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The behaviour of the natural oxide of MANET as permeation barrier under cyclic loads: Self-healing

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Abstract

A gas permeation technique has been employed to determine hydrogen permeation rates for oxidised tubular MANET (**MA**rtensitic for **NET**) specimens under cyclic tensile loads. The results obtained over the temperature range 400–873 K and for driving pressures of 100 kPa indicate a permeation reduction factor (PRF) of up to 100. Similar measurements performed under cyclic tensile loads (220 MPa 35% UTS, cyclic rate 10 min/cycle) resulted in a PRF of only 50. However, continuous measurements under tensile cyclic load, i.e. the sample was kept in contact with the hydrogen (with ~1000 ppm H_2O) for an extended period, has shown a recovery of the initial PFR implying the possibility of barrier self-healing.

1. Introduction

The low solubility of hydrogen in liquid Pb–17Li together with its high permeability in most of the candidate structural materials has resulted in the need to develop effective permeation barriers. The most common routes chosen in attempting to reduce permeation losses have recently been reviewed [1]. These barriers should not only hinder the permeation flux but also have sufficient adhesion to the substrate; be chemically stable; and not crack during thermal and mechanical cycling.

So far the testing methods used on promising barriers have not incorporated the application of stress to the barrier. Although some indication of the cracking resistance of some barriers [2] has been obtained by mechanical testing on coated tensile specimens, it is preferable to directly measure the permeability of any structural/barrier system under cyclic tensile loads. A dedicated apparatus to measure the hydrogen permeability of structural material, both coated and uncoated, under cyclic tensile loads has been constructed at the Institute for Advanced Materials, JRC-Ispra Site [3].

An effective route to obtain a permeation barrier is the growth of oxide layers on the surface of the structural material [4]. MANET (**MA**rtensitic for **NET**) is particularly suitable for this approach because of the formation of chromium and manganese oxides in the presence of low oxygen partial pressures [5].

2. Experimental

2.1. Materials

The material studied is the martensitic stainless steel MANET II, a development of MANET [6]. The MANET II steel used in this study has 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 test specimens were subjected to the following heat treatment to produce a fully 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, and slow cooling to room temperature.

2.2. Apparatus and experimental method

The apparatus used in this study (Fig. 1) was constructed from standard ultra high vacuum components together with some specially fabricated all steel parts (SS 304).

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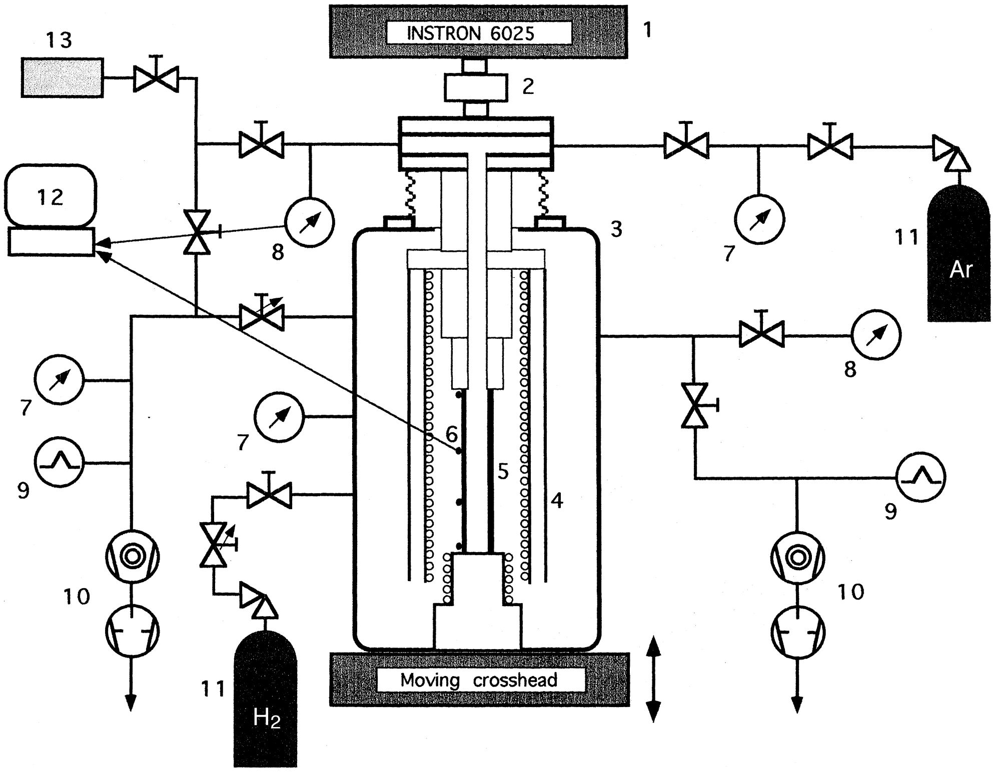

Fig. 1. Schematic of the experimental facility. 1 Instron test machine, 2 Load cell, 3 H_2 chamber, 4 Furnace, 5 H_2 permeation specimen, 6 Thermocouple, 7 Vacuum gauge, 8 Baratron, 9 Mass spectrometer, 10 UHV-system, 11 Gas bottle, 12 Data acquisition and 13 Calibrated volume.

