Diffusion and Surface-Limited Transport Parameters of Deuterium in Incoloy 800

Final Report

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G.A. Esteban, A. Perujo, L.A. Sedano,
B. Mancinelli, K. Douglas
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DIFFUSION AND SURFACE-LIMITED TRANSPORT PARAMETERS OF DEUTERIUM IN INCOLOY 800

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ABSTRACT

A gas permeation technique has been used to obtain the complete set of diffusion-limited deuterium transport parameters (diffusivity D, Sieverts' constant Ks and permeability Φ) and the surface rate constants (adsorption σK1 and recombination σK2) in INCOLOY 800. A diffusion-limited transport model is applied to derive the bulk transport parameters, whereas a non-symmetric surface limited transport model has been applied to obtain the surface rate constants for the bare and oxidised material. The diffusion-limited transport parameters have been evaluated in the temperature range 427 to 664 K, whereas the surface-limited transport parameters have been evaluated in the temperature range 427 to 780 K, both of them using deuterium driving pressures ranging from 10^4 to 1.5·10^5 Pa. The deuterium diffusive transport parameters obtained are: D(m^2s^-1) = 3.87·10^-2 exp(-47.8 (kJ·mol^-1)/RT), Kd(mol·m^-3·Pa^-1/2) = 0.102 exp(-7.8 (kJ·mol^-1)/RT), Φ(mol·m^-1·s^-1·Pa^-1/2) = 3.94·10^8 exp(-55.6 (kJ·mol^-1)/RT). The deuterium surface rate constants for a non-oxidized surface has been evaluated as: σK1(mol·m^-2·s^-1·Pa^-1) = 2.67·10^10 exp(-40.1 (kJ·mol^-1)/RT) and σK2(mol^-1·m^-4·s^-1) = 2.58·10^8 exp(-24.5 (kJ·mol^-1)/RT). For an oxidized surface the deuterium surface rate constants has been evaluated as: σK1(mol·m^-2·s^-1·Pa^-1) = 4.14·10^-6 exp(-44.3 (kJ·mol^-1)/RT), σK2(mol^-1·m^-4·s^-1) = 4.00·10^4 exp(-28.6 (kJ·mol^-1)/RT). All the results are compared to different types of steels and different states of oxidation. The inhibition of hydrogen isotope permeation by means of the growth of an oxide layer on the specimens has been confirmed.

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1. INTRODUCTION

The CrNiFe alloy INCOLOY 800 is increasingly being used as a steam generating (SG) material of nuclear power reactors. Its high strength and corrosion resistance properties in the presence of high-temperature water or steam make this alloy a suitable candidate material to construct the steam generator of future thermonuclear fusion reactors. Thereby, INCOLOY 800 is expected to be employed in the reactor design option of the European Helium-Cooled Pebble Bed (HCPB) Blanket [1].

Some important issues to be defined when analysing the feasibility of a particular option of the reactor design are the tritium economy and the radiological safety. In relation with these matters, the evaluation of the tritium inventory absorbed within structures and released out of the breeding blanket to non-radiologically protected zones is mandatory. One of the main paths for tritium release to the environment is the following: first, the helium coolant circuit receives tritium that permeates either from the first wall (FW) or the breeding zone (the last one having minor importance with respect to the FW, 0.78 g/d to 8.5 g/d [1]); then, tritium is carried by the helium to the steam generator where tritium is able to be absorbed in and diffuse through the heat exchanger walls, and be carried by the steam to the thermodynamic cycle. Thereby, tritium may reach non-radiologically protected zones of the power plant.

The amount of tritium that is acceptable to be released to the environment during usual operation is about 20 Ci/day. A permeation reduction factor (PRF) of 20 in the heat exchanger walls has been evaluated to accomplish the previous condition [1]. Additionally, high PRF values will reduce the amount of hydrogen needed in the tritium recovery columns of the fuel cycle and, consequently, diminish the size and operational costs of that system.

As a result, this high-temperature material INCOLOY-800 needs a detailed analysis in relation with the hydrogen isotope transport characteristics. Several works [2-9] have been carried out in order to characterise tritium permeation through INCOLOY 800 together with other high-temperature SG alloys and study the inhibition of this effect by the growth of oxide layers on its surface, i.e. the use of oxide layers as effective permeation barriers.

In the present work besides permeability $\Phi$, the diffusive deuterium transport parameters diffusivity $D$ and Sieverts' constant $K_s$ have been evaluated in the
temperature range 427 to 664 K. These parameters allow the evaluation of transient kinetics in gas transport through the diffusivity and the total capacity of gas absorption by means of the Sieverts’ constant. The permeation rate in steady-state conditions can be evaluated with the permeability $\Phi = D \cdot K_s$. Knowing the whole set of diffusive parameters is of great importance, even when only gas-surface reactions on oxide layers (permeation barriers) are supposed to control the transport, because the total gas absorption capacity is controlled by the Sieverts’ constant. Moreover, the normal operation of the heat exchanger may undergo thermal transients that provoke stresses and induce cracks and other imperfections in the oxide film [9]. As a consequence, direct paths of diffusion through the bulk of the material (characterised by the previous diffusive transport parameters) are allowed during an important period of time before self-healing oxidation restores a perfect oxide layer.

Additionally, the present experiment evaluates the surface rate constants of adsorption $\sigma k_1$ (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) and recombination $\sigma k_2$ (mol$^{-1}$ m$^{-4}$ s$^{-1}$), either for “as-received” or oxidized surfaces. For its evaluation a non-symmetric surface limited model has been applied, taking into account the different physical state of the surfaces of the specimen: one exposed to the feeding gas at high temperatures (completely oxidised) and the surface exposed to the vacuum region (no oxide detected). These surface-limited transport parameters have been evaluated in the temperature range 427 to 780 K. That range covers the nominal temperature range foreseen during the operation of the steam generator: 523 – 723 K [1].

