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Corrosion Behaviour of Al based TPB in flowing Pb-17Li

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**Institut für Materialforschung
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Zusammenfassung

Korrosionsverhalten von tritiumpermeationshemmenden Schichten auf Aluminiumbasis in strömendem Pb-17Li

Das Korrosionsverhalten von drei unterschiedlich hergestellten Fe-Al Schichten auf ferritisch-martensitischen Stählen wurde im Flüssigmetallkreislauf „PICOLO“ in strömendem Pb-17Li bei 480 °C bei Einsatzzeiten bis zu 10000 h untersucht. Die Schichten wurden im FZK mittels HDA (Hot-Dip Aluminising), von CEA mittels CVD (Chemical Vapour Deposition) und von JRC Ispra mittels VPS (Vacuum Plasma Spraying) hergestellt.

Es konnte gezeigt werden, dass Schichten, die mittels HDA und VPS hergestellt worden sind, in strömendem Pb-17Li bei bis zu 10000 h keinen Korrosionsangriff aufzuweisen hatten. Dagegen konnte eine Wechselwirkung der CVD beschichteten Proben mit dem Flüssigmetall detektiert werden. Mit zunehmender Auslagerungsdauer nimmt die Dicke der Schicht und auch deren Aluminiumkonzentration in der Fe-Al-Schicht signifikant ab.

Abstract

The corrosion behaviour of three Fe-Al coatings prepared by means of chemical Vapour Deposition (CVD) by CEA, Hot-Dip Aluminising (HDA) by FZK and Vacuum Plasma Spraying (VPS) by IRC Ispra on ferritic-martensitic steels was studied in the PICOLO loop in flowing Pb-17Li at 480 °C for up to 10000 h.

In spite of the fact that the Fe-Al layers which were produced by means of HDA and VPS are not yet optimised with respect to the formation of reproducible uniform thick layers, the corrosion resistance could be demonstrated in flowing Pb-17Li at 480 °C up to 10000 h.

An interaction between CVD coated specimens and the eutectic melt was clearly observed. With increasing exposure time the thickness and the concentration of Al in the Fe-Al layer decreased considerably.

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1. Introduction

In a water-cooled liquid lead-lithium (WCLL) blanket concept, the tritium permeation from the breeder zone through the structural material into the cooling water circuit must be minimised for reasons of safety and economy. The tritium leakage from the breeder to the coolant must be reduced 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).

Several coating materials (e.g. TiC/TiN, W) and different coating techniques have been investigated [2-8]. On the basis of the results obtained in the European fusion technology programme 1996 – 1998, Fe-Al base coatings with alumina on the surface have been selected as the reference material for TPB [9-12].

A large number of methods are available to deposit Fe-Al 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. The preparation procedures and the characterisation of each coating were investigated by means of several analytical methods. The results were summarised in reports [9, 13-15]. Several qualification tests are strongly required for the final selection of the reference process [13]. These experimental tests include the measurement of the hydrogen permeation in gas phase and in the presence of Pb-17Li with and without mechanical stresses applied to the specimens. Self-healing tests in Pb-17Li are foreseen as well in order to investigate the in-situ formation of an alumina scale on the Fe_xAl_y layer. Irradiation experiments are also necessary and are planned beyond 2001. Compatibility studies in flowing Pb-17Li were performed on three different prepared coatings. The results obtained will be discussed in this paper.

2. Experimental

Low activation ferritic-martensitic steels are foreseen as structural material [17] for a common fusion reactor. Hence, such steels were used as base materials to investigate the different aluminide coatings. The Japanese steel F82H-mod. was aluminised by means of CVD and VPS. MANET II steel was coated by hot-dip aluminising process. Preparation and characterisation of CVD, hot-dip aluminising and VPS were described elsewhere [9, 13-15].

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.

CVD coating of F82H-mod. samples was performed by CEA Grenoble, France. JRC Ispra, Italy was responsible for coating the F82H-mod. by means of VPS. The MANET II specimens were aluminised by hot-dip aluminising process carried out in FZK Karlsruhe, Germany.

For corrosion measurements on coated materials in flowing Pb-17Li, the test loop PICOLO, which is described in [18], was used. The temperature in the test section was 480 °C, chosen exposure times are given in table 1 for the different coated specimens.

| Base Material | Coating procedure | Exposure time / h |
|----------------------|--------------------------|-------------------------------|
| MANET II | HDA | 1004, 2034, 3022, 4046, 10000 |
| F82H-mod. | CVD | 4982, 7700, 10000 |
| F82H-mod. | VPS | 3022, 8710, 10000 |

Table 1: Times of exposure for different coated specimens in flowing Pb-17Li at 480 °C.

After exposure the specimens were cut into pieces. One piece of each long-exposed coated specimen was cleaned with a mixture of acetic acid, ethanol and hydrogen peroxide in order to remove solidified Pb-17Li from the surface.

Post test analysis consisted of metallurgical examination and EDX line scan analysis on the cross sections of the exposed specimens. Metallurgical examination was carried out to study the influence of the liquid melt on the coating, the adherence to the base material and the quality of the layers after exposure. EDX point analysis was performed on polished cross sections on some selected specimens.

3. Results

3.1 Vacuum Plasma Spraying (VPS)

An etched micrograph of the unexposed VPS specimen is shown in Fig. 1. Two layers, which are separated by a band of pores, can be observed on the structural material F82H-mod. The external layer shows a rough surface and a thickness variation between 20 and 40 µm. The

internal layer seems to be very homogenous in thickness of around 70 μm and shows good adherence to the basic material.

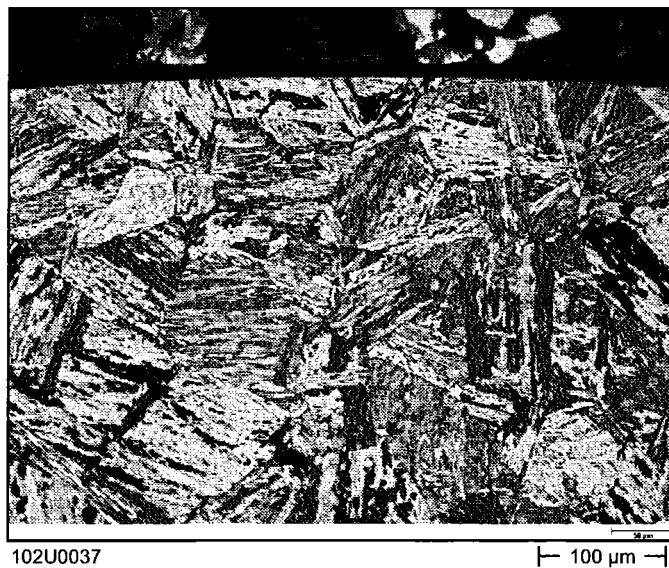


Fig. 1: Micrograph of an etched cross section of an unexposed VPS specimen.

