TiAlN/TiMoN Coatings as Hydrogen Barriers

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Abstract: We evaluated the hydrogen barrier properties of a multi-layered coating of TiAlN/TiMoN. Coatings facilitated reductions of the hydrogen permeabilities to 1/1,000 of that of the uncoated substrate. The experiment confirmed that the coatings composed of fine crystal grains were highly effective as hydrogen barriers, and that this barrier property became even more efficient if multiple layers of the coatings were applied. The crystal grain boundaries of the coating and interfaces of each film in a multi-layered coating can serve as hydrogen trapping sites. We speculate that fine crystal structures with multiple crystal grain boundaries and multi-layered coating interfaces will contribute to the development of hydrogen barriers.

Key words: Hydrogen permeation, multi-layered-coating, microstructure, hydrogen traps.

1. Introduction

There have been many attempts to replace fossil fuels with hydrogen gas, and many hydrogen energy systems that use high-pressure hydrogenare being developed. Hydrogen in many metallic materials, such as carbon steel, stainless steel, and aluminum alloys, affects their mechanical properties negatively. Steels mainly composed of high-strength ferrite and martensite structures have exceptionally high hydrogen diffusibilities and often exhibit hydrogen embrittlement.

Their widespread industrial application demands not only the clarification of the interactions between high-pressure hydrogen and relevant materials but also the development of technology that prevents the penetration of hydrogen into these materials. Previous studies have shown that when steel is exposed to a hydrogen gas atmosphere, the hydrogen on the surface is relatively easily dissociated from a molecular state to an atomic state, penetrating the material and causing hydrogen embrittlement [1, 2].

Engineers and researchers of various systems, including fusion reactors, fuel cells, H_2S-corrosion resistant components, and vacuum devices, have developed barrier films that prevent hydrogen penetration of the material. Some ceramic coatings of Al_2O_3, TiN and TiC were reported as effective hydrogen barriers [3-5].

Thin alumina deposited on amorphous tungsten oxide by a filtered vacuum arc method can reduce hydrogen permeation by a factor greater than 3,000, even for only thicknesses of 500 nm. However, plasma-sprayed coatings of alumina on steels are not very effective permeation barriers since the films contain many defects [4, 5]. These differences can be accounted for by the microstructures of the coating, which differ considerably depending on how they are formed, thereby influencing the hydrogen permeation behavior.

TiN films consisting of fine crystal grains, with diameters of about 100 nm or less, provided superior hydrogen-permeation barriers. Applying a coating of TiN on a stainless steel substrate reduced the hydrogen permeation by a factor of about 100 to 5,000 compared with uncoated substrates [3]. The grain boundaries of the films can be trap sites for hydrogen and microcrystalline structures with many grain boundaries are expected to provide effective hydrogen-barrier performance.

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In recent years, hard coatings for cutting tools have become necessary to achieve high wear resistance performances under extremely severe environments. Typically, these improvements have been achieved by multiple element additions and multilayered structures. The coatings deposited by arc ion plating method have unique structures in which hard layers are combined with functional layers, or the stacking period of the layers is adjusted to achieve a variety of characteristics. However, no reports on hydrogen permeation behavior of multi-layered-coatings have been published.

In this research, the influence of multi-layer on the hydrogen permeation behavior was studied, and the correlations between the influencing factors were analyzed.

2. Experimental Details

2.1 Characterization of Coatings

Coatings were deposited using the arc ion plating method. AISI 316L austenitic stainless steel was used as the substrate. The substrate was set in the film deposition device, evacuated, and its surface was subjected to ion bombardment treatment in an argon atmosphere. The substrate temperatures were 573-773 K. The reaction gases were C_2H_2 and N_2, maintained at pressures of 7-8 Pa. The substrate bias voltage was -135 V.

Multiple evaporation sources with a plate target are equipped on the lateral side of a vacuum chamber, and a substrate table is set in the chamber. The multiple evaporation sources are typically arrayed in the vertical direction to ensure film thickness uniformity in the vertical direction and to provide a wide coating area. The table is rotated by a rotating mechanism so that a large quantity of substrates can be coated uniformly along the circumference.

