



# The hydrogen permeation behaviour of aluminised coated martensitic steels under gaseous hydrogen, liquid Pb–17Li/hydrogen and cyclic tensile load

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## Abstract

This paper describes the results of in-situ hydrogen permeation measurements of aluminised martensitic steels (F82H-mod. and MANET) under gaseous hydrogen and liquid Pb–17Li/hydrogen while being subjected to a cyclic tensile load. The results are presented in terms of the permeation reduction factor (PRF) of the coating. The vacuum plasma sprayed (VPS) coated specimens exhibited only a moderate PRF when tested under gaseous hydrogen (in comparison to previously reported data) but an even lower PRF when tested under liquid Pb–17Li/hydrogen. In particular, the coated MANET tube exhibited an increasing permeation rate with time for sequential measurements carried out at 830 K, which was attributed to the effect of wetting of the surface by the Pb–17Li. Although thermodynamic calculations have indicated that the aluminide coating should form alumina down to very low aluminium contents ( $x_{Al} = 0.0133$  in oxygen-saturated Pb–17Li at 773 K), they also show that the thermodynamically favoured product is  $LiAlO_2$ . © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Current designs of the European water-cooled Pb–17Li blanket [1] envisage the use of permeation barriers as a means of overcoming the high tritium permeation rates exhibited by structural martensitic steels [2–5]. These barriers should not only hinder the permeation flux but also have sufficient adhesion to the substrate, be chemically stable and not deteriorate under thermomechanical cycling. Although many coatings have been proposed, the aluminium-based coatings [6,7] appear the most promising types of barrier currently available to satisfy these requirements. Some indications of the cracking resistance of aluminide coatings have been obtained by mechanical testing on coated tensile specimens [8]. However, it was considered imperative to directly measure the permeability of any structural material/coating system under cyclic loads and in con-

tact with Pb–17Li [9,10] to obtain realistic permeation reduction factors (PRF).

The base materials to be coated are the martensitic steels F82H-mod. and MANET (heat No. 51482). F82H-mod. was chosen as the coating qualification base material, whereas MANET was used for the cyclic tests due to its availability in the form of tubes. This paper describes the results of in situ hydrogen permeation measurements of vacuum plasma sprayed (VPS) aluminised martensitic steels (F82H-mod. and MANET) under gaseous hydrogen and liquid Pb–17Li/hydrogen while being subjected to a cyclic tensile load. The results are interpreted with regard to the expected thermodynamic stabilities of the coating/liquid metal system.

## 2. Experimental

### 2.1. Materials

The base materials to be coated were the martensitic steels F82H-mod. and MANET (heat No. 51482). The F82H-mod. specimens were discs 48 mm in diameter and

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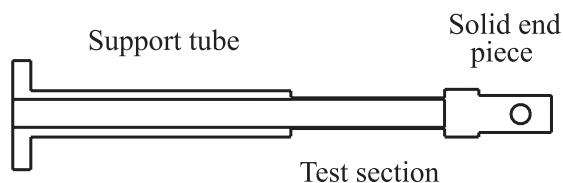


Fig. 1. Schematic diagram of the MANET test assembly.

0.5 mm in thickness, while the MANET test section consisted of a MANET tube (24 mm in outer diameter, 1 mm in wall thickness and 100 mm in length). This tube was welded, at one end, to a 6 mm thick-walled MANET II tube (machined from a solid plate, heat No. 50761) with an ultra-high vacuum (UHV) flange (SS 304) for connection to the rest of the UHV system and, at the other end, to a solid MANET II end piece for attachment to the Instron testing machine, to form the MANET test assembly (Fig. 1).

The VPS deposition of aluminium was carried out in a VPS installation supplied by Plasma Technik, using an aluminium powder (Metco Al 54 supplied by Metco Spa). The VPS parameters used to produce the aluminium coatings were the same as previously described [11]. The whole of the external part of the MANET test assembly was covered in a uniform VPS aluminium layer from the bottom of the solid end piece to within a few millimetres of the welded flange [12].

A specific heat treatment is necessary to produce a fully martensitic structure with an optimum balance of mechanical properties for each of the base steels used in this study.

