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Characterising materials for walls of fusion reactors

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Abstract

Experiments in which a permeation flux through a membrane specimen is modulated have been shown to provide valuable insight into permeation processes. In particular, surface and bulk effects can be separately identified from the experimental data. This approach requires an analytical model of the process in terms of absorption steps and bulk transport. A basic model has been developed to account for permeation through a binary membrane comprising a coating and a substrate. The interface reaction kinetics including trapping are taken into account in terms of rate constants. It is shown that given adequate knowledge of the substrate then the permeation parameters of the coating can be deduced. This greatly extends the range of materials which can be examined, particularly those materials which cannot be obtained as foils such as ceramics. Some strategies for first wall reactor materials combine a low diffusivity ceramic coating on a mechanical substrate; such binary (and even more complex) structures can now be assessed through the modulated permeation method, taking full account of the interface. As an example, recent measurements on a titanium carbide–molybdenum alloy system (TiC–TZM) are discussed.

Keywords: Hydrogen; Trapping; Diffusion; Molybdenum; Titanium carbide

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1. Introduction

The permeability of hydrogen isotopes in first wall materials is a crucial research subject in fusion reactor technology [1]. Preventing the loss of tritium is required to increase the economic viability of the fusion reactors and also permeation of tritium to the surroundings poses a radiological hazard. Recent strategies to reduce hydrogen permeation combine low diffusivity/permeability coatings on a mechanical substrate. The coatings can be put into two categories; one is the compact oxidation films formed by oxidation of metal construction materials, and the other is the thin films created by chemical vapor deposition, ion sputtering, ion implanting, plasma assisted deposition etc. TZM, a molybdenum alloy with small additions of Ti and Zr, owing to its very high tensile strength and high thermal and electrical conductivity, has been proposed as a candidate divertor material for future fusion reactors. A rather large amount of permeation data, showing wide scatter, particularly in solubility and diffusivity of hydrogen in molybdenum, suggest that the permeation process may be convolved with processes other than pure lattice transport [2–4]. Recent reports on hydrogen permeation in TZM show that the permeation data are not so different from those of pure molybdenum. It is claimed that slow surface processes and/or trapping of hydrogen is important in these materials [5–7].

In order to reduce hydrogen permeation further, chemical vapour deposition (CVD) coating of TZM with TiC, which has very close thermal expansion coefficient to TZM, is an attractive option. Several attempts have been made to deduce the permeation parameters, (solubility and diffusivity) and even surface reaction rates of hydrogen in TiC and it is suggested that TiC could be a reasonable permeation barrier in fusion technology applications [8,9].

In this paper we present modulated permeation measurements on bare TZM and CVD coated TiC on a TZM substrate to reveal the possibility of identifying permeation characteristics of hydrogen in substrate and coating materials. This involves the measurements and analysis of the frequency dependence of phase lag and modulation amplitude ratio of hydrogen flux in modulated permeation experiments.

2. Experiments

Experiments are performed in a double ultra high vacuum system in which a foil specimen separates two chambers termed input and output. The modulation of the input pressure was provided by a large stainless steel bellows fitted to the input chamber. The input chamber

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pressure was monitored using capacitance monometers. The output chamber, with a fixed volume, was continuously pumped by a magnetically levitated turbo-molecular pump via a calibrated leak. The output chamber pressure was monitored using an ion gauge. Hydrogen was introduced into the input chamber to the desired equilibrium pressure via a palladium thimble which ensured high purity. Temperature was measured using calibrated chrome/nickel thermocouples with a common fixed reference. The temperature stability achieved was 0.1 K. With the exception of the absolute pressure setting, control of the equipment was fully automated.

Steady state conditions were first established between input and output chambers before commencing sinusoidal modulation of the input pressure, p_s, with an amplitude of $0.1p_s$. After sufficient time had elapsed to allow transients to decay, measurements were made of the pressure waveform in the input and output chambers for cycle times ranging from 20 s to 8000 s. Further experimental details and methods of data analysis have been reported previously [10,11].