The thicknesses of the coatings ranged between 2.0 and 2.6 μm.

Crystal phase analyses of the coatings were carried out using X-ray diffraction and electron-beam diffraction. The thicknesses of the coating cross-sections were measured and the microstructures were observed via scanning electron microscopy. The coating surface roughness and crystal grain analyses were carried out using scanning probe microscopy (SPM). Crystal grain size measurements and crystal phase analysis inside the coatings, via coating cross-sectional analysis, were conducted using transmission electron microscopy (TEM).

Using SPM, the sample surfaces in the atmosphere can be easily measured at high resolutions. The properties of the coating surface can be analyzed using image analysis software. A method that binarizes the unevenness of the surface and generates an image can be applied to better understand the crystal grains of the coating. From a crystal cross-section in a plane parallel to the substrate surface (coating surface), the average value for the crystal grain size can be calculated by assuming that the crystals are spherical [6, 7]. In this study, the crystal grain size measurements were performed by a coating cross-sectional analysis using TEM, as this provided high-accuracy result. The diameters of 20 crystals taken from five arbitrary cross-sections in a plane parallel to the substrate surface were determined from a TEM image, and an average diameter of these 20 crystals was calculated.

2.2 Hydrogen-Permeation Tests

Hydrogen-permeation tests were performed on the coated stainless steel samples. These tests were based on the differential-pressure methods [3]. A gas chromatograph was used in this study. The samples (diameter: 35 mm; thickness: 0.1 mm) were set on a susceptor, which could be held in place at temperatures up to 773 K. The apparatus was evacuated to ~10^{-6} Pa. After the test temperature stabilized, hydrogen (purity of 99.995%) was introduced into the susceptor side of the chamber at a filling pressure of 400 kPa. The permeation area was 6.6 cm^2.

The amount of hydrogen that permeated the sample was quantitatively measured by gas chromatography. The sample was maintained with a susceptor made of silicone fiberglass. This was maintained at the test temperature under a vacuum, and hydrogen pressure was applied to its coated side. A measurement began when the quantity of hydrogen that permeated the sample reached a constant level. A metallic gold seal, with a low hydrogen reaction rate and high shielding properties against gas, was used as the material to maintain the sample. Three test temperatures of 573, 673, and 773 K were used. Under these test conditions, the hydrogen permeation of a coated sample is limited by the speed of hydrogen diffusion in the coating [8]. The sample was maintained at the test temperature, and the hydrogen permeation began. The hydrogen permeation became constant after three hours, and thus, this measured value was defined as the hydrogen permeability.

The permeability, ϕ, is defined by the expression

$$\phi = (Jd)/ (A\Delta p^{n}) \qquad (1)$$

where J is the permeation flux of hydrogen through a sample of area A and thickness d, under a partial pressure gradient Δp across the sample called the driving pressure. The exponent n represents different permeation regimes: diffusion-limited and surface-limited when $n = 0.5$ and 1, respectively. Hydrogen permeation through a thin-film-coated steel sample is known to be diffusion-limited when the driving pressure is between 10^{4} and 10^{5} kPa [3].

The permeation flux was continuously measured. After 30 min, for example, the standard deviation decreased below 10% among the data for permeation flux through the non-coated stainless steel substrate at 773 K under a hydrogen pressure of 400 kPa.

