Experimental refutation of the deuterium permeability in vanadium, niobium and tantalum

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Deuterium permeability through Nb, V, and Ta was measured in the temperature range between ~300-500 ºC and 100 to 1000 mbar. For the three materials, the permeation rate at 500 ºC was between two and three orders of magnitude below expected values which were obtained by combining diffusivity and solubility data and which have been traditionally accepted due to the insufficient experimental available data. Comparison with existing literature suggests a complex dependence of permeability with temperature, what helps explain this discrepancy. Given the important role of the surface condition on the permeability, additional deuterium permeation tests were carried out in vanadium for more realistic sample preparation. Results indicate that native oxides formed at room temperature introduce a permeation reduction of several orders of magnitude, what must be considered for practical applications.

Keywords: Permeability, deuterium, vanadium, tantalum, niobium

1. Introduction

Unique gas retention and transport characteristics of group V elements (V, Nb, Ta) have long attracted a significant interest, in particular among the nuclear fusion community. The nominally high hydrogen isotope permeability and diffusion at the expected operational temperatures, together with the negative activation energy for the solubility present these materials as a promising choice for the fabrication of tritium recycling structures. However, before seriously considering these materials, one should question the accuracy of the available data, given the remarkable lack of direct experimental measurements in support of the traditionally accepted transport properties of these materials. Furthermore, it must be considered that the generally most accepted data have been obtained by combining results from different authors and methods. The extensive literature review presented in this paper shows that existing experimental results not only contradict the semi-empirical values assumed for these materials but also present a broad dispersion.

Within the fusion field, tritium transport is of special concern, a tight inventory control being required not only for fuel availability but also for safety reasons due to its radioactivity. The design of tritium related systems as well as the possible existence of leakages to other components might be underestimated affecting the safety of the reactor. For this, deuterium permeability data for the three materials was obtained in a relevant range of temperatures, according to requirements which have in general been established for the blanket design [1, 2]. Experimental difficulties together with the role of surface oxidation which may become a major issue for practical uses are also assessed.

2. Experimental procedure

High purity (99.9 %) niobium and tantalum from Goodfellow, and vanadium supplied by Eagle Alloys were examined. The samples, 0.5, 1.0, and 0.9 mm thickness respectively were cut to meet the system required dimensions and grinded/polished when necessary in order to minimize surface process effects. A new gas permeation system (Thermoperm II) has been commissioned for these experiments, as a replica of Thermoperm I apparatus developed within F4E activities for hydrogen/metal interaction studies [3, 4]which allows one to obtain data for hydrogen/deuterium permeability through metal membranes from ~300 to 550 ºC and 0.1 to 1000 mbar. A small oven (Thermocoax heating element and copper base) is in direct contact with the sample in the pressure side, and two thermocouples are spot welded on the opposite face for temperature control. The measuring principle is based on the gas evolution permeation technique [5], the experimental procedure consisting on maintaining a driving gas pressure level on one sample surface while vacuum conditions (~ 10^{-3} mbar) are held in the opposite site. Permeated flux from high to low concentration regions is measured at each temperature under steady-state conditions using a Pfeiffer Smart Test leak detector (10^{-12} mbar l/s sensitivity for D_2). The system was carefully checked and validated using high purity alpha-iron, and 316-L stainless steel (both materials which were exhaustively characterized by different laboratories as part of above-referenced F4E-contract). The reproducibility of the method is shown in figures 1 and 2 which compare data obtained for Thermoperm I and II for stainless steel and iron respectively. Excellent agreement is observed with values present in the literature.