An EDX depth profile was measured on the cross-section of the unexposed VPS specimen. The spectra is shown in Fig. 2. The two crosses in the corresponding secondary electron (SE) picture (Fig. 2) show the area in between which the spectra was recorded. With increasing depth the Al content decreases from 20 to 0 wt.%. The steel elements Fe and Cr show the opposite trend: with increasing depth the content of these elements increase up to the steel composition. The external layer consists of FeAl phase, the internal layer of $\alpha\text{-Fe(Al)}$.

A cross section of a VPS specimens after 8710 h of exposure is given in Fig. 3. Solidified Pb-17Li interspersed into the external layer can be observed on specimens that were not cleaned following corrosion testing. The internal layer is not effected by the liquid eutectic melt. An EDX profile measured on a cleaned VPS specimen after 8710 h of exposure confirms this fact as well (see Fig. 4). The thickness of the internal layer remains constant with around 70 μm and the phase found corresponds to $\alpha\text{-Fe(Al)}$. The thickness of the external layer (FeAl-phase) is only around 10 μm after exposure.

Two VPS specimens were exposed up to 10000 h in flowing Pb-17Li. The EDX spectra obtained for both 10000 h specimens are comparable. Hence, in the following only one of the 10000 h spectra will discussed. The measured EDX depth profile and the corresponding SE image showing solidified Pb-17Li are given in Fig. 5. The sample surface appeared to be rather rough. In the external layer near to the sample surface a few pores can be observed. The

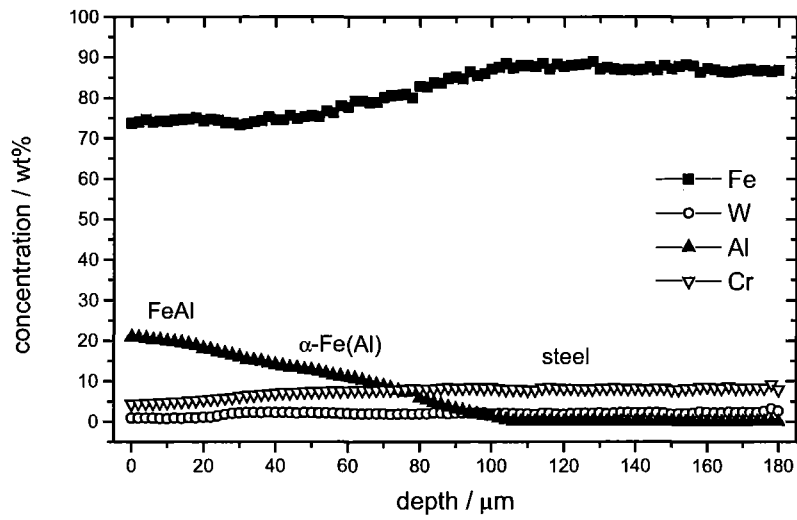
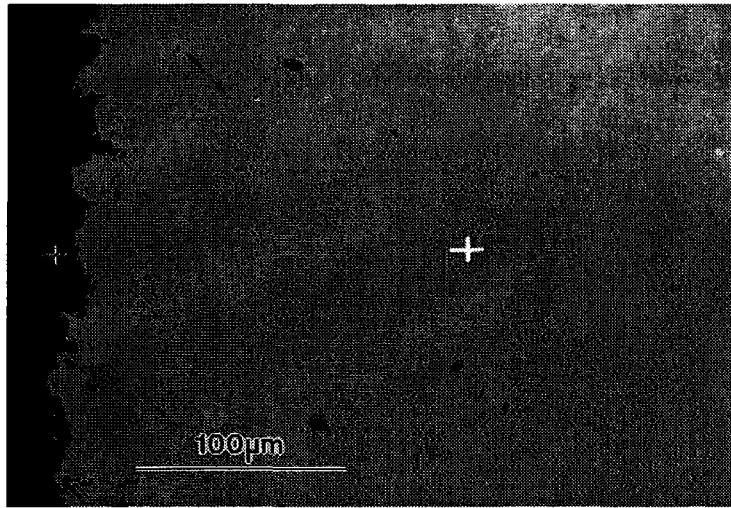
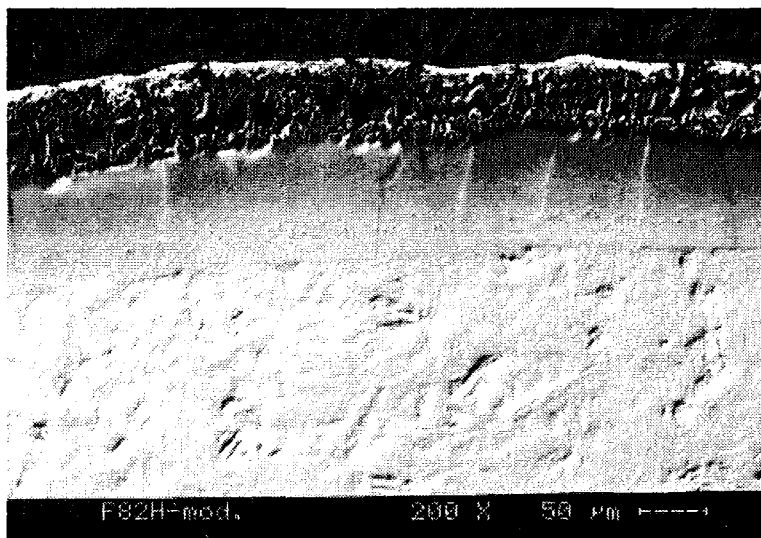


Fig. 2: SE image of the cross section of an unexposed VPS specimen and the corresponding EDX concentration profile.