For MANET, the treatment is  
1348 K/30 min, fast cool + 1023 K/2 h,

whereas, for F82H-mod., it is  
1313 K/30 min, fast cool + 1023 K/1 h.

This heat treatment procedure was also used to transform the VPS aluminium layer into a low aluminium-containing aluminide coating [13].

## 2.2. Apparatus and testing procedure

The method chosen for the current investigation was a gas-phase technique, previously described in detail for disc specimens [14]. For the cyclic tests on the tubular specimens, a specific apparatus was designed and built from standard UHV components together with some specially fabricated all-steel parts (SS 304) [9]. Following the initial proving tests of as-received and oxidised MANET [9,10], the VPS aluminide-coated tubular specimen of similar geometry was studied.

The procedure for the investigation on tubular specimens was as follows. The test specimen was heated

stepwise under high vacuum  $<10^{-6}$  Pa to 400 K to degas both the specimen and the 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. This pressure was then maintained constant by using the output from a second Baratron (range – 133.3 kPa) to control hydrogen inlet via an electromagnetic valve. 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 signal from the Baratron measuring the pressure rise due to the permeating hydrogen, together with the thermocouple outputs, was 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. Repeating the experiment at various temperatures between 520 and 873 K gave rise to the temperature dependence of the permeation flux.

The Instron testing machine model 6025 was operated under load control. A tensile load was applied in a triangular loading cycle (2 min/cycle) from zero to a maximum, then back to zero. The maximum load used for any test was 312 MPa, which corresponds to a maximum of 45% of the UTS of the steel depending on the test temperature.

## 3. Results and discussion

### 3.1. Results for aluminised F82H

The results of the VPS coated F82H-mod. disc are depicted in Fig. 2, where it can be seen that they do not follow the expected Arrhenius form. Previous results for aluminide-coated MANET have yielded permeation

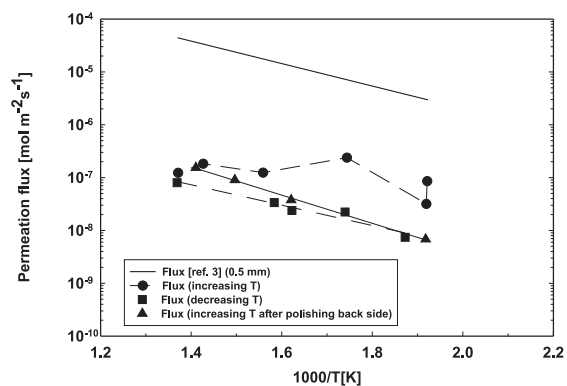


Fig. 2. Permeation rate of hydrogen through VPS aluminide-coated F82H-mod. specimen. The high-pressure side was 103 kPa.

fluxes either parallel to or greater than the slope of the uncoated steel. The results obtained for the coated F82H-mod. disc show an initial tendency for a slope parallel to that of the uncoated steel (up to 573 K), followed by a practically horizontal section up to 743 K, indicating possible oxidation of the specimen. This oxidation process effectively reaches a limit at around 743 K in that no further reduction in permeation fluxes was observed. Then the specimen was cooled down, with re-measuring at various points during the cooling process.

In order to determine whether the oxidation occurred on the deposited side of the specimen or on the reverse (non-deposited) side, the specimen was extracted from the permeation rig and the non-coated 'reverse side' mechanically polished. A new set of measurements was then made in which, as can be seen from the final curve in Fig. 2, most of the reduction was due to the oxidation of the front, coated side rather than the non-deposited side. The permeation reduction factor observed for this coating was approximately 500 at 623 K.

### 3.2. Results for aluminised MANET tube under pure hydrogen gas

The results of the hydrogen gas permeation experiments are depicted graphically as an Arrhenius plot of the permeation flux (Fig. 3). The measurements for the 'as-received' MANET were taken using an uncoated tube in the same installation and the value obtained agreed very well with the reported literature value for MANET II [2].