A systematic procedure has been followed in order to assure adequate surface condition, consisting on prior sample cleaning with detergent and ultrasonic bath and, once the sample is mounted, annealing in high vacuum up to ~ 400 ºC for about 70 h before the onset of the experiments. For these materials, extended than usual preparatory baking periods for surface cleaning were

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needed in order to attain signal stabilization at reasonabletimes. Prolonged experiments lead to additional difficulties as a consequence of the elevated temperatures, such as the appearance of leaks and heating problems due to Thermocoax degradation in the hydrogen atmosphere [6]. In addition, the high deuterium absorption of these materials produced an increasing background for consecutive runs, introducing an additional error in the measurements. For this reason, attempts to perform experiments at low pressures were in general unsuccessful, and regular tests were performed above 100 mbar. A temperature range from ~250 to 500 ºC was considered, with small variations depending on the material.
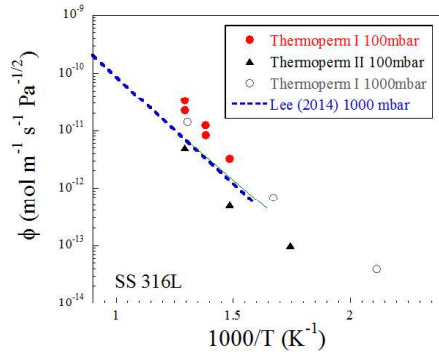

Fig. 1. Permeability for 316L stainless steel obtained in Thermoperm I and II, and comparison with literature data [7].
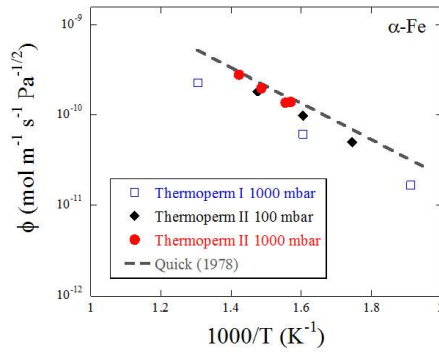

Fig. 2. Permeability for α-Fe obtained in Thermoperm I and II, and comparison with literature data [8].

3. Literature revision

The most widely accepted values for H isotope transport properties for V, Ta, and Nb can be found in several compilation books and review articles mainly focused on fusion applications such as those prepared by Steward in 1983 [9] or Reiter in 1994 [10]. These values have been repeatedly quoted attending to their application in tritium extraction and recovery related technologies [11, 12, 13, 14] and even recommended in ITER reports [15]. Such works present this set of materials as having remarkably high hydrogen permeability when compared to other BCC crystal structures (e. g. ~ 3 orders of magnitude higher than α-Fe at 550 ºC). Also, negative activation energy is given which is derived from the solubility behaviour (solubility decreases with temperature). These

properties make these materials particularly attractive to be used as membranes for gas separators in fusion, providing efficient tritium permeation but also minimizing gas absorbance at the operating temperatures. However, one must be aware that permeability data has been deduced from experimental solubility and diffusivity taken from separate references which, in some cases, were obtained under very different conditions. For example, Steward uses vanadium solubility data of Veleckis and Edwards obtained from 246 to 554 ºC but diffusivity measurements from Volk & Alefeld in the narrower range from -20 to 340 ºC. Attention should be paid to the remarkable discrepancy which exists between calculated and experimentally obtained values as shown in figure 3.
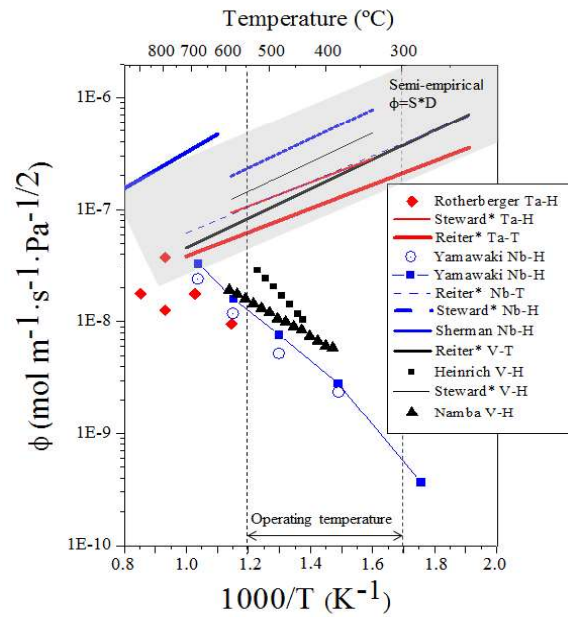

Fig. 3. Literature review for H permeability in V, Nb and Ta. Shaded area indicates calculated values. * Undetermined temperature range validity/extrapolated.

