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An overview on tritium permeation barrier development for WCLL blanket concept

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Abstract

The reduction of tritium permeation through blanket structural materials and cooling tubes has to be carefully evaluated to minimise radiological hazards. A strong effort has been made in the past to select the best technological solution for the realisation of tritium permeation barriers (TPB) on complex structures not directly accessible after the completion of the manufacturing process. The best solution was identified in aluminium rich coatings, which form Al_2O_3 at their surface. Two technologies were selected as reference for the realisation of coating in the WCLL blanket concept: the chemical vapour deposition (CVD) process developed on laboratory scale by CEA, and the hot dipping (HD) process developed by FZK. The results obtained during three years of tests on CVD and HD coated specimens in gas and liquid metal phase are summarised and discussed.

1. Introduction

To guarantee adequate radiological protection of personnel and populations the design of the water cooled lithium–lead (WCLL) blanket for the DEMO fusion reactor required the deposition of permeation barriers on the cooling tubes and blanket module surface.

Aluminium rich coatings, which form Al_2O_3 at their surface were selected as reference coatings in the framework of the European Fusion Technology Program [1]. Aluminised coatings can be obtained by several deposition techniques; the most promising are hot dipping (HD) and chemical vapour deposition (CVD).

The aim of the herein-reported experimental campaign was to investigate the efficiency of aluminised coatings as TPB by performing comparative tests between coated samples and bare ones, and to verify if the results obtained in the past on similar specimens were due to unexpected problems during the manufacturing process or to inadequacy of coating technique on tubular geometry. The experiments were carried out with the 'Vivaldi' device described elsewhere [2].

2. Experimental

2.1. Materials

Twelve tubular specimens coated with alumina were tested. Six specimens were coated by FZK using the hot dipping technique, while the other six were coated at CEA-Grenoble using the CVD procedure. The base metal was the low activation Eurofer 97 martensitic steel. The specimens, in form of hollow cylinder 10 mm in external diameter and 1 mm thickness, with a length of 250 mm, were prepared by an external manufacturer and delivered to FZK and CEA by ENEA Brasimone. All the specimens were leak tested before delivery.

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2.2. Experimental set up and procedure

Schematically the Vivaldi installation can be divided into:

- the permeation chamber containing two tubular specimens;
- UHV lines for gas supply, high vacuum pumping and measurements;
- electric heating systems for tests and degas.

The two permeation specimens, the coated and the bare one, were placed in the permeation chamber to carry out comparative tests in the same operating conditions, determining in a precise way the PRF (permeation reduction factor) of the coated sample.

Hydrogen gas at a known, fixed pressure was admitted to the permeation chamber and permeated through the samples, causing a pressure rise in the inner volume. To evaluate the permeation flux through specimens the inner volume was calibrated so that the pressure rise could be converted into an amount of gas in moles permeating per unit area of the sample. Simply by comparing the steady state fluxes in the coated and the bare specimen it was possible to evaluate the PRF.

Experiments in Pb–16Li eutectic alloy were performed charging the liquid metal in the permeation chamber from a crucible using a pressurisation technique. The liquid metal and permeation chamber temperatures were accurately controlled to prevent any kind of thermal stress on specimens. As the liquid metal requires some days to wet the specimen surface, and it has to be saturated with hydrogen, it was heated at 673 K producing a small continuous flow of hydrogen bubbling through the liquid for several days, with a mass flow rate of 10 N l/h.

After the permeation tests, coated specimens were extracted from the test section and cut to prepare samples for metallographic observations. Elemental analysis was performed too, when necessary, by means of the SEM-EDS (energy dispersive spectroscopy) system.

3. Results

3.1. Permeation tests

The permeation experimental campaign was started performing tests in the gas phase, in order to have a reference permeability value for both the coated and the bare specimens, and to establish the starting point on the basis of which to determine the effect of liquid metal on the reliability of the coating. The specimens were tested in sequence and compared, in terms of permeation behaviour, with the identical bare sample.

