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1998

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Zusammenfassung

Entwicklung von Tritiumpermeationshemmenden Schichten auf F82H-mod. Blechen und MANET Rohren nach dem Hot-Dip Aluminierverfahren mit anschließender Wärmebehandlung

In der vorliegenden Arbeit werden die Ergebnisse von tauchaluminierten Blechproben aus F82H-mod. und Rohrproben aus MANET diskutiert. Die anschließende Wärmebehandlung an den getauchten Proben (1040°C, 0.5 h / 750°C, 1 h bzw. 1075°C, 0.5 h / 750°C, 2 h) entspricht der Vergütungsvorschrift für F82H-mod. bzw. der für MANET.

Das Hot-Dip Aluminierverfahren mit anschließender Wärmebehandlung eignet sich als Beschichtungsmethode sowohl für Blechproben als auch für die Innen- und Außenbeschichtung von Rohren. Die Zusammensetzung und Dicke der hergestellten Schichten ist unabhängig vom eingesetzten Stahl. Des weiteren wird gezeigt, daß die hergestellten Aluminidschichten in Pb-17Li beständig sind, der PRF genügend hoch ist und die einzelnen Prozeßschritte mit der ITM Geometrie und der Fabrikationssequenz vereinbar sind.

Abstract

The present work describes the results of hot dip aluminised F82H-mod. sheets and MANET tubes. The subsequent heat treatment on the aluminised samples (1040°C, 0.5 h / 750°C, 1 h or 1075°C, 0.5 h / 750°C, 2 h) corresponds to the standard heat treatment for F82H-mod. and MANET steel, respectively.

It could be shown that hot dip aluminising with a subsequent heat treatment is a suitable technique to produce TBP on sheet materials and on tubes as well from the inside or the outside. The aluminide layers produced are compatible with Pb-17Li, the PRF is sufficiently high and the process is compatible with the ITM geometry and the fabrication sequence.

Content

1. **Introduction** 3

2. **Preparation of the coating** 4
2.1 Materials 4
2.2 Sample preparation 4
2.3 Aluminising process 5
2.4 Heat treatment 6

3. **Basic characterisation of the coating** 8
3.1 Aluminised samples 8
3.1.1 Metallographical examination 8
3.1.2 Analytical examination 10
3.1.3 VICKERS micro hardness 11
3.2 Aluminised and subsequent heat treated samples 12
3.2.1 Surface Investigations 12
3.2.1.1 XPS 12
3.2.1.2 Low angle XRD 13
3.2.1.3 SEM / EDX 13
3.2.2 Metallographical examination 19
3.2.3 Analytical examination 23
3.2.4 VICKERS micro hardness 25

4. **Preliminary tests** 27
4.1 Compatibility with Pb-17Li 27
4.2 Compatibility with water 27
4.3 Permeation measurements 27

5. **Compatibility with ITER test module preparation** 27

6. **Summary** 28

7. **References** 30

1. Introduction

One of the main issues in the design of blankets for a future fusion reactor is the permeation of tritium through the structural material into the secondary circuit [1-3]. In the case of the water-cooled Pb-17Li liquid blanket the concentration of T in the cooling water has to be minimised for safety and economical reasons. The martensitic steel MANET at present foreseen as structural material for ITER cannot be used without any further protection to reduce the tritium permeation. One of the most promising methods entails the use of coatings which have low diffusion rates and / or low hydrogen recombination or adsorption constants.

It is well known that thin alumina scales can reduce the tritium permeation rate by several orders of magnitude [4-6]. Hence, aluminised coatings have been considered as reference choice for the present programme (1997-98).

The requirements raised up to the Permeation Barrier fabrication technique are the following:

- producing, at the end of the fabrication process, a permeation barrier on a structural material in the required metallurgical state;
- producing coating with acceptable performances;
- compatible with the ITM geometry and fabrication sequence.

Previous results concerning fabrication and / or qualification tests led to a selection of four coating techniques: CVD, Hot Dip Aluminising, HIP and Spray Technique.

