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Surface coating with a high resistance to hydrogen entry under high-pressure hydrogen-gas environment

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ABSTRACT

Development of a surface coating with high resistance to hydrogen entry under a high-pressure hydrogen-gas environment is presented. Two aluminum-based coatings were developed on the basis of preliminary tests: two-layer (alumina/Fe–Al) and three-layer (alumina/aluminum/Fe–Al) coatings, deposited onto cylindrical and pipe (Type 304 austenitic stainless steel) surfaces by immersion into a specially blended molten aluminum alloy. The coated specimens were exposed to hydrogen gas at 10–100 MPa at 270 °C for 200 h. Specimen hydrogen content was measured by thermal desorption analysis; hydrogen distributions were analyzed by secondary ion mass spectroscopy. Both coatings showed high hydrogen-entry resistance at 10 MPa. However, resistance of the two-layer coating clearly decreased with an increase in pressure. In contrast, the three-layer coating showed excellent hydrogen-entry resistance at a wide pressure range (10–100 MPa), achieved by the combined effect of alumina, aluminum, and Fe–Al layers.

1. Introduction

Hydrogen energy has potential for the realization of a sustainable society, because it can be produced from various sources of renewable energies and does not emit carbon dioxide (CO_2). However, it is essential to resolve many technical problems in relation to hydrogen use, such as improvements in fuel cell technologies, hydrogen production and storage, and development of materials and systems capable of withstanding cyclic loads in a hydrogen environment. In the

Abbreviations: AES, Auger electron spectroscopy; EDX, energy dispersive X-ray; GC–MS, gas chromatography-mass spectrometry; HE, hydrogen embrittlement; OM, optical microscopy; SEM, scanning electron microscopy; SIMS, secondary ion mass spectroscopy; TDA, thermal desorption analysis.

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case of metallic materials, characteristic tensile and fatigue properties are often degraded by hydrogen, a phenomenon known as hydrogen embrittlement (HE) [1–44]. To ensure the safe and reliable use of metallic materials in a hydrogen environment, tolerant materials and systems must be employed to prevent accidents due to HE failure.

HE is caused by hydrogen dissolved in metallic materials. Accordingly, if new technologies inhibiting hydrogen entry into materials under high-pressure hydrogen environments are developed, HE can be mitigated. Barrier coatings for hydrogen-entry obstruction are one of the most promising technologies under investigation, with many studies on barrier coatings reported thus far [45–75]. Most of these studies have been performed under a low-pressure hydrogen-gas environment (~kPa). It is known that oxide layers function as an effective barrier for hydrogen entry; in particular, aluminum oxide (Al_2O_3) layers have displayed extremely high barriers for hydrogen entry.

Roberts et al. [51] measured tritium permeability (Q_T) of Al_2O_3 under hydrogen partial pressures ranging from 2 to 50 kPa and temperatures ranging from 1200 to 1450 °C, by circulating a mixture of hydrogen, tritium, and helium gases in a sintered Al_2O_3 pipe. Q_T was converted to hydrogen permeability (Q_H) by using $Q_H/Q_T = (m_T/m_H)^{1/2}$, where m_T is the tritium mass and m_H is the hydrogen mass [76]. As a result, the Q_H of Al_2O_3 was found to be approximately 10^4 times less than that of metallic materials such as vanadium, niobium, molybdenum, and uranium.

Yamada-Takamura et al. [66] deposited an Al_2O_3 layer of thickness ranging from 50 to 500 nm on a tungsten oxide (WO_3) film by using a filtered vacuum arc method. They measured the Q_H of the coated WO_3 film by utilizing a unique property in which coloration of WO_3 reacts with hydrogen. The Q_H of the coated film was approximately 10^2–10^3 times less than that of a non-coated specimen.

Forcey et al. [57] deposited an Al_2O_3 multilayer coating on an austenitic stainless steel alloy (AISI 316L) and martensitic steel (DIN 1.4914) by pack aluminizing method and measured the Q_H of the coated specimens by hydrogen permeation method at a pressure of 100 kPa and temperatures ranging from 250 to 600 °C. The coating structure was composed of Al_2O_3 and Fe–Al layers; the effects of coating thickness ranging from 18 to 44 μm and aluminum concentrations in the Fe–Al layer on Q_H were investigated. The results implied that Q_H of the coated specimens at 600 °C was approximately 10^3 times less than that of non-coated specimens. Furthermore, based on observations that the Q_H of the coated specimens was not dependent on layer thickness and Fe–Al layer composition, Forcey et al. [57] suggested that the low Q_H of the coated specimens was because of the Al_2O_3 layer.