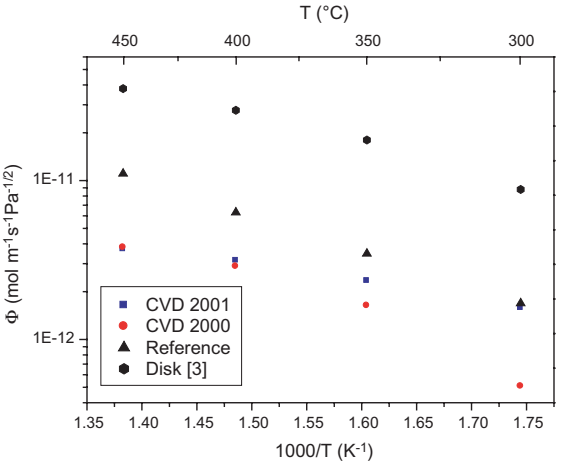

Fig. 1. Permeability of CVD coated samples compared with bare specimen and disk in gas phase [3].

In Fig. 1 are shown the Arrenhius plots of permeability for CVD coated specimens compared with the reference specimens. The behaviour of specimens produced in 2000 and 2001 is absolutely similar, confirming that the coating were produced using the same, probably not optimised, procedure. The activation energy for permeation in gas phase is 48 kJ/mol, close to the value of pure bare Eurofer [3], while in liquid metal it decreases to 39 kJ/mol. A moderate increase of the PRF is present in liquid metal. The similar behaviour of specimens produced at different times confirmed that the coating procedure was not adequate.

In the case of HD coated samples, three of them didn't show any permeation barrier effect, and it was not possible to measure the permeability. They were leak tested and demonstrated the presence of cracks. Since all the specimens were leak tested before the delivery, the defects appeared only after the coating.

The permeability of HD coated specimens is about 30 times lower with respect to the uncoated specimens. The values of permeability obtained at different temperatures can be well fitted to an Arrenhius plot, demonstrating a good stability of the coating. In Fig. 2 are reported the values of permeability in the gas phase, while in Fig. 3 are compared the permeabilities of CVD and HD coated samples in liquid metal phase.

In Table 1 the values of PRF determined comparing the steady state fluxes through the bare specimen and CVD and HD coated ones are reported. Also the PRFs obtained comparing the flux through a coated sample with that in a disk shaped sample [3], are reported.

No significant improvement of the deposition processes can be identified in terms of PRF for both techniques, as the experimental tests gave the same results on specimens produced at different times.

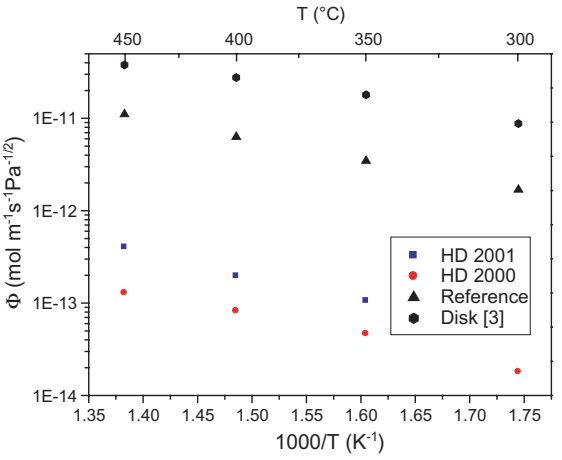

Fig. 2. Permeability of HD coated samples compared with bare specimen and disk in gas phase [3].

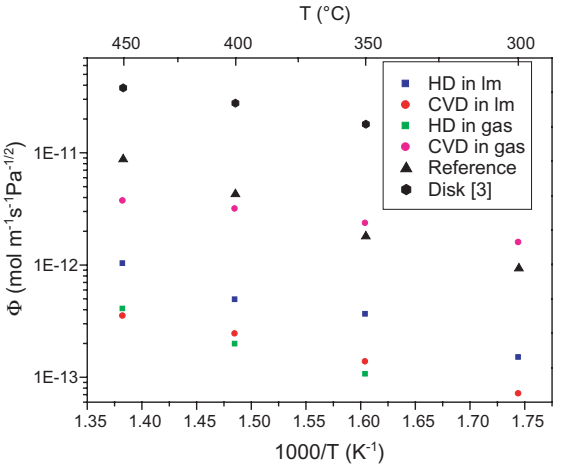

Fig. 3. Permeability of CVD and HD coated specimens in liquid metal phase compared with reference and gas phase results [3].

