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Letter to the Editors

Alumina sputtered on MANET as an effective deuterium permeation barrier

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Abstract

This paper describes the reduction of the effective deuterium permeation rate of MANET obtained by the deposition of an alumina coating on the surface. The measurements of the permeation rate of deuterium were performed by a gas-phase permeation technique over the temperature range 533–773 K and for deuterium driving pressures in the range from 10^3 to 10^5 Pa. The maximum observed reduction in permeation, compared to the bare MANET steel, is around 4 orders of magnitude.

1. Introduction

The permeation rate of hydrogen and its isotopes through materials is important in many technological applications. For example, the presence of hydrogen can produce embrittlement in steels. Equally important is the control of tritium losses due to permeation through structural materials used in high-temperature gas-cooled reactors and in fusion reactors. In particular, in the fusion reactor blanket, where the tritium-containing breeder material will be in contact with steel coolant tubes at temperatures in the range 500–800 K. It could thus be a critical factor in determining the economic viability of fusion power as well as posing radiological hazards [1]. One of the most promising routes available to attempt for reducing permeation is the use of deposited layers on the surfaces. The deposited material itself should have a low permeability and/or a low recombination coefficient (so-called permeation barriers).

It is known that the hydrogen permeabilities of different materials at a given temperature cover a very wide range (many orders of magnitude), with some materials such as oxides very much less permeable than others such as steel. Either the growth of oxide layers or the application of surface coatings can be used to provide effective hydrogen and tritium permeation barriers. In general, non-metals seem to be the most promising materials from the point of view of permeation barriers. Oxides such as Al_2O_3 or Cr_2O_3 or carbides such as SiC or TiC have been proposed. There are a large number of potential coating techniques available, for example: CVD; electroplating; sputter-ion-plating; VPS; aluminising. Previous measurements have shown that Al_2O_3 is one of the most promising materials for use as permeation barriers [2]. The aluminising (i.e. pack aluminising, vapour aluminising, hot-dipping, etc.), would appear to be one of the most effective methods. Since the permeation barrier effectiveness of these coatings is probably related to the presence of the surface oxide, it should be possible to regenerate a damaged permeation barrier by in situ oxidation ('self-healing') because the aluminising process produces a reservoir of Al solution in the metallic substrate. In addition, it is possible both to aluminise components before assembly and to aluminise in situ (for example by plasma spraying followed by heat treatment).

In the present investigation, the material chosen as substrate for the deposit is the martensitic steel DIN

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1.4914 (MArtensitic for NET, MANET). It is a Nb-bearing steel which has better swelling resistance, lower sensitivity to helium embrittlement and more suitable thermophysical properties than the austenitic stainless steel AISI 316L [3]. MANET is a candidate material for the first wall and structure for the demonstration power reactor DEMO.

2. Experimental

The material studied was MANET II, a development of MANET [4]. The MANET II sample consisted of a disc, 48 mm in diameter and 0.5 mm in thickness. It was machined from a slab of material supplied by Forschungszentrum Karlsruhe from the Net-heat (No. 50803) with the following composition (wt%): C 0.11, Cr 10.3, Ni 0.65, Mo 0.58, V 0.19, Nb 0.14, Si 0.18, Mn 0.85, S 0.004, P 0.005, B 0.0072, N 0.030, Al 0.012, Co 0.006, Cu 0.010, Zr 0.014, Zn 0.001, Sb 0.0004, As 0.010, Fe balance. The membrane underwent the following heat treatment in order to produce a fully δ-ferrite free martensitic phase: heating at 1243 K for 2 h; austenising at 1348 K for 0.5 h; quenching to room temperature; tempering at 1023 K for 2 h; slow cooling to room temperature. Both sides of the disc were coated with alumina by closed-field unbalanced magnetron sputtering to a thickness of about 1.5 μm and the reactive gas was controlled by optical emission monitoring. The deposition was performed in the Institute for Design, Manufacture and Marketing at the Salford University. The exact coating procedure was a proprietary method and more details cannot be disclosed.