2. BASIC THEORY

In this section the basic theory and terminology concerning gas diffusive and surface-limited transport is summarised.

2.1. Diffusive transport

The amount of gas dissolved into the volume unit of solid in equilibrium at a certain pressure $p$ and temperature $T$ is referred to as the solubility (or the equilibrium concentration) $c_{eq}$ (mol m$^{-3}$) of the gas in the solid. It is described by the Sieverts’ law, $c_{eq} = K_s \cdot p^{1/2}$, which states that the gas solubility in a material is proportional to the square root of the external gas partial pressure, $p$ (Pa), through the temperature dependent Sieverts’ constant, $K_s$ (mol m$^{-3}$ Pa$^{-1/2}$). The Sieverts’ constant may be
described by the Arrhenius equation \( K_s = K_{s0} \exp \left( \frac{-E_s}{RT} \right) \), \( K_{s0} \) (mol m\(^{-3}\)Pa\(^{-1/2}\)) being the pre-exponential factor, \( R \) (J K\(^{-1}\)mol\(^{-1}\)) the ideal gas constant and \( E_s \) (J mol\(^{-1}\)) the activation energy of the solution process. Depending on the sign of the solution energy, \( E_s \), the material is characterised as endothermic or exothermic, when \( E_s \) is positive or negative respectively.

The first Fick’s law accounts for a diffusive flux of gas through a solid lattice due to a gradient concentration through the spatial co-ordinate. In the absence of source terms and temperature gradients it can be expressed as \( \dot{J}(r,t) = -D \nabla c(r,t) \), where \( \dot{J}(r,t) \) (mol m\(^2\) s\(^{-1}\)) is the H diffusive local flux dependent on time \( t \) and the position within the material \( r \), \( c(r,t) \) (mol m\(^3\)) is the local H concentration in the material and \( D \) (m\(^2\)s\(^{-1}\)) is the diffusivity. The continuity equation expresses that every increase of the gas concentration in a differential volume is due to a net inlet of diffusive flux, \( \frac{\partial c(r,t)}{\partial t} = -\nabla \dot{J}(r,t) \), the second Fick’s law is derived as \( \frac{\partial c(r,t)}{\partial t} = D \nabla^2 c(r,t) \). The diffusivity \( D \), with respect to temperature, behaves in the Arrhenius manner \( D = D_0 \exp \left( \frac{-E_d}{RT} \right) \), \( D_0 \) (m\(^2\)s\(^{-1}\)) being the pre-exponential diffusivity and \( E_d \) (J mol\(^{-1}\)) the activation energy for diffusion.

If a sheet of material with a certain thickness “d” is exposed from one of its sides to a high gas driving pressure \( p_h \) whereas the other one is maintained at a low pressure level \( p_l \), the steady state gas flux through that specimen is described by the transport parameter of permeability \( \Phi \) (mol m\(^{-1}\)Pa\(^{-1/2}\)s\(^{-1}\)) = \( D \cdot K_s \), through the Richardson’s law \( J = \frac{\Phi \cdot \left( p_h^{1/2} - p_l^{1/2} \right)}{d} \).

2.2. Surface-limited transport

In many occasions it has been experimentally proved and theoretically studied [10-14] that under certain conditions (i.e. low pressure level, presence of impurities, degradation and/or oxidation of the surface), the H transport regime becomes surface-limited, i.e. H transport within the material is limited by the physico-chemical reactions (adsorption, dissociation, desorption, recombination) occurring at the surface.
of the material, rather than diffusion-limited, where H transport is limited by the
diffusion of H atoms through the host matrix of the bulk of the material.

The evaluation of such process rates leads to consider one adsorption flux and
one recombination flux. Hence, the H flux entering the material J can be expressed as
J=σk_1p-σk_2c^2, σk_1 (mol m^{-2}s^{-1}Pa^{-1}) and σk_2 (m^3s^{-1}mol^{-1}) being the adsorption and
recombination rate constants, respectively. σ is the surface roughness expressing the
ratio between the real and the geometrical areas of the surface.

If a specimen of material is exposed to a certain partial pressure of hydrogen
"p", for enough time to reach a saturation state, an equilibrium concentration in the
bulk c_{eq}, is reached. Thus, recombinative and adsorptive fluxes show dynamic
equilibrium cancelling each other: 0=σk_1p-σk_2c_{eq}^2. In the described equilibrium state
Sieverts’ law, c_{eq}=K_p p^{1/2}, is fulfilled. Hence, a direct relationship between surface rate
constants, σK_1, σK_2, and Sieverts’ constant, K_s, arises:

\[ K_s = \sqrt{\frac{σk_1}{σk_2}} \]  
(1)

It is worth noting that once the Sieverts’ constant is known and using the
previous expression (1), it is only necessary to evaluate one of the surface rate
constants in order to define completely the surface-limited H transport. Furthermore,
the most reliable attempts in theoretically defining the surface-limited transport regime
[12, 13] calculate the adsorption constant σk_1 rather than σk_2; for σk_1 can be easily
evaluated in terms of a simple kinetic theory. The conclusions reached in those works
propose the following expressions for the adsorption constant:

For Baskes’ approximation [12]:

\[ σk_1 = \frac{2Cσσ}{(2mT)^{1/2}} \exp\left(\frac{-E_s}{RT}\right), \quad (E_s=\max(0, E_s+E_d)) \]  
(2)

For Pick and Sonnenberg’s approximation [13]:

\[ σk_1 = \frac{Cσ}{(2mT)^{1/2}} \]  
(3)

C being a kinetic constant equal to 4.376 mol K^{1/2}u^{1/2}Pa^{-1}m^{-2}s^{-1}. “s” is the “sticking
coefficient” expressing the probability that a H atom remains “sticked” to an
adsorption surface site; it is activated with an energy of 2E_c because both the two
atoms from the H_2 molecule must surpass the sticking barrier E_c, s = s_0 \exp\left(\frac{-2E_c}{RT}\right),
m is the H isotope atomic mass (a.m.u.), T the temperature (K) and R the ideal gas’ constant (8.314 J K⁻¹mol⁻¹).