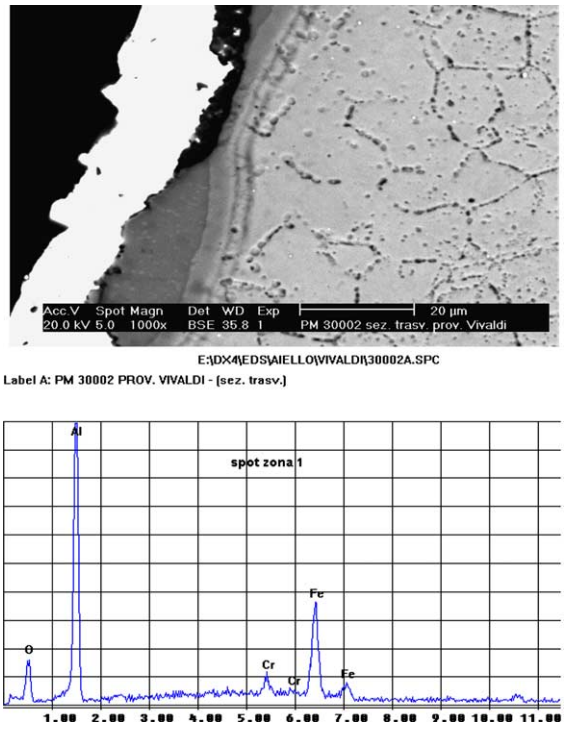

Fig. 4. CVD coated specimen transversal section and EDS.

3.2. Metallographic results

After extraction from the permeation chamber, the coated specimens were cutted to prepare transversal and longitudinal sections to be examined by SEM. Looking at the CVD coating section in Fig. 4, four different areas can be observed. The upper one, very thin, is the alumina coating. The second one is the FeAl phase, the third one is the α-Fe(Al) bulk, while the last one is the Eurofer bulk material. The alumina area is interrupted and the Fe–Al phase was partially removed by the liquid metal. Examining the composition of the damaged area with EDS this appears to be rich in aluminium. In the

Table 1
Permeability (in mol m^{-1} s^{-1} $Pa^{-1/2}$) in gas and liquid metal phase and PRF

T (°C)	CVD gas	CVD PbLi	HD gas	HD PbLi	Reference Eurofer	Disk Eurofer 97 [3]
300	6.23e–13	1.28e–13		1.49e–13	3.53e–12	8.79e–12
350	1.20e–13	2.34e–13	1.06e–13	2.81e–13	6.50e–12	1.80e–11
400	1.75e–12	3.34e–13	1.96e–13	4.91e–13	1.14e–11	2.77e–11
450	1.23e–12	4.35e–13	4.02e–13	1.14e–12	1.82e–11	3.79e–11
Mean PRF refer	9	8	32	17		
Mean PRF disk	25	20	98	45		

past the CVD coated specimens were tested only in gas phase because the low value of PRF suggested little value in any further test in liquid metal, and therefore a comparison between the past and the present results is not possible. In any case, the low value of PRF, especially in gas phase, is probably due to the limited surface of steel covered with a coating of good quality, considering that several separations between the coating and the substrate can be observed.

A comparison between the present and the past CVD coating is possible observing Fig. 5, in which the transversal section specimens produced in 2000 and 2001 are compared. Voids and separations between the bulk material and the coating are evident in both sections.

The coating on the cap of the HD coated specimen was found to be severally damaged after exposure to liquid metal. The liquid metal produced large separations, and the typical columnar structure of α-Fe(Al) is absent. A brittle intermetallic phase of Fe–Al can be observed in Fig. 6. As reported in [4] an incorrect thermal treatment of hot dipping alumina coated specimen makes it sensitive to corrosive attack in liquid lead–lithium.

