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Derivation of hydrogen transport parameters in carbon fibre composites by modelling transient release in isovolumetric desorption experiments

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Abstract

A non-stationary model has been developed to determine the hydrogen diffusivity (D) and Sieverts' constant (K_s) in carbon fibres composites (CFC), from isovolumetric desorption experiments using short loading times. For homogeneous materials such as nickel the model predictions and the experimental results are in good agreement. Assuming the CFC as homogeneous specimen, apparent values of D and K_s for two types of CFC (NB11 and N11(SEP)) were obtained. The model was successfully refined in order to account for CFC non-homogeneity. The determinant role of the fibre on the total K_s of hydrogen in CFC and the role of the porosity on the hydrogen D and K_s in matrix is explicitly illustrated. The model capabilities suggest its use as a tool for the design of CFC from the point of view of their hydrogen transport properties. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Low Z, satisfactory behaviour under irradiation and good thermomechanical properties make carbon fibre composites (CFC) attractive as candidate plasma facing materials. Because of the variability of hydrogen transport data in the literature for D and K_s in CFC and graphites [1–3], only specific data for each CFC should be used for fusion reactor design.

Isovolumetric desorption (ID) [4] is a powerful classical technique to obtain transport parameters in materials. Due to the small hydrogen diffusivity in CFC, the measuring times are too long to ensure instrument stability. Therefore, it seemed interesting to develop a non-stationary model in order to derive transport parameters for loading times shorter than the typical saturation ones. The developed model has been successfully checked [5] using existing results for nickel (Ni) [6,7]. Considering the CFCs N11(SEP) and NB11(SEP) to be homogeneous, the apparent values of D and K_s were derived. Nevertheless, the experimental release curves showed clearly the overlapping of two different processes.

This paper will show that when the model is refined to account for non-homogeneity the quality of the fitting to the experimental curves is substantially improved. Two NB11 specimens with different sizes (length $= 60$ mm and diameters, $\phi = 6$ and 12 mm) have been used to test this non-homogeneous model.

The H diffusivity found for the matrices of the studied CFC is 6–7 orders of magnitude higher than that for the fibres. The fibres determine the H solubility in the studied CFC. The porosity can explain the large D values in the two matrixes and also the large K_S found in the N11 matrix.

2. Isovolumetric desorption experimental method

The experimental method has been previously described in detail [4], here a short description is given for completeness. The measurement of D and K_s was accomplished by placing the samples (four cylinders) in the release chamber (RC), and loading them at constant pressure (100 kPa) of hydrogen during a loading time τ. For times τ sufficiently long, the sample could be

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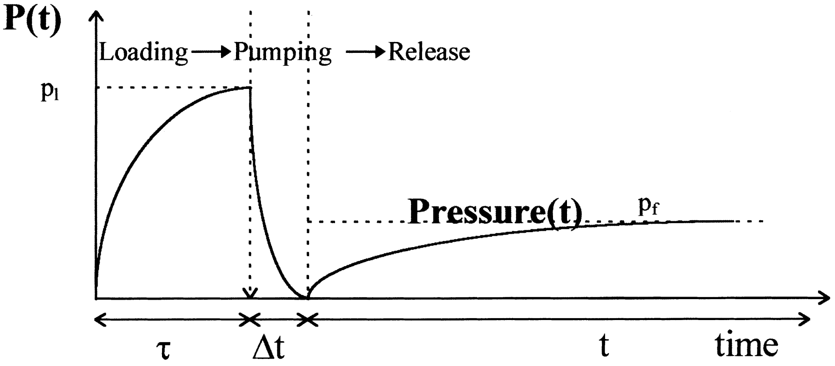

Fig. 1. Three phases in isovolumetric desorption experiments.

saturated with hydrogen. Once the time τ was reached, a very fast transient phase (~30 s) followed in order to obtain the maximum vacuum (~10^{-7} Pa) in the RC. This transient caused the release of the H loaded into the sample. Measurements were performed isothermally (±3–4 K for $T = 1200$ K) in isovolumetric conditions.

The release phase represented the main part of the experiment (Fig. 1). A capacitance manometer of 133 Pa full-scale measured the pressure increase in the RC, during the release phase, against absolute time and temperature. The background signal (to be subtracted from the total pressure signal) coming from the contribution of the RC walls was determined by identical measurements without sample. The measuring frequency was higher in the initial phase of the experiment, when the pressure variation is fastest [4].