3. EXPERIMENTAL

3.1. Material

The material studied is the high-temperature SG CrNiFe alloy INCOLOY 800, its nominal chemical composition (wt%) being shown in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Si</th>
<th>Al</th>
<th>C</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>30.8</td>
<td>20.5</td>
<td>0.64</td>
<td>0.56</td>
<td>0.46</td>
<td>0.36</td>
<td>0.065</td>
<td>0.004</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Clean INCOLOY 800 is highly susceptible to oxidation, the characteristic of such oxide being dependent on the initial conditions of the material and its chemical and thermal exposure. The most probable oxides to be expected under oxidizing conditions are the chromium oxide Cr₂O₃ and the MnCr₂O₄ spinel (that have been identified as the responsible of the gas permeation inhibition [8,9]); the presence of Mn in the spinel oxide is explained by its higher diffusivity through Cr₂O₃ as compared to Cr [15]. However iron oxides are also possible depending on the surface preparation (Bittner et al. [16] found that electropolished samples formed iron oxide) and on the chemistry of the media (a reducing high-pressure steam chemistry enhances the iron oxide formation [4]). Conversely to chromium oxides and CrMn spinels, iron oxide has not been found to significantly reduce the permeation rate below that of the unoxidized metal [9]. The mechanical consistency of the oxide layer shows a notable improvement when rising the oxidation temperature or when pre-annealing the material with pure hydrogen [6].

The tested specimen consisted of a thin disc with a 0.4-mm thickness and 48-mm diameter. This physical configuration of the specimen permits, on the one hand, to account for surface effects if they are present, because large surface areas are available for transport in comparison with short diffusive lengths. On the other hand, it makes feasible the H isotopes transport study using an infinite-slab (1-d) geometry approximation.
Before setting the specimen into the experimental rig, the specimen was chemically degreased with acetone and ethanol, then rinsed in distilled water and finally dried in a vacuum furnace before insertion into the experimental rigs.

Some technological problems arose when measuring diffusive transport parameters. For the study of bulk diffusion and absorption, the surface oxidation may impede the normal transport. Due to the oxidation susceptibility of INCOLOY 800, in several occasions the sample had to be extracted and cleaned or be changed to eliminate the presence of oxide. In this manner, diffusive transport parameters could be obtained in the temperature range of 427 to 664 K. Oxide growth and the corresponding gas permeation reduction could not be prevented at temperatures higher than 664 K.

When measuring the surface effects, the oxidation of the specimen at high temperature was allowed to proceed to a final stable situation where the steady-state permeation rate did not change as the time passed. After the permeation tests, the specimen was analysed by means of Secondary Neutral Mass Spectroscopy (SNMS); an oxide layer about 100 nm with an enrichment of Mn, Cr and O in the first 30 nm was detected on the surface directly exposed to deuterium gas. The surface exposed to vacuum did not show any noticeable oxide presence. The deuterium gas used had 99.7% purity with a maximum H₂O content lower than 15 ppm.

3.2. Permeation experiment

A schematic view of the installation used is shown in Figure 1. This installation and the procedure for a measurement have been described in earlier works [17-20]. Here we will briefly describe them for completeness. The rig comprises standard ultra high vacuum stainless steel components. The ultra high vacuum needed before any measurement is obtained by two pumping units (UHV1 and UHV2); both of them comprise a turbomolecular and a two-stage rotary pump. A good level of vacuum, about \(10^{-6}\) Pa, is reached prior to system bake-out, and about \(10^{-7}\) Pa, afterwards. Several Penning gauges (PG) together with a quadrupole mass spectrometer (QMS) control the quality of the vacuum reached. The specimen (S) is placed between two flanges set into a resistance furnace allowing measurements at an experimental temperature of 723 K and lower. A nickel/chromium-nickel thermocouple (T1) held in a well (drilled into one of the flanges) permits temperature control with stability of ± 1 K. Two gold O-rings ensures the leak tightness of the specimen.
A single run of the experiment consists of holding one surface of the specimen at a certain high gas pressure level; forcing its permeation through the specimen to the low-pressure region (Figure 1).

Figure 1. Schematic view of the permeation facility.
The desired driving pressure is controlled by a high-pressure transducer (HPT) and a pressure controller (PC), whereas a capacitance manometer (P1) with a full scale reading of 100 Pa measures the pressure increase due to permeation through the sample. The low-pressure volume is calibrated in every test to allow a direct conversion of the pressure level into the amount of permeated gas Q(t). Likewise, the pressure increase rate may be converted into the amount of gas permeated per specimen unit area and time (gas flux, \( J(t) = \frac{\partial Q(t)}{\partial t} \)). The modelling of the experimental pressure increase p(t), due to the gas permeation in the low-pressure region, makes it possible to derive the transport parameters in the diffusion or surface-limited transport regimes (Figure 2).