- The HIP method can only be used for the inside coating of the tubes (water side).
- The Spray techniques are foreseen as a repair method.
- CVD techniques have been considered for the outside coating of the tubes (Pb-17Li side).
- The Hot Dip Aluminising technique is the only method which has the capability to coat the tubes as well on the inside or the outside.

In September 1996, the Tritium Permeation Barrier Working Group decided to divide the programme 1997-1998 in two parts: The year 1997 should be used to prepare qualified coatings for the reference tests which will be performed in the year 1998 in different laboratories. The qualified coatings have to be characterised by means of different analytical techniques which were defined in the 1st meeting on Tritium Control & Permeation Barriers held in Brasimone on March 4-5, 1997. The results achieved for each coating technique have to be summarised in a report which should be contributed to the members of the TPB group by December 1997 / January 1998.

In this report in hand the complete characterisation of aluminised coatings by means of hot dip procedure will be presented. The results obtained on the structural materials F82H-mod. sheets and on MANET tubes will be discussed. The guidelines for the coating qualification worked out by the TPB group have been considered.

2. Preparation of the Coating

2.1 Materials

The substrate materials to be aluminised were the martensitic steels F82H-mod. and MANET II. F82H-mod. has been chosen as first reference material since it is available in sufficient quantities (see minutes of the 1st meeting on Tritium Control & Permeation Barriers; Brasimone Centre on March 4-5, 1997) as sheet. MANET II has been selected additionally for pipe specimens. The chemical composition of these steels is given in table 1.

	C	Si	Mn	P	S	**Cr**	Ni	Mo	V	Nb	**Fe**
F82H-mod.	0.09		0.156			**8.36**	0.021	<0.0003	0.162	0.01	**Bal.**
MANET II	0.10	0.18	0.76	0.004	0.005	**10.37**	0.65	0.58	0.21	0.16	**Bal.**

Table 1: Chemical composition of F82H-mod. and MANET II (wt%).

Al used for the Al melt had an initial purity of 99.5% with the main impurities being Fe and Si. With increasing immersion time the melt became enriched in the main steel components Fe and Cr.

2.2 Sample Preparation

In order to demonstrate the usability of the hot dipping process as a coating process for both flat surfaces and pipes two kind of samples with different geometries have been used. The material was delivered as 20 mm thick sheets (F82H-mod.) and as rod material 12 mm in diameter (MANET II) in a tempered condition. Sheet specimens of 50 x 15 x 1 mm were machined by erosion. Pipes were machined (∅=10 mm x 1 mm x 100 mm) by drilling a hole into the rod. Each sample had a small hole on one side for fixing during the aluminising process.

After machining the samples were degreased in acetone and finally cleaned ultrasonically in ethanol. As a final surface preparation the cleaned specimens were dipped into a flux solution (solution of KCl, NaCl and Na_3AlF_6 (ratio 5:4:1) in water) and dried.

2.3 Aluminising Process

Aluminising has been carried out by using the facility shown in figure 1.

