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Hydrogen in the martensitic DIN 1.4914: a review

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Abstract

The martensitic steel DIN 1.4914 (MArtensitic for NET, MANET) is a candidate material for the first wall and structure of the demonstration power reactor DEMO. This paper reviews the values obtained for all the hydrogen transport parameters in MANET using gas-evolution and permeation methods. It also discusses the susceptibility of the material to oxidation and its influence on those parameters.

Keywords: Steel; Embrittlement

1. Introduction

The martensitic stainless steel DIN 1.4914 (MANET, MArtensitic for NET) is a candidate material for the first wall and structure for the demonstration power reactor DEMO. MANET is a Nb bearing steel which has better swelling resistance, lower sensitivity to helium embrittlement and more suitable thermophysical properties when compared with austenitic stainless steel AISI 316L [1].

In a fusion reactor the hydrogen interaction with materials is an important issue concerning safety, fuelling and reliability. Many computer codes are available for estimating the inventory, permeation and recycling of tritium in a predefined reactor configuration. These codes require as input all the hydrogen (tritium) transport parameters for the structural material which rule the gas–material interaction (diffusivity, solubility, permeability, surface reaction constants, trap density and trap energy). Hydrogen–material interaction properties in MANET have been studied by Forcey et al. [2] using a permeation method and by our group using both a gas evolution method [3,4] and a permeation method. In both studies, MANET had been given the recommended standard heat treatment to produce a δ-ferrite free, fully martensitic structure.

This paper reviews all the hydrogen–material interaction properties of MANET and discusses the influence on these parameters of its oxidation susceptibility.

2. Experimental method and materials

A detailed description of the experimental apparatuses and methods can be found in earlier reports [3,4]. Here, only a small description is presented for completeness.

The gas evolution method (isovolumetric desorption) involves two phases: loading of the sample at 10^5 Pa of H_2 at a given temperature (isothermal and isobaric loading) and, after a short pump down of the experimental chamber to less than 10^{-3} Pa, the recording as a function of time of the pressure increase due to the degassing of the sample together with the installation walls. Another measurement made under the same conditions without the sample follows each run to allow for the apparatus' walls contribution. After this measurement, a subtraction of the two pressures vs. time release curves is made, to obtain the net contribution due only to the sample. By a nonlinear least squares fitting process using a diffusion controlled gas release model, one can obtain directly the diffusivity constant D and the Sieverts' constant K_S of hydrogen in the sample.

On the other hand, the permeation method (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. The pressure vs. time plot shows two different characteristic zones: a non-steady zone where the gas flows from one to the other volume at a rate depending on time and a steady-state zone where a linear behaviour is established, corresponding to a maximum constant flow

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rate. The linear zone crosses the time axis at τ_l (the ‘time lag’) that is linked to the diffusivity D by $D=d^2/6\tau_l$, where d is the sample thickness. The steady-state permeation flux can be obtained from the derivative of the pressure in the linear (steady-state) zone, and from it the evaluation of the permeability is straightforward. The experimental installation is provided with a system of valves that allows a ‘reverse permeation’ experiment (experiment with exchanged upstream and downstream volumes); this assures the experimenter that both sides of the specimen have the same surface conditions.

It should be noted that in the first technique the diffusivity and solubility are obtained directly from the experiment and the permeability calculated using Richardson’s law while in the second technique, the permeability and the diffusivity are obtained directly from the experiment while the solubility is derived from them.

The material studied is MANET II, a development of MANET [5]. The MANET II samples consist of cylinders 6 mm in diameter by 60 mm length, and discs of 48 mm in diameter and 0.5 mm in thickness, respectively, for the gas evolution and permeation technique. They were machined from a slab of material supplied by Kernforschungszentrum Karlsruhe 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 and Fe balance. The samples underwent 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, slow cooling to room temperature. Before the samples were inserted into the measuring equipment, they were mechanically polished. Thus, only oxide layers resulting from exposure to air at room temperature should have been present.

3. The hydrogen transport parameters

3.1. Diffusivity

In Fig. 1 the diffusivity of hydrogen and deuterium in MANET is depicted. Lines a (for H_2), b (for D_2) and f (for H_2) are obtained by the gas evolution method while the others (c for D_2, and d and e for H_2) correspond to the permeation method. All of them are in good agreement independently of the method used and taking into account the isotope effect. It is our opinion that the values represented by the line c [6] corresponds to a non-oxidised surface (less that 50 Å oxide layer) because the authors have been very careful in avoiding any oxidation of the surfaces of the sample during the measurements. The other values (d and e [2] and a, b and f [7]) correspond to surface slightly oxidised. In particular, the values depicted by line f correspond to an oxidised surface of about 300 Å that was obtained by keeping the samples in the experimental rig and repeating the measurement till no change in the diffusivity of the material was found (‘saturation’ was achieved).