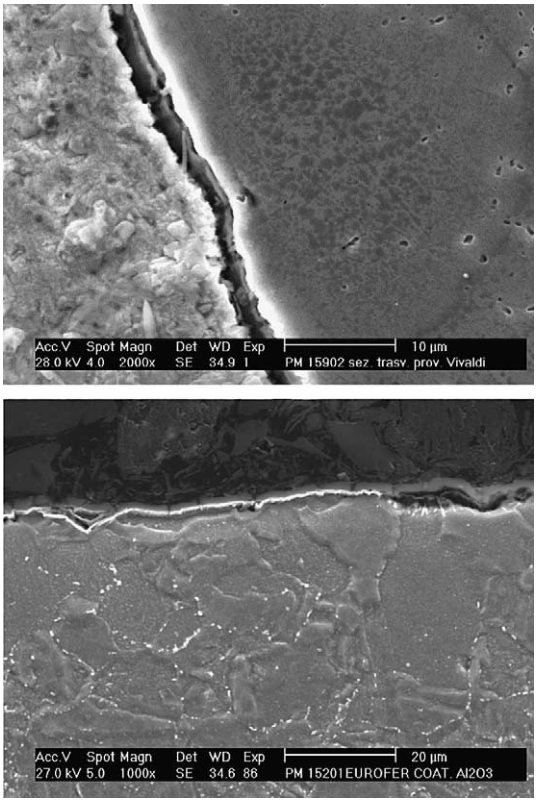

Fig. 5. Comparison between CVD 2000 and CVD 2001 coating micrograph.

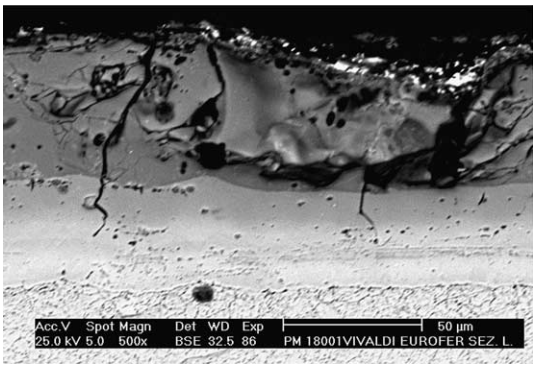

Fig. 6. Transversal section of HD coated specimen.

4. Discussion

The PRFs evaluated in gas phase for CVD and HD coated specimens in this experiment are lower than those found in literature [1] which were obtained from permeation through disc shaped samples coated in the same way. It has to be pointed out that two experimental campaigns were performed to verify if the obtained results were due to unexpected problems during fabrication or to unrecoverable deficiencies of the coating techniques when working on cylindrical geometry. For that reason manufacturers were requested to improve the quality of coatings.

When examining the results obtained in liquid metal phase by CVD coated specimens it is evident a low efficiency of the coating is probably due to unpredicted problems during the deposition phase that made the coating unstable in liquid metal. This is an unexpected phenomenon considering that CVD alumina coating was expected to be inert in Pb–16Li. The increase in the barrier effect in liquid metal could be explained based on the closure of small porosities on the surface, and a resulting increase in the surface not directly exposed to gas. This assumption is confirmed by the activation energy, that is almost the same of the bare specimen. In any case post test examinations confirmed the presence of large area on which the lead–lithium removed the coating. Probably several days are necessary for this action, and during this phase the permeated fluxes change. This effect is stronger at high temperatures, as shown by permeation plots. At the end of this phase, the permeated flux reach a final, constant, value. The poor quality coating had been removed and only a limited surface is still coated by good adherent alumina.

The HD coated specimens present a similar behaviour. The main result in this case is the presence of defects in the welded area, that seem to have been induced by the coating procedure. The defects were not present before the deposition of coating. Moreover one of the defected specimens was leak tested before mounting it in

Vivaldi. We can say that the defects are induced in a stressed area, like welds, but they are closed by aluminium that, during the specimens heating, is removed due to stress recovery.

In any case it can be assumed that no improvements were made to deposition processes, considering that the results and activation energy, are almost the same as obtained in the past and are very far from literature data on permeation through similar samples.

5. Conclusion

The results achieved in VIVALDI device appear unexpected, but show that at this stage the selected deposition processes have not yet reached technological maturity. The barrier effect is practically negligible considering the design prescription of 75, and the value of activation energy is not significantly different from that for the bare material. SEM analysis showed marked coating separations in different zones and in some points the metal surface was practically free of coating.

The HD process induced strong stresses in the welded area of specimens, that in some cases produce cracks.

The coatings are believed to have not correctly prepared, and do not represent an acceptable fabrication procedure.

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