Effects of deformation on hydrogen absorption and desorption properties of titanium

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A R T I C L E   I N F O

A B S T R A C T

In this study, we analyzed the effects of deformation on hydrogen absorption and desorption properties of titanium to improve such properties. Hydrogen was introduced into commercially pure (99.5%) titanium by the electrochemical method. The amount and existing state of hydrogen were examined using hydrogen desorption curves obtained by thermal desorption spectroscopy. Hydrogen absorption was promoted by applying tensile deformation prior to charging, which leads to hydride formation within a short charging time. The amount of hydrogen absorbed decreased when the volume fraction of deformation twins exceeded about 0.2. It was considered that hydrogen was mainly trapped by dislocations forming hydride while a large fraction of deformation twins hindered dislocation motion, thus reducing dislocation density leading to a decrease in the amount of absorbed hydrogen. Almost half the charged hydrogen was released when in-plane compressive stress was applied to a charged plate specimen at room temperature due to hydride decomposition under compressive stress.

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1. Introduction

Titanium absorbs a large amount of hydrogen as hydride (gravimetric density: 4 mass%, volumetric density: 148 kg/m^3) owing to the negative enthalpy of formation of TiH$_2$ (-131 kJ/mole H$_2$), that requires high temperatures for the release of hydrogen under atmospheric pressure [1]. To make titanium more attractive as a hydrogen storage material, it is desirable to explore processes for hydrogen release under ambient conditions while accelerating absorption. In this study, deformation was applied to titanium as a method of improving its hydrogen absorption and desorption properties.

There have been many reports on the formation kinetics and configuration of hydride in hcp materials including titanium, especially under the influence of stress [2–4]. However, there was little study on the behaviour of hydrogen in deformed titanium and on the kinetics of hydride formation in connection with defects, which can serve as trapping sites of hydrogen and become preferential sites of hydride formation [5,6]. In hcp metals, mechanical twins are formed under deformation and their number increases linearly with applied deformation [7–10]. The contribution of twins to total deformation is small [11,12], because the relative atomic movement is limited. Most of the plastic flow occurs by the motion of dislocations, even in hcp metals.

However, the presence of a number of twins and their interactions were considered to hinder the motion of dislocations [13]. Therefore, deformation twins and twin boundaries play a role in hydrogen absorption by affecting dislocation density. The role of twin in hydrogen absorption properties was analyzed in this study.

Liu and Nakasa reported the result of an experiment on anomalous hydrogen absorption behavior during electrochemical charging that may be caused by hydride decomposition under compressive stress [14]. We previously measured hydrogen release from hydrogenated titanium during compressive or tensile deformation using a tensile testing machine fitted with a vacuum chamber and a quadropole mass spectrometer [15]. The results showed that the release of hydrogen was observed only under compressive stress. On the basis of these findings, hydrogen release from hydrogenated titanium under compressive stress was measured and analyzed.

2. Materials and experimental procedure

Commercially pure (99.5%) titanium of 1 mm or 0.1 mm thickness was used in the experiments. Anode electrochemical charging was conducted at a potential of -1.5 V (vs. a Ag/AgCl reference electrode) in a 323 K aqueous H$_2$SO$_4$ solution of pH 2.0, which corresponds to the conditions in the corrosion region of the Pourbaix diagram of titanium [16].

Three-pole electrochemical charging was employed in hydrogen charging. A specimen, a platinum plate serving as a counter electrode, and a Ag/AgCl reference electrode were immersed in H$_2$SO$_4$ solution under a constant potential by using a potentiostat. Hydrogen desorption curves were measured by thermal desorption analysis to assess the amount of hydrogen together with its existing state in the material. The specimen was heated in high-purity argon gas at a heating rate of

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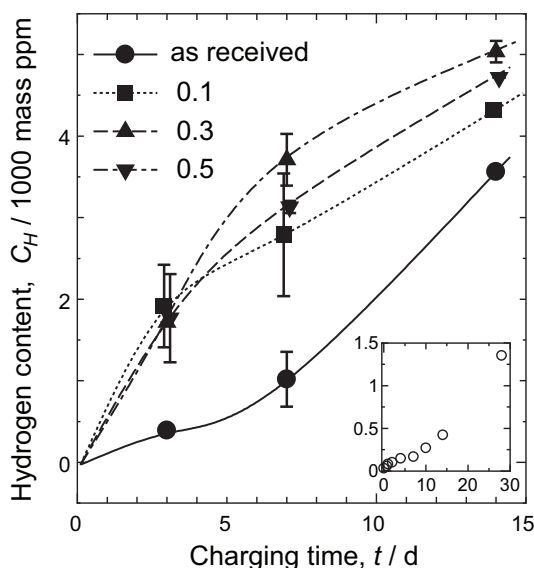E-mail address: h-suzuki@me.sophia.ac.jp (H. Suzuki).