The method chosen for the deuterium permeation measurements during the current investigation is a gas-phase technique where, after evacuating the apparatus to an ultra-high vacuum (10^{-6} Pa), so that both sides of a sample are initially in contact with vacuum, one side of the sample (the ‘high-pressure side’) is instantaneously exposed to deuterium gas at a known, fixed pressure. Gas permeates through the sample and is released at the other side (the ‘low-pressure side’), where it causes a pressure rise in an initially evacuated, calibrated volume that is sealed off from the turbomolecular pump at the same time as deuterium gas is introduced into the high pressure side. The pressure rise is measured using a Baratron capacitance manometer with a full scale reading of 100 Pa (1 mbar). Since the volume is calibrated, either the pressure rise could be converted into an amount of gas in moles permeating through unit area of the sample ($Q(t)$) or the rate of pressure rise could be converted into an amount of gas in moles permeating through unit area of the sample per second ($J(t)$).

The apparatus is constructed from standard stainless steel UHV components [5]. Bakeout of the entire system is made possible using heating tapes. Residual pressures lower than 10^{-6} Pa (10^{-8} mbar) prior to system bakeout at 573 K and less than 10^{-7} Pa afterwards are obtained before any experiment. High pressure deuterium gas, with a nominal purity of 99.7% (H_2O $3 \leqslant 2$ ppm and O_2 $\leqslant 2$ ppm), is taken from a cylinder and admitted to the sample via two pressure controllers which enable the pressure to be set at any value between 0.1 and 150 kPa (1.0–1500 mbar). The sample is heated by a resistance furnace and the temperature may be set at values up to 773 K by a temperature controller with a thermocouple held in a well drilled into one of the flanges holding the sample, allowing a temperature stability of ±1 K. An analysis of the high-pressure gas and the permeated gas are made with a quadrupole mass spectrometer. It is thus possible to check for possible contaminants and to distinguish permeation from outgassing. The volume of the low pressure side of the sample is measured by a gas expansion method (Sieverts' method) using a calibrated volume (9.13×10^{-5} m^3) which is permanently attached to the apparatus.

3. Theory

Following a step change in the high pressure at time $t = 0$, the permeation flux J of deuterium atoms (mol m^{-2} s^{-1}) through a membrane of uniform thickness, d, where the high pressure, p, is always very much higher than the pressure on the low pressure side (which is the case during the present measurements) is given by the one-dimensional solution of Fick's law and can be expressed [6] as

$$J = \frac{DK_S p^{1/2}}{d}\left[1 + 2\sum_{n-1}^{\infty}(-1)^n \exp\left[-D\frac{n^2\pi^2}{d^2}t\right]\right], \tag{1}$$

where D (m^2 s^{-1}) is the diffusion coefficient of the membrane and K_S (mol m^{-3} $Pa^{-1/2}$) the Sieverts constant. The half-power pressure dependence of permeation rate arises from the fact that the deuterium molecule dissociates before dissolving into metals.

At steady-state conditions (i.e., $t \to \infty$) Eq. (1) becomes

$$J = \frac{\Phi}{d} p^{1/2}, \tag{2}$$

where $\Phi = DK_S$ (mol m^{-1} s^{-1} $Pa^{-1/2}$) is defined as the permeability of the material and is normally found to vary in the Arrhenius manner, i.e.,

$$\Phi = \Phi_o \exp\left[-\frac{E_p}{RT}\right], \tag{3}$$

where Φ_o is a constant, E_p the activation energy for permeation and R the molar gas constant (8.314 J K^{-1} mol^{-1}). To assume that the permeating flux is given at steady state by Eq. (1) implies that no surface effects are present, i.e. that those effects are characterised by times which are negligible in comparison to the diffusion characteristic time. If the surface effects are predominant, the system operates in the surface limit regime, and the permeation flux depends linearly on the driving pressure and is independent of thickness of the layer [5].