Perujo et al. [59] deposited an Al_2O_3 multilayer coating (Al_2O_3/Fe–Al layers) on martensitic steel (DIN 1.4914) by a vacuum plasma spraying technique and measured its deuterium permeability. Effects of pressures (p) ranging from 3 to 50 kPa on the deuterium permeation rate (J_D) of the coated specimen were investigated. The Al_2O_3 multilayer coating showed a high resistance to hydrogen entry with J_D values proportional to p at $p < 20$ kPa and $p^{0.5}$ at $p > 20$ kPa. The pressure dependence of J_D obtained by Perujo et al. indicates that deuterium permeation follows a surface reaction-controlled process such as absorption and dissociation at $p < 20$ kPa and a diffusion-controlled hydrogen transport process at $p > 20$ kPa.

Song [67] exposed austenitic stainless steel coated with an Al_2O_3 layer (150-μm thickness) by a plasma spraying method to high-pressure hydrogen gas at a pressure of 24 MPa and temperature of 200 °C for 14 d, followed by the measurement of its hydrogen content. The hydrogen content of the coated hydrogen-exposed specimen was 30.2 ppm, while that of the non-coated hydrogen-exposed specimen was 39.5 ppm. The hydrogen-entry resistance of the Al_2O_3 layer under exposure to high-pressure hydrogen gas (~MPa) obtained by Song is significantly degraded, compared with that found under a low-pressure hydrogen-gas environment (~kPa) [51,53,57,59,63,66,68].

Lorthan Jr. et al. [45] performed tensile tests of an austenitic stainless steel alloy (SUS304L) with a titanium layer coating under a 69-MPa hydrogen-gas atmosphere. The hydrogen content of the coated specimen was not determined. They report that the reduction of area for the coated specimen hardly decreased in the hydrogen-gas environment, while that of a non-coated specimen significantly decreased.

Murray et al. [54] measured the tensile strength of a precipitation-hardened martensitic steel coated by $A1_2O_3$, SiO_2, or Si_3N_4 after exposure to high-pressure hydrogen gas (13.8 MPa, 202 °C for 24 h). The hydrogen content of each coated specimen was not determined. The result showed that hydrogen exposure of the $A1_2O_3$ coating had a smaller effect on the area of reduction, compared with the other coatings.

As mentioned above, most studies on surface coatings have been performed under low-pressure hydrogen-gas environments (~kPa), though there are some studies on surface coatings under higher pressures (~MPa) as well [45,54,60,67]. The results reported by Song [67] and Perujo et al. [59,63] indicate that the resistance of surface coatings to hydrogen entry may decrease with an increase in hydrogen pressure. Hence, the investigation of surface coatings in hydrogen-gas environments at pressures of 1 kPa is not sufficient to develop new coatings that are able to resist hydrogen entry under much higher hydrogen-gas pressures such as 100 MPa. The development of such a new coating necessitates investigations under high-pressure hydrogen-gas environments.

With this goal, this study describes the preparation and detailed investigation of a surface coating with high resistance to hydrogen entry under exposure to a high-pressure hydrogen-gas environment (ranging from 10 to 100 MPa). For the design of high-pressure components subjected to fatigue loading such as storage cylinders and pipes for fuel cell vehicles, hydrogen stations and hydrogen pipelines, a safety factor is generally applied to the component materials. Considering the safety factor, the high-pressure components are operated under cyclic stresses much lower than the yield stress of the materials. In this viewpoint, this study pursued the development of new surface coatings with an excellent strength under fatigue loading within the elastic stress regime of base steels. On the basis of preliminary hydrogen-entry and durability tests for several coatings, aluminum-based multilayer coatings were selected as candidates. Specimens were coated with a specially blended aluminum alloy based on Al–Si, not an ordinary pure aluminum. Keeping in mind that these coatings are deposited on the inner surfaces of storage