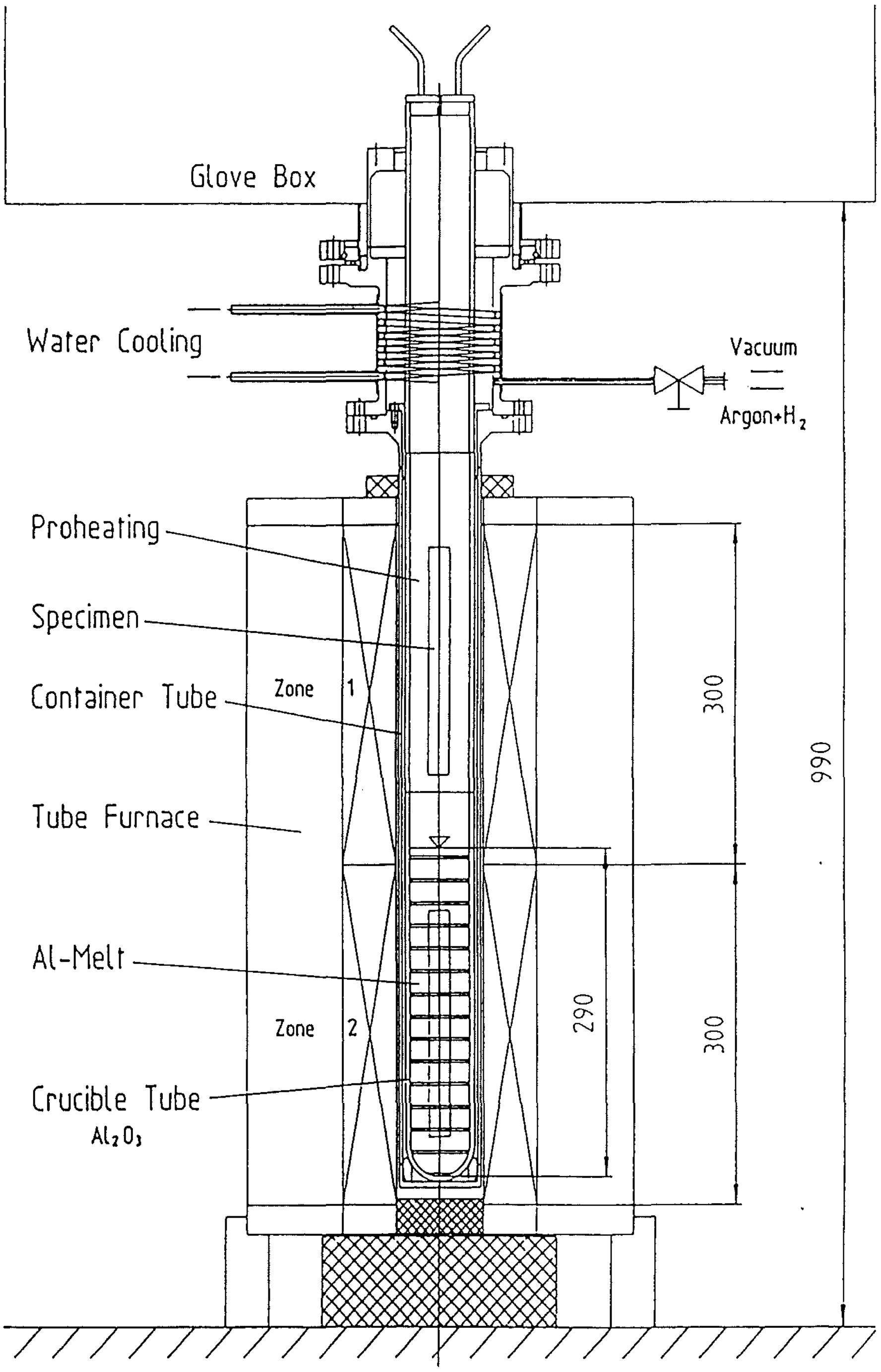

Figure 1: Aluminising facility.

On its bottom a glove box is connected gas tight to a heated alumina crucible. As working atmosphere a reducing Ar-5%H_2 mixture was used since oxidation of the Al melt had to be avoided. The alumina crucible was filled with small Al pieces and heated up to 700°C by a furnace. The temperature was measured by a NiCr-Ni thermocouple which was protected by an alumina tube and placed directly in the Al melt. The samples, fixed by a hook and stainless steel wire to a crane system, were dipped into the melt. After 30 s of exposure they were pulled out of the melt. Cooling down took place in the glove box by natural cooling rate.