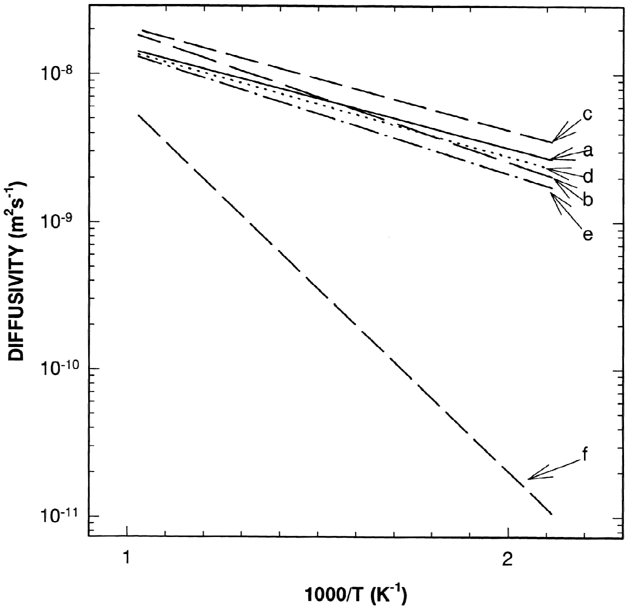

Fig. 1. Diffusivity of hydrogen and deuterium in MANET measured by gas evolution method [7] (lines a, b and f) and by a gas permeation method (lines c [6], d and e [2]).

MANET kept at a temperature of 900 K for 10 days at 10^5 Pa of pure H_2 (0.8 ppm of H_2O, 0.1 ppm of O_2, 0.01 ppm of CO_2 and 0.1 ppm of CH_4) reduces the hydrogen diffusivity due to the presence of oxides in the surface. The presence of Mn in the steel (0.85 wt.%) made it less resistant to oxidation. This was also observed by Stott et al. [8] in Fe–Cr alloys with different Mn concentrations. Wild [9] assigned this effect to the higher diffusivity of Mn as compared to Cr in Cr_2O_3 (2 orders of magnitude at 1070 K). Therefore, mixed oxides of Cr–Mn (spinel $Cr_xMn_yO_4$) are found in the surface and these increase in thickness with time. Fig. 2 shows the XPS spectrum of the MANET surface before and after oxidation with the clear presence of Mn oxides in the oxidised sample.

The Arrhenius’ equation, Eq. (1), gives the diffusivity of deuterium in MANET for the non-oxidised case [6], while Eq. (2) gives the diffusivity of hydrogen in oxidised MANET:

$$D(\mathrm{m^2\,s^{-1}}) = 1.01\times10^{-7}\exp\left(-\frac{13210\ \mathrm{J\,mol^{-1}}}{RT}\right) \tag{1}$$

$$D(\mathrm{m^2\,s^{-1}}) = 1.85\times10^{-6}\exp\left(-\frac{47460\ \mathrm{J\,mol^{-1}}}{RT}\right) \tag{2}$$

where $R=8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and T is the temperature in K.