3. Modelling ID experiments

A non-stationary model was developed [5] to include any loading time τ, to accurately account for the gas balance during the pumping phase, and to consider the evolution of the sample surface in equilibrium with the H released in the RC.

The model solves the diffusion equation without source for an infinite cylindrical geometry for each phase. Final hydrogen concentration in one phase is used as the initial concentration for the following one.

For the loading phase the initial concentration is assumed to be zero and the boundary condition is given by $c_L = K_S\sqrt{P_L}$, (P_L is the loading pressure and c_L is the surface concentration).

Using Duhamel's method [8], the general solutions for the transient pressure, $p(t)$, in the RC can be derived:

$$p(t) = \frac{RT}{(V_1 - 4V_S)2N_A} V_s \frac{4}{a^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \left\{ \Psi_n(D, K_s)(1 - e^{-D\alpha_n^2 \tau}) + A(t) \right\} \tag{1}$$

with

$$A(t) = c_{\Delta t}(1 - e^{-D\alpha_n^2 \tau}) + \frac{c_f - c_{\Delta t}}{1 - e^{-\gamma\tau}} \left(1 - e^{-D\alpha_n^2 \tau} - \frac{e^{-\gamma t} - e^{-D\alpha_n^2 t}}{1 - \frac{\gamma}{D\alpha_n^2}} \right),$$

where $R = 8.314$ J mol^{-1} K^{-1}, V_1 is the RC volume, V_s the sample volume, N_A the Avogadro's number, a the cylinder's radius, α_n are the roots of Bessel's equation: $J_0(a\alpha_n) = 0$, $c_{\Delta t}$ and c_f being the equilibrium concentrations at the end of the pumping phase and release phase. The β and γ constants parametrize the transient evolution of the surface as temporary boundary conditions, t is the time and $\Psi_n(D, K_S, p_L, \beta, \tau, \Delta t)$, expressed in Eq. (1) as $\Psi_n(D, K_S)$, is a function [5].

The real free parameters of the model are D and K_S. The model is not very sensitive to β (and γ). It is more sensitive to β than γ, due to β entering in $\Psi_n(D, K_S)$, and in the initial concentration for the release phase. The value of β was included in order to introduce the fall to an unknown value of the pressure in the RC, after 30 s of pumping. Then, β can be roughly evaluated and related to the gas balance during the pumping phase as: $\beta = (1/2\Delta t)\ \ln\ (P_{\Delta t}/P_L) \approx 10^{-2}$, for typical values of $\Delta t = 30$ s and $p_{\Delta t}/p_L = 10^{-7}$.

Using commercial software [9] the experimental curves were fitted to Eq. (1). The soundness of the model was verified by comparing its predictions for different τ, T, and p_L with existing results for Ni [7] (averaging data from 20 independent measurements), and with the values for Ni obtained in the calibration of our facility with τ at saturation [8]. About 18 tests were conducted for temperatures ranging from 300 to 800 K and τ as short as 1 h (with τ at saturation = 20 h).

The ability of the homogeneous model to reproduce the measured H release from CFC was considered unsatisfactory although the experimental curves are fitted over the whole release time within an experimental error of ±5% [5]. We use the word "apparent" to qualify the values of D and K_s (with ~30–40% of error) derived

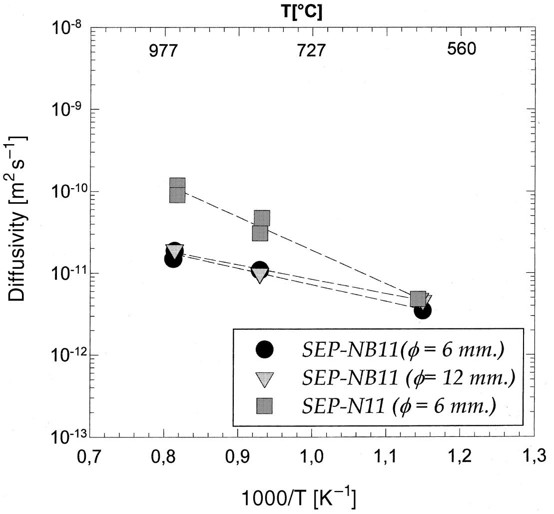

Fig. 2. Apparent hydrogen diffusivity D in NB11 and N11.

from this approach. These D and K_s for N11(SEP) and NB11(SEP) are shown in Figs. 2 and 3, respectively.