2.4 Heat Treatment

In order to optimise the coating structure in view of the demands of a tritium permeation barrier a suitable heat treatment has to be carried out after aluminising. The goal of a successful heat treatment process must be:

- complete incorporation of solidified Al on the sample surface into the steel matrix by diffusion
- transformation of the brittle intermetallic scale Fe_2Al_5 which has been formed during the aluminising process into more ductile phases (preferable FeAl or α-Fe(Al))
- formation of a thin alumina scale on top of the coating as a very efficient tritium permeation barrier with potential for self healing
- the formed alumina scale has to be compatible with Pb-17Li and / or water under the particular conditions required dependent on whether the tubes have to be coated from the inside or outside
- the preparation process of the coating has to be compatible with the heat treatments admissible for the steel to guarantee the original mechanical properties of the structural material under working conditions after coating
- the whole coating system should be kept as thin as possible since Al is an activating element and is not desired in the matrix of low activation steels

The heat treatment was carried out in a horizontal quartz rig. The aluminised samples were cleaned ultrasonically in ethanol, dried and placed in alumina crucibles which were positioned in the hot zone of the furnace. The working rig was flushed with Ar 6.0 and finally a flow rate of 5 l/h and a pressure of 1.25 bar were set. The heating rate was about 25 K/min. After the required holding time the crucibles were removed from the hot zone of the furnace and cooled down in air. Time and temperature regimes of the chosen heat treatments are listed in table 2.

type / material	aluminising conditions (T / t)	heat treatment
A F82H-mod.	700°C / 30 s	1040°C / 0.5 h / air cooling 750°C / 1 h / air cooling
B F82H-mod.	700°C / 30 s	1075°C / 0.5 h / air cooling 750°C / 2 h / air cooling
C MANET II	700°C / 30 s	950°C / 2 h / air cooling 750°C / 2 h / air cooling
D MANET II	700°C / 30 s	1075°C / 0.5 h / air cooling 750°C / 2 h / air cooling

Table 2: Time and temperature regime of the heat treatment after aluminising.

Extended investigations have shown that the fulfilment of the demands listed above requires reaustenitisation and subsequent tempering of the aluminised samples. Type A is the standard heat treatment of steel F82H-mod. Type B and D heat treatment corresponds to the standard heat treatment for MANET steel. Additionally an aluminised F82H-mod. sheet was austenised and tempered under MANET conditions (Type B) for better comparison of the results obtained. Type C was selected as alternative applications for MANET II. Reaustenisation at 950°C instead of 1075°C results in smaller martensitic grains. Up to now it is not yet clear whether a decrease of martensitic grains and therefore very possibly a decrease of the creep properties will be accepted in view of the substrate properties.

3. Basic Characterisation of the Coating

3.1 Aluminised Samples

3.1.1 Metallographical examination

Generally, the thickness of the layers formed during hot dip aluminising on the two steels are in the same range. No difference in the immersion behaviour of F82H-mod. and MANET II could be observed. In the following chapter the results obtained for each steel will be discussed.

F82H-mod. (sheet specimens)

After aluminising the samples were homogeneously covered by an overlayer of solidified Al melt as seen in figure 2a and b. The thickness of this layer varies strongly. On the bottom side

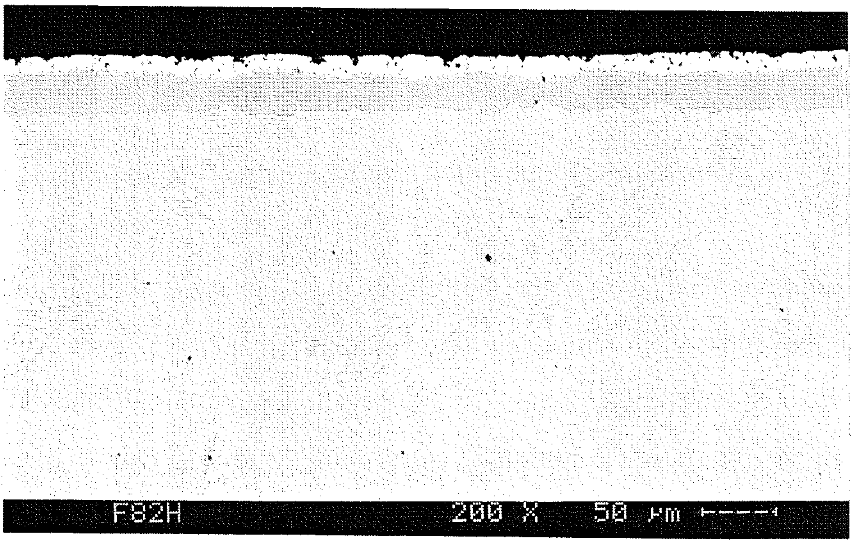

Figure 2a: Cross section of aluminised F82H-mod. sheet (x 200).