Materials investigated in this work were 0.1 mm foils of bare TZM (a Mo alloy with 0.5% Ti and 0.08% Zr) and 1 μm TiC+TZM prepared by CVD and supplied by Metallwerk Plansee, Austria. Measurements were made within the temperature range of 573–723 K and over a pressure range of 1.3 kPa to 133 kPa.

3. Analysis

Modulated experiments are analysed in terms of two characteristic independent variables (phase and ratio of relative modulation amplitude) as functions of the modulation frequency [12–16]. The permeation process is treated as a sequential combination of surface and bulk processes which give rise to characteristic behaviour of the phase and the amplitude variations with the modulation frequency, ω. The modelling of modulated permeation has been extended to laminated composites. Although this approach could readily be incorporated into the overall modulated permeation model, it is of limited applicability since it presumes implicitly that the interface between coating and substrate is in dynamic equilibrium. It was found that a more thorough strategy was required to allow for the possibility that reaction kinetics are responsible for limiting the flow. It is also possible that local disorder in the interface region, being not unlike the disorder associated with heavily work hardened material, could lead to trapping and accumulation.

The model is conveniently handled in a matrix form in which each step of permeation path (surface processes, bulk diffusions in the coating and the substrate and the interface in between them) is described by matrices linking concentrations and fluxes. Time variation is incorporated through a linearized harmonic analysis [16].

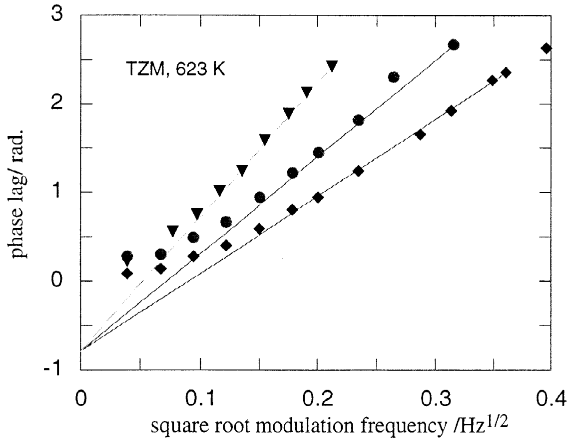

Fig. 1. Measured variation of phase lag, Φ, with root frequency, $\omega^{1/2}$, for TZM at 623 K. Symbols: ♦ 133 kPa; ● 13.3 kPa; ▼ 1.3 kPa.

4. Results and discussion

Figs. 1 and 2 show the variation of phase lag, Φ, and relative modulation amplitude ratio, Λ, with root angular frequency, $\omega^{1/2}$, for 0.1 mm TZM at 623 K for three different base pressures. Similar responses are obtained at other temperatures. These data show behaviour which the model identifies as strongly characteristic of bulk diffusion limited flow together with diffusivity impeded by trapping. The diffusion limited flow is strongly associated with the zero frequency extrapolation of the phase variation at high frequencies together with the value of 0.5 for the relative modulation amplitude ratio at zero frequency; note how all

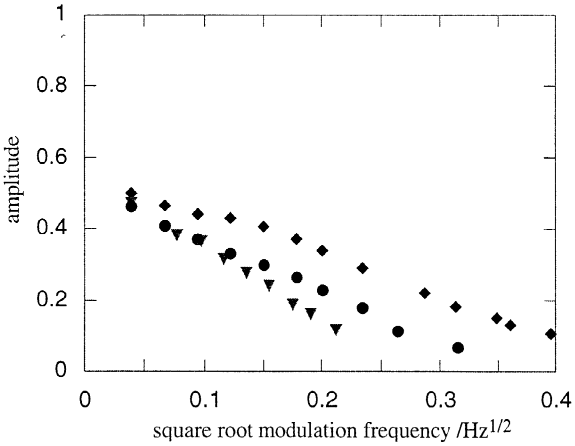

Fig. 2. Measured variation of relative amplitude modulation ratio, Λ, with root frequency $\omega^{1/2}$ for TZM at 623 K. Symbols: ♦ 133 kPa; ● 13.3 kPa; ▼ 1.3 kPa.

