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Investigation of hydrogen transport behavior of various low-alloy steels with high-pressure hydrogen gas

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ABSTRACT

The apparent hydrogen diffusivity and the saturated hydrogen content of Cr–Mo and Ni–Cr–Mo steels were determined with high-pressure hydrogen gas. Surface effects on hydrogen entry and exit were also investigated by using palladium-coated samples and by diffusion analysis using the finite-element method. Hydrogen contents of hydrogen-exposed cylindrical specimens of various sizes were measured by means of gas chromatography–mass spectrometry to obtain the saturated hydrogen content. The diffusivity was determined by fitting the solution of a diffusion equation to the experimental hydrogen contents determined by desorption at various constant temperatures. In the specimens examined, surface effects were significant at room temperature. The temperature dependences of the diffusivity were reasonably consistent with reference data mainly measured with electrochemical charging. These results were interpreted in terms of hydrogen trapping. Ordinary electrochemical charging represents a more severe condition than exposure to high-pressure hydrogen, for example, at 100 MPa.

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Introduction

Fuel-cell vehicles have recently become commercialized, and the necessary hydrogen filling stations are gradually being built. In terms of safety, these fuel-cell vehicles and their

associated hydrogen stations have been designed to use metallic materials with a high resistance to hydrogen embrittlement, such as type 316L austenitic stainless steel and A6061-T6 aluminum alloy. However, such metals have lower strengths and are more expensive than conventional steels such as carbon or low-alloy steels. For the widespread

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commercialization of hydrogen-energy systems, expected to occur in the near future, conventional steels that have higher strengths and lower costs will have to be widely used. Consequently, many experiments on the tensile, fatigue, and hydrogen-diffusion properties of such materials in high-pressure hydrogen gas need to be performed, and appropriate design methods will have to be established on the basis of the resulting scientific understanding [1–3].

Yamabe et al. [3] investigated the effect of hydrogen on the fatigue-crack growth (FCG) and fracture-toughness properties of Cr–Mo steels. We found that the effects of hydrogen on these properties were dependent on the tensile strength and microstructure of the materials. Furthermore, we showed that the rate of FCG was accelerated by hydrogen, but there was an upper limit on the hydrogen-accelerated FCG rate for Cr–Mo steels with a tensile strength of less than about 900 MPa. In contrast, Matsuo et al. [4] and Nishiguchi et al. [5] reported that the relative reduction in area of carbon steels decreased with increasing hydrogen content. The susceptibility of steels to hydrogen embrittlement is therefore believed to be related to the distribution of dissolved hydrogen, irrespective of the fact that precharged specimens were tested in air and noncharged specimens were tested in gaseous hydrogen [6,7]. The macroscopic hydrogen distribution in the steels under nonloaded conditions can be calculated from their hydrogen diffusivity and their saturated hydrogen content, provided that hydrogen entry and exit occur by a diffusion-controlled process. It has also been reported that the hydrogen diffusivity of various steels decreases with increasing tensile strength [8].

There have been many studies on the hydrogen-diffusion behavior of metals that are relevant to the practical significance of this behavior [9–26]. Studies have also been made on the hydrogen-diffusion behavior of low-alloy steels [21–26]; however, in these studies, only hydrogen diffusivity was determined mainly with electrochemical charging [21–24]. Consequently, the hydrogen content of such steels exposed to high-pressure hydrogen gas has not been determined directly. It is also unclear whether or not the state of steels subjected to electrochemical charging is identical to that of steels exposed to hydrogen gas [27,28]. To interpret the results of tensile and fatigue tests in high-pressure hydrogen gas precisely, it is essential to understand the distribution of hydrogen dissolved under practical conditions involving gaseous hydrogen, rather than that produced by electrochemical charging. Mine et al. [29,30] reported a method for the determination of hydrogen diffusivity and saturated hydrogen content by using disc-shaped specimens of various thicknesses exposed to high-pressure hydrogen gas. They applied this method to austenitic stainless steels (γ -stainless steel) and they found that the hydrogen diffusivity and solubility were reasonably consistent with the reference values determined by a permeation method with low-pressure hydrogen gas. However, their method mainly used precharged disc-shaped specimens with a thickness of less than 1 mm. Consequently, because the hydrogen diffusivity of carbon and low-alloy steels is much larger than that of γ -stainless steels, almost all the hydrogen desorbed from the specimens before their hydrogen content could be measured. Mine's method is therefore unsuitable for determining the hydrogen diffusivity and solubility of carbon and low-alloy steels.

Our current study focused on the desorption of hydrogen from samples exposed to high-pressure hydrogen gas. We used a desorption-based technique to determine the temperature dependence of the hydrogen diffusivity as well as the saturated hydrogen content of Cr–Mo and Ni–Cr–Mo steel samples, most of which were taken from storage cylinders used for hydrogen filling stations. Five low-alloy steels with tensile strengths of around 900 MPa were used, and cylindrical specimens with $2r_0 = z_0 = 7, 10, 15,$ and 19 mm, where r_0 was the radius of the specimen and z_0 was its thickness, were sampled from the steels. These cylindrical specimens were larger than those used by Mine et al.; consequently, rapid desorption of hydrogen from the specimens was suppressed. The specimens were exposed to high-pressure hydrogen gas at 100 MPa and at room temperature (RT; ~ 25 °C), 50 °C, or 85 °C for 200–300 h. After the hydrogen exposure, the hydrogen that desorbed from the specimens was measured by means of gas chromatography–mass spectroscopy (GC–MS) at a rising or constant temperature. The hydrogen contents of specimens of different sizes were measured to identify the specimen size necessary to achieve saturation with hydrogen. The hydrogen diffusivity was determined by fitting the solution of the nonsteady diffusion equation to the experimental hydrogen-desorption profile by the least-squares method.

Surface effects on the entry and exit of hydrogen were also investigated by using palladium-sputtered low-alloy steel [14,19]. To interpret these surface effects, we used a finite-element method (FEM) to perform a diffusion analysis in which the surface effects were taken into account. The results that we obtained are useful in understanding tensile and fatigue data for high-pressure hydrogen gas; moreover, they permit the estimation of the amount of hydrogen that will permeate into storage cylinders at hydrogen stations or into pipes used to carry high-pressure hydrogen gas.

Experimental procedures

Materials

Four JIS–SCM435 steels (Cr–Mo steels, Materials A to D) and one JIS–SNCM439 steel (Ni–Cr–Mo steel, Material E) were used in this study. Table 1 lists the chemical composition and Vickers hardness for each of these steels. Materials A, B, C, and E were sampled from real storage cylinders for hydrogen stations, whereas Material D was sampled from a round bar. These steels were quenched and tempered.

Specimens and hydrogen exposure

To clarify the effects of the specimen size on the hydrogen contents of steels exposed to hydrogen, four cylindrical specimens with $2r_0 = z_0 = 7, 10, 15,$ and 19 mm were sampled from each of the steels. The surfaces of these specimens were finished with #2000 emery paper. Identical experimental results were obtained when the surfaces were finished with #600 emery paper. Based on our previous study [31], a native oxide layer with a few nanometers thickness is formed on the surface and surface reactions of hydrogen, such as

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