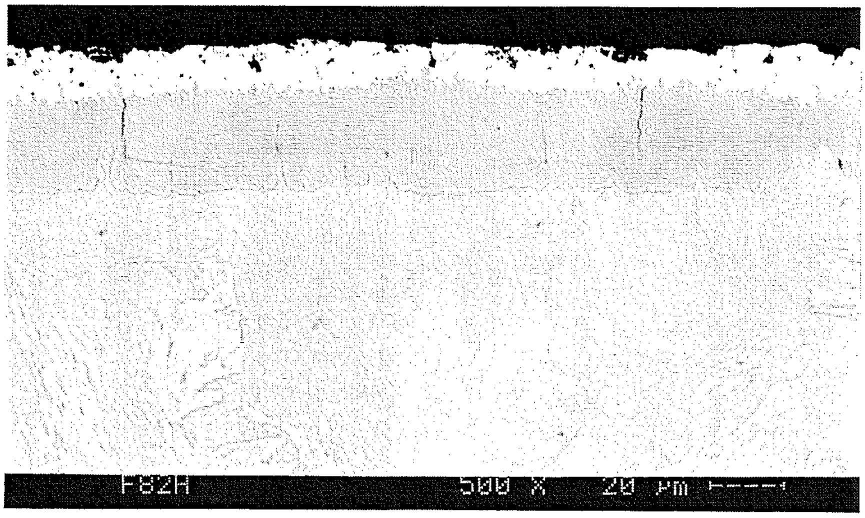

Figure 2b: Cross section of aluminised F82H-mod. sheet (x 500).

of each sample a drop of Al solidified during the cooling phase since no tools were used to remove the melt drop. Beneath the Al overlayer at about 20-30 µm thick, intermetallic scale has been formed mainly by Al diffusion into the steel substrate. The interface between the substrate and the intermetallic scale is smooth although the scale grew somewhat tongue like into the substrate, figure 2b. The interface between the Al overlayer and the intermetallic scale appears very inhomogeneous. This pattern is a good indication for two alternative processes: Crystal growth and dissolution of the crystals formed and transport into the Al melt. Some cracks could be observed across the intermetallic scale.

MANET II (pipe specimens)

As an example the cross section of an aluminised pipe (inside) is shown in figure 3a and b.

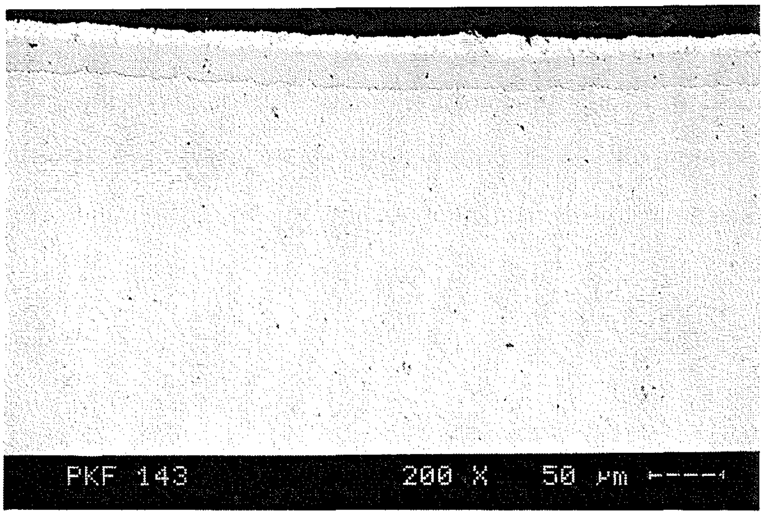

Figure 3a: Cross section of aluminised MANET pipe (inside wall, x 200).

