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Corrosion behaviour of Al based tritium permeation barriers in flowing Pb–17Li

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Abstract

Tritium permeation barriers on low-activation steels are required in fusion technology in order to reduce the tritium permeation rate through the structural material into the cooling water system. Al–Fe layers with alumina on top can fulfil the required reduction rate. Three techniques were selected to produce such a multi-layered coating system: chemical vapour deposition (CVD) by CEA, hot-dip aluminising (HDA) by FZK and vacuum plasma spraying (VPS) by JRC Ispra. A sufficient corrosion resistance against Pb–17Li attack is also required for the coating. Therefore, the corrosion behaviour of these three coatings on ferritic–martensitic steels was studied in the PICOLO loop of FZK in flowing Pb–17Li at 480 °C up to 10 000 h. Corrosion effects could not be found on HDA and VPS coated specimens even up to the longest time of exposure. The total thickness of the two-layered system remained unchanged at around 130 μm for all examined HDA and VPS specimens. In contrast to this, corrosion effects could be inspected on CVD coated specimens.

1. Introduction

In a water-cooled liquid lead–lithium blanket concept, the tritium permeation from the breeder zone through the structural material into the cooling water circuit must be minimised to a level less than 1 g/d [1]. This can be realised by coating the structural material with a suitable layer, a so-called tritium permeation barrier (TPB).

On the basis of the results obtained in the European fusion technology programme 1996–1998, Al–Fe base coatings with alumina on the surface have been selected as the reference material for TPB [2–5]. A large number of methods are available to deposit Al–Fe layers but previous results concerning fabrication and/or qualification tests led to a selection of three techniques: chemical vapour deposition (CVD) by CEA, hot-dip aluminising (HDA) by FZK and vacuum plasma spray (VPS) technique by JRC Ispra. Several qualification tests are strongly required for the final selection of the reference process and among others the corrosion resistance of the coatings in a Pb–17Li melt is of great interest.

2. Experimental

The Japanese steel F82H-mod. was aluminised by means of CVD and VPS methods. MANET II steel was coated by HDA process. Preparation and characterisation of CVD, HDA and VPS were described elsewhere [2,6–8]. Cylindrical, coated corrosion test specimens had dimensions of 8 mm in diameter and around 35 mm in length. They had threads on both ends, thus they could be mounted to a stack of 12 pieces fixed in the central position of the test section tube.

For corrosion measurements on coated materials in flowing Pb–17Li at 480 °C, the test loop PICOLO was used, which is described in [9]. The chosen exposure times are given in Table 1 for the different coated specimens. Post-test analysis consisted of metallurgical

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Table 1
Exposure times for different coated specimens in flowing Pb–17Li at 480 °C

Base material	Coating procedure	Exposure time (h)
MANET II	HDA	1004, 2034, 3022, 4046, 10 000
F82H-mod.	CVD	4982, 7700, 10 000
F82H-mod.	VPS	3022, 8710, 10 000

examination and EDX line scan analysis on the cross sections of the exposed specimens.

3. Results

3.1. Vacuum plasma spraying

Two layers, which are separated by a band of pores, can be observed on the unexposed VPS specimen. The external layer shows a rough surface and a thickness variation between 20 and 40 μm. The internal layer seems to be very homogeneous in thickness of around 70 μm and shows good adherence to the basic material.

An EDX depth profile was measured on the cross section of the unexposed VPS specimen. With increasing depth the Al content decreases from 20 wt% to zero, the content of the steel elements Fe and Cr increases with increasing depth up to the steel composition. The external layer consists of the AlFe phase, the internal layer of α-Fe(Al).

The line scan profile of unclean VPS specimens after 8710 h exposure has revealed that solidified Pb–17Li has interspersed into the external layer. The internal layer is not affected by the liquid eutectic melt and remains constant at around 70 μm and the phase found corresponds to α-Fe(Al). The thickness of the external layer (AlFe phase) is only around 10 μm after exposure.