The unsuccessful results to accurately derive H diffusivity and Sieverts' constant using a homogeneous model and the direct observation of two different time processes overlapping during the release, justified the need of a non-homogeneous/non-stationary release model for CFC. The preferential paths for the release of H from the CFC can be investigated in terms of the time constants of the diffusion processes.

Due to the material nature (matrix **M**: ∼60 vol% or more depending on each CFC) a direct contribution to the released flux, should come from the amount of gas directly loaded into the matrix (**M→RC**). Another contribution should come from the amount of gas loaded in any of the fibres. They are considered here as identical infinite long cylinders. The collective contribution of identical fibres is accounted for by the ratio of fibre volume to the total sample volume. The amount of H in each fibre should cross the matrix before contributing to the increase of the pressure in the **RC** (**F→M→RC**). Other processes potentially present like **M→F→M→ (...)→RC** or/and **F→M→F→M→ (...)→RC** should be neglected in a first approximation. The transport is assumed radial and diffusion controlled. Then, at a given temperature, two fluxes working in parallel should govern the H kinetics during the loading and release in the composite with characteristic times $a^2/(D_M\alpha_0^2)$ and $a^2/(D_{FM}\alpha_0^2)$ respectively, and the experimental curve should be reproduced by the addition of two homogeneous-like contributions. One with the matrix characteristics (D_M, $(K_s)_M$), and the other with the solubility of the hydrogen in the matrix with a time constant equivalent to a system fibre–matrix in series (D_{MF}, $(K_s)_F$). Then there are 4 main parameters to fit the experimental curve.

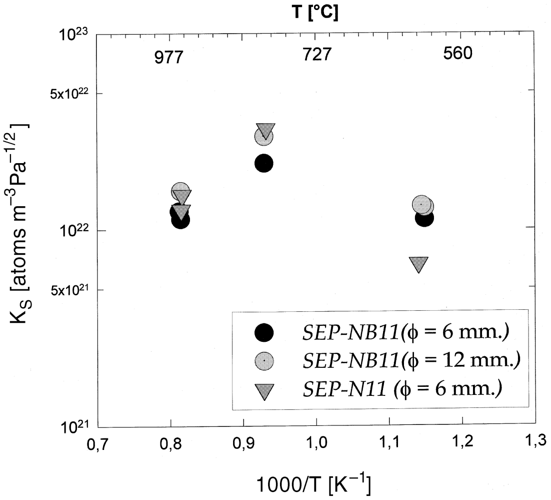

Fig. 3. Apparent hydrogen Sieverts' constant K_S in NB11 and N11.

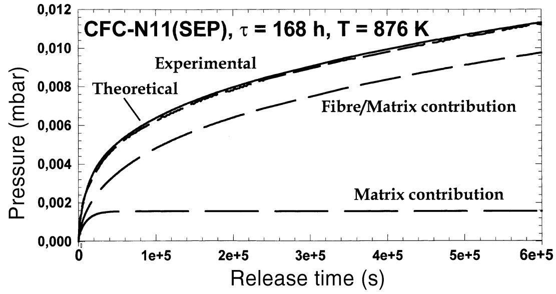

Fig. 4. Fitting with a non-homogeneous/non-stationary model. The soundness of the fit is manifest.

Fig. 4 shows an example of a fitting obtained with the non-homogeneous model. Once D_{MF} is obtained, D_F can be deduced. Figs. 5 and 6 show the values of D and K_s in the fibre and in the matrix.

4. Results and discussion

As a test of the model's quality, the D and K_S values for two NB11 specimens with different size (Figs. 5 and 6) are quite similar. The differences can arise from a non-negligible axial flux contribution (∼25% for the case $\phi = 12$ mm). The fibres show large K_S values and determine the H apparent solubility in N11 and NB11 as can be seen by comparing the data in Figs. 3 and 6. This is probably due to the existence of voids between carbon filaments or to the doping of the material used to glue the carbon filaments together to form the carbon fibre. Fig. 5 shows just a gap in the diffusivity pre-exponential