Fig. 1. Dependences of amount of hydrogen absorbed by titanium on charging time and tensile strain (0.1, 0.3, or 0.5) applied prior to charging. Inserted graph shows hydrogen absorption properties measured with the same material under a charging condition of a potential of −1.0 V (vs. a Ag/AgCl reference electrode) in 303 K aqueous H_2SO_4 solution of pH3.0.

100 K/h. The amount of released gas was measured using a gas chromatograph every 5 min.

In the experiment examining the effect of tensile deformation on hydrogen absorption properties, tensile deformation was applied to a specimen of 1 mm thickness and 20 mm gauge length at a displacement rate of 0.1 mm/min at room temperature prior to electrochemical charging. The specimen was annealed at 973 K for 3 h before deformation for full anneal heat treatment [17]. The strain applied was chosen to be 0.1, 0.3, or 0.5. Strain was obtained by dividing the displacement of a cross-head of a testing machine by the gauge length of the specimen. After tensile deformation, the surface of the specimen was polished with #800 emery paper to minimize the effects of surface changes caused by deformation.

In the experiment examining the effect of compressive stress on hydrogen desorption properties, specimens of 20 mm × 5 mm and 0.1 mm thickness annealed at 973 K for 30 min were charged electrochemically at 323 K for 3 days. Under the charging conditions used in this study, uniform hydride phase was formed up to approximately 30 μm from the surface of the specimen and precipitated hydride is observed up to 50 μm from the surface in the metallographic examination. Therefore, the specimen of 0.1 mm thickness used in the experiments contains hydride throughout the thickness.

3. Results and discussion

3.1. Effect of tensile deformation on hydrogen absorption properties

The relationship between charging time and the amount of hydrogen absorbed by the specimens that was deformed uniformly with different strains is shown in Fig. 1. The inserted graph in Fig. 1 shows hydrogen absorption properties measured with the same material under a charging condition of a potential of −1.0 V (vs. a Ag/AgCl reference electrode) in a 303 K aqueous H_2SO_4 solution of pH 3.0. This data was used as a reference for hydrogen absorption property of the material, and the effect of deformation on the property is measured and compared at three charging time. At the start of charging, the amount of hydrogen increases linearly with absorption time, then the relationship becomes parabolic due to hydride formation [18,19]. In the as-received material, the linear relation at the early stage is not apparent. This may be related to hydride decomposition on the surface due to the compressive stress caused by the formation of a hydride phase on the surface [14]. The amount of hydrogen at a certain charging time increases with deformation, except at a strain of 0.5. The reason for this will
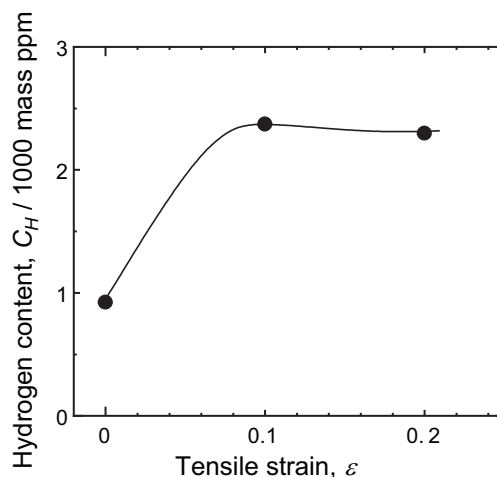

Fig. 2. Dependence of amount of hydrogen absorbed by titanium on tensile strain applied at 373 K prior to charging.

be discussed later. Results of X-ray diffraction (XRD) measurement show that the hydride phase of $TiH_{1.924}$ appears within a shorter charging time with increasing deformation. Therefore the effect of tensile deformation prior to hydrogen charging is the promotion of hydride formation.

The role of dislocations and deformation twinning in hydrogen absorption was analyzed experimentally by controlling the number of twins under a fixed strain. Since deformation twinning is strongly dependent on temperature [9,11], a fixed strain was applied to the specimen at temperatures from 77 to 373 K. The volume fraction of twins was measured by the point count method. A grid of 12.5 μm square was overlaid on an 800 μm × 600 μm optical micrograph. The test points at the intersections of the grid that were located on a twin were counted, and the ratio of their number to the total number of test points was defined as the volume fraction of deformation twins. The measurement was conducted in at least 10 micrographs to obtain the average volume fraction.