Two VPS specimens were exposed up to 10 000 h in flowing Pb–17Li. SE images show that the sample surface appeared to be rather rough (see Fig. 1). In the external layer near to the sample surface a few pores can be observed. The external layer has a variable thickness between 5 and 40 μm. Solidified eutectic alloy has diffused into the cavities of the surface. The internal layer remained unchanged against the corrosion attack. Thickness of around 70 μm, homogeneous structure and good adhesion to the structural material do not shift compared to the unexposed VPS specimen. The external layer corresponds to the composition of AlFe phase and the internal layer to that of α-Fe(Al).

A comparison of the Al concentrations obtained for the different exposure times revealed: In the external layer the measured Al concentration varied between 18 and 25 wt% which corresponds to the AlFe phase. The Al concentration in one 10 000 h VPS specimen was higher than in the unexposed specimen, the Al concentration in the other 10 000 h VPS specimen was lower. Beneath the porous band, the Al concentration decreases from around 17 wt% down to zero. This composition corresponds to α-Fe(Al). The lowest value of Al in the internal layer was measured after the exposure of 8710 h, while the concentrations in the two specimens after 10 000 h of exposure were exactly the same as in the unexposed material. There is, however, no systematic influence of exposure time on the composition of the layers. The difference in the Al concentrations measured is not a corrosion effect but it seems that the VPS coating process is not yet 100% reproducible in the laboratory.

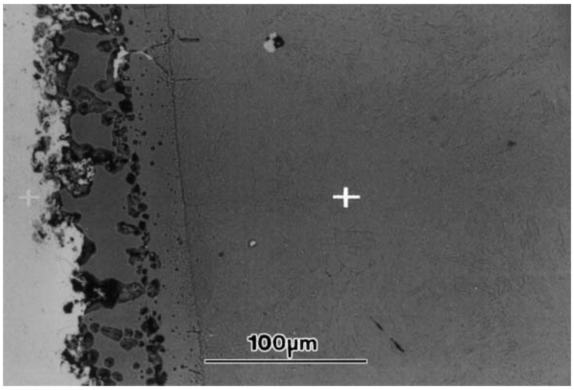

Fig. 1. SE image of the cross section shows the AlFe phase, a porous band, the α-Fe(Al) phase and the steel F82H-mod (from left to right) of a VPS specimen after 10 000 h.

3.2. Hot-dip aluminising

The samples exposed between 1000 and 10 000 h did not show any visible damage of the surface layers. These observations are in agreement with results obtained previously [10,11].

A metallurgical cross section of an exposed HDA MANET specimen after 4000 h of exposure showed solidified Pb–17Li on top of a two-layered system on the sample surface. The external layer (about 25 μm in thickness) is separated from the internal layer (about 105 μm) by a band of pores whose formation is due to the Kirkendall effect. The transition of the internal layer to the steel looks very sharp.

An SE image of an HDA specimen exposed for 10 000 h showing solidified Pb–17Li are given in Fig. 2. The measured EDX spectra of this specimen revealed a continuous decrease of the Al concentration from the surface to the bulk material. In the near surface region the concentration of Al is around 40 wt%. The existence of the compound Al_2O_3 detected by low angle XRD analysis on original material on the surface [7] is probably responsible for this relatively high value of Al. Subsequently, the Al content decreases from around

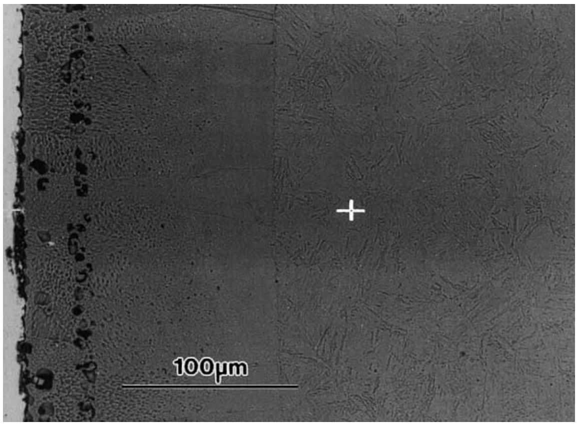

Fig. 2. The two phases AlFe and α-Fe(Al) separated by pores are measured by means of EDX on the steel MANET II in the cross section of a HDA specimen after 10 000 h.