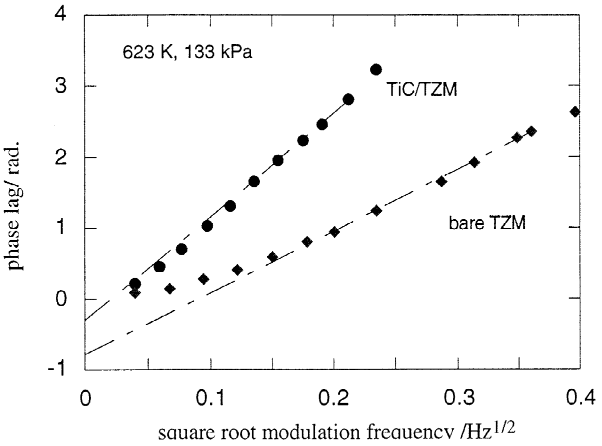

Fig. 3. Measured variation of phase lag Φ with root frequency $\omega^{1/2}$ for TiC–TZM at 623 K at a base pressure of 133 kPa. The results for base TZM are included for comparison. Symbols: ● TiC–TZM; ♦ TZM.

phase lag curves on extrapolation pass through $-\pi/4$. The pressure dependence indicates that bulk diffusivity increased when higher pressures (higher internal concentrations) give rise to reduced phase shift at a given frequency as traps are becoming more filled and less effective as delaying sites. This pressure effect also indicates that the traps are saturable and hydrogen is trapped as atoms. If the nature of the lattice–trap equilibrium (by Sievert's law) were that of molecular trapping, the trapped concentration should be an increasing fraction of the total hydrogen concentration, as the lattice concentration increases. This would give the opposite effect of traps becoming more effective as delaying sites and would increase the phase shift at a given frequency [15].

Figs. 3 and 4 show the variation of phase lag, Φ, and relative modulation amplitude ratio, Λ, with root angular frequency, $\omega^{1/2}$, for the same 0.1 mm TZM foil but now coated with 1 μm of TiC. The results combine the trapping impeded diffusivity of the substrate with both the low diffusivity of the coating and the reaction kinetics at the interface. The model reveals that the importance of the interface is signalled by the zero frequency intercept of the phase lag variation at high frequencies. In Fig. 3 this no longer passes through $-\pi/4$ but through a somewhat greater value of about -0.3. In Fig. 4 the value of 0.5 for the relative modulation amplitude ratio at zero frequency also indicates that the surface processes on TiC are fast compared with the overall permeation process. Our model suggests that the transport of hydrogen through TiC is mainly atomic and in this case extremely slow interface kinetics would shift the intercept of the extrapolated phase characteristic towards zero. Further modelling and results on permeation in the TiC–TZM system will be reported elsewhere [16].

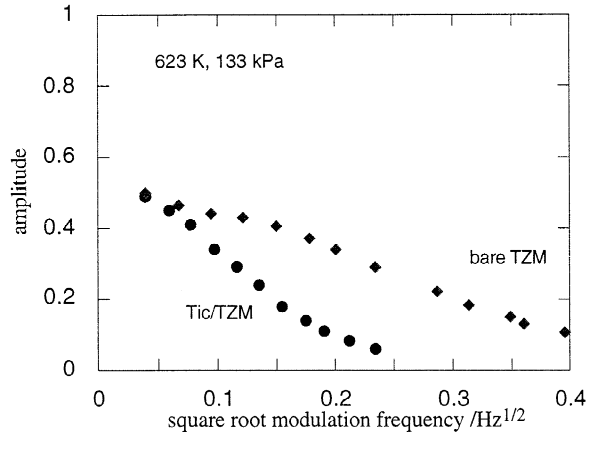

Fig. 4. Measured variation of relative amplitude modulation ratio, Λ, with root frequency $\omega^{1/2}$ for TiC–TZM at 623 K at a base pressure of 133 kPa. The results for base TZM are included for comparison. Symbols: ● TiC–TZM; ♦ TZM.

5. Conclusions

Modulated permeation experiments have been performed on foils of TZM, bare and coated with TiC. Results reveal that hydrogen is reversibly trapped within the bulk during permeation in TZM. It has been found that diffusion through a TIC coating is atomic. Both diffusion through the coating and slow interface kinetics reduce the permeation through a TiC coated TZM foil.

Acknowledgments

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