Fig. 2 shows the relationship between tensile strain and the amount of hydrogen absorbed by the specimens deformed at 373 K. At this temperature, the volume fraction of deformation twins is approximately 0.01 in the strain range applied; therefore only the effect of dislocation on absorption of hydrogen is shown. Hydride is formed in the material because the amount of absorbed hydrogen readily exceeds the solubility limit of titanium at room temperature [20]. The amount of absorbed hydrogen increases rapidly with strain when the applied strain is small, then gradually becomes almost constant. This suggests that hydride formation is strongly related to dislocations. Although the binding energy of hydrogen to various types of defects in titanium has not yet been reported, dislocations are considered to be major trapping sites for hydrogen compared with other defects such as twin boundaries [13].

Fig. 3 shows the relationship between the volume fraction of deformation twins and the amount of absorbed hydrogen under a constant tensile strain of 0.1. The amount of hydrogen is not affected by the volume fraction of twins until it reached about 0.2. As mentioned earlier, deformation is mainly caused by dislocation motion. On the other hand, with increasing number of twins, their contribution to total deformation increases; furthermore secondary twins occur, thereby reducing the equivalent size of grains. Both factors cause a decrease in dislocation density that leads to a smaller number of trapping sites for hydrogen and hydride, thus reducing the amount of absorbed hydrogen. At a strain of 0.5, the volume fraction of deformation twins that increases linearly with applied deformation exceeds the threshold value mentioned above,
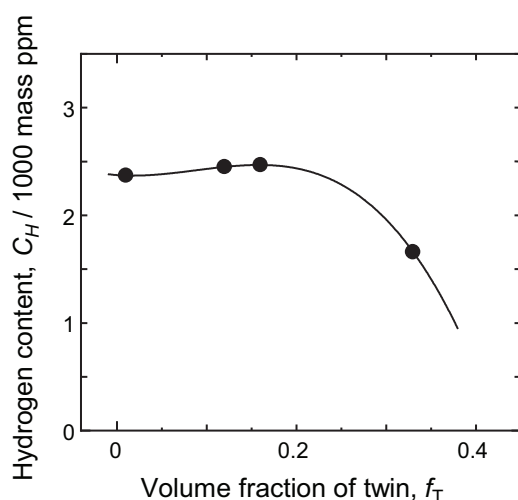
Fig. 3. Dependence of amount of hydrogen absorbed by titanium on the volume fraction of deformation twins. The tensile strain is 0.1 for all tests.

Fig. 4. Relationship between hydrogen content of titanium after bending around a bar of diameter ϕ and reciprocal of the diameter. The hydrogen content after charging without deformation is also shown.

therefore the amount of hydrogen becomes smaller than at a strain of 0.3 as shown in Fig. 1.

3.2. Effect of compressive stress on hydrogen desorption properties

The role of compressive stress in hydrogen desorption was assessed by applying compressive stress to plate specimens at room temperature. We found in preliminary experiments that hydrogen released from hydride in the vicinity of the surface tends to diffuse into the bulk of the material [15] when a thick specimen was used. Furthermore, when compressive stress was applied normal to the surface of the specimen, material flow occurred in the in-plane direction, thereby causing tensile deformation. In both cases, hydrogen release from the material was not clearly observed. Therefore, to clarify effect of compressive stress on hydride decomposition, it is necessary to apply only in-plane compressive stress to a thin specimen.

A hydrogen-charged titanium specimen was attached to an aluminium sheet of 1 mm thickness with adhesive. A combined specimen was bent around a fixed-diameter round bar, with the titanium plate placed between the aluminium sheet and the bar at room temperature. The neutral plane of bending stress was located within the thickness of the aluminium sheet; therefore, only in-plane compressive stress was applied to the titanium specimen and the magnitude of the stress could be controlled by adjusting the diameter of the bar. The gradient of compressive stress within the specimen thickness was considered to be small since the thickness ratio of aluminium to titanium was sufficiently large. The exact compressive stress within the titanium plate could not be evaluated analytically since the precise thickness and properties of the adhesive layer were not clearly defined. Thus, the effect of compressive deformation was shown in terms of the diameter of the bar, which corresponds to the magnitude of compressive stress within the specimen. The titanium specimen was removed from the fixture and the aluminium plate shortly after the experiment, and the amount of hydrogen was measured. The kinetics of decomposition of hydride under compressive stress was not examined in this study, but the release of hydrogen from the specimen was believed to occur during bending.