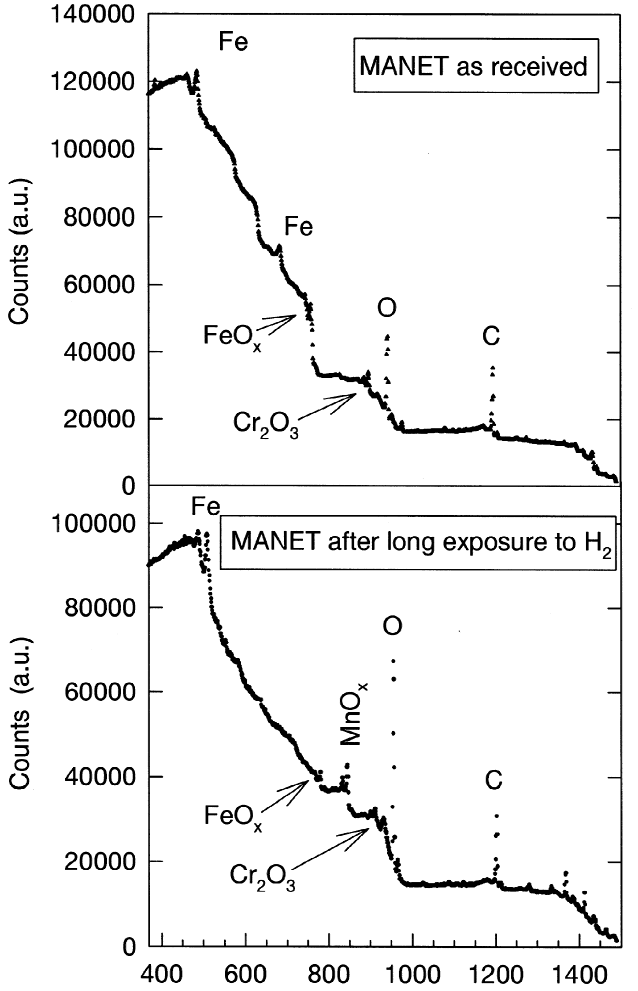

Fig. 2. XPS spectrum of non-oxidised (top) and oxidised (bottom) MANET, showing the presence of Mn and Cr oxides.

3.2. Solubility

In contrast with the case of the diffusivity, no appreciable change (roughly the experimental error, which for the gas evolution method is estimated to be ~10%) in the solubility was found after exposing the sample to hydrogen as described above. However, the change was not random as expected for an experimental error, but it was always in the increasing solubility direction. This trend shows that the solubility of the oxide is much larger than that of the substrate material because it increases the total solubility, although the amount of material is negligible in comparison to the base material (300 Å oxide and 6 mm of material).

The Sieverts' constant is given for the MANET by Eq. (3):

$$K_s(\text{mol D}_2\ \text{m}^{-3}\ \text{Pa}^{-1/2}) = 0.27\exp\left(-\frac{26670\ \text{Jmol}^{-1}}{RT}\right) \tag{3}$$

3.3. Permeability

The value for the permeability of deuterium in MANET is given for the non-treated sample by Eq. (4)

$$P(\text{mol D}_2\ \text{m}^{-1}\ \text{s}^{-1}\ \text{Pa}^{-1/2}) = 4.2 \times 10^{-8}\exp\left(-\frac{42380\ \text{Jmol}^{-1}}{RT}\right) \tag{4}$$

This value has been obtained directly by the permeation method. Obviously for the case of oxidised material and for diffusive behaviour the permeability can be obtained by using Richardson's law, employing the appropriate diffusivity and solubility equations.

3.4. Surface reaction rates constants

Measurements of the permeation rate of deuterium in MANET were performed using a gas permeation technique in the temperature range 560–740 K and at upstream pressures in the range 9 Pa–5×10^4 Pa. From these measurements and following the approach of Ali-Khan et al. [10], Serra and Perujo [11] calculated the surface adsorption (σk_1) and surface release (σk_2) constants of deuterium in MANET, where σ is the surface roughness factor and is the ratio of the real area to the geometric area of the surface. The surface conditions of the studied sample were slightly oxidised with an oxide thickness of about 150 Å. The oxide was of the same type as the one discussed in the diffusivity section.

The values for the two surface rate constants are given by the following Arrhenius equations:

$$\sigma k_1(\text{mol m}^{-2}\ \text{s}^{-1}\ \text{Pa}^{-1/2}) = 7.66 \times 10^{-6}\exp\left(-\frac{55217\ \text{Jmol}^{-1}}{RT}\right) \tag{5}$$

$$\sigma k_2(\text{mol}^{-1}\ \text{m}^4\ \text{s}^{-1}) = 2.59 \times 10^{-5}\exp\left(-\frac{5781\ \text{Jmol}^{-1}}{RT}\right) \tag{6}$$

3.5. Trapping

Trapping is a process that delays the flow of deuterium (hydrogen) in a solid via the capture and release of deuterium atoms by sites other than the ordinary solution ones.

Measurements of diffusivity, solubility and permeability of deuterium in MANET were performed by the permeation method in the temperature range 373–743 K with deuterium driving pressures in the range 0.5–100 kPa. This range of temperatures includes the onset (low temperatures) of deuterium trapping effects in this martensitic steel. The results in the whole range of temperature were interpreted [6] using a trapping model based upon Oriani's model [12]. The results gave 1.5×10^{25} trap sites m^{-3} with an average energy of 48 kJ mol^{-1}.

The trapping process in MANET is very pronounced in the low-temperature interval (up to 523 K). This result can be used as a reference for the evaluation of the effects of the presence of hydrogen in steels damaged by neutron irradiation.

4. Conclusions

A review has been presented of the parameters governing the hydrogen/deuterium interaction with the martensitic steel MANET, a DEMO structure candidate material. This set of parameters can be used to calculate the inventory, recycling and permeation of hydrogen/deuterium/tritium in fusion reactor design concepts in non-steady-state conditions with appropriate numerical codes. When the value for a given isotope has not been presented, the use of a scaling law (isotopic effects) will provide the value for the required isotope.

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