Fig. 3 shows some interesting features. Firstly, as the experiment progressed with time, no significant changes are observed between the initial set of measurements (1st series) and later ones. This indicates that no significant changes occurred at the surface of the tube, which could have effected the permeation barrier efficiency of the

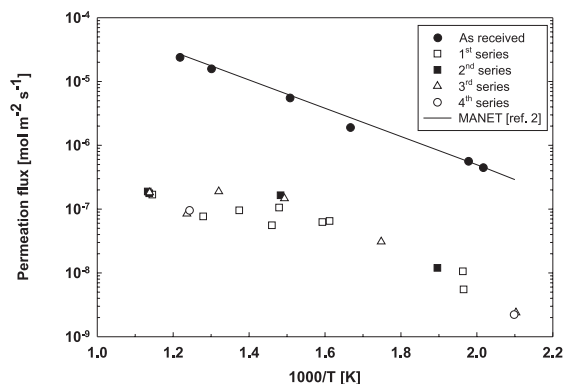


Fig. 3. Permeation rate of hydrogen through VPS coated MANET under hydrogen during heating/cooling cycles. The upstream hydrogen pressure was 100 kPa.

coating. This implies that the coating was stable to repeated temperature changes in the range of 479–878 K. Secondly, it should be noted that a flattening of the curves is evident for temperatures above 723 K. This we attribute to the difficulty in correctly assigning a temperature to the surface of the tubular test section. As it was impossible to physically attach thermocouples to the surface of the tube (as this would have damaged the coating), a bundle of four thermocouples (covering the length of the test section) was placed parallel and as close to the test section as possible and held in place with wire fittings. The method of assigning the temperature of the test section consisted of fitting a curve to the temperature data obtained from the four thermocouples. This may have led to an overestimation of the true temperature of the test section, so flattening the curve. (Note that this is not seen in the case of the uncoated 'as-received' test section because the thermocouples could be firmly attached.) The obtained PRF values range from 117 (523 K) to 44 (723 K).

### 3.3. Results for aluminised MANET tube under liquid Pb–17Li/hydrogen

Following the completion of the tests in pure hydrogen gas, the apparatus was dismantled and a circular crucible, with an attached bubbling tube, welded to the solid base of the test assembly. Argon gas was flushed through the inner volume of the test section during the welding procedure to prevent any oxidation of the inner surfaces. Once attached, the crucible was filled with Pb–17Li in an argon-filled glove box and a thermocouple inserted in a stainless steel thermocouple pocket immersed in the Pb–17Li. The apparatus was then re-assembled with the crucible bubbling tube attached to the hydrogen inlet of the apparatus in such a way as to permit hydrogen bubbling through the Pb–17Li.

Permeation tests under Pb–17Li and hydrogen were then started with a hydrogen pressure of 100 kPa. The first series of measurements was started at a low temperature around 543 K, and the test section temperature was increased step-wise to a maximum of 873 K. This data series, shown in Fig. 4 as '1st series', clearly shows that at 830 K (which was maintained for 12 days), an increase in the permeation flux with time was observed. Moreover, this increase in the permeation flux remained when the test section was cooled step-wise, measuring the permeation rate at intervals. We have postulated that the increase in the permeating flux was due to a reaction of the surface of the coating with the liquid Pb–17Li. Further heating and measuring of the test section showed no additional change.

In addition, Fig. 4 clearly shows that there was minimal influence of cyclic loads, corresponding to 40% of the UTS of MANET, on the permeation flux. The measured PRF of the VPS aluminide coating was

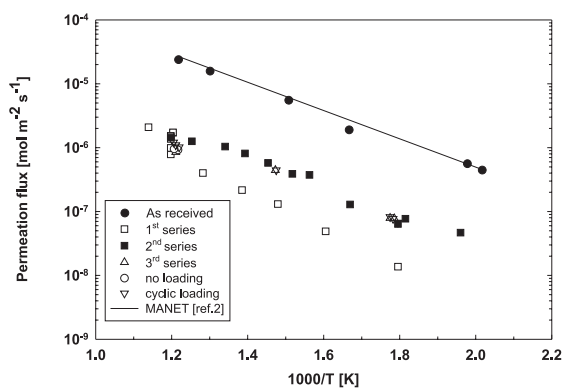


Fig. 4. Permeation rate of hydrogen through VPS coated MANET under liquid Pb–17Li/hydrogen during heating/cooling cycles. The upstream hydrogen pressure was 100 kPa.

between 15 and 20 depending on the temperature. Further cyclic load tests using loads corresponding to a maximum of up to 45% of the UTS of MANET showed similar results, i.e., an almost negligible effect on the PRF. Specific tests were performed to investigate if there was a significant difference in the temperature of the support tube under the experimental conditions of gaseous hydrogen and liquid Pb–17Li/hydrogen. In particular, these tests were to assess if the increased permeation rate under liquid Pb–17Li occurred through a noticeable increase through the support tube or as a result of increased permeation through the test section.

