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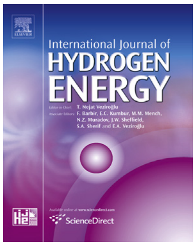

Elucidating the hydrogen-entry-obstruction mechanism of a newly developed aluminum-based coating in high-pressure gaseous hydrogen

Junichiro Yamabe [a,b,c,*], *Tohru Awane* [b,d], *Saburo Matsuoka* [b]

[a] *International Research Center for Hydrogen Energy, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*

[b] *Research Center for Hydrogen Industrial Use and Storage (HYDROGENIUS), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*

[c] *International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*

[d] *Kobe Material Testing Laboratory Co., Ltd., 47-13 Ni-jima, Harima-cho, Kako-gun, Hyogo 675-0155, Japan*

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ABSTRACT

This study presents a precise hydrogen-barrier mechanism of a newly developed three-layer (alumina/aluminum/ferro-aluminum) aluminum-based coating in high-pressure gaseous hydrogen. After exposure to high-pressure gaseous hydrogen, the hydrogen content of the specimen with a palladium-sputtered aluminum-based coating was the same as that of the specimen with aluminum-based coating, but without palladium. Furthermore, the hydrogen content of the coated specimens increased with a decrease in the specimen size. These results indicate that the hydrogen entered by a diffusion-controlled process. The effective diffusivity of the coated specimen was approximately one thousandth of that of base steel (type 304 stainless). Such excellent resistance could not be obtained with a two-layer coating (alumina/ferro-aluminum). Analysis of local hydrogen concentrations by secondary ion mass spectroscopy demonstrated that the extremely low effective hydrogen diffusivity of the three-layer-coated specimen was attributed to hydrogen trapping at the aluminum–ferro-aluminum interface, and not to the hydrogen-entry obstruction by the aluminum layer.

Introduction

In anticipation of the forthcoming commercialization of fuel cell vehicles and hydrogen stations, numerous components are being developed for use with high-pressure hydrogen. In the design of such components, susceptibility of materials to hydrogen embrittlement (HE) must be considered; this is dependent on various factors such as hydrogen gas pressure, temperature, and loading conditions [1–9]. Data on the HE

Abbreviations: AES, auger electron spectroscopy; HE, hydrogen embrittlement; SIMS, secondary ion mass spectroscopy; TDA, thermal desorption analysis.

[*] *Corresponding author.* International Research Center for Hydrogen Energy, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan. Tel.: +81 92 802 3247.

E-mail address: yamabe@mech.kyushu-u.ac.jp (J. Yamabe).

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susceptibility of various metals have been provided by NASA [10]. Recently, a few methods of evaluating hydrogen compatibility and suitability of materials have been proposed [11–15].

Barrier coatings prevent hydrogen entry into a material, resulting in the effective prevention of HE. Many studies have been reported on the use of such barrier coatings [16–60]. In these studies, mainly permeation tests of coated specimens with a hydrogen isotope at low pressure (<1 MPa) or electrochemical charging have been carried out. To summarize, aluminum-based (or alumina-based) and titanium-based coatings provide a significant reduction in hydrogen permeability [16–40]. Moreover, most studies on aluminum-based (or alumina-based) coatings under low pressure concluded that the top alumina layer obstructed hydrogen entry although it was not clarified whether hydrogen dissociation or diffusion was responsible for the effect. Recently also extensive investigations on zinc-based coatings mainly with electrochemical charging have been performed [45–51]. For steels in corrosion environments, there are studies on surface coatings with organic compounds [59,60].

In contrast, there exist only a few studies that have investigated these coatings at high hydrogen pressure [19,29,46,61]. Lorthan Jr. et al. [36] reported the effectiveness of a titanium-based coating based on tensile tests of coated austenitic stainless steel in hydrogen gas at 69 MPa. Murray et al. [19] reported that an alumina layer effectively prevented the tensile-strength reduction of precipitation-hardened martensitic steel after exposure to hydrogen gas at 13.8 MPa and 202 °C for 24 h. However, these studies did not determine the hydrogen content of the coated specimens; thus, it was not clarified whether these coatings resisted the entry of hydrogen under high-pressure conditions.