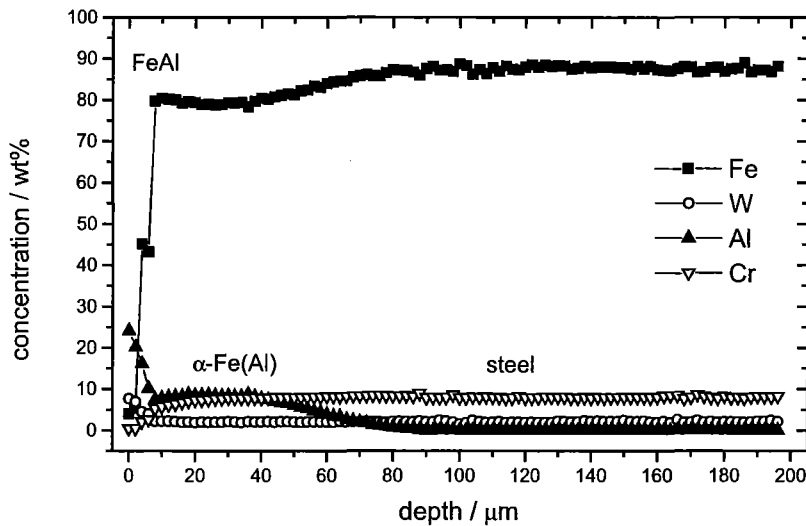
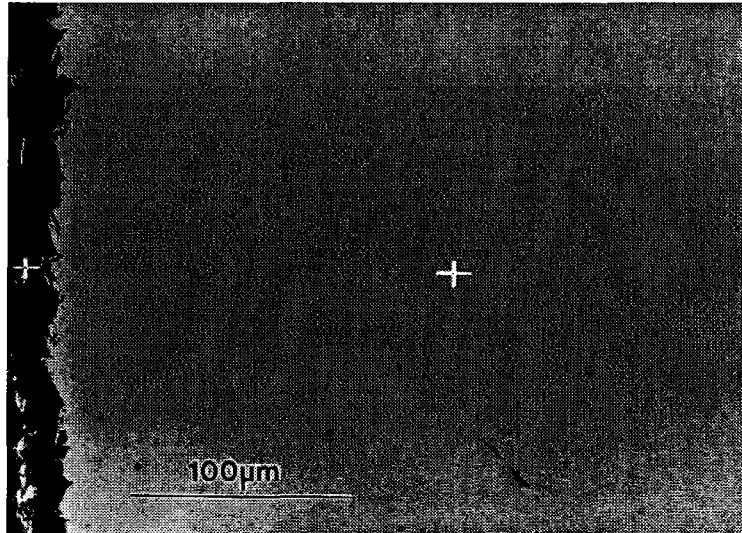


Fig. 3: Micrograph of the cross section of VPS specimen after 8710 h of exposure.

Fig. 4: SE image of the cross section of VPS specimen after 8710 h and the corresponding EDX concentration profile.

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 , homogenous structure and good adhesion to the structural material does not shift compared to the unexposed VPS specimen. The external layer corresponds to the composition of an FeAl phase and the internal layer to that of $\alpha\text{-Fe(Al)}$.

For a better comparison the Al concentrations obtained for the different exposure times were drawn in one graph (see Fig. 6). In the external layer the measured Al concentration varied between 18 and 25 wt% which corresponds to FeAl phase. The Al concentration in one

10000 h VPS specimen was higher than in the unexposed specimen, the Al concentration in the other 10000 h VPS specimen was lower.

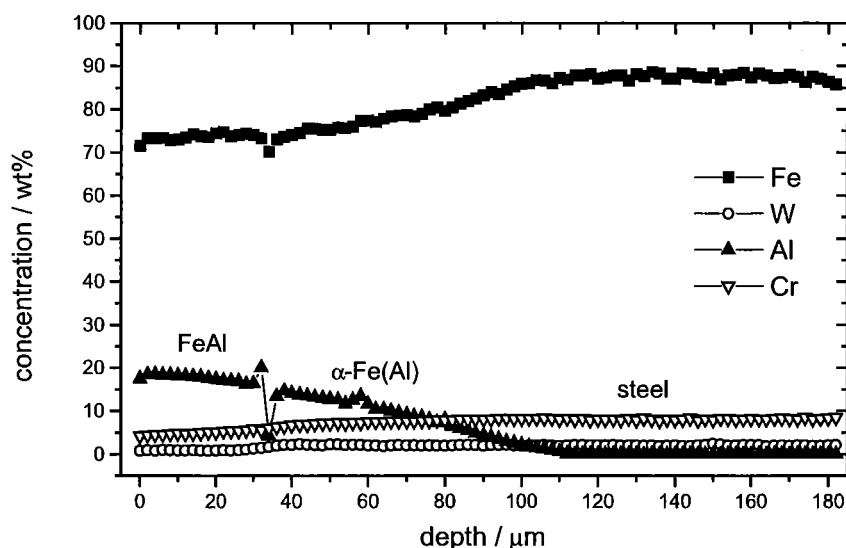
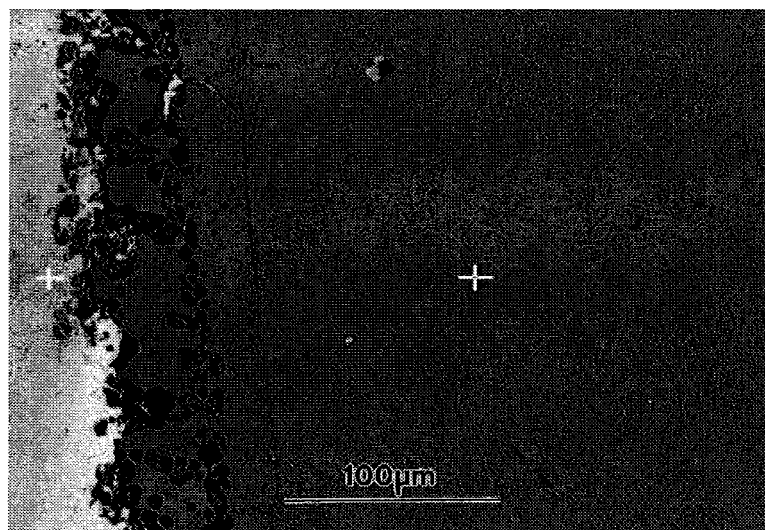


Fig. 5: SE image of the cross section of VPS specimen after 10000 h and the corresponding EDX concentration profile.

