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The permeation of tritium through 316L stainless steel with multiple coatings

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Abstract

TiN + TiC + TiN and TiN + TiC + SiO_2 films were deposited on the surface of 316L austenitic stainless steel by means of physical vapor deposition (PVD). The thickness of the films was about 2–3 μm. The film is compact, oxidation-resistant, and has good adherence with the substrate below 500°C. Tritium gas permeation of 316L with multiple films was examined, and it was found that the tritium permeability in 316L with a TiN + TiC + TiN film was 4–5 orders of magnitude lower, and in 316L with a TiN + TiC + SiO_2 film was 4–6 orders of magnitude lower than that in 316L with a Pd film at about 200–500°C. At about 600°C, the permeability of 316L with the multiple coating was 3–4 orders of magnitude lower than that in 316L with a Pd film. The result shows that the tritium permeation barrier is formed by multiple coating above 300°C, and it is stable below 500°C. However, the barrier is partly destroyed at about 600°C because of oxidation; although this results in degradation of the barrier, it still plays a positive role. These films may be useful as coatings for the first wall, tritium blanket, and heat exchanger in fusion reactors for tritium permeation resistance. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Tritium gas-driven permeation (GDP) in materials is one of the problems facing fusion reactor operation [1–5]. 316L stainless steel is a candidate structural material for fusion reactors, but the tritium permeability is high in 316L. At present, the prevention of tritium permeation through metal structural materials is not aimed at the inherent permeability of the metal. Coatings on the surface of metals produced by physical vapor deposition (PVD) may be a better approach.

The purposes of investigating coatings are to determine the conditions for forming tritium permeation-barrier coatings, conditions of stability of the barriers, and the identification of coating materials with low permeability at high temperature. Shan et al. [1,3] investigated the diffusion and permeation of tritium through TiC and TiN + TiC films produced by chemical vapor deposition and through natural oxide films on the surface of 316L. The tritium permeability through the three kinds of film is lower by several orders of magnitude compared to 316L with a Pd film at 200–500°C. The tritium permeability of 316L with a natural oxide film is 2–3 orders of magnitude lower than that of bulk only. The resistance to permeation of tritium of TiC and TiN + TiC films is better, but they begin to oxidize in air at about 390°C and the color becomes grey on oxidation above 450°C, resulting in their degradation as a barrier.

In this work, TiN + TiC + TiN and TiN + TiC + SiO_2 multiple films were coated on the surface of 316L for improving the oxidation-resistance and permeation of TiC films at high temperature.

2. Experiment

2.1. Sample preparation

Multiple films were deposited on the surface of double-cup shaped samples of 316L stainless steel, as described in [1]. TiN + TiC + TiN films were deposited by means of hollow cathode deposition (HCD), and TiN + TiC + SiO_2 films, by means of HCD plus E-type

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electron gun ion plating. The outside layer of these multiple films was TiN or SiO_2, the middle TiC, and the inside TiN. These films are designated as TiN/TiC/TiN/316L and SiO_2/TiC/TiN/316L. Samples with TiC and SiO_2 films only were similarly fabricated.

2.2. Sample annealing

The samples with TiN + TiC + TiN and TiN + TiC + SiO_2 films were annealed in a mixture of hydrogen and argon at 350°C and in argon at 300–500°C, respectively, and subsequently cooled rapidly to room temperature. Samples with TiC and SiO_2 films only were similarly annealed for surface analysis.

2.3. Observation and analysis

The surface and adherence of the films to the substrate was examined by scanning electron microscopy (SEM), and surface analysis was done by secondary ion mass spectroscopy (SIMS) and infrared spectroscopy (IR).

2.4. Test procedure

The details of the apparatus and method of tritium permeability measurement have been described previously [1,2]. It basically consists of measuring the rate of permeation through a membrane at a controlled temperature from an upstream region pressurized at 200 Pa to a downstream region under vacuum by a proportional counter tube.

3. Results and discussion

3.1. SEM observations

The thickness of the deposited films was 2–3 μm. The diffusion bonding of films to the substrate was very good, as shown in Fig. 1. After annealing in argon at temperatures in the range 300–500°C, no cracks were found between the films and substrate. The films were compact, oxidation-resistant, and did not spall off below 500°C.