![Figure 2. Characteristic permeation curve.](image-url)
4. MODELLING

In this section the two models applied to simulate the experimental permeation tests will be developed. The diffusion-limited model has been explained elsewhere [21], here, it will be briefly explained for completeness. Additionally, a non-symmetric surface-limited model has been developed accounting for different characteristics in the two surfaces of the specimen.

4.1. Diffusion-limited model

The present theoretical model analyses a diffusion-limited transport regime, where the diffusion of hydrogen atoms through the lattice of the material is the rate-limiting phenomenon rather than surface reactions (gas adsorption/dissociation and recombination/desorption).

Figure 3 shows the scheme of the gas transport through a sheet of material with a thickness “d” that is exposed on one side to a certain gas driving pressure $p_h$, whereas the other side is left under vacuum conditions ($p_l$).

\[ J_s(x) = -D \frac{\partial c}{\partial x} \]

\[ x = 0 \quad x = d \]

Figure 3. Scheme of the permeation process through 1-d slab. Diffusion limited regime.

The solution of this problem is obtained by solving the second Fick’s law in the one dimension slab:

\[ \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} \]  \hspace{1cm} (4)

the boundary conditions being the following:
\[ c(\varepsilon=0, t) = c_0 \]
\[ c(\varepsilon=d, t) = 0 \]  \hspace{1cm} (5)
and the initial condition:
\[ c(\varepsilon,t=0) = 0 \]  \hspace{1cm} (6)

The analytical solution of the equation with the previous boundary and initial conditions is [22]:
\[ c(\varepsilon,t) = c_0 \left( 1-\frac{\varepsilon}{d} \right) - \frac{2c_0}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi \varepsilon}{d} \right) \exp \left( -D \frac{n^2 \pi^2}{d^2} t \right) \]  \hspace{1cm} (7)

The flux generated by any concentration gradient is defined by first Fick's law as:
\[ J(\varepsilon,t) = -D \frac{\partial c(\varepsilon,t)}{\partial t} \]  \hspace{1cm} (8)

Consequently, taking into account Sieverts' law, \( c_0 = K_s p_b^{1/2} \), the resultant flux at \( \varepsilon=d \), i.e. desorbing to the low pressure region, can be evaluated from (7) and (8) as:
\[ J(d,t) = -D \frac{\partial c(\varepsilon,t)}{\partial t} \bigg|_{\varepsilon=d} = \frac{DK_s p_b^{1/2}}{d} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -D \frac{n^2 \pi^2}{d^2} t \right) \right] \]  \hspace{1cm} (9)

From this Eq. (9) the steady state permeation flux (\( t \rightarrow \infty \)) is derived as:
\[ J = \frac{DK_s}{d} p_b^{1/2} = \frac{\Phi}{d} p_b^{1/2} \]  \hspace{1cm} (10)

which is the Richardson's law mentioned above.

The total amount of gas permeated to the low-pressure region is evaluated by accounting for all the gas flux released during the considered time period \( t \), from Eq. (9):
\[ Q(t) = A \int_0^t J(\varepsilon, \tau) d\tau = \frac{\Phi p_b^{1/2}}{d} A t - \frac{\Phi p_b^{1/2}}{6D} A - 2\frac{\Phi p_b^{1/2}}{6D} A \sum_{n=1}^{\infty} (-1)^n \exp \left( -D \frac{n^2 \pi^2}{d^2} t \right) \]  \hspace{1cm} (11)

"A" being the surface area of the specimen. Taking into account the ideal gas approximation, the pressure increment due to this amount of gas is:
\[ p(t) = \frac{RT_{eff}}{V_{eff}} \left[ \frac{\Phi p_b^{1/2}}{d} A t - \frac{\Phi p_b^{1/2}}{6D} A - 2\frac{\Phi p_b^{1/2}}{6D} A \sum_{n=1}^{\infty} (-1)^n \exp \left( -D \frac{n^2 \pi^2}{d^2} t \right) \right] \]  \hspace{1cm} (12)

where the \( V_{eff} \) is the effective volume where the permeated gas is retained, provoking the measuring pressure rise. This volume is precisely calibrated in each experimental permeation test.
In the general equation (12) two regimes may be separated: one predominant at the first stage of the permeation test (whose influence disappears as the time goes by) and a second one characteristic of the steady state permeation.

The steady state permeation may be represented by:

\[ P_{\infty}(t) = \frac{RT_{\text{eff}}}{V_{\text{eff}}} \left( \frac{\Phi p^{'1/2}_b}{d} A t - \frac{\Phi p^{'1/2}_b d}{6D} A \right) \]  

(13)

What is depicted by a straight line in the Figure 2. This straight line crosses the abscissa axis in the time co-ordinate known as time-lag \( \tau_L = \frac{d^2}{6D} \).

From the experimental permeation curve there are two different methods to derive the transport constants. The first one performs a linear least-squares fitting to the steady-state permeation region with a linear equation \( p(t) = St + B \) (Eq. 13) deriving the permeability \( \Phi \) from the value of the slope \( S = \frac{RT_{\text{eff}}}{V_{\text{eff}}} \frac{\Phi p^{'1/2}_b}{d} \), and deriving the diffusivity \( D \) from the value of \( B = \left( \frac{RT_{\text{eff}}}{V_{\text{eff}}} \frac{\Phi p^{'1/2}_b d}{6D} A \right) \) or the time-lag value \( \tau_L = t(y = 0) = -\frac{B}{S} = \frac{d^2}{6D} \).

In the second method a non-linear least-squares fitting is performed with the general expression (12) in both the steady-state region and the transitory region by considering the permeability \( \Phi \) and the diffusivity \( D \) the fitting parameters.