The strong scatter of the concentration gradient of Al beneath the FeAl phase results from the interaction of the electron beam with the porous band in between the two layers. A correct quantitative analysis is not possible in this region. Beneath the porous band, the Al concentration decreases from around 17 wt% down to 0. 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 10000 h of exposure were exactly the same as in the unexposed material.

There is, however, no systematic influence of exposure time to 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.

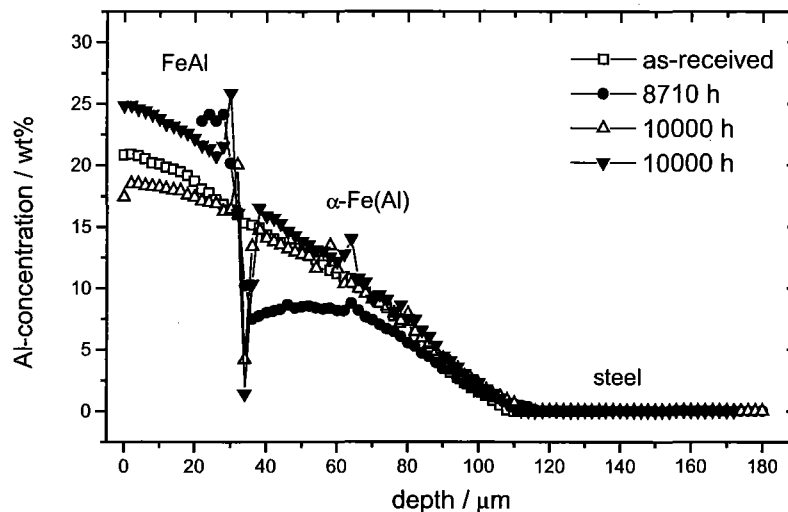


Fig. 6: Concentration profiles of Al in internal and external layers of individual VPS specimens after exposure to Pb-17Li at 480 °C for 0, 8710 and 10000 h.

The microstructure of the F82H-mod steels remained unchanged even up to 10000 h exposure time at 480 °C. This is in agreement with the results obtained previously on bare F82H-mod. material which also showed no bulk effect [19, 20].

3.2 Hot-Dip Aluminising (HDA)

The samples exposed between 1000 and 10000 h did not show any visible damage of the surface layers. These observations are in agreement with results obtained previously [21, 22]. Unetched cross sections of HDA specimens are shown after 1000, 2000 and 3000 h of exposure in Fig. 7 a - c. The external layer is separated from the internal layer by a band of pores whose formation is due to the Kirkendall effect. Some pores can be observed near by the surface of the specimen. The thickness of the external layer is around 35 μm after 1000 h, 30 μm after 2000 h and about 35 μm after 3000 h of exposure. These deviations in thickness are due to the preparation process of hot-dip aluminising which is not automated until now but is still in laboratory scale.

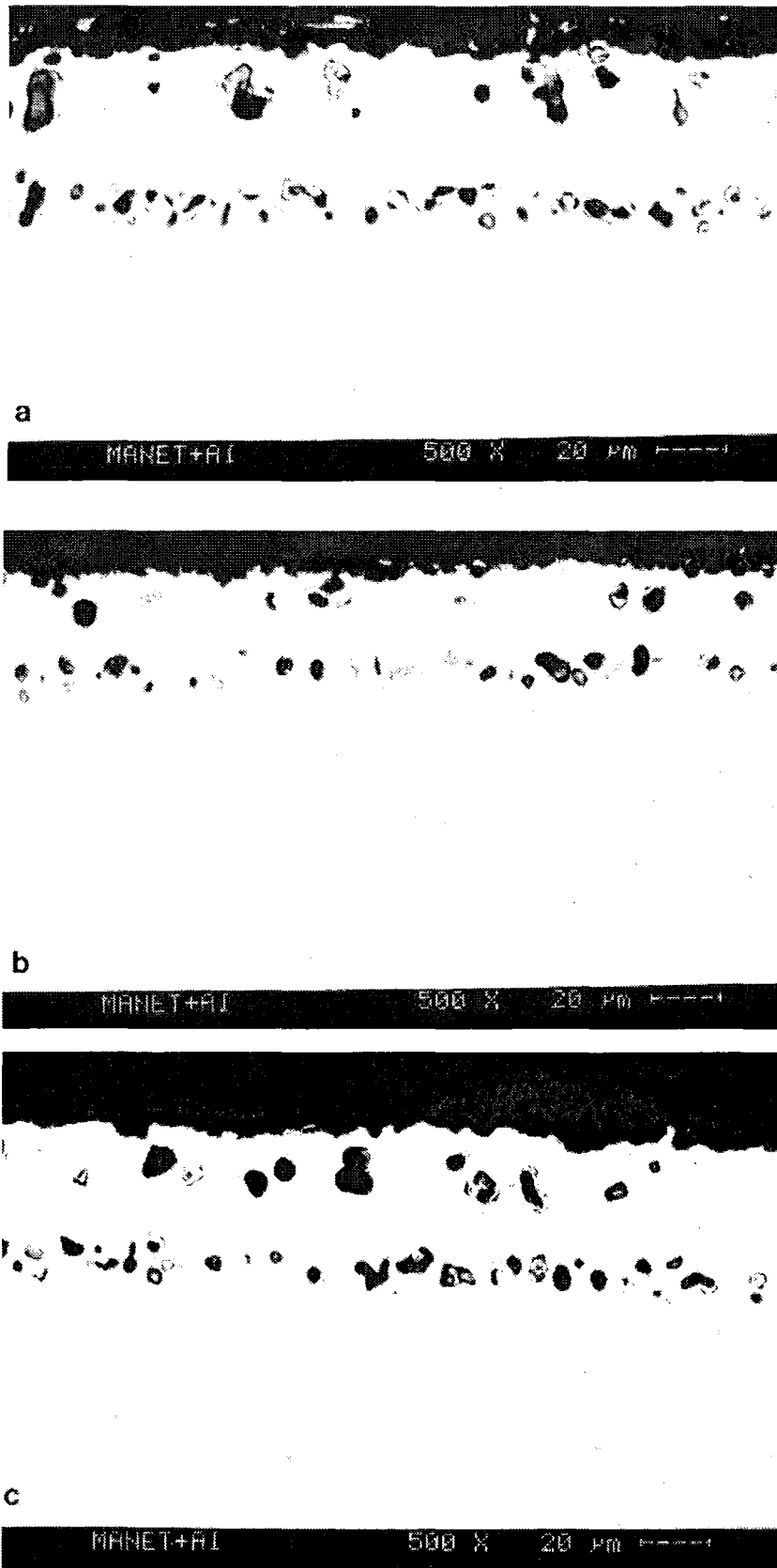


Fig. 7: Unetched cross sections of HDA specimens after a) 1000 h, b) 2000 h and c) 3000 h of exposure to Pb-17Li at 480 °C.