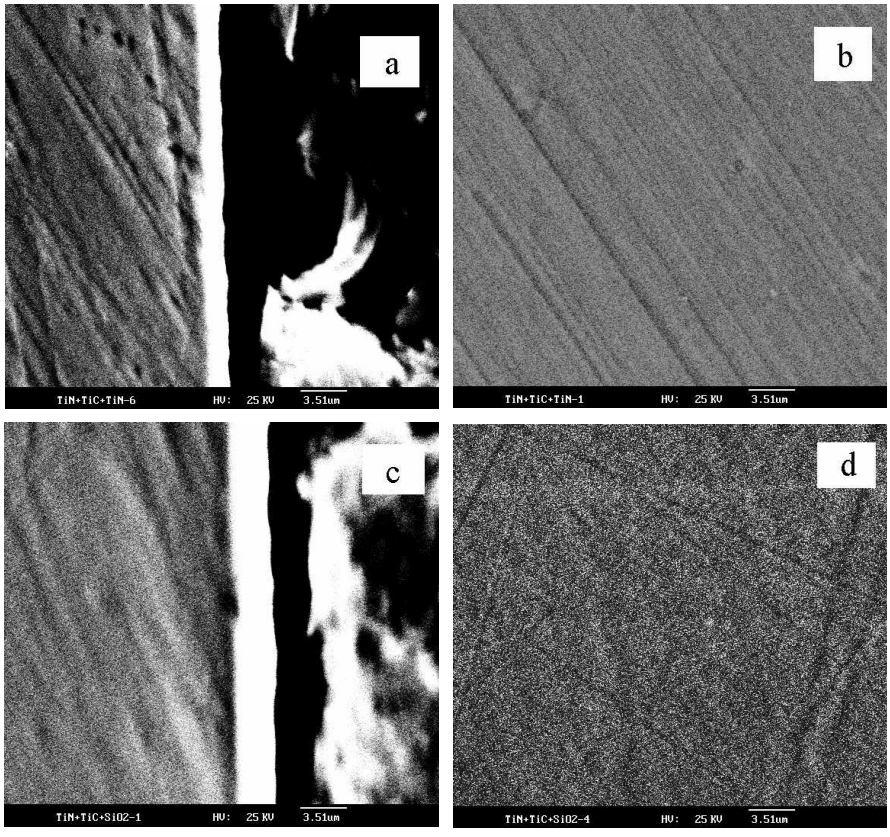


Fig. 1. SEM images of multiple coatings: (a) TiN + TiC + TiN (cross-section); (b) TiN + TiC + TiN (surface); (c) TiN + TiC + SiO_2 (cross-section); (d) TiN + TiC + SiO_2 (surface).

3.2. Tritium permeation

The relationship between tritium permeability and temperature in various materials is shown in Fig. 2. The Pd film on the surface of 316L prevents oxide formation. Tritium permeability Φ in 316L is controlled by bulk diffusion, and it follows an Arrhenius relation $\phi = \phi_0 \exp(-E/RT)$. The natural oxide film, TiN + TiC + TiN and TiN + TiC + SiO_2 films on the surface of 316L result in tritium permeation by both bulk diffusion and surface reaction, and the permeability may deviate from an Arrhenius relation. In the temperature range of 200–500°C, the tritium permeability in 316L with a natural oxide film is 2–3 orders of magnitude lower than that in 316L with a Pd film. The multiple film is better than natural oxide film. The tritium permeability in 316L with a TiN + TiC + TiN film is 4–5 orders of magnitude lower, and the permeability in 316L with a TiN + TiC + SiO_2 film is 4–6 orders of magnitude lower than that in 316L with a Pd film. Although the resistance to tritium permeation was degraded at 600°C, the tritium permeability of 316L with these films was still 3–4 orders of magnitude lower than 316L with a Pd film at this temperature. Shan et al. [1] found that a TiC film is oxidized and destroyed above about 450°C. On the contrary, the TiN and SiO_2 films coated on the outside of a TiC film were found to improve the oxidation-resistant property of TiC at high temperature, in this work. The resistance to oxidation of TiN + TiC + SiO_2 is better than that of TiN + TiC + TiN, which may be because the oxidation resistance of SiO_2 is better than that of TiN.