4.2. Surface-limited non-symmetric model

This theoretical model analyses a surface-limited transport regime, where the gas-surface reactions adsorption and recombination limit the permeation through the slab rather than the diffusion through the bulk of the specimen. Thereby, diffusion is supposed to proceed infinitely faster than the surface processes and the dissolved gas concentration is simultaneously equilibrated through the whole thickness of the specimen at each period of time (Figure 4). As a consequence, the specimen concentration can be considered as an exclusive function of time \( c = c(t) \).

In the basic scheme of the surface-limited permeation, one surface of the specimen is exposed to a certain gas driving pressure \( p_b \), whereas the other side is left under vacuum conditions (low pressure level \( p_l \)). The involved H fluxes coming from
surface reaction processes are the recombination \( J_{o,h}=(\sigma k_2)c^2 \), \( J_{o,l}=(\sigma k_2)'c^2 \), and adsorption \( J_{l,h}=(\sigma k_1)p_h \), \( J_{l,l}=(\sigma k_1)'p_l \). The sub-indexes indicate "o" out, "i" in, "l" low-pressure-region, "h" high-pressure-region. \((\sigma k_1)\) and \((\sigma k_2)\) are the surface-rate constants for the high-pressure region whereas \((\sigma k_1)'\) and \((\sigma k_2)'\) correspond to the low-pressure region.

![Diagram](image)

Figure 4. Scheme of the permeation process through 1-d slab. Surface-limited regime.

When the continuity equation is considered in the slab, one can state that any gas concentration increase with time is due to a net incoming gas flux into the slab. This fact is expressed by the following equation:

\[
V_s \frac{dc(t)}{dt} = A \left[ (\sigma k_1)p_h + (\sigma k_1)'p_l \right] - A \left[ (\sigma k_2)c(t)^2 + (\sigma k_2)'(c(t))^2 \right]
\]

or:

\[
\frac{dc}{dt} = \left[ \frac{(\sigma k_1)p_h + (\sigma k_1)'p_l}{d} \right] - \left[ \frac{(\sigma k_2) + (\sigma k_2)'}{d} \right] c^2
\]

which is the Ricatti's equation \( \frac{dc}{dt} + b^2 c^2 = a^2 \) with the \( a \) and \( b \) coefficients defined as:

\[
a = \sqrt{\frac{(\sigma k_1)p_h + (\sigma k_1)'p_l}{d}}, \quad b = \sqrt{\frac{(\sigma k_2) + (\sigma k_2)'}{d}}.
\]

When enough time passes a steady-state permeation occurs and the concentration in the whole specimen stabilises \( c(t\to\infty)=c_f \). Attending these assumptions Eq. (15) becomes:
\[ 0 = \left[ \frac{(\sigma k_1) p_h + (\sigma k_1)' p_l}{d} \right] - \left[ \frac{(\sigma k_2) + (\sigma k_2)'}{d} \right] c_r^2 \]  

(16)

And, from this equation (16), the final concentration built up in the specimen is evaluated as:

\[ c_r = \frac{\sqrt{(\sigma k_1) p_h + (\sigma k_1)' p_l}}{\sqrt{(\sigma k_2) + (\sigma k_2)'}} = \sqrt{\frac{a}{b}} \]  

(17)

The solution of the Ricatti's equation (Eq. 15) with the initial and final conditions \( c(t=0) = 0 \) and \( c(t\to\infty) = c_r \) is the following [22]:

\[ \frac{c_r - c(t)}{c_r + c(t)} = \exp(-2abt) \quad \text{or} \quad c(t) = c_r \left( \frac{1 - \exp(-2abt)}{1 + \exp(-2abt)} \right) = c_r \tanh(abt) \]  

(18)

The flux permeating to the low-pressure region is evaluated as:

\[ J(t) = J_{o,l} - J_{u,l} = (\sigma k_2)' c^2 - (\sigma k_1)' p_l = (\sigma k_2)' c^2 \tanh(abt) - (\sigma k_1)' p_l \]  

(19)

Consequently, the total amount (in mol units) of gas permeated to the low-pressure region is:

\[ Q(t) = A \int_0^t J(t') dt' = A \left[ (\sigma k_2)' c^2 t - \frac{(\sigma k_2)' c_r^2}{ab} \tanh(abt) - (\sigma k_1)' \int_0^t p_l(t') dt' \right] \]  

(20)

The integral term \( (\sigma k_1)' \int_0^t p_l(t') dt \) can be neglected due to the low value of \( p_l(t) \), i.e. the incoming flux \( J_{i,l} = (\sigma k_1)' p_l \) is negligible in relation to the outcoming flux \( J_{o,l} = (\sigma k_2)' c^2 \) in the low pressure region. Moreover, the incoming flux from the high pressure region \( J_{i,h} = (\sigma k_1) p_h \) is much larger than the incoming flux from the low pressure region \( J_{i,l} = (\sigma k_1)' p_l \), even when the surfaces are non-symmetric. These two suppositions have been proved for the experimented specimen (when modelling the experience and introducing in eq. (20) the maximum value of \( p_l \) of the permeation curve no different results were obtained in comparison to those obtained with the neglecting suppositions). The pressure increment in the effective experimental volume due to this amount of gas is evaluated from Eq. (20) (ideal gas approximation):

\[ p(t) = p_s(t) = \frac{RT}{V_{eff}} A(\sigma k_2)' c_r^2 \left[ t - \frac{1}{ab} \tanh(abt) \right] \]  

(21)

Considering the definition of \( a, b, c_r \) and the relationship between the surface-rate constants of the same surface in Eq. (1), the previous equation can be expressed
only as a function of the Sieverts' constant $K_*$ and the unknown parameters $(\sigma k_1)$ and $(\sigma k_1)'$:

$$p(t) = \frac{RTA}{V_{\text{eff}}} \left( \sigma k_1 \right)' \frac{(\sigma k_1)p_b}{(\sigma k_1) + (\sigma k_1)'} \left[ t - \frac{dK_*}{\sqrt{(\sigma k_1)p_b \left[ (\sigma k_1) - (\sigma k_1)' \right]}} \tanh \left( \frac{\sqrt{(\sigma k_1)p_b \left[ (\sigma k_1) - (\sigma k_1)' \right]}}{dK_*} t \right) \right]$$

(22)

In this expression (22) two regimes can be differentiated as in the diffusive regime: one predominant at the first stage of the permeation test (whose influence disappears as the time passes) and a second one with a linear dependence of time (steady-state permeation).