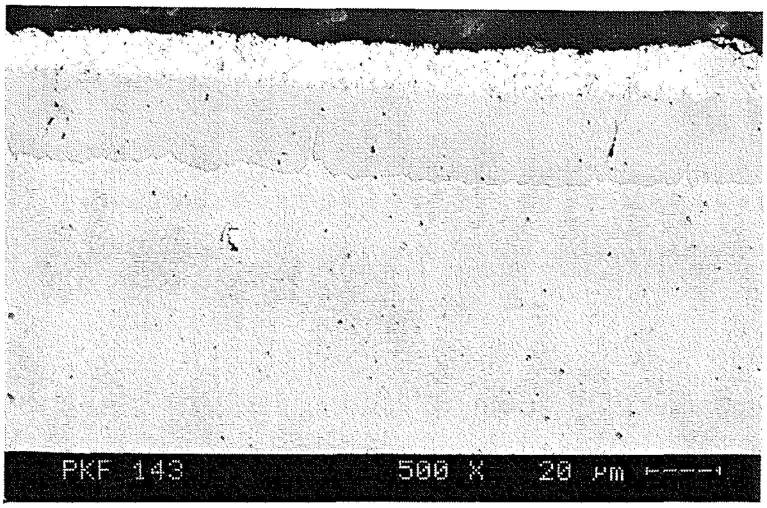

Figure 3b: Cross section of an aluminised MANET pipe (inside wall, x 500).

The MANET pipes have revealed a very similar scale structure and chemical composition like the F82H-mod. sample sheets after aluminising. The inside and outside surfaces of the pipes were homogeneously covered by about a 2-8 µm thick overlayer of solidified Al melt. Beneath the Al overlayer about a 8-12 µm thick intermetallic scale had been formed.

3.1.2 Analytical examination

SEM/EDX point analyses of hot dip aluminised samples (F82H-mod. sheets and MANET tubes) have shown that the main part of the scale corresponds to Fe_2Al_5 phase. Just beneath the solidified Al the interface of the intermetallic scale shows a higher Al concentration compared to the rest of the scale indicating the existence of the $FeAl_3$ phase. The striation like precipitates in the Al melt were found to be $FeAl_3$ phase as well.

F82H-mod. (sheet specimens)

EPMA line scan analysis of an aluminised F82H-mod. sheet is given in figure 4. In the first few microns the Al content decreases continuously from nearly 100 at% down to around 71 at%. The values measured for the iron content show the opposite trend: from 0 at% at the near surface region up to around 28 at% in the depth of 5 µm. At a depth area of about 5 to 25 µm the concentration of all elements measured stay rather consistent. This composition