3. Results and Discussion

3.1 Hydrogen Permeation Behavior

Fig. 1 summarizes the hydrogen permeation behaviors of the samples prepared in this study and previous study [3]. The TiC, TiN, TiAlN, and multi-layered TiAlN/TiMoN coatings were dense and exhibited excellent adhesion to the AISI 316 L austenitic stainless steel substrate. The hydrogen permeability of all the coated samples decreased compared with that of the substrate alone, confirming the effectiveness of the coatings as hydrogen barriers.
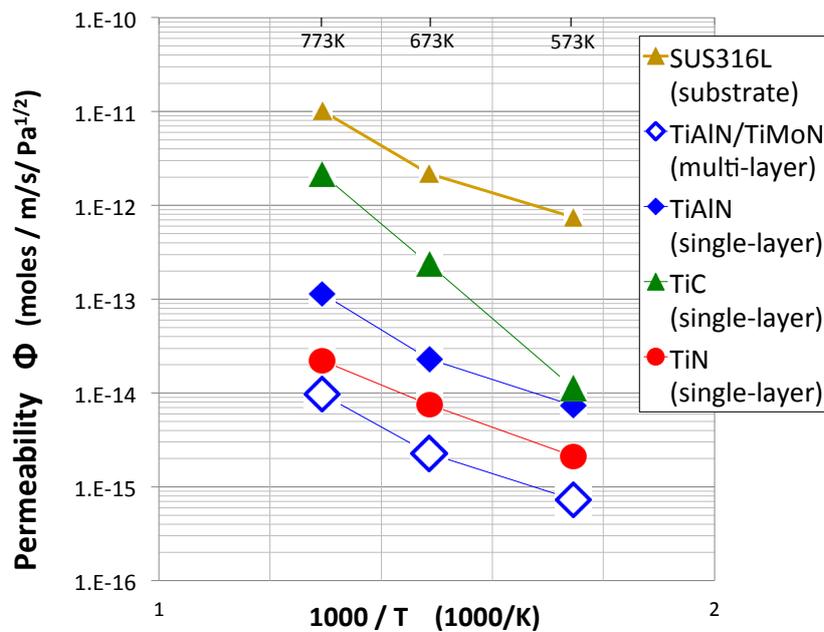

Fig. 1 Hydrogen-permeation behaviors of coatings.

A comparison of the results obtained at a test temperature of 573 K showed that the hydrogen permeabilities of the TiAlN-coated, TiN-coated, and TiAlN/TiMoN multi-layered coating samples were 1/100, 1/100 or less, and 1/1,000 of that of the uncoated substrate, respectively.

The hydrogen permeability varied greatly with the test temperature, with greater variations at lower temperatures. This permeability, shown in Fig. 2, is believed to reflect the hydrogen diffusion in the coating. The implication is that in these hard coatings, lower temperatures result in lower diffusion coefficients of hydrogen. In other words, the highly sloped lines of the hydrogen permeability of each sample versus temperature indicate that the hydrogen diffusion activation energies are large.

3.2 Effect of Microstructure of Coatings on Hydrogen Permeation Behavior

Based on previous research of the forms of hydrogen found inside materials, examples of hydrogen trapping sites are lattice defects (atom vacancies, dislocation, and crystal grain boundaries), impurity atoms, precipitates, inclusion interfaces, and voids. At hydrogen trapping sites, the diffusion of hydrogen is limited. For a hydrogen atom to escape from a trap site and continue to diffuse, a certain amount of activation energy is necessary [1, 2].

Hydrogen diffusion behaviors inside metal materials, especially the mechanism of hydrogen embrittlement of steel, have been studied extensively. The quantity limit and solid solubility of hydrogen inside a crystal lattice are determined from the hydrogen quantity of a pure iron sample in a high-purity hydrogen gas environment and equilibrium. Solid solubility is the ratio of the number of hydrogen atoms to the number of normal lattice points, whereas the hydrogen concentration is proportional to the square root of the hydrogen gas pressure. Although the solid solubility of hydrogen in steel may be affected by the purity of the sample and

surface conditions, the results of various research studies performed at approximately 673 K or above concur that the temperature dependence is nearly a linear Arrhenius plot [1, 2]. This is attributed to an essential phenomenon associated with the solid solution state, such as the inter-lattice position occupied by the hydrogen. Furthermore, the good data correlation for various samples indicates that the quantity of hydrogen that iron can absorb at 673 K or above is not strongly affected by lattice defects, such as impurities and crystal grain boundaries.