The temperature profile of the support tube was measured by thermocouples brazed to the outer surface at known intervals above the welding between the test section and the thick-walled support. Tests were performed using an uncoated MANET tube identical in all respects to that used previously. The general shape of the temperature profiles is similar in both cases, which is to be expected, as the major heat-transfer mechanisms are conduction and convection. The only significant difference arises as a consequence of the level of the liquid Pb–17Li. For a given test-section temperature, the tests under liquid Pb–17Li effectively extend the constant temperature region 0.5 cm above the level of the weld.

For example, taking the tests at 673 K, due to the longer constant zone temperature under liquid Pb–17Li, the support tube effectively exhibits a 20–25 K higher temperature than that for a similar test under hydrogen gas. This difference effectively holds for the full range of temperatures tested and as such would form an insignificant change in the overall permeation.

Only a negligible contribution to the total permeation flux can be envisaged to originate from the support section. This is because the whole test assembly was coated at the same time; the support section had a wall thickness of 6 mm (in comparison to the 1 mm test

section thickness) and the temperature of the support section was lower than that of the test section and decreased towards the upper flange. Therefore, the observed increase in permeation rate with time at 830 K (maintained constant for 12 days) can only be attributed to an increased flux from the area in contact with the liquid Pb–17Li. During the testing, we attributed this phenomenon to the effect of wetting of the surface by the Pb–17Li because, although thermodynamic calculations have indicated that the aluminide coating should form alumina down to very low aluminium contents ( $x_{Al} = 0.0133$  in oxygen-saturated Pb–17Li at 773 K) [15,16], they also show that the thermodynamically favoured product is  $LiAlO_2$  [15,16].

Despite previous results indicating good bulk corrosion resistance of aluminide coatings in flowing Pb–17Li at 723 K [17], it would be premature to assume that no surface interaction occurs. Indeed, a high-temperature (1023 K) study of the stability of alumina in liquid Pb–17Li indicated the transformation of  $Al_2O_3$  into  $LiAlO_2$  and  $LiAl_5O_8$  [18]. Further work is needed to elucidate any possible surface reaction between the coatings and the liquid Pb–17Li.

#### 4. Conclusions

The observed effectiveness of VPS aluminide coating in reducing the  $H_2$  permeation flux of F82H-mod. martensitic steel (PRF = 500 at 623 K) has been found to be lower than that previously observed for coated MANET [11].

Gas permeation tests of coated MANET tubes under pure  $H_2$  yielded lower PRF (117 at 523 K and 44 at 723 K) than observed for F82H-mod. and previous MANET disc specimens [11], and an even lower PRF (approximately 20, from 523 to 723 K) was observed after maintaining the test section under liquid Pb–17Li at 830 K for 12 days.

We attribute the low PRF of the coating under liquid Pb–17Li/hydrogen to the wetting of the surface by the Pb–17Li, probably indicating the reaction of the surface  $Al_2O_3$  with the liquid Pb–17Li to form  $LiAlO_2$ . The observed reduction in the PRF of the VPS coating under liquid Pb–17Li raises doubts as to the suitability of any tritium permeation barrier based on aluminium-containing coatings with alumina at the surface for use in contact with liquid Pb–17Li.

Cyclic loading tests, using a triangular wave form, a 2 min cycling rate and a load corresponding to a UTS of around 40–45% of MANET II, showed minimal effects on the measured PRF. This may be due in part to the initial low PRF measured in that any further defects produced by cyclic load have only a small effect.

In the light of the small PRF measured under liquid Pb–17Li, we recommend that the whole liquid Pb–17Li

tritium cycle be re-assessed and, if possible, modified to design around the need to incorporate tritium permeation barriers of any type.

### Acknowledgements

We would like to thank Mr A. Crippa for producing the VPS aluminium coatings used in this study.

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