From Eq. (22) for high values of time ($t \to \infty$) the steady state permeation may be represented by:

$$p_\infty(t) = \frac{RTA}{V_{\text{eff}}} \left( \sigma k_1 \right)' \frac{(\sigma k_1)p_b}{(\sigma k_1) + (\sigma k_1)'} \left[ t - \frac{dK_*}{\sqrt{(\sigma k_1)p_b \left[ (\sigma k_1) - (\sigma k_1)' \right]}} \right]$$

(23)

The previous expression implies a straight line in Figure 2. This straight line crosses the abscise axe in the time-lag $\tau_L$ from Eq. (23), $p_\infty(\tau_L) = 0$:

$$\tau_L = \frac{1}{ab} = \frac{dK_*}{\sqrt{(\sigma k_1)p_b \left[ (\sigma k_1) - (\sigma k_1)' \right]}}$$

(24)

Once again, the first method to derive the transport constants performs a least-squares linear fitting to the steady-state permeation region with the linear equation:

$p(t) = St + B$ (Eq. 23) where the slope is $S = \frac{RTA (\sigma k_1)'(\sigma k_1)p_b}{V_{\text{eff}} (\sigma k_1) + (\sigma k_1)}$ and the crossing with the abscises axe is $B = -\frac{RTA dK_*}{V_{\text{eff}}} \frac{(\sigma k_1)'}{\sqrt{(\sigma k_1) + (\sigma k_1)'}}^{3/2}$. Instead of B, the time-lag value

$$\tau_L = \frac{B}{S} = \frac{dK_*}{\sqrt{(\sigma k_1)p_b \left[ (\sigma k_1) - (\sigma k_1)' \right]}}$$

can be used. The second method is a non-linear least-squares fitting with the general expression (22) in both the steady-state region and the transient region considering the surface rate constants $(\sigma k_1)$ and $(\sigma k_1)'$. 


the fitting parameters (Sieverts' constant $K_s$ could be introduced as another unknown parameter but deteriorating the convergence of the fitting routine; thus, it has been preferred to previously evaluate the Sieverts' constant by means of the diffusive test).

5. RESULTS AND DISCUSSION

5.1. Transport regime definition

The INCOLOY 800 specimen has been tested in the temperature range 427 to 780 K, using deuterium driving pressures ranging from $10^4$ to $1.5 \cdot 10^5$ Pa. The specimen showed great susceptibility to oxidation; in search of the bulk transport parameters the specimen had to be extracted and mechanically polished or changed to eliminate any presence of oxide. The maximum temperature achieved without noticeable effect due to oxide on transport has been 664 K.

Conversely, for surface rate constants evaluation the oxidation of the specimen was allowed to proceed. The specimen was maintained with high gas pressure on one of its sides at a high temperature (where oxidation was observed to initiate) for enough time (several days) to have permeation fluxes and the oxide layer stabilised.

A group of permeation tests with different driving pressures have been performed before and after oxidation of the specimen. The measured steady state permeation fluxes $J$ are depicted versus the gas driving pressures "p" for different experimental temperatures in Figure 5; it can be noticed how the oxidation process provokes an abrupt change in the transport regime. The pressure dependence of fluxes close to a 0.5 power relationship (characteristic of a pure diffusive transport regime) becomes a 1 power (characteristic of a pure surface limited transport regime) after oxidation. This experimental verification permits to consider pure surface and diffusion limited transport regimes and use the corresponding models (the ones explained above) rather than an intermediate transport regime [17].
Figure 5. Flux dependence on pressure indicating the type of transport regime.
5.2. Diffusive regime

A series of permeation test have been performed in the temperature range from 427 to 664 K and driving pressures ranging from $10^4$ to $1.5 \times 10^5$ Pa avoiding the influence of any surface effect. The experimental permeation curves were modelled to obtain the diffusive transport parameters. A linear least-squares fitting routine was applied to the steady state permeation region with Eq. (13); from the slope of each straight line and its corresponding time-lag $\tau$, values of $D$ and $\Phi$ are obtained whereas $K_s$ is derived from them as $K_s = \Phi/D$. These values are used as initial entry parameters in a non-linear least-squares fitting routine with the general equation of permeation (Eq. 12). Subsequently, the series of values of $D$, $K_s$ and $\Phi$ obtained at each temperature are fitted to an Arrhenius expression.