18 wt% down to zero. This corresponds to the α-Fe(Al) phase. The concentration of the steel components Fe and Cr increases from the surface to the steel side. The amount of Mn (also a steel component) remains more or less constant.

3.3. Chemical vapour deposition

F82H-mod. steel specimens were coated with a layer system of AlFe and Al_2O_3 by means of CVD at CEA Grenoble. EDX analysis was performed on the cross section of an unexposed specimen. The composition of the coating near the surface is about 20 Al, 65 Fe and 4 Cr, in wt%. The Al profile decreases continuously from the surface to the substrate and is detected at a distance of about 13 µm from the surface. The external layer corresponds to the AlFe phase and has a thickness of approximately 7 µm. In the 6 µm thick internal layer the Al content decreases from about 18 wt% to zero which fits well to α-Fe(Al) phase.

The concentration profiles of the different elements recorded on the CVD specimen after 4982 h correspond to the results seen for the non-exposed specimen. The amounts of Fe and Cr increase with increasing depth whereby the amount of Al decreases. The internal layer consists of the α-Fe(Al) phase and reaches a thickness of around 6 µm. The AlFe phase can be found in the external layer. The detected thickness is about 4 µm for this phase. The oxygen content throughout the measured area was below the detectable limit.

Two CVD specimens were exposed to Pb–17Li up to 10 000 h, but the results obtained are not identical. Hence the results of the EDX spectra will be discussed for each specimen separately. The phases AlFe and α-Fe(Al) were analysed by EDX line scans on the first specimen. The concentrations of Fe, Al and Cr are comparable to the results achieved on the two other CVD specimens. The thickness of the internal phase is around 5 µm, that of the external phase only 2 µm.

The SE image of the second 10 000 h CVD specimen is given in Fig. 3. The concentration profiles of Fe and Cr still correspond to the other measured spectra: the content of these two elements increases with increasing depth over a distance of about 6 µm. These concentration profiles fit to the phases AlFe and α-Fe(Al). But the element Al can hardly be detected. Only a slight increase of the Al content in the near surface region was observed. The layer on the steel seems to be inhomogeneous but porous. The reason for the very low Al content in this layer could be a leaching effect of Al out of the layer into the Pb–17Li. The solubility of Al in the eutectic melt is around 2.5 magnitudes higher than for Fe [12].

The Al concentration profiles obtained on the CVD specimens are presented in one diagram for better comparison (see Fig. 4). It can be seen that increasing ex-

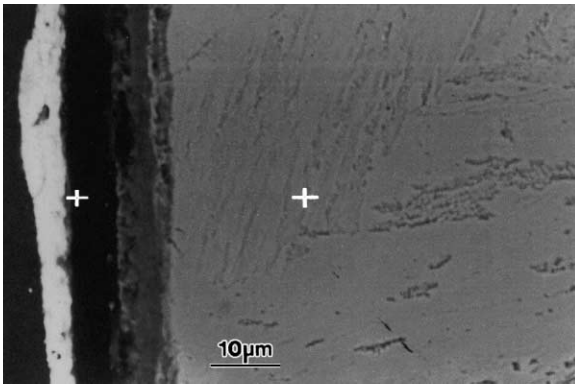

Fig. 3. A thin Al–Fe layer on F82H-mod. can be seen in a SE image made on a cross section of a CVD specimen after 10 000 h of exposure. The light layer on top (left side) is remaining Pb–17Li.