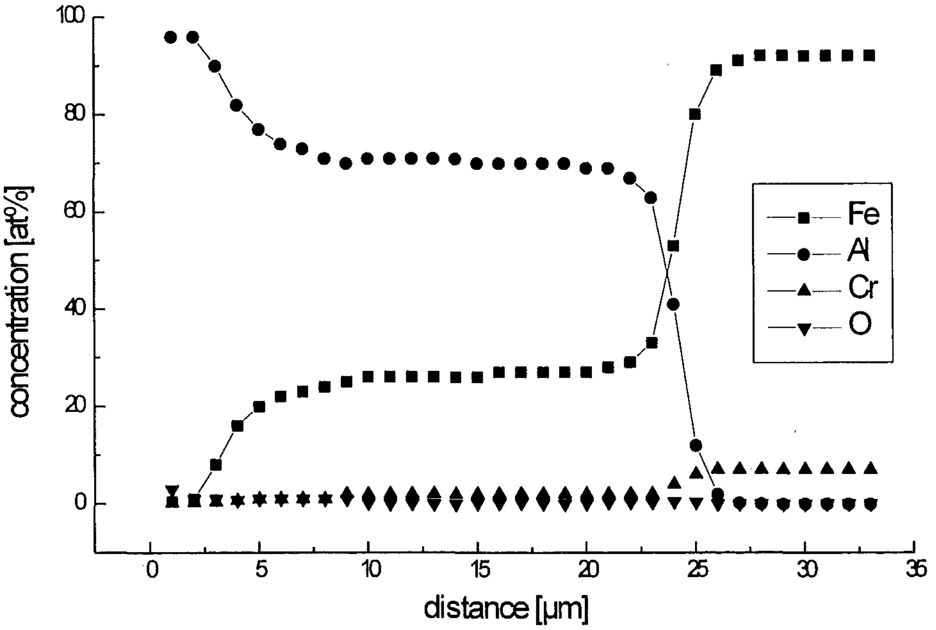

Figure 4: EPMA line scans of an aluminised F82H-mod. sheet.

conforms to Fe_2Al_5 phase as well. On the transition zone from Fe_2Al_5 phase to the steel matrix, the concentration of the elements rapidly changes.

MANET II (pipe specimens)

Line scan measurements obtained on the aluminised MANET tube show the same trend for the elements analysed as observed for the aluminised F82H-mod. sheet (see figure 5). The only difference observed is the decrease in thickness of the Fe_2Al_5 layer, which is less than on the sheet samples. This observation is in agreement with the metallographical examination mentioned above.

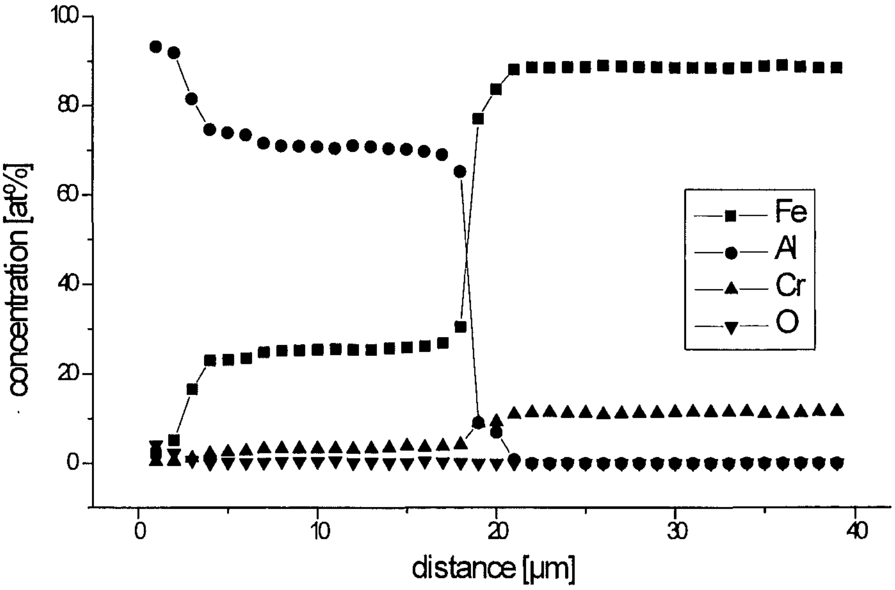

Figure 5: EPMA line scans of an aluminised MANET tube.

3.1.3 Vickers micro hardness

The micro hardness of the formed intermetallic scale after the aluminising process was about 1000-1100 HV 0.05, independent of the structural material. This is in agreement with micro hardness values for the compound Fe_2Al_5 reported in the literature. The micro hardness of the substrate remained unchanged compared to the virgin material.