3. Experimental results

3.1 Permeation under ideal conditions

Results for 100 mbar deuterium permeation through V, Nb, and Ta are given in figure 4. A positive Arrhenius activation energy is observed for all three materials, as well as permeability values between 2-3 orders of magnitude below semi-empirical predictions at 500 ºC.

The equations relating the permeability of each material variation with the temperature are:

$$\phi_V \ (mol/m \cdot s \cdot Pa^{0.5}) = 6.0E-3 \cdot \exp(-11798/T)$$

$$\phi_{Nb} (mol/m \cdot s \cdot Pa^{0.5}) = 0.5 \cdot \exp(-16690/T)$$

$$\phi_{Ta} \ (mol/m \cdot s \cdot Pa^{0.5}) = 2.9E-2 \cdot \exp(-13187/T)$$
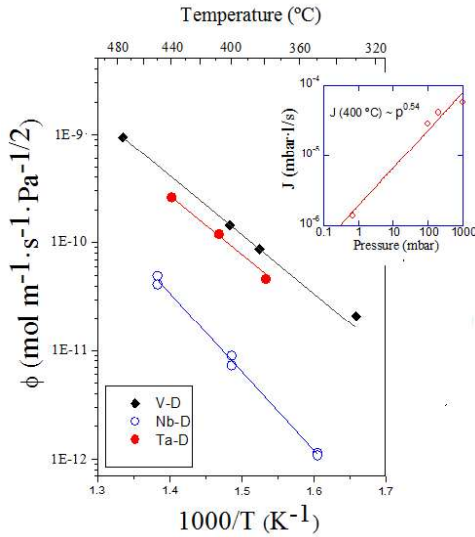
Fig. 4. Experimental deuterium permeabilities through V, Ta, and Nb (driving pressure ~ 100 mbar). Inset: Permeated flux as a function of pressure for V at 400 ºC.

However, these results are in the order of most of the experimentally obtained values at the same temperature and regardless the pressure range considered. Permeation tests at different pressures for V in figure 4 show half-power flux dependence with pressure. This indicates diffusion limited permeation regime for this material, as expected above 10 Pa according to existing studies [16].

3.2 Permeation under realistic conditions

Additional tests were carried out for vanadium sample under deliberately relaxed cleaning conditions, the usual preliminary annealing in vacuum being omitted. The aim is two-fold: on the one hand, evaluate the real tritium permeation capability which must be expected under fusion operating conditions, and on the other hand address the experimental difficulties related to surface condition and which probably are responsible for the large dispersion of data.

Figure 5 shows permeability results as a function of inverse temperature before and after different treatments. Comparison with results obtained during ideal conditions and with examples taken from the literature is provided.
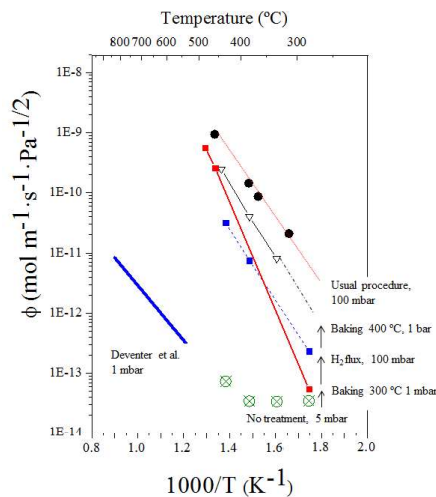

Fig. 5. Surface condition effect on D-V permeability.