In some cases for coated materials, it is possible to use a two-slab model [7] to evaluate the intrinsic permeability of the permeation barrier layer. However, this approach is only valid if the precise thickness and composition of the surface layer is known and there are no defects such as cracks, in the layer. The other situation where this model fails is in the case where surface effects are present. For these reasons, the most widely used criterion to assess the effectiveness of permeation barrier layers is to quote a 'reduction factor'. This is defined to be the factor by which the steady state permeation rate of a hydrogen isotope through a sample is decreased by the presence of a permeation barrier.

4. Results and discussion

The measured values of the permeation rate for the coated disc over the temperature range 533–773 K at 50 K intervals and for a deuterium driving pressure of 10^5 Pa, are shown as Arrhenius plots in Fig. 1. A reduction of 1 order of magnitude at 773 K and 2 orders of magnitude at 533 K was observed in the initial measurements (open triangles). The pressure dependence of the deuterium permeation rate of the specimen was investigated at the constant temperature of 773 K and over the pressure range 10^3–10^5 Pa. The results are presented in Fig. 2 as deuterium permeation rate versus driving pressure on a log–log scale. The complete set of data for each specimen was fitted to an expression of the form $J = ap^n$. The value found for n of 0.74 indicates a strong surface contribution to the kinetics of permeation. Therefore no attempt was made to calculate the intrinsic permeability of the barrier layer using the two-layer diffusion model [7].

Repeating the measurements, with a deuterium pressure of 10^5 Pa and at 773 K, a gradual decrease of the permeation rate was observed and eventually a reduction of 4 orders of magnitude in the present temperature range (solid triangle in Fig. 1) was obtained. A plausible explanation for these results is that during the measurements, a better adherence of the layer to the substrate was achieved with a possible presence of an interdiffusion zone (see (SERRA 1) in Fig. 3). In the SEM pictures of the cross-section of the sample after permeation measurements (SERRA 1) in Fig. 3, the elemental compositions were determined by semi-quantitative EDX. The compositions (wt%) were in point 1: O = 31.6, Al = 59.7, Cr = 0.8 and Fe = 7.8; at point 2: O = 3.5, Al = 17.1, Cr = 7.6 and Fe = 71.8; at point 3: O = 1.8, no Al, Cr = 10.5 and Fe = 87.4; at point 4: O = 2.9, Al = 17.2, Cr = 8.5 and Fe = 71.4. In addition, during the measurements, the micro-cracks on the aluminide layers of the sample might be filled by the

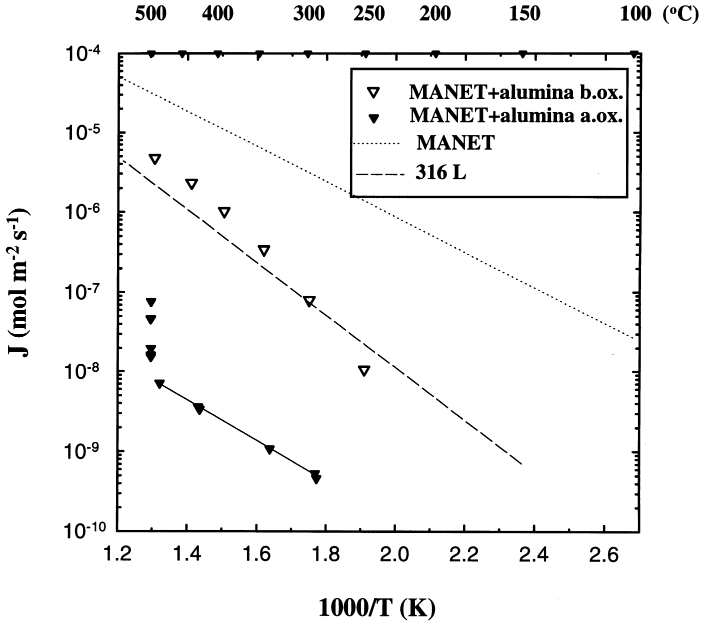

Fig. 1. Arrhenius plot of the permeation rate of deuterium through bare and alumina coated MANET II, before and after deuterium exposure at 773 K in the permeation rig. The upstream deuterium pressure was 10^5 Pa.