A metallurgical cross section of an exposed HDA MANET specimen after 4000 h of exposure is shown in Fig. 8. The sample was not cleaned after exposure hence solidified Pb-17Li can be seen on the surface. Two uniform layers can be easily observed, they are separated by a porous band. The external layer has a thickness of about 25 μm , the internal layer of about 105 μm . The transition of the internal layer to the steel looks very sharp.

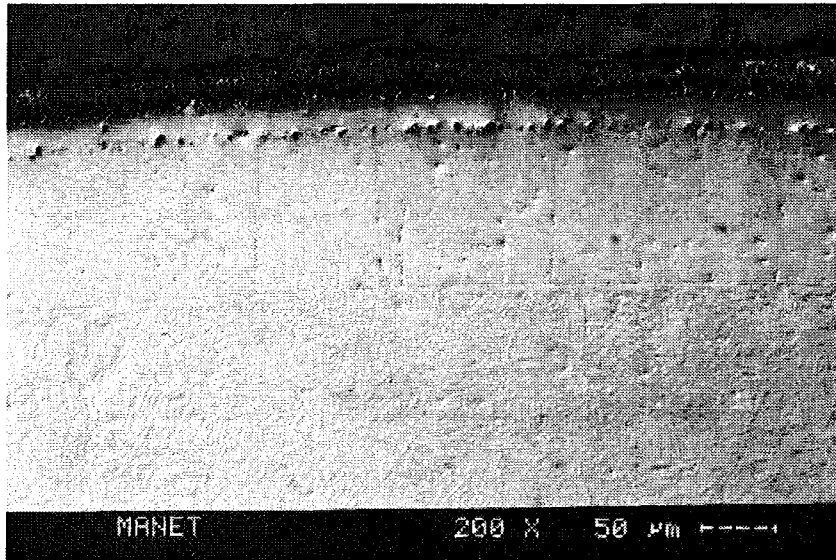


Fig. 8: Micrograph of the cross section of HDA specimen after 4000 h exposure at 480 °C.

EDX depth profile was recorded on a HDA specimen exposed for 10000 h. The measured EDX spectra and the corresponding SE image showing solidified Pb-17Li are given in Fig. 9. The Al concentration decreases continuously 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 [15] is probably responsible for this relatively high value of Al. Subsequently, the Al content decrease from around 18 wt% down to 0. This corresponds to the $\alpha\text{-Fe(Al)}$ 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) stayed more or less constant.

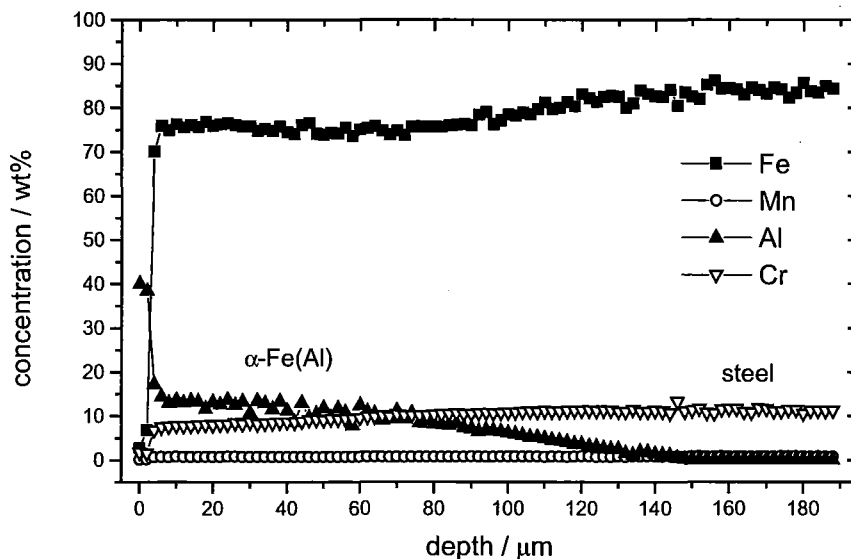
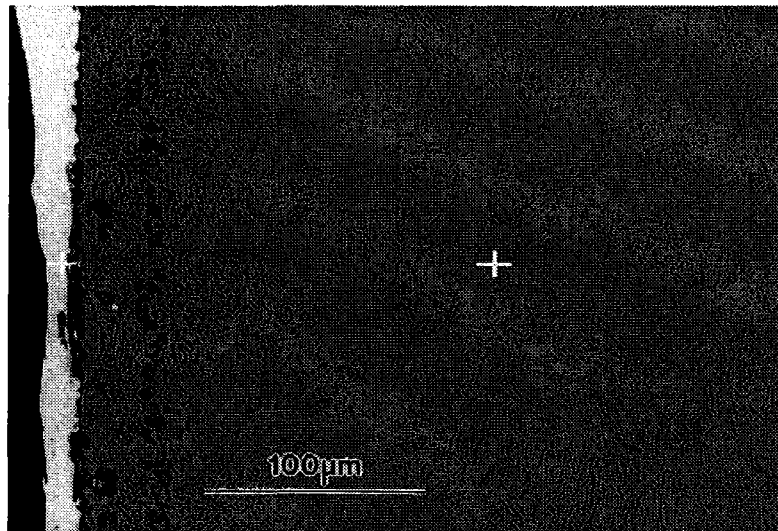


Fig. 9: SE image of the cross section of a HDA specimen after 10000 h and the corresponding EDX depth profile.

3.3 Chemical Vapour Deposition (CVD)

F82H-mod. steel specimens were coated with a layer system of Fe-Al by means of CVD at CEA Grenoble. EDX analysis was performed on the cross section of an unexposed specimen. The SE image and the corresponding EDX spectra are shown in Fig. 10. 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. Al is detected at a distance of about 13 μm from the surface. The external layer corresponds to FeAl-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 0 which fits well to $\alpha\text{-Fe(Al)}$ phase. An element mapping of Al was performed on this specimen and the result is shown in Fig. 11. The concentration of the element in question is proportional to the number of points. The Al content is higher in the external layer and decreases continuously from the surface to the steel. This corresponds well to the EDX depth profile discussed before.