The tritium permeabilities were found to be as follows:

$$\Phi_1 = 3.24 \times 10^{-5} \exp(-60075/RT),$$
$$\Phi_2 = 4.10 \times 10^{-7} \exp(-68749/RT),$$
$$\Phi_3 = 3.25 \times 10^{-8} \exp(-78362/RT),$$
$$\Phi_4 = 2.81 \times 10^{-7} \exp(-99798/RT),$$

where Φ is in mol m^{-1} s^{-1} $Mpa^{-1/2}$, $R = 8.314$ J K^{-1} mol^{-1}, T the temperature in K and the subscripts 1–4 refer to the film types designated in Fig. 1. The magnitude of the permeability activation energy E scales with the resistance to tritium atom diffusion, and hence tritium permeability.

3.3. Preliminary analysis of the mechanism of tritium permeation in TiC and SiO_2

TiC and SiO_2 serve as the primary tritium permeation barriers in the multiple films [1,4,5]. Because TiN or SiO_2 were coated on the outside of a TiC middle layer in the multiple films, it is difficult to analyze the contribution of the TiC layer alone. So, as previously described, samples with a single layer of TiC or SiO_2 were annealed in a mixture of argon and hydrogen and the surfaces analyzed by SIMS and IR. Although the argon in the annealing gas is inert, the hydrogen is not: a CH_4^- adsorption peak was found in SIMS, as shown in Fig. 3. This has also been previously reported in another study [1]. But the CH_4^- peak overlaps an O_2^- peak due to the same ratio of mass to electric charge (M/e) and hence, one cannot judge that the peak is for CH_4^- or O_2^- from these data alone. So IR was done, and the result is shown in Fig. 4. The adsorption peaks, 2962 and 2876 cm^{-1}, of the TiC film after annealing correspond to, respectively, the non-symmetry

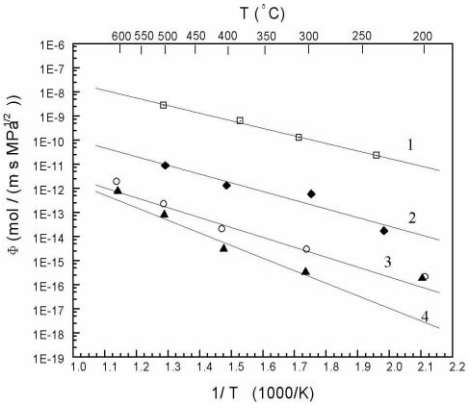


Fig. 2. The relationship between tritium permeability of various materials and temperature: 1 – Pd/316L [2]; 2 – natural oxide film/316L [3]; 3 – TiN + TiC + TiN/316L; 4 – TiN + TiC + SiO_2/316L.

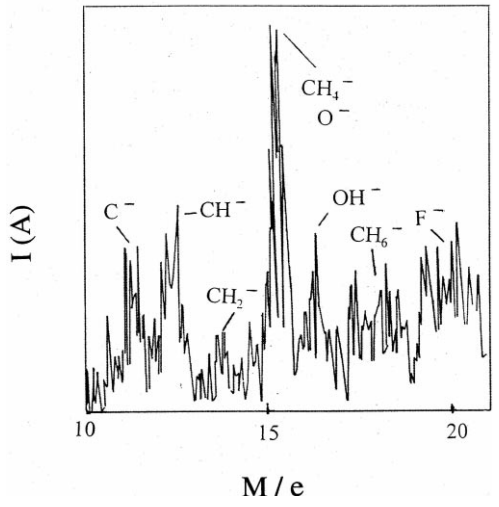


Fig. 3. SIMS spectrum of TiC film after annealing in a mixture of hydrogen and argon.

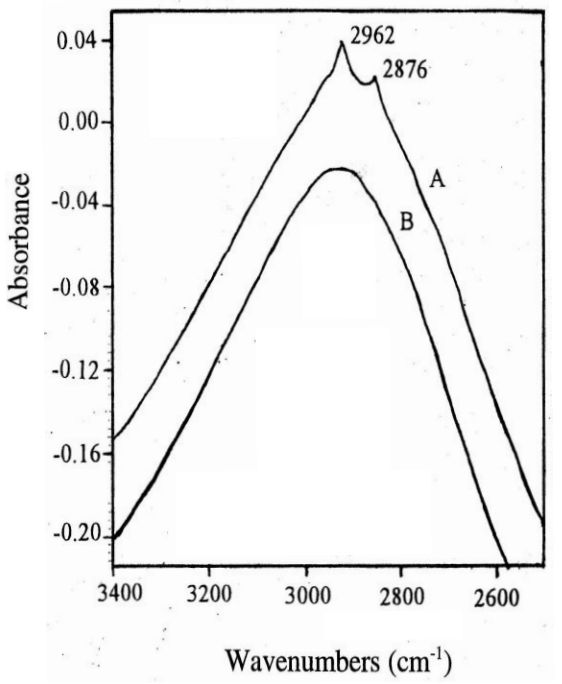


Fig. 4. Infrared spectra of TiC film: A – after annealing in a mixture of hydrogen and argon; B – No annealing.

