarify which factor is essential.

The planes that intersect (100) at an angle of 45 degree with the direction [011] as shown in Fig. 5(a) are (010), (001), (110), (101), $(1\bar{1}0)$ and $(10\bar{1})$. The trace of the crack on $(0\bar{1}1)$ is at the angle of about 70 degrees with the direction [011] as shown in Fig. 5(b). Since the traces of (110), (101), $(1\bar{1}0)$ and $(10\bar{1})$ on $(0\bar{1}1)$ must be at the angle 35.3 degrees with [011], they are eliminated from candidates. The traces of (010) and (001) must be at the angle 90 degrees with [011]. These coincide with the observation considering the deformation. Thus, it is considered that the cracks of 100-specimen were developed on {100}. In the case of 111-specimen, the traces of $(\bar{1}11)$, $(1\bar{1}1)$, (011), (101), (100) and (010) on (111) are at angles of 30 degrees with $[11\bar{2}]$ (Fig. 6(a)). Only (100) and (010) intersect to $(\bar{1}10)$ at an angle of 35 degrees with $[11\bar{2}]$ in them (Fig. 6(b)). Therefore, it is considered that cracks of both 111 and 100-specimen were developed on {100}.

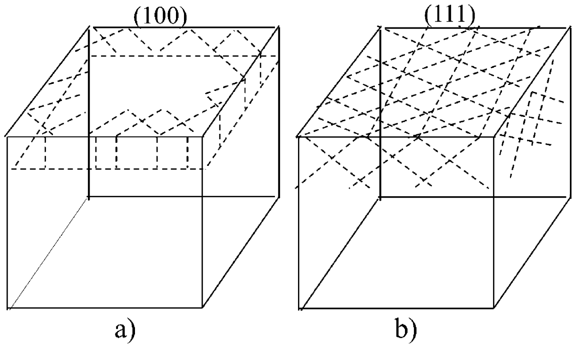


Fig. 7. Schematic illustration of {100} cracks in hydrogen charged specimens in which hydrogen charged from (100) plane, a), or (111) plane, b).

In the present work, the specimens did not sustain external stress. Since the hydride layer on the surface was restricted to the matrix that was not affected by hydrogen, the internal stress induced by hydride formation was probably different depending on the specimens' orientation. Then, the present results indicate that cracks develop along {100} independent of stress condition in nickel-hydride. Namely, {100} cracking is preferred in nickel-hydride. Pielaszek[9] suggested that the binding energy along {100} decreases due to the formation of dislocation cell wall along {100} and hydrogen concentration on it at the same time.

Figure 7 is the schematic illustration of the distribution of the cracks along {100} on the specimens. The broken lines denote cracks along {100}. The upper surfaces are the charged planes. There were cracks with the circumstance on the surface in the 100-spceimen, but over the surface in the111-specimen. In the 100-spceimen, {100} planes are parallel or perpendicular to the surface. Stress should act parallel to the surface in order to induce cracks along (010) or (001). It is considered that no crack was induced, since the stress acts to press the center of the 100-specimen. Cracking due to hydrogen in the 111-specimen is not restricted, because {100} planes tilt to the surface.

The authors$^{5)}$ have been proposed that slips along {111} and brittle fractures along {100} occur alternately in hydrogen embrittlement in nickel. In the present paper, it is proposed that cracks develop along {100} independent of stress condition in nickel-hydride. Then, it is considered that the slips along {111} induce a crack along {100} in nickel-hydride formed in front of the main crack. The fracture surface is macroscopically {100} independent of the tensile direction.

5. Conclusion

Surfaces of nickel single crystal charged hydrogen under the high fugacity of hydrogen were investigated in detail. Nickel α phase was transformed into the hydride by hydrogen. A lot of cracks were observed on the nickel-hydride layer. The cracks are along {100} independent of the plane charged hydrogen, though the distribution of the cracks on the surface depends on it.

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