Song [29] exposed austenitic stainless steel coated with an alumina layer to hydrogen gas at 24 MPa and 200 °C for 14 days and then measured its hydrogen content. As a result, the resulting hydrogen content of the hydrogen-exposed specimen (30.2 mass ppm) was slightly lower than that of the non-exposed sample (39.5 mass ppm), even though the hydrogen permeability of the alumina-coated specimen was approximately 10^3 times smaller compared to that of the non-coated specimen under low pressure [21]. Yamabe et al. [61] exposed cylindrical specimens made from austenitic stainless steel coated by an approximately 10-nm thick passivation layer to hydrogen gas at pressures of 10 and 100 MPa at 270 °C for 200 h. The coating showed good resistance to hydrogen entry at a pressure of 10 MPa; however, this excellent resistance was degraded at a pressure of 100 MPa. These previous studies infer that the development of a new surface coating that can resist hydrogen entry under much higher hydrogen pressures, such as 100 MPa, requires investigations to be conducted under high pressure.

Yamabe et al. [62] conducted intensive investigations of various coatings under high-pressure hydrogen, and demonstrated that a three-layer aluminum-based coating, consisting of alumina, aluminum, and ferro-aluminum (Fe–Al), prepared with a specially blended aluminum alloy by a hot dipping method had excellent durability and high resistance to hydrogen entry. It was also demonstrated that the three-layer aluminum-based coating had a higher resistance to hydrogen entry than a two-layer (alumina/Fe–Al) aluminum-based coating prepared by the same hot dipping method. This result indicates that the hydrogen-entry-obstruction effect of the two- and three-layer coatings was not due to the alumina layer only, which showed extremely high resistance to hydrogen entry under low-pressure hydrogen gas in the kilopascal range. The only difference in the coating structure between the three- and two-layer coatings was the existence of the aluminum layer; thus, it was concluded that the aluminum layer, and not the alumina layer, strongly contributed to the obstruction of hydrogen entry at high pressures. As mentioned above, many previous studies conclude that the alumina layer exhibits a high resistance to hydrogen entry; however, the results obtained under high pressure cannot be explained in terms of the obstruction caused by the alumina layer to hydrogen entry. Thus, this is a clear indication that the mechanism of hydrogen-entry obstruction under high pressure is different compared to the low-pressure condition.

In addition to the hydrogen-entry-obstruction effect, an important precondition for a coating to be successful in structural applications is that the coating remains intact (no cracks) under mechanical loading [57]. The high-pressure components subjected to fatigue loading such as storage cylinders and pipes are generally designed in consideration of a safety factor. The safety factor is defined as the tensile strength of a material to the allowable design stress and its value is 3.5–4.0 for design by rule or 2.4–3.0 for design by analysis [13]. Considering the safety factor, the high-pressure components are operated under cyclic stresses lower than the yield stress of the materials [13–15]. Under such a loading condition, it is confirmed that the developed three-layer aluminum-based coating shows a good durability from fatigue tests of coated specimens [62].

Our previous study [62] clarified that the aluminum layer had a strong impact on hydrogen-entry obstruction although the exact mechanism was not investigated. Thus, the present study aims to elucidate a precise mechanism of the hydrogen-entry-obstruction effect of the three-layer (alumina/aluminum/Fe–Al) aluminum-based coatings under high hydrogen pressure (*e.g.*, 100 MPa). Type 304 austenitic stainless steel was used as a base steel, and the following investigations, which were not conducted in our previous study [62] were performed: (1) hydrogen permeation tests of sheet specimens fabricated from pure aluminum and type 304 austenitic stainless steel under low hydrogen pressure; (2) hydrogen-content measurements of the aluminum-based-coated specimens with and without a sputtered palladium (Pd) overlayer after exposure to hydrogen; (3) hydrogen-content measurements of the differently sized coated specimens after exposure to hydrogen; and (4) analysis of local hydrogen concentration at interfaces in the coated specimens by secondary ion mass spectroscopy (SIMS).

Materials and experimental methods

Material, specimens, and Al-based coating

The base material was type 304 austenitic stainless steel, composed of 0.05 C, 0.47 Si, 1.54 Mn, 0.030 P, 0.024 S, 8.09 Ni,