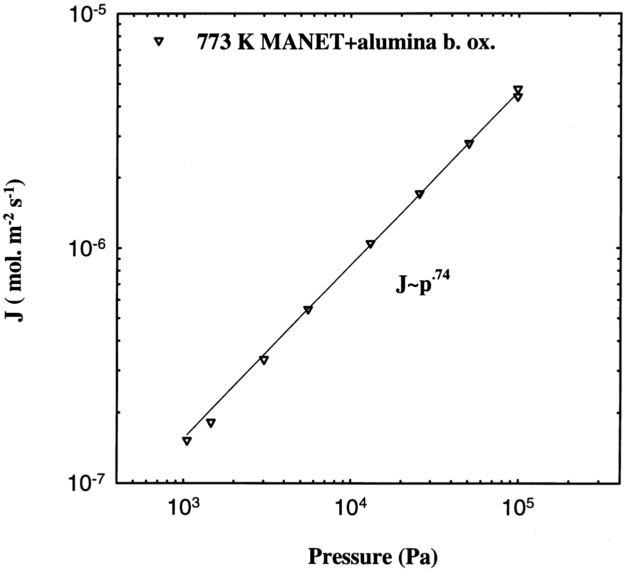

Fig. 2. Permeation rate of deuterium through the sputtered alumina specimen versus the driven pressure at 773 K, before oxidation in the permeation rig.

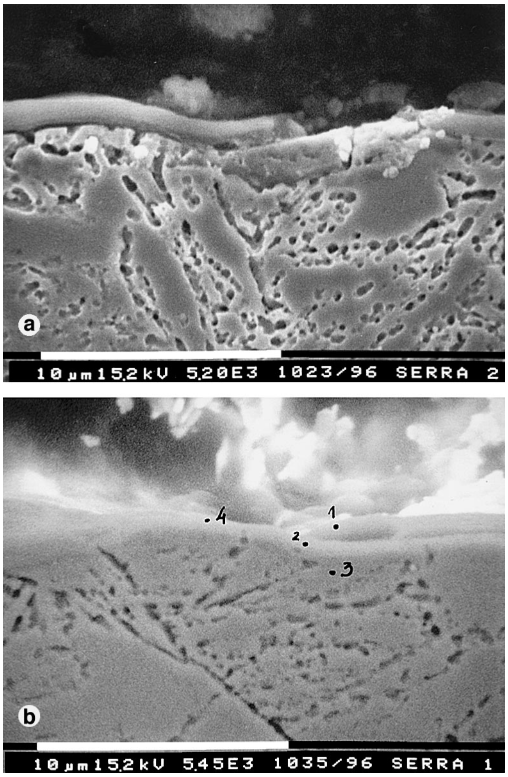

Fig. 3. SEM pictures of the cross-section of (a) the as-received sputtered alumina MANET II (SERRA 2) and (b) the same sample after permeation measurements (SERRA 1).

formation of oxides ('self-healing') (compare (SERRA 1) with (SERRA 2) in Fig. 3). Therefore, an increase of the barrier efficiency was obtained and hence the observed strong decrease of the effective deuterium permeation rate. During the time that the sample was in the rig, it was held either in an ultra-high vacuum or under a deuterium atmosphere. Probably the presence of small quantities of H_2O and O_2 in the deuterium gas (few ppm) and the temperature were the cause of in situ oxidation of the sample. Since the gas used was extremely pure ($\leqslant 2$ ppm H_2O and O_2), the impurities also came out from the wall of the equipment.

5. Conclusion

An investigation on the use of sputtered alumina as a permeation barrier shows that it is possible to reduce the permeation rate of hydrogen isotopes through MANET by around 4 orders of magnitude over the temperature range 573–773 K. These very positive preliminary results encourage a complete cycle of tests to develop these type of coatings.

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