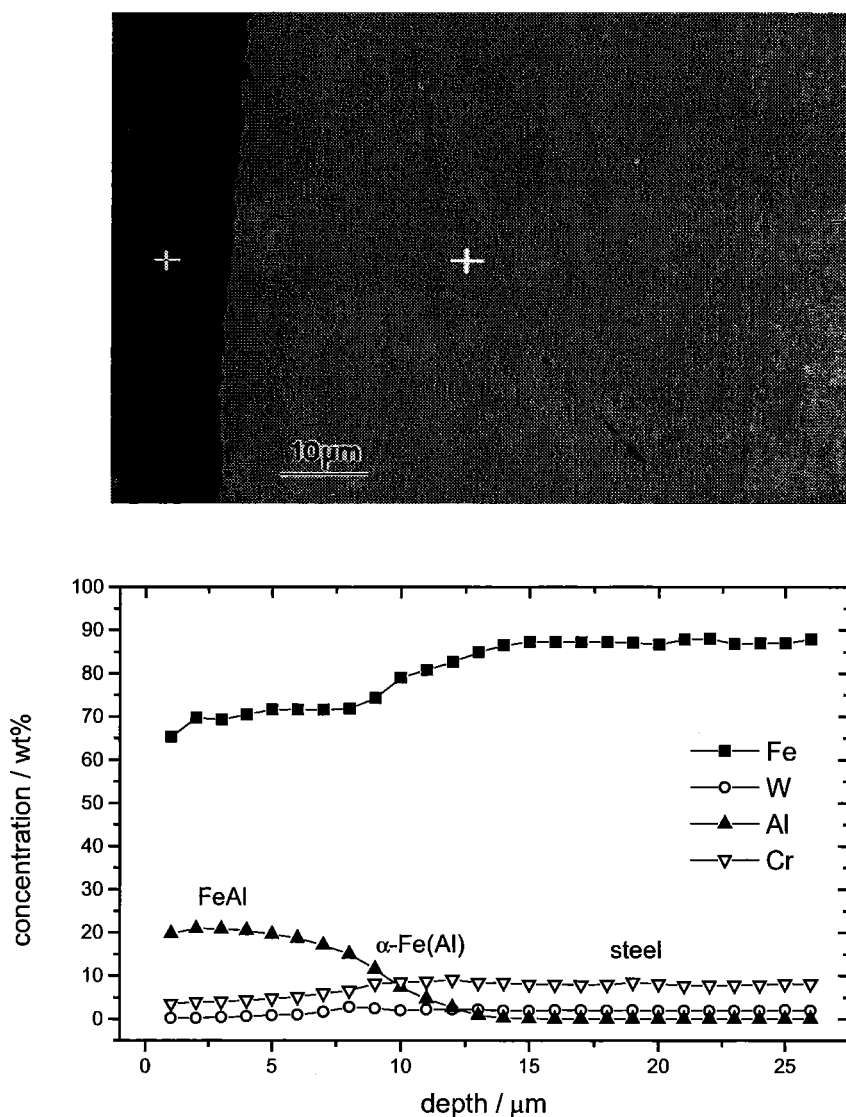


Fig. 10: SE image measured on the cross section of a CVD coated specimen and the corresponding EDX depth profile.

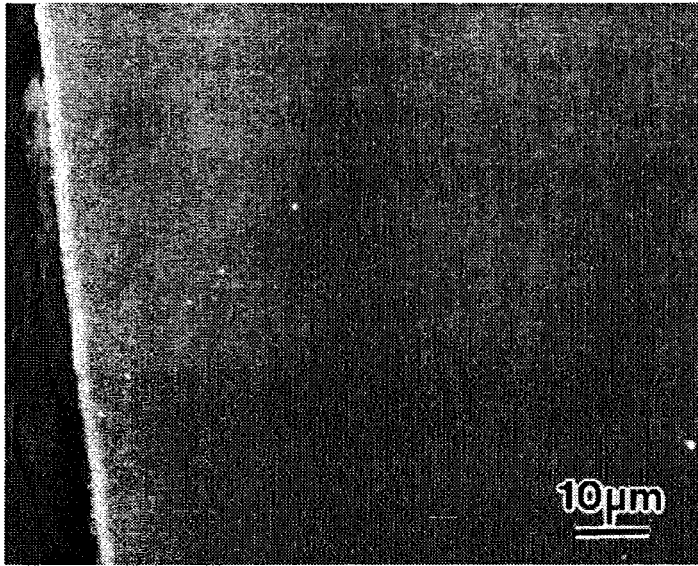


Fig. 11: An element mapping of Al on a non-exposed CVD specimen.

The CVD specimens were exposed to Pb-17Li up to 10000 h. In the following the results obtained for the different exposure times will be discussed separately.

The SE image and the corresponding EDX depth profile of the CVD specimen after 4982 h of exposure are given in Fig. 12. The concentration profiles of the different elements correspond to the results seen for the non-exposed specimen. The amount of Fe and Cr increase with increasing depth whereby the amount of Al decreases. The internal layer consists of α -Fe(Al) phase and reaches a thickness of around 6 μm . FeAl-phase can be found in the external layer. The thickness detected is circa 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 10000 h, but the results obtained are not identical. Hence the EDX spectra will be discussed for each specimen one after another. In the first EDX line scan presented (see Fig. 13), the phases FeAl and α -Fe(Al) are analysed. 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 , of the external phase only 2 μm .