The permeability has been evaluated as (Figure 6):

$$\Phi (\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}) = 3.94 \times 10^{-8} \exp(-55.6 \text{ (kJ} \cdot \text{mol}^{-1})/RT)$$

The diffusivity has been evaluated as (Figure 7):

$$D (\text{m}^2 \cdot \text{s}^{-1}) = 3.87 \times 10^{-7} \exp(-47.8 \text{ (kJ} \cdot \text{mol}^{-1})/RT)$$

The Sieverts' constant has been evaluated as (Figure 8):

$$K_s (\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1/2}) = 0.102 \exp(-7.8 \text{ (kJ} \cdot \text{mol}^{-1})/RT)$$

In Figure 6 it can be noticed how the present result of permeability approximates well to those obtained by J.T. Bell et al. [5] and J. Schaefer et al. [6]. The dispersion of the experimental points around the theoretical Arrhenius lines is minimum for $\Phi$ ($R^2 = 0.992$) and $D$ ($R^2 = 0.987$). Conversely, this dispersion is higher for $K_s$ ($R^2 = 0.597$); this result accounts for the error propagation when evaluating $K_s$ from $\Phi$ and $D$.

To the knowledge of the authors $K_s$ and $D$ of any hydrogen isotope have not been independently studied in INCOLOY 800 hitherto. The obtained parameters have been compared with the parameters characteristic of several types of steel in Figures 9 and 10. It can be noticed how well INCOLOY 800 matches the results of austenitic stainless steel rather than the results of the ferritic-martenstisitic ones. This fact confirms the soundness of the results, because it is reasonable that INCOLOY 800 with very high Cr and Ni contents (20.05 and 30.8 %wt, respectively) approximates better the type of steel with higher Cr and Ni contents (17.3 and 12.4 %wt for the SS316L) than the ferritic-martenstisitic steels with low Cr and Ni contents (between 8 and 10 %wt for Cr and lower than 1% wt for Ni). At this point, it is worth mentioning the work performed by P. Jung where chemical composition of the alloys are directly related to the magnitude of the hydrogen isotope transport parameters [23]. Furthermore, the
diffusion activation energy of deuterium in INCOLOY 800 $E_d=47.8$ kJ·mol$^{-1}$ is analogous to the high values detected for the austenitic stainless steel 316L ($E_d=42.5$ kJ·mol$^{-1}$ [26] or 59.7 kJ·mol$^{-1}$ [27]), departing from the typical low values of the ferritic-martensitic ones (all the referenced steels of this type show $E_d<16.0$ kJ·mol$^{-1}$ [21, 24-26]). The low solution energy obtained for INCOLOY $E_s=7.8$ kJ·mol$^{-1}$ (the slope of the curve corresponding to INCOLOY 800 is one of the lowest in Figure 10) approximates to that obtained by Forcey et al. for the austenitic SS316L, $E_s=6.9$ kJ·mol$^{-1}$.

The foreseen effect of trapping on diffusivity and Sieverts' constant has not been noticed throughout the whole temperature range; the sudden increment of $K_s$ and decrease of $D$ at temperatures approximately below 300°C has not been observed. The absence of any martensitic lath in INCOLOY 800 acting as trapping centres might explain that this usual effect in the ferritic-martensitic steels has not been detected in this case.
Figure 6. Arrhenius plot of the fitted deuterium permeability in INCOLOY 800: (1) Hydrogen [5], (2) Hydrogen (extrapolated from experimental high temperatures (923 – 1223 K) [6]; (3) Deuterium (this work).
Figure 7. Arrhenius plot of the fitted deuterium diffusivity in INCOLOY 800.
Figure 8. Arrhenius plot of the fitted deuterium Sieverts' constant in INCOLOY 800.
Figure 9. Diffusivity for INCOLOY 800 compared with reference steels. (1), (2) and (3) H_P, H_D and H_T, respectively, in OPTIFER-IVb [24], (4) Batman (H_D) [21], (5) F82H (H_D) [21], (6) MANET (H_P) [25], (7) MANET (H_P) [26], (8) SS 316L (H_P) [26], (9) SS 316L (H_P) [27], (10) a-Fe (H_P) [28], (11) INCOLOY 800 (H_D) (this work).
Figure 10. Sieverts' constant of INCOLOY 800 compared with reference steels. (1), (2) and (3) H_P, H_D and H_T, respectively, in OPTIFER-IVb [24], (4) Batman (H_P) [21], (5) F82H (H_D) [21], (6) MANET (H_P) [25], (7) MANET (H_P) [26], (8) SS 316L (H_P) [26], (9) SS 316L (H_T) [27], (10) α-Fe (H_P) [28], (11) INCOLOY 800 (H_D) (this work).
5.2. Surface-limited regime

After maintaining the specimen at high temperature (623 K) and high deuterium pressure (1 bar) in one of its sides during several days, the oxide layer on the surface facing the gas atmosphere stabilised. Then, a series of permeation test were performed in the temperature range from 427 to 780 K and driving pressures ranging from $10^4$ to $1.5 \times 10^5$ Pa in search of the surface rate constants.

The experimental permeation curves were simulated with the non-symmetric model to obtain the surface rate constants of the non-oxidized and oxidized surfaces. A linear least-squares fitting routine was applied to the steady state permeation region with Eq. (23); from the slope of each straight line and its corresponding time-lag $\tau_{ts}$, values of $(\sigma k_1)$ and $(\sigma k_1)'$ are obtained. The value of $K_s$ previously evaluated has been used here. These $(\sigma k_1)$ and $(\sigma k_1)'$ values are used as initial entry parameters in a non-linear least-squares fitting routine with the general permeation equation expressed in (22). Subsequently, the series of values of $(\sigma k_2)$ and $(\sigma k_2)'$ are obtained from $(\sigma k_1)$ and $(\sigma k_1)'$ by means of Eq. (1). Then, all the groups $(\sigma k_1)$, $(\sigma k_1)'$, $(\sigma k_2)$ and $(\sigma k_2)'$ are fitted to Arrhenius expressions.