In contrast, it is known that with Ni, the hydrogen solid solubility varies considerably between single and multi-crystal samples [9]. Some studies emphasized that at temperatures of 573 K or lower, the solubility of iron alloys is also influenced by the surface adsorption reaction and lattice defects [10]. Other sources indicate that the hydrogen diffusion coefficient in steel is dependent on the crystal grain size [10]. That is, if the crystal grain size is small, the diffusion coefficient also decreases [10]. This suggests that when the diffusion speed of hydrogen is relatively low, the influence of crystal grain boundaries cannot be ignored. The hydrogen diffusion coefficient in ionically or covalently bonded substances, such as ceramic coatings, is several times lower than that in steel [5, 11], which suggests that the hydrogen trapping site effect works very efficiently.

In multi-layered coatings, as crystal grain boundaries become hydrogen diffusion barriers, the interfaces of the films may also become hydrogen diffusion barriers.

Fig. 2 shows the result of the TEM cross-section observation of the TiAlN/TiMoN multi-layered coating. Many layers of a crystalline coating with thickness of around 5-10 nm were laminated onto a TiAlN single-layer coating (Fig. 3). All these coatings were crystalline (Figs. 4 and 5).

As shown in Fig. 1, the TiAlN/TiMoN multi-layered coating exhibited the lowest hydrogen permeability of all the coatings in this study, demonstrating
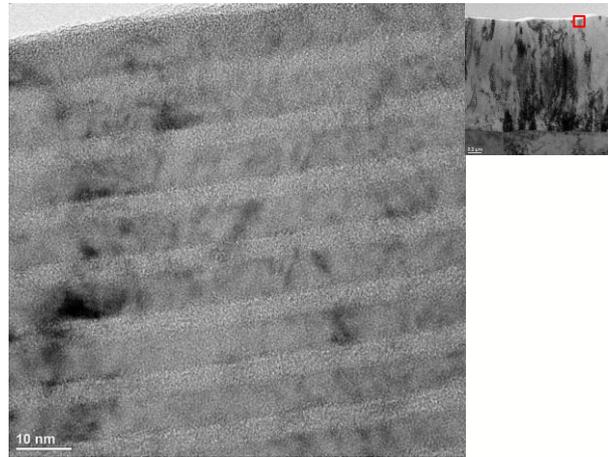
Fig. 2   TEM image of cross section of the upper part of TiAlN/TiMoN multi-layer coating.
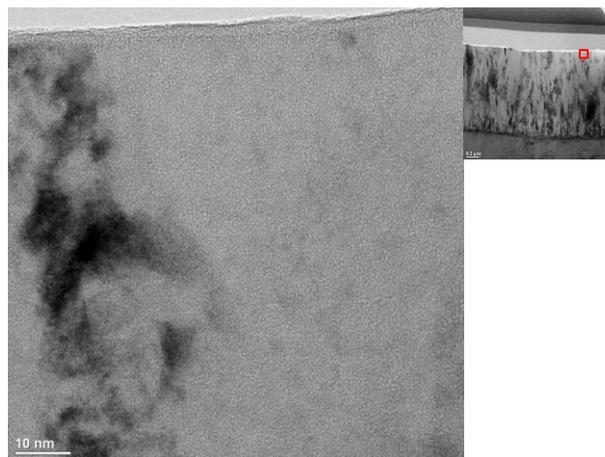

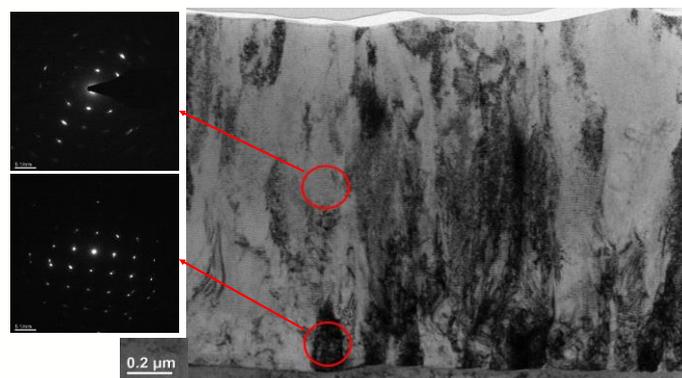**Fig. 3   TEM image of cross section of the upper part of TiAlN coating.**