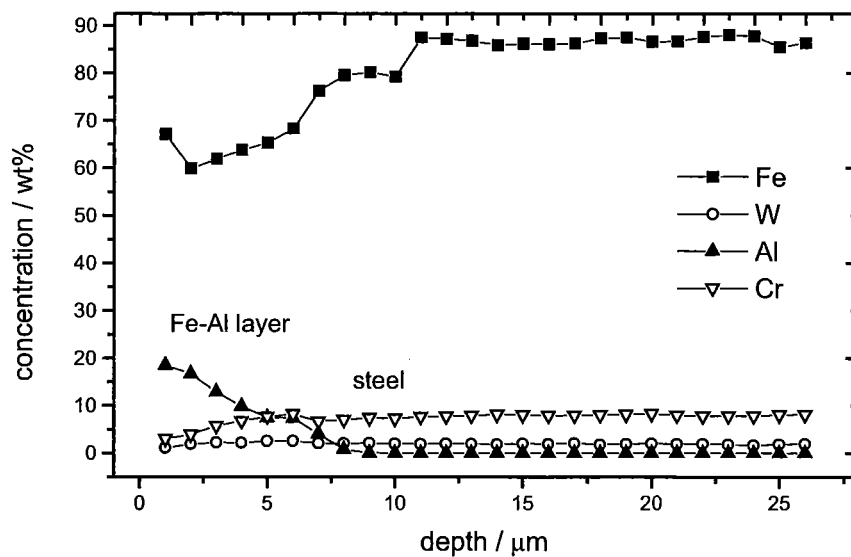
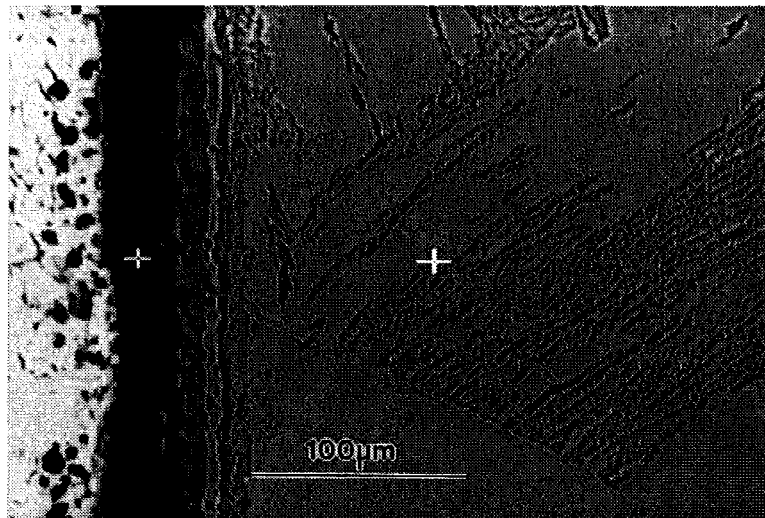


Fig. 12: SE image of a cross section of a CVD specimen after 4982 h of exposure with the corresponding EDX depth profile.

The EDX depth profile measured on the second 10000 h CVD specimen is given in Fig. 14 together with the corresponding SE image. The concentration profiles of Fe and Cr correspond to the other measured spectra: with increasing depth the content of these two elements increases over a distance of about 6 μm . These concentration profiles fit to the phases FeAl and $\alpha\text{-Fe}(\text{Al})$. 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 not

homogenous but porous. The reason for the very low content of Al in this layer could be a leaching 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 [23].

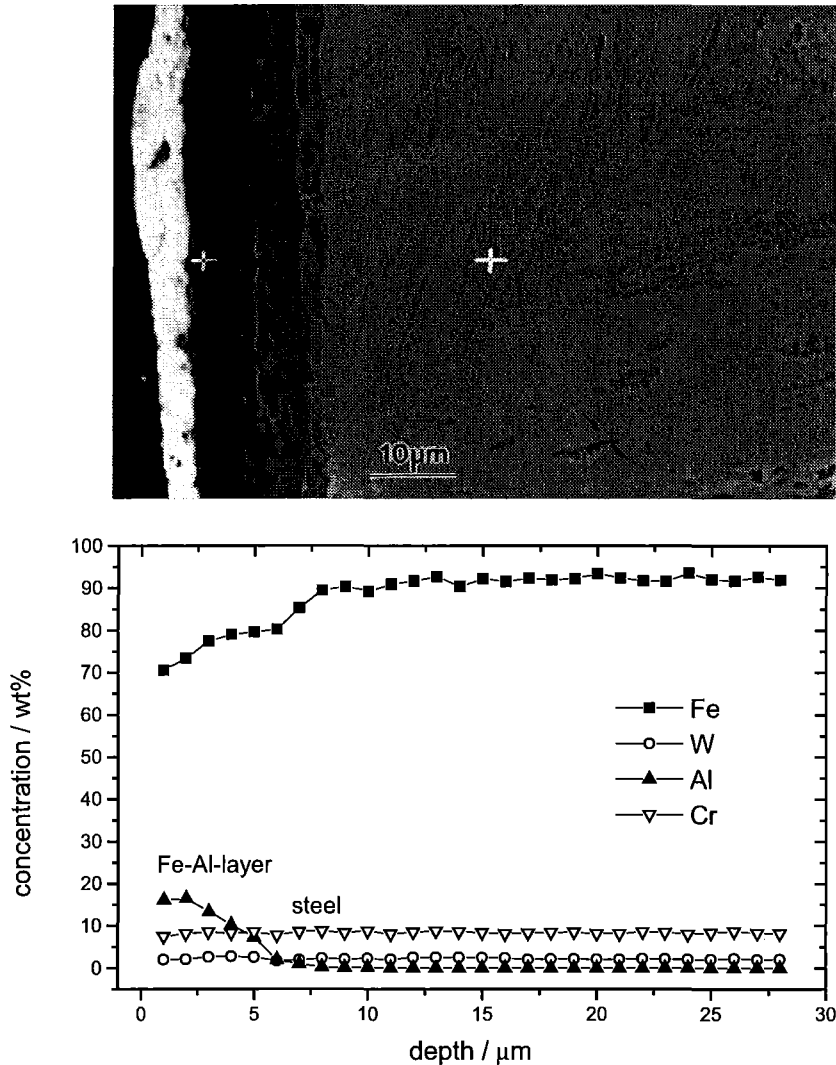


Fig. 13: SE image of a cross section of a CVD specimen after 10000 h of exposure with the corresponding EDX depth profile.

The Al concentration profiles obtained on the CVD specimens are drawn in one diagram for better comparison (see Fig. 15). It can be seen that increasing exposure times influences the thickness and the Al concentration in the Fe-Al layer unfavourable. The overall thickness of the layer decreases from around 13 μm (value of the unexposed specimen) down to less than 6 μm after 10000 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 10000 h of exposure.