The permeation method used (isovolumetric permeation) consists of the measurement of the pressure increase in an ultra-high vacuum, calibrated volume (the downstream side), due to the gas flow, through a thin sample, from another volume kept at constant pressure (the upstream side). The specimen under study divides the two volumes involved.

Following a step change in the pressure of the high pressure side at time $t = 0$, the permeation flux J of hydrogen atoms through a membrane of uniform thickness d, where the high pressure p, is always very much greater 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 as:

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

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 hydrogen dissociates before dissolving into metals.

Under steady-state conditions (i.e., $t \rightarrow \infty$) Eq. (1) becomes $J = P/dp^{1/2}$ (mol m^{-2} s^{-1}). Where $P = DK_S$ (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., $P = P_0 \exp(-E_p/RT)$, where P_0 is a constant and E_p is the activation energy for permeation. 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. However, if the surface effects are significant, the system operates in the surface limited regime, and the permeation flux is linearly dependent on the driving pressure and is independent of thickness of the layer. In this case, the surface parameters become important.

The tests were conducted on a tubular MANET II stainless steel specimen (wall thickness of 1 mm). The test specimen was heated stepwise, under high vacuum $<10^{-6}$ Pa to 400 K to degas the specimen and apparatus. Upon reaching the desired test temperature the internal volume of the test specimen was isolated from the UHV system and hydrogen gas (100 kPa) introduced into the hydrogen chamber. The pressure rise due to the flux of hydrogen permeating through the tube was measured using a Baratron absolute pressure gauge (range 1330 Pa). The hydrogen driving pressure was maintained constant at 100 kPa by using the output from a second Baratron (range 133.3 kPa) to control the hydrogen inlet via an electromagnetic valve.

The signal from the Baratron measuring the pressure rise due to the permeating hydrogen together with the thermocouple outputs were collected and stored on a data recorder. Following the establishment of steady state permeation the internal permeated hydrogen was expanded into an evacuated calibrated volume.

Using the one-dimensional solution of Fick's law (Eq. (1)) the permeability at a given test temperature can be obtained from the permeated hydrogen flux and the specimen dimensions. Repeating the experiment at various temperatures between 520 and 900 K gives rise to the temperature dependence of the permeability.

The Instron testing machine model 6025 was operated under load control. A tensile load was applied in a triangular loading cycle (10 min/cycle) from zero load to a maximum of 312 MPa then back to zero. The load of 312 MPa corresponds to a maximum of 45% of the UTS of the steel depending on the test temperature.

3. Results and discussion

The presence of water at a concentration $\leqslant 1000$ ppm in the hydrogen gas used for the tests resulted in the oxidation of the MANET II specimens. The fact that the MANET II surface readily oxidises can be attributed to a more negative free energy for oxidation of the Cr than the other main constituent of the alloy. Many factors such as alloy composition, the oxidation temperature and the partial pressure of oxygen in contact with the metal surface govern the rate at which the oxidation process proceeds. At temperatures above 900 K, the proportion of Mn in the steel (0.85 wt%) plays an important role. Wild [7] assigned this effect to the higher diffusivity of Mn as compared to Cr in Cr_2O_3 (2 orders of magnitude at 1070 K). Stott and co-workers [8] also observed this effect in Fe–Cr alloys with different Mn concentrations. Therefore, mixed oxides of Cr–Mn (spinel $Cr_xMn_yO_4$) are expected to be found in the surface and these increase in thickness with time.

The permeation flux of hydrogen was reduced by up to two orders of magnitude (a factor 100 at 450 K and 10 at 820 K, see Fig. 2) as a result of the oxidation of the surface. The measured value of the hydrogen permeation flux for the unoxidised case is also depicted in Fig. 2 together with the values found in literature [5]. The good agreement between the unoxidised and literature values demonstrates that the experimental procedure is correct.