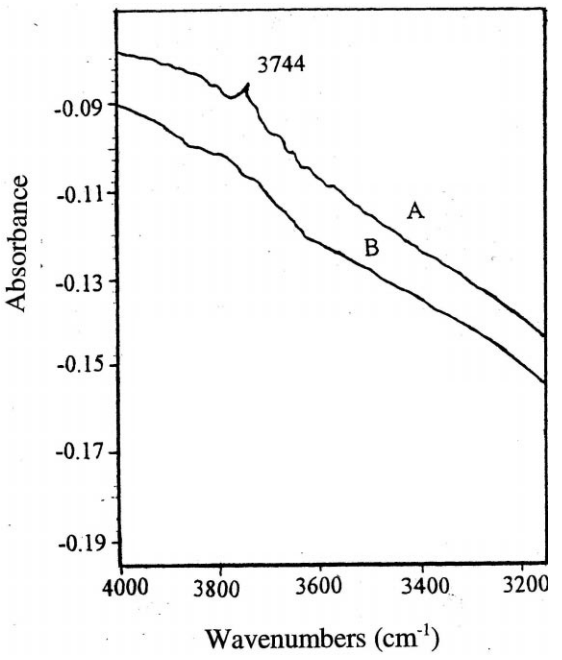
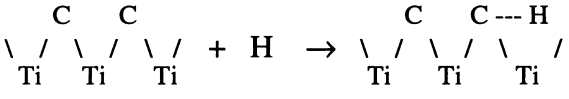


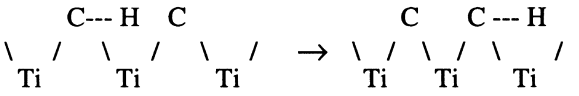
Fig. 5. Infrared spectra of SiO_2 film: A – after annealing in the mixture of hydrogen and argon; B – No annealing.

and symmetry stretch frequency of methyl ($-CH_3$) and hence correspond to a typical C–H bond. Because the peaks were not found for the TiC film without annealing, it appears that the hydrogen in the annealing gas is adsorbed by carbon in the host lattice of TiC to form C–H bonds. Since the CH_4^- is in a static state, H^+ can migrate from a site occupied by a carbon ion to a neighboring site only when the C–H bond is broken at high temperature. Because the C–H bond is strong and difficult to break, this implies that hydrogen bonding to C makes tritium permeation in TiC films difficult, which agrees with the tritium permeability in 316L with the TiC coating being several orders of magnitude lower than that in the substrate. The process may be represented schematically as follows, where the symbol '\ /' means a Ti–C bond and '–' means a C–H bond.

(a) The C–H bond forming process can be represented as



and (b) the H^+ migration process can be represented as



The arguments for reduced tritium permeation in SiO_2 are similar. In this case, an adsorption peak (3744 cm^{-1}) in the infrared spectrum of SiO_2 film after annealing was also found, as shown in Fig. 5. The peak corresponds to isolated OH^- and indicates the formation of O–H bonds. In turn, this suggests that the role of O–H bonds in the tritium permeation process in SiO_2 film is similar to that of the C–H bond in TiC film.

4. Conclusions

TiN + TiC + TiN and TiN + TiC + SiO_2 films were deposited on the surface of 316L by PVD. The thickness of films was about 2–3 μm. The films were compact, oxidation-resistant, and had good adherence to substrate below 500°C. The tritium permeability in 316L with a TiN + TiC + TiN film and with a TiN + TiC + SiO_2 film was, respectively, 4–5 and 4–6 orders of magnitude lower than that in 316L with a Pd film at about 200–500°C. The permeability was 3–4 orders of magnitude lower than that in 316L with Pd film at about 600°C. The tritium permeation barrier is formed by

multiple coatings above 300°C, and it is stable below 500°C. However, the barrier is partly destroyed at about 600°C, resulting in degradation of the barrier. These films may be useful as a tritium permeation barrier for the first wall, tritium blanket and heat exchanger in fusion reactors.

Acknowledgements

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