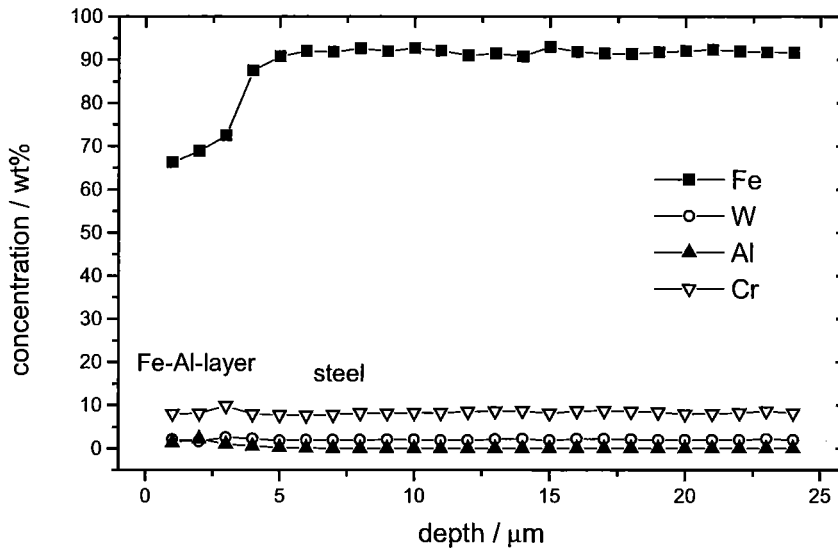
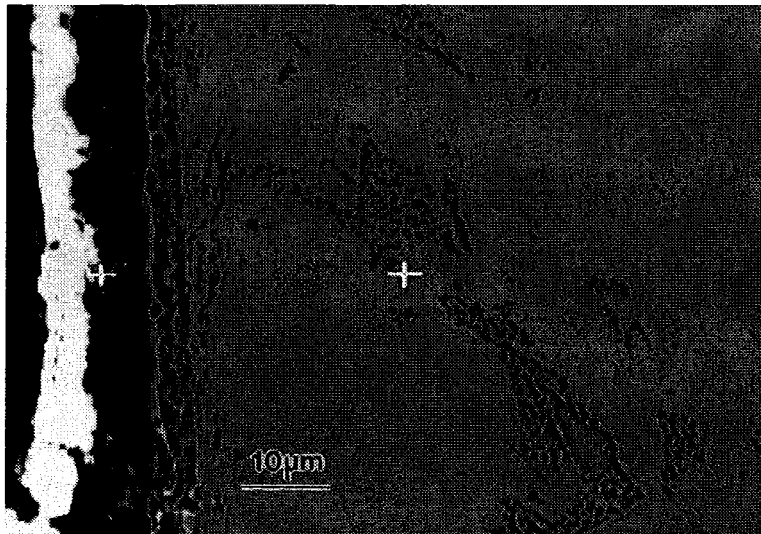


Fig. 14: SE image of a cross section of a CVD specimen after 10000 h of exposure with the corresponding EDX depth profile.

As observed on the VPS specimen the microstructure of the CVD coated F82H-mod steels is not affected at 480 °C even after long exposure times. This was also observed for the VPS F82H-mod. specimens.

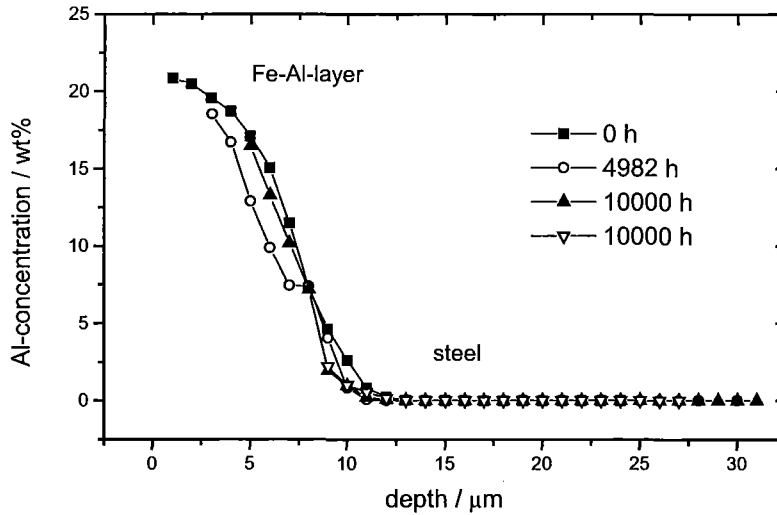


Fig. 15: Concentration profiles of Al obtained for the individual CVD specimens after and without exposure to Pb-17Li.

4. Discussion and Conclusions

The corrosion behaviour of three Fe-Al 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 for up to 10000 h.

In spite of the fact, that the Fe-Al layers which were produced by means of HDA and VPS are not yet optimised with respect to the formation of reproducible uniform thick layers, the corrosion resistance was demonstrated in flowing Pb-17Li at 480 °C up to 10000 h. No systematic tendencies in the concentration profiles attributed to a corrosion attack were observed. The coating procedures for both techniques are still in development which can lead to a varying in the 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 Fe-Al layer decreased considerably. The Fe-Al phases formed are the same for all three coating methods. It is not obvious why the Fe-Al layers produced by means of CVD should not withstand a corrosion attack while the Fe-Al 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 $\alpha\text{-Al}_2\text{O}_3$) is formed on the surface [15] which protects the Fe-Al layer against

corrosion attack of the melt. The stability of the alumina layer on the Fe-Al layer in Pb-17Li is in agreement with the thermodynamic data concerning the oxygen potential of the liquid alloy [24]. The CVD coating technique used here is a low temperature process ($T = 450\text{ }^{\circ}\text{C}$). Therefore, only the $\gamma\text{-Al}_2\text{O}_3$ phase, which is meta stable, can be formed during the coating process. How far the corrosion resistance of α - and $\gamma\text{-Al}_2\text{O}_3$ against Pb-17Li attack is different can only be speculated at the moment. Fact is, that 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 $\alpha\text{-Al}_2\text{O}_3$ layer by means of CVD on an Fe-Al phase without the use of an additional high temperature heat treatment is still a problem. Another important point is the thickness of the layers. The layers 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 Fe-Al layers formed by HDA and VPS. This issue should be taken into account for the selection of an appropriate coating process for the fabrication of tritium permeation barriers, too.

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