For the oxidized surface (high pressure region) the adsorption constant has been evaluated as (Figure 11):

$$\sigma k_1 (\text{mol m}^2\text{s}^{-1}\text{Pa}^{-1}) = 2.67 \times 10^{-10} \exp(-40.1 \text{ (kJ mol}^{-1})/RT) \quad (R^2=0.974)$$

and the recombination constant (Figure 12):

$$\sigma k_2 (\text{mol}^{-1}\text{m}^4\text{s}^{-1}) = 2.58 \times 10^{-9} \exp(-24.5 \text{ (kJ mol}^{-1})/RT) \quad (R^2=0.969)$$

For the non-oxidized surface (low pressure region) the adsorption constant has been evaluated as (Figure 11):

$$(\sigma k_1)' (\text{mol m}^2\text{s}^{-1}\text{Pa}^{-1}) = 4.14 \times 10^{-6} \exp(-44.3 \text{ (kJ mol}^{-1})/RT) \quad (R^2=0.988)$$

and the recombination constant (Figure 12):

$$(\sigma k_2)' (\text{mol}^{-1}\text{m}^4\text{s}^{-1}) = 4.00 \times 10^{-4} \exp(-28.6 \text{ (kJ mol}^{-1})/RT) \quad (R^2=0.939)$$

The resulting surface rate constants for the high pressure region (oxide present) are more than 3 orders of magnitude lower than the resulting surface rate constants for the low pressure region (oxide absent). This fact shows the great influence of the oxide on the surface parameters entailing the inhibition of the hydrogen isotope transport.

The Arrhenius plots of the surface rate constants obtained for INCOLOY 800 are compared with other works in Figures 13 and 14. The values for $\sigma k_1$ and $\sigma k_2$ obtained here for the oxidized surfaces are the lowest of all the steels reviewed. This
feature confirms the possibility of generating effective permeation barriers with an oxide layer on INCOLOY 800 whenever the oxide stability is assured.

Baskes and Pick & Sonnenberg models have been applied for INCOLOY 800 with the diffusive transport parameters previously evaluated. The Baskes model yields an activation energy of adsorption 55.6 kJ·mol$^{-1}$ comparable to the experimental 40.1 and 44.3 kJ·mol$^{-1}$; the existent gap between the experimental and theoretical values may be attributed to sticking coefficients of 5.26·10$^{-10}$ and 8.17·10$^{-6}$ corresponding to oxidized and non-oxidized surfaces, respectively. The Pick & Sonnenberg model denotes a major mismatch because the model foresees no activation energy for adsorption when the experimental results accounted for it. The model could be congruent with the experimental values provided the sticking coefficient was activated with the energies of 40.1 and 44.3 kJ·mol$^{-1}$ for oxidized and non-oxidized surfaces respectively.
Figure 11. Arrhenius plot of the fitted deuterium adsorption constant in INCOLOY 800: (1) low pressure side, (2) high pressure side.
Figure 12. Arrhenius plot of the fitted deuterium recombination constant in INCOLOY 800: (1) low pressure side, (2) high pressure side.
Figure 13. Arrhenius plot of adsorption rate constants. (1) and (2) Pick & Sonnenberg [13] model and Baskes [12] model respectively for INCOLOY 800 (with sticking coefficient s=1 and roughness σ=1); (3) D$^+$ implantation in MANET [29]; (4) H$_2$, 316 SS ion beam cleaned [30], (5) H$_2$, 316 SS oxidized both surfaces [30], (6) D$_2$, bare MANET [18]; (7) D$_2$, MANET [20], (8) D$_2$, oxidized MANET [18]; (9) D$_2$, Inconel 600 [31], (10) D$_2$, 304 SS [32], (11) D$_2$, bare OPTIFER-IVb [17], (12) D$_2$, bare INCOLOY 800 (this work), (13) oxidized INCOLOY 800 (this work).
Figure 14. Arrhenius plot of recombination rate constants. (1) and (2) Pick & Sonnenberg [13] model and Bakes [12] model respectively for INCOLOY 800 (with sticking coefficient s=1 and roughness $\sigma$=1); (3) D$^+$ implantation in MANET [29]; (4) H$_2$, 316 SS ion beam cleaned [30], (5) H$_2$, 316 SS oxidized both surfaces [30], (6) D$_2$, bare MANET [18]; (7) D$_2$, MANET [20], (8) D$_2$, oxidized MANET [18]; (9) D$_2$, Inconel 600 [31], (10) D$_2$, 304 SS [32], (11) D$_2$, bare OPTIFER-IVb [17], (12) D$_2$, bare INCOLOY 800 (this work), (13) oxidized INCOLOY 800 (this work).
6. CONCLUSIONS

The gas permeation technique has been used to investigate deuterium transport in INCOLOY 800. Two well-differentiated transport regimes have been discriminated: a diffusion limited and a surface limited regime, both of them have been individually simulated with their respective theoretical model. Satisfactory diffusive transport parameters $D$, $K_s$ and $\Phi$ have been obtained in the temperature range 427 to 664 K. In accordance with previous results obtained for permeability, the complete set of diffusive transport parameters shows an analogous tendency to the austenitic steel departing from the ferritic-martensitic ones.

The surface rate constants of adsorption $\alpha k_1$ and recombination $\alpha k_2$ have been evaluated in the temperature range 427 to 780 K. The state of each surface of the specimen has been differentiated by means of a non-symmetric model. A gap close to four orders of magnitude between the surface rate constants evaluated in the presence and in the absence of oxide has been evidenced. The layer of the spinel oxide $\text{Mn}_x\text{Cr}_y\text{O}_z$ has demonstrated to be an effective hydrogen isotope transport barrier.
7. REFERENCES


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