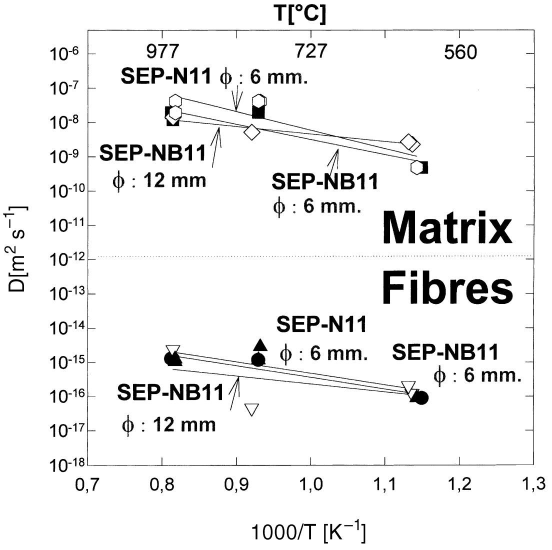

Fig. 5. Hydrogen diffusivity in the fibre and in the matrix for NB11 and N11.

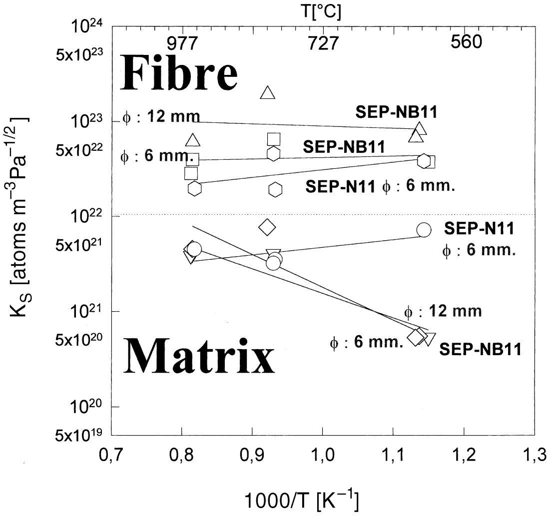

Fig. 6. The Sieverts' constant of hydrogen in the fibre and in the matrix for NB11 and N11.

factor (D_0 in the Eq. $D = D_0 \exp(-E_D/RT)$) for fibre and matrix suggesting that the same processes govern the H diffusion in carbon for both subsystems. Such gap may be explained assuming a reduction of the mean-free-path of H in the matrix due to the existence of connected pores ranging from 5 to 50 nm. The exothermal solubility behaviour shown by the material with the highest porosity (N11) indicates that porosity could have a non-negligible impact on the value of K_s for the matrix. Connected pores would load H without significant thermal influence but, in addition, they would favour the intake of H in the matrix material.

5. Conclusions

A non-stationary and non-homogeneous model has been developed to determine the hydrogen diffusivity (D) and Sieverts' constant (K_s) in CFC, from isovolumetric desorption. The suitability of the developed model has been shown by its application to obtain hydrogen transport data in a CFC material using two specimens of different size.

The separated accounting on fibre and matrix contributions should track H-isotopes better in the first wall of a fusion machine and support the preliminary design of CFC materials as plasma facing components.

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References

[1] V. Malka, H.D. Rohrig, R. Hecker, Tritium technology in fission, fusion and isotope application, in: Proc. Conf. Dayton, OH, 1980, Am. Nucl. Soc. (1980) 102.
[2] K. Ashida, K. Watanabe, J. Nucl. Mater. 183 (1991) 89.
[3] H. Atsumi, S. Tokura, M. Miyake, J. Nucl. Mater. 155–157 (1988) 241.
[4] S. Alberici, A. Perujo, J. Camposilvan, Fusion Technol. 28 (1995) 1108–1113.
[5] L.A. Sedano, CEC EUR 17320 EN Report, 1997, Catalogue: CL-NA- 17320-EN-C, Italy.
[6] W.M. Roberston, Z. Metallk. 64 (1973) 436.
[7] M. Caorlin, J. Camposilvan, F. Reiter, in: Proc. 8th AIV Nat. Vac. Congress, L'Aquila, Italy, vol. 2, 1983, p. 713.
[8] H.S. Carslaw, J.C. Jaeger, Conduction of Heat in Solids, 2nd ed., Oxford Science Publications, Oxford, p. 29.
[9] MATHCAD 6.0+, Ver. MS4.00, User's Guide.