Fig. 4 shows the relationship between the amount of hydrogen after deformation at room temperature and the reciprocal of the diameter of the bar. The amount of hydrogen at the origin of the horizontal axis was set equal to that before bending. With decreasing
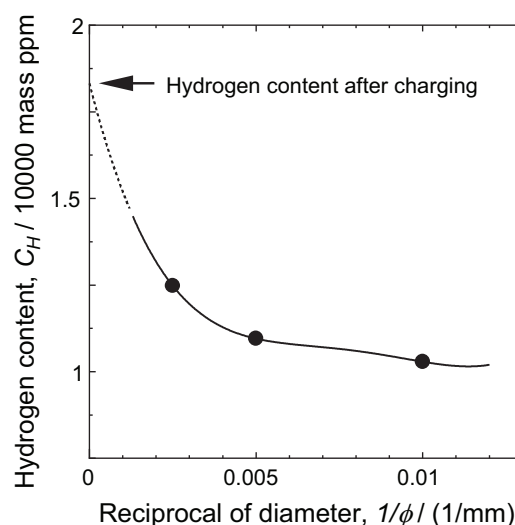
diameter of curvature of bending corresponding to higher compressive stress, the amount of hydrogen after deformation decreases to almost half the amount of charged hydrogen.

The decrease in the amount of hydrogen from the bent specimen can be attributed to the decomposition of titanium hydride under compressive stress. Liu and Nakasa compared the XRD profiles of specimens at various charging time [14] and found that the peaks of titanium hydride disappeared when the density of hydrogen at the surface decreases drastically. In this study, the thermal desorption spectrums obtained from charged and deformed specimens are compared. The height of the peaks in the spectra decreases as the diameter of the bar decreases, while the position of the peaks does not change. No new peaks appear after deformation. This leads to the conclusion that hydrogen desorption is caused by decomposition of titanium hydride. Effect of compressive stress on hydrogen desorption was examined using specimens without prior deformation; therefore discussion of the role of twins on desorption property is out of the scope of the present study.

4. Conclusion

Deformation was applied to commercially pure titanium to analyze the effects of deformation on its hydrogen absorption and desorption properties:

1. Hydrogen absorption was promoted by applying tensile deformation prior to charging, leading to hydride formation within a short charging time. It was considered that hydrogen was mainly trapped by dislocations followed by hydride formation and that a large fraction of twins hindered dislocation motion, thus reducing dislocation density and decreasing the amount of absorbed hydrogen.
2. By applying in-plane compressive stress to a charged titanium specimen, almost half the hydrogen was released due to hydride decomposition at room temperature.

References

[1] Y. Fukai, The Metal-Hydrogen System: Basic Bulk Properties, Springer-Verlag, Berlin, 1993, p. 31.

[2] D.S. Shih, I.M. Robertson, H.K. Birnbaum, Acta Metall. 36 (1988) 111–124.

[3] H. Numakura, M. Koiwa, Acta Metall. 32 (1984) 1799–1807.

[4] E. Conforto, D. Caillard, Acta Mater. 55 (2007) 785–798.

[5] I.M. Robertson, H.K. Birnbaum, P. Sofronis, in: J.P. Hirth, L. Kubin (Eds.), Dislocation in Solids, vol. 15, North-Holland, Amsterdam, 2009, pp. 249–293.

[6] I. Jacob, M. Bereznitsky, O. Yeheskel, R.G. Leisure, Appl. Phys. Lett. 89 (2006) 201909.

[7] M.H. Yoo, J.R. Morris, K.M. Ho, S.R. Agnew, Metall. Mater. Trans. A 33A (2002) 813–822.

[8] L. Capolungo, I.J. Beyerlein, C.N. Tome, Scr. Mater. 60 (2009) 32–35.

[9] A.M. Garde, R.E. Reed-Hill, Met. Trans. 2 (1971) 2885–2888.

[10] H. Sasano, H. Kimura, J. Jpn. Inst. Met. 41 (1971) 933–939.

[11] E. Fukushima, A. Goto, Mater. Sci. Technol. 9 (1972) 255–261.

[12] R.J. McCabe, G. Proust, E.K. Cerreta, A. Misra, Int. J. Plast. 25 (2009) 454–472.

[13] S. Nemat-Nassar, W.G. Guo, J.Y. Cheng, Acta Mater. 47 (1999) 3705–3720.

[14] J. Liu, K. Nakasa, J. Jpn. Inst. Met. 55 (1991) 1086–1092.

[15] H. Suzuki, N. Kirihara, H. Taniguchi, N. Hanada, K. Takai, Y. Hagihara, unpublished work, presented at MH2008, Reykjavik, Iceland.

[16] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, 1966, pp. 213–222.

[17] Properties and selection: stainless steels, tool materials and special-purpose metals, in: Metals Handbook, vol. 3, 9th ed., ASM international, Metals Park, OH, 1980, p. 374.

[18] M. Tsutsui, N. Fujise, J. Jpn. Inst. Met. 39 (1975) 460–466.

[19] I.I. Phillips, P. Poole, L.L. Shreir, Corros. Sci. 12 (1972) 855–866.

[20] H. Numakura, Bull. Jpn. Inst. Met. 31 (1992) 526–529.