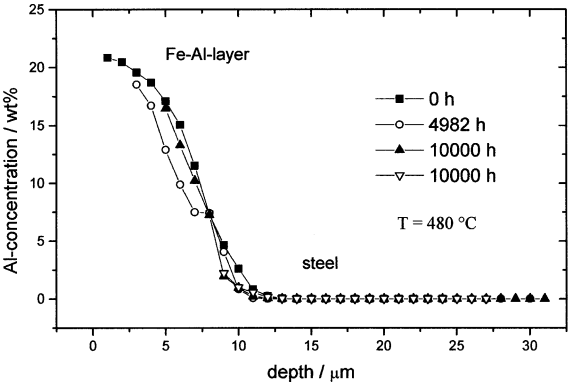

Fig. 4. Al concentration profiles obtained for the individual CVD specimens before and after exposure to Pb–17Li.

posure times influence the thickness and the Al concentration in the Al–Fe layer unfavourably. The overall thickness of the layer decreases from around 13 μm (value of the unexposed specimen) down to less than 6 μm after 10 000 h of exposure. The maximum Al content achieved is 21 wt% in the unexposed CVD specimen and only 2 wt% of Al can be detected after 10 000 h of exposure.

4. Discussion and conclusions

The corrosion behaviour of three Al–Fe coatings prepared by means of HDA, VPS and CVD on ferritic–martensitic steels was studied in the PICOLO loop in flowing Pb–17Li at 480 °C up to 10 000 h. The microstructure of the MANET II and F82H-mod. steels remained unchanged even up to 10 000 h exposure time at 480 °C. This is in agreement with the results obtained previously on bare MANET II and F82H-mod. materials which also showed no bulk effect [13,14].

In spite of the fact that the Al–Fe layers which were produced by means of HDA and VPS are not yet optimised with respect to the formation of reproducible and uniform thick layers, the corrosion resistance was demonstrated in flowing Pb–17Li at 480 °C up to 10 000 h. No systematic tendencies in the concentration profiles attributable to corrosion attack was observed. The coating procedure for both techniques is still in development which can lead to a varying Al concentration.

An interaction between CVD coated specimens and the eutectic melt could be clearly observed. With increasing exposure time the thickness and the concentration of Al in the Al–Fe layer decreased considerably. The Al–Fe phases formed are the same for all three coating methods. It is not obvious why the Al–Fe layers produced by means of CVD should not withstand a corrosion attack while the Al–Fe layers formed by HDA and VPS are resistant against Pb–17Li. One reason could be that the coating procedures by means of HDA and VPS include a high temperature heat treatment. During this process an alumina layer (the stable compound α-Al_2O_3) is formed on the surface [9] which protects the Al–Fe layer against corrosion attack of the melt. The stability of the alumina layer on the Al–Fe layer in Pb–17Li is in agreement with the thermodynamic data concerning the oxygen potential of the liquid alloy [15]. The CVD coating technique used here is a low temperature process ($T = 450$ °C). Therefore, only the γ-Al_2O_3 phase, which is thermodynamically less stable, can be formed during the coating procedure. This observation is in agreement with the Ostwald's rule of successive transformation (law of stages) which says that if a compound forms different phases firstly the phase is formed with the highest energy. Step by step this phase can be transformed into a lower energy phase. But not only the thermodynamic is responsible for this transformation but also the kinetics.

The low temperature CVD heat treatment has resulted in a reduced stability of the aluminide layer in the eutectic melt compared to HDA and VPS coatings. The formation of an α-Al_2O_3 layer by means of CVD on an Al–Fe phase without the use of an additional high temperature heat treatment is still a problem. Another important point is the thickness of the layers. Those formed by HDA and VPS techniques are around 10 times thicker than the layers produced by CVD. In the case of CVD-produced layers corrosion attack was much more dramatic than in the case of the thick Al–Fe layers formed by HDA and VPS.

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