The deuterium permeability of the sample "as mounted" shows two different trends (green symbol in the plot). The slope at above ~ 400 ºC is in excellent agreement with permeability data reported by Deventer at al. for a sample for which a thick surface layer containing large amounts of carbon and oxygen was found. [17]. However, a different limiting mechanism is observed at lower temperatures. Permeation tests as a function of temperature were repeated after sample heating in high vacuum up to 300 ºC for ~ 60 h (red line). A significant increase on the permeability is observed. Further sample surface cleaning *in situ* was intended by introducing a H_2 purge gas flow at 400 ºC in the vacuum system as a reducing agent (blue line). Similar results, with increased permeation at lower temperatures, were obtained. Finally, new baking at 400 ºC for ~15 h was carried out. New measurements performed at 1 bar quadruplicate previous values, while sample for which usual cleaning procedure was carried out shows x3 higher permeation values, with similar activation energy. According to this simple test, native oxides produced at room temperature reduce in about 4 orders of magnitude the permeation rate, what might be unacceptable for pragmatic purposes. Results also indicate that annealing in vacuum at 300 ºC mostly prevents this effect, in agreement with the vanadium oxide decomposition at 290 ºC given by Kiss et al. [18].

4. Discussion

Very limited experimental data for H isotope permeation in materials of group V have been published. Moreover, inconsistent results are obtained even for similar pressures and temperatures. The experimental difficulties, and the by no means simple task of avoiding surface effects are most probably the primary reasons, both related with the high reactivity of this class of materials. Many of the few published experimental works in this topic highlight and address the difficulty for obtaining oxygen-free surfaces. Sputter etching method has been suggested to minimize surface influence [19, 20] giving rise to varying results which are still well below theoretical predictions. For the here presented measurements, steps were taken in order to avoid surface effects. The ~ $p^{1/2}$ dependence for the permeated flux was obtained at Ciemat for pressures from 0.7 to 1000 mbar is indicative of low surface influence, yet the existence of surface effects cannot be completely ruled out. Despite dispersion, and considering all three materials without distinction, a general trend is observed for data collected in figure 3. The slope of the Arrhenius plot decreases with temperature, hence different mechanisms seem to dominate H isotope permeation depending on the temperature range. The only experimental evidence for negative activation energy was obtained by Sherman & Birnbaum [21] under high temperature (> 636 ºC) and carefully controlled oxidation conditions. However, data acquired at lower temperatures gradually turned to an opposite temperature dependence. The change was

reported as being reversible, what indicates a possible modification in the permeation mechanism rather than surface effect derived from surface reduction-oxidation. The data obtained in this work, with activations energies ~ 100 kJ/mol, is undoubtedly in agreement with this tendency.

The significant and general deviation of experiments from the expected values should be consequence first of the extrapolation of the calculated values to an inadequate range of temperatures and second the difficulty for avoiding surface effects. One must be aware not only of a notable reduction over the expected permeation values but also a further reduction of several orders of magnitude when extremely clean surface conditions are not met. Similar deuterium permeability as for vanadium before any treatment has been observed for intentionally oxidized 316 stainless steel [22], what should be taken into account when selecting materials for practical applications. Candidate materials should be tested under similar and as close as possible to operating conditions.

5. Conclusions

Deuterium permeability through Nb, V, and Ta was measured in the temperature range between ~300-500 ºC. Comparison with existent data suggests a complex dependence with temperature. Although it is evident that further analysis and experiments in a wider range of pressures and temperatures should be considered to fully characterize H isotope permeability in these materials, it is clear that the use of traditionally accepted values should be avoided. Furthermore, special attention should be paid to surface oxidation in these materials for practical applications, given the permeability reduction of more than 3 orders of magnitude observed at ~ 450 ºC due to the presence of native oxides formed at room temperature, and their high stability.

Acknowledgments

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