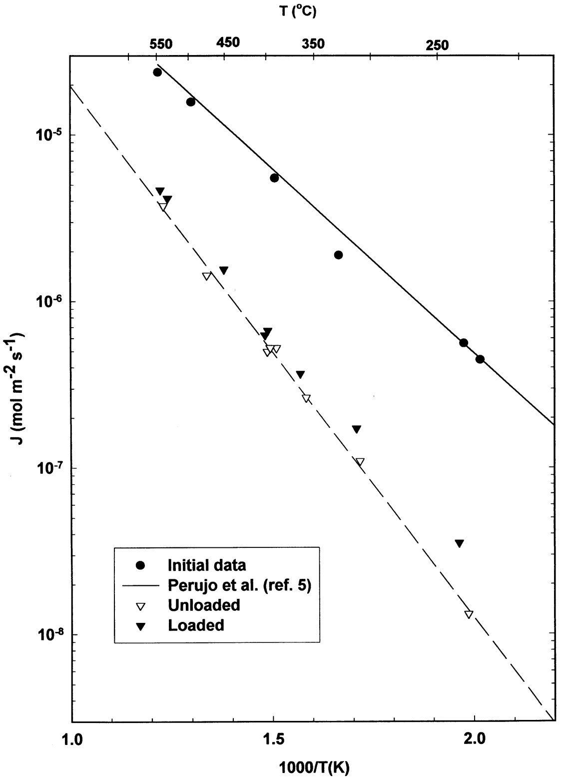

Fig. 2. Arrhenius plot of the permeation rate of hydrogen through bare and oxidised MANET II with and without cyclic tensile loading (first experimental data set). The upstream hydrogen pressure was 100 kPa.

Cyclic tensile loading of 200 MPa at 523 K (~35% UTS of MANET) with a cyclic rate of 10 min/cycle yielded an increase in permeating flux of about a factor 3. The increase in the permeating flux can only be attributed to cracking of the surface oxide layer because a previous study on an unoxidised MANET II specimen did not yield any change in the permeation flux when similar tensile loads were applied [2]. Continuous application of loading corresponding to around 35% UTS of the steel at different test temperatures resulted in smaller changes in the permeation flux. At temperatures of 623 K and higher no change in the permeation flux was observed. This effect seems to indicate that the oxidation kinetic is faster than the crack propagation under cyclic tensile loads at those temperatures and therefore no changes in the permeation flux take place because the oxide heals faster than cracks appear.

A second set of experiments was conducted (Fig. 3) starting from an unoxidised surface. In this case the oxidation only resulted in a PRF of 20 at 400 K and 10 at 820 K (see Fig. 3). An applied cyclic tensile loading corresponding up to 30% UTS at 400 K did not result in any appreciable change in the permeation flux. An increase of a factor 3 in the permeation flux was obtained when a load corresponding to 45% UTS was applied to

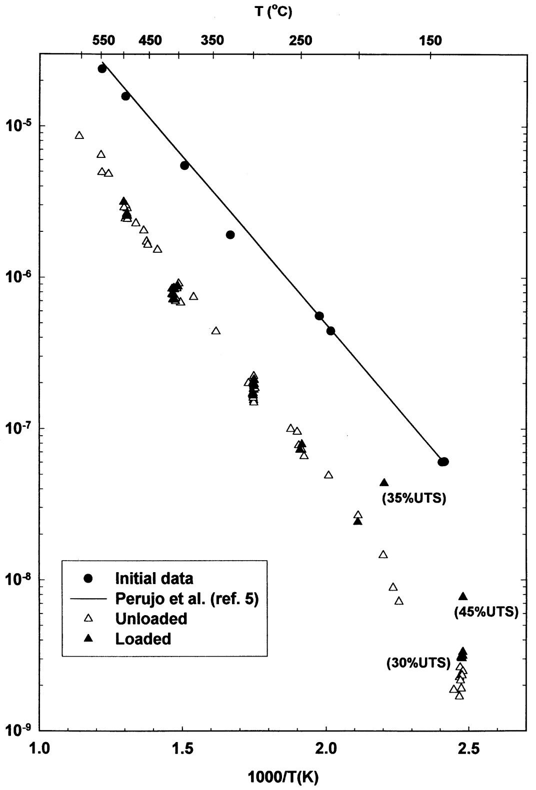

Fig. 3. Arrhenius plot of the permeation rate of hydrogen through bare and oxidised MANET II with and without cyclic tensile loading (second experimental data set). The upstream hydrogen pressure was 100 kPa.

the specimen. The initial permeation flux was again obtained after cycling for 24 h in presence of hydrogen (1000 ppm H_2O). As in the previous set of measurements (Fig. 2), an increase of the permeation flux was observed when loading to up to 35% UTS at different test temperatures. However, in this case, no change was noticed at temperature above 500 K, indicating once more that above this temperature the oxidation kinetic was faster than the cycling frequency and the characteristic time for permeation.

It is worthwhile here to note that we cannot talk of characteristic time for diffusion in this case because the permeation is not strictly diffusion controlled. The pressure dependence of the hydrogen permeation rate of the specimen at a constant temperature of 773 K over the pressure range 10^3–10^5 Pa is of the form $J = 8 \times 10^{-11}\ p^{0.9}$, indicating a strong surface contribution in the kinetic of permeation. This is in agreement with values for the absorption coefficient of an oxidised MANET II specimen (5×10^{-11} mol m^{-2} s^{-1} Pa^{-1}) found in the literature [9]. Therefore, all the results presented are given as permeation rates and not as permeability of the material and no attempt was made to calculate the intrinsic permeability of the oxide layer using a two-layer diffusion model [10].