Fig. 4   TEM image and diffraction pattern of TiAlN/TiMoN multi-layer coating.
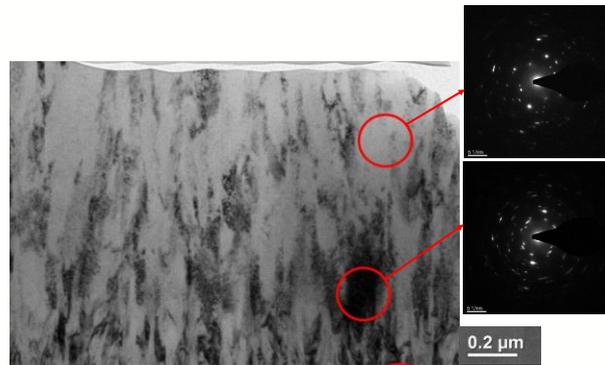
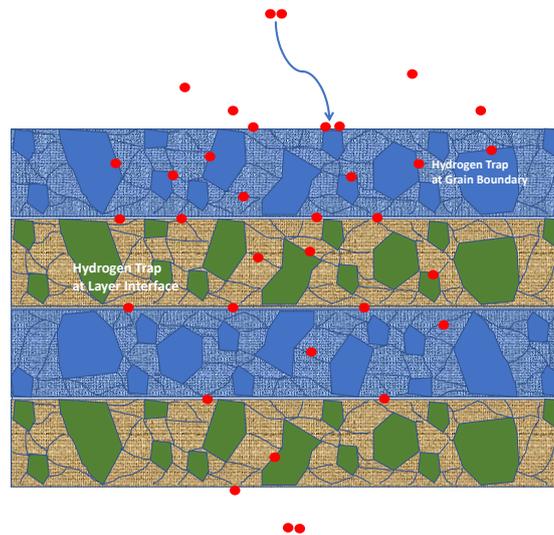**Fig. 5   TEM image and diffraction pattern of TiAlN coating.**

Fig. 6   Schematic illustration of hydrogen traps at grain boundary and layer-interface. Hydrogen atoms can be trapped at grain boundary and layer-interface in coatings.

that the interface effectively served as a hydrogen diffusion barrier.

Fig. 6 shows a schematic diagram of the film interface serving as a hydrogen trap. The hydrogen atoms that diffuse into the coating are believed to be trapped in the crystal grain boundaries and at the film interface.

Based on the findings above, we believe that in the fine crystal grain coating and the multi-layered coating, the crystal grain boundary and film interfaces serve as hydrogen diffusion barriers to reduce the hydrogen permeability, and that these hydrogen barrier coatings are more efficient when they possess these microstructures.

4. Summary

This study confirmed that the multi-layered coating of TiAlN/TiMoN was dense and effectively served as hydrogen barriers.

When compared at a test temperature of 573 K, the hydrogen permeabilities of the TiAlN-coated, TiN-coated, and TiAlN/TiMoN multi-layered coating samples were 1/100, 1/100 or less, and 1/1,000 of that of the uncoated substrate, respectively.

The tests confirmed that coatings with fine crystal grains were highly efficient hydrogen barriers. It is speculated that these coatings possessed many crystal grain boundaries that served as barriers to the diffusion of hydrogen.

According to previous research on the forms of hydrogen inside materials, examples of hydrogen trap sites are lattice defects (atom vacancies, dislocation, and crystal grain boundaries), impurity atoms, precipitates, inclusion interfaces, and voids. However, which defects in the coatings affect the hydrogen barrier, as well as the extent of this influence, are subjects of future research. The diffusion movement of hydrogen is limited at hydrogen trapping sites.

We speculate that the hydrogen atoms that diffuse into the coating are effectively trapped in the crystal grain boundaries and at the film interfaces. Among all the coatings tested, the TiAlN/TiMoN multi-layered coating exhibited the lowest hydrogen permeability.

The results of this study indicate that, in the fine crystal grain and the multi-layered coatings, the crystal grain boundaries and film interface served as hydrogen diffusion barriers to reduce the hydrogen permeability, and these hydrogen barrier coatings were more efficient when these microstructures were present. As such, we speculate that development of coating microstructures will become increasingly important for the development of hydrogen barrier coatings in the future.

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