To confirm and characterise the growth of the oxide layer on the MANET II specimen, X-ray photoelectron spectroscopy (XPS) measurements were conducted on the specimen after oxidation (specimen of Fig. 3). The XPS analysis was performed from 0 to 35 nm at 5 nm intervals in order to check the composition at different depths. At the surface Cr was in the form of Cr_2O_3 while neither Fe or Mn oxides were detected. The absence of Mn oxide can be in part attributed to the low mobility of Mn in the Cr_2O_3 at the maximum temperature used in the test (823 K) [7]. The oxide thickness was measured to be between 10 and 15 nm.

All the above indicates that self-healing of the surface oxide layer occurs with reasonable fast kinetics at temperatures above 500 K (certainly above 623 K, Fig. 2).

In order to check further the self-healing characteristic of the oxide layer, the specimen was left at a constant load of 204 MPa (35% UTS, strain = 0.92%) at 673 K for 116 h. The permeation rate was measured at 0, 1094, 1324, 5554, 5754 and 7000 min, respectively. The measurements at 0 and 7000 min corresponded to an unloaded condition. If self-healing occurred, the values at zero loads, i.e. measurements at 0 and 7000 min, should show a net reduction and the values obtained under load should show a decreasing trend. This is in fact what was observed (see Fig. 4). A second set of measurements at the same temperature with a load changing from 207 (strain = 0.94%) to 229 MPa (strain = 1.03%) resulted in a slight increase in the permeation rate and exhibited the same trend as before when the stress was eliminated. It could be argued that the changes are small and therefore it may be a consequence of the experimental uncertainty. However, the net trend exhibited by the data cannot correspond to an experimental error because the errors should behave randomly without a preferred direction. Secondly the same trend was observed twice at two different UTS values. As we believe that this phenomena is not due to experimental error, one should be able to quantify the kinetics of the oxidation process and in both cases it should be approximately the same value, despite the minor variations between the two sets of experiments. A linear fitting of the permeation flux as a function of time under load for the two set of data yielded similar slopes: -1.73×10^{-11} and -2.61×10^{-11}, respectively. These slopes are a qualitative measurement of the kinetic of oxidation that corresponds to the speed with which the permeation flux reduces with time.

4. Conclusions

The behaviour of a natural oxide layer as hydrogen permeation barrier on MANET II has been studied. The

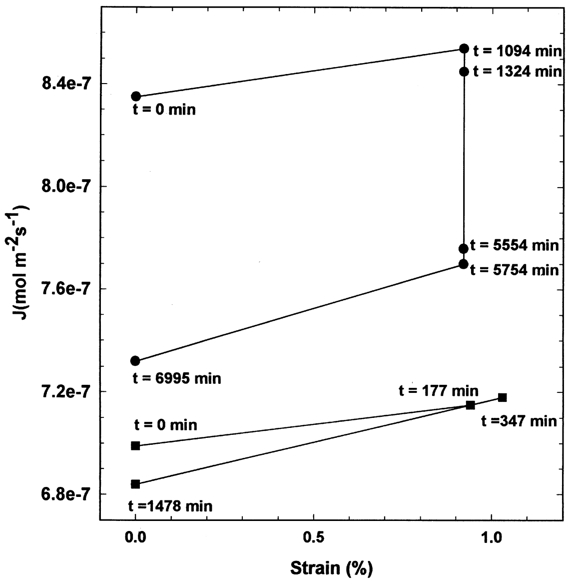

Fig. 4. Plot depicting the change of permeating flux as a function of the applied engineering strain. The reduction of the flux in time is obvious (self-healing).

permeation reduction factors obtained are similar to those found in the literature (PRF of up to 100) [3].

The oxidised layer exhibits self-healing characteristics in the temperature range of operation of the structural blanket material. This is one of the main requirements for a permeation barrier to function effectively in the expected working environment of a fusion reactor. The experimental method chosen to investigate the self-healing (applied stresses of up to 40% UTS and strains of up to 1.3%) ensures that the data are directly usable by the blanket design teams without the need of extrapolations from indirect measurements. The stresses applied to the specimen are larger than those expected for the material when in operation.

The self-healing property of the oxide layer formed on the MANET II surface opens the possibility for better performances by other deposited barriers (e.g. Al_2O_3), because even if they might not heal, the underlying material at a crack site may oxidise and the newly formed oxide should be able to stand considerable stresses by re-oxidising after cracking in a reasonably short time.

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