3.2 Aluminised and subsequent heat treated samples

3.2.1 Surface Investigation

3.2.1.1 XPS

F82H-mod. (sheet specimens)

In the XPS spectra of samples type A and B the elements Al and O can be clearly detected. Some small peaks present in the spectra result in surface contamination i. e. carbon and nitrogen. No photopeaks of the steel elements Fe or Cr were detected in the spectra. In figure 6 the Al 2p photopeaks of each sample investigated are shown. An increase of the binding energy of the Al 2p peak from type A to B can be observed. Additionally, the FWHM decreases from around 2.5 eV down to 2.2 eV. The conclusion of these observations can be summarised as follows: The surface exists of pure alumina. The heat treatment type A leads to different alumina compounds but is not sufficient to form α-Al_2O_3. In contrast to these results type B heat treated samples exist mainly of α-Al_2O_3 on the surface.

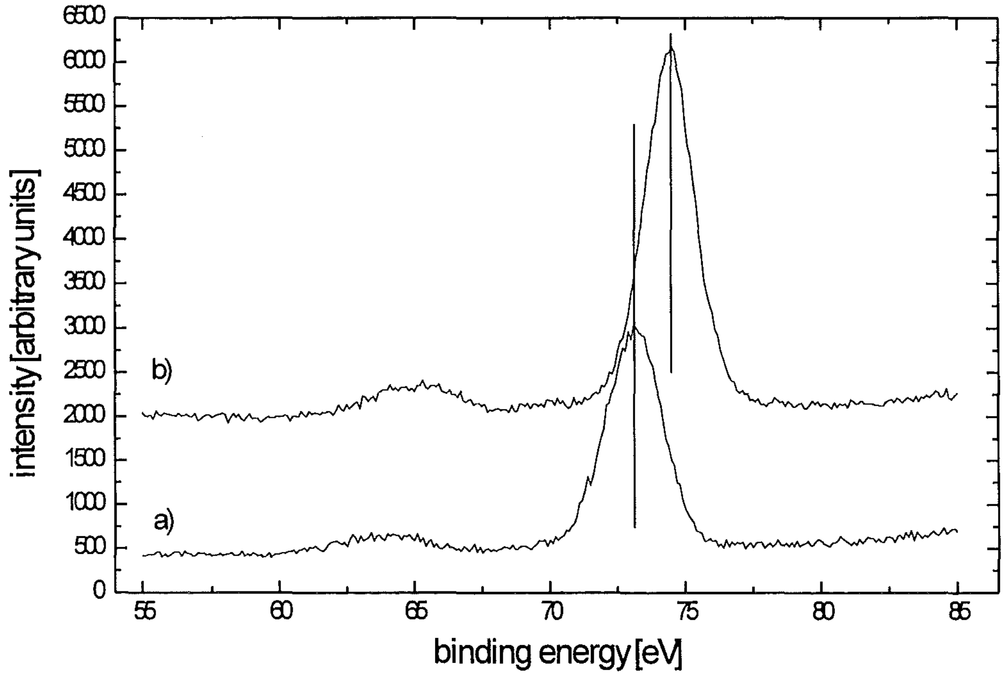

Figure 6: Al 2p photopeak of samples heat treated at a) 1040°C, 30 s and 750°C, 1 h and b) 1075°C, 30 s and 750°C, 2 h.

3.2.1.2 Low angle XRD

F82H-mod. (sheet specimens)

The aluminised and subsequent heat treated F82H-mod. samples were analysed with low angle XRD in order to get information concerning the compounds existing on the surface. The spectrum revealed for type A sample is given in figure 7. The main reflex comes either from FeAl or Fe_3Al phases or from both. These two compounds can not be exactly related with this method. The spectrum for type B samples is given as well in figure 7. In comparison with type A spectra, more additional reflexes can be observed for type B. These peaks can be clearly related to α-Al_2O_3. For better comparison the signals for this compound were added into the spectra as lines. It can be easily seen that α-Al_2O_3 is formed at 1075 °C within 30 min, but not at 1040 °C. It is known that α-Al_2O_3 is also built at 1040 °C but unfortunately at this temperature the transformation requires longer times. This result is in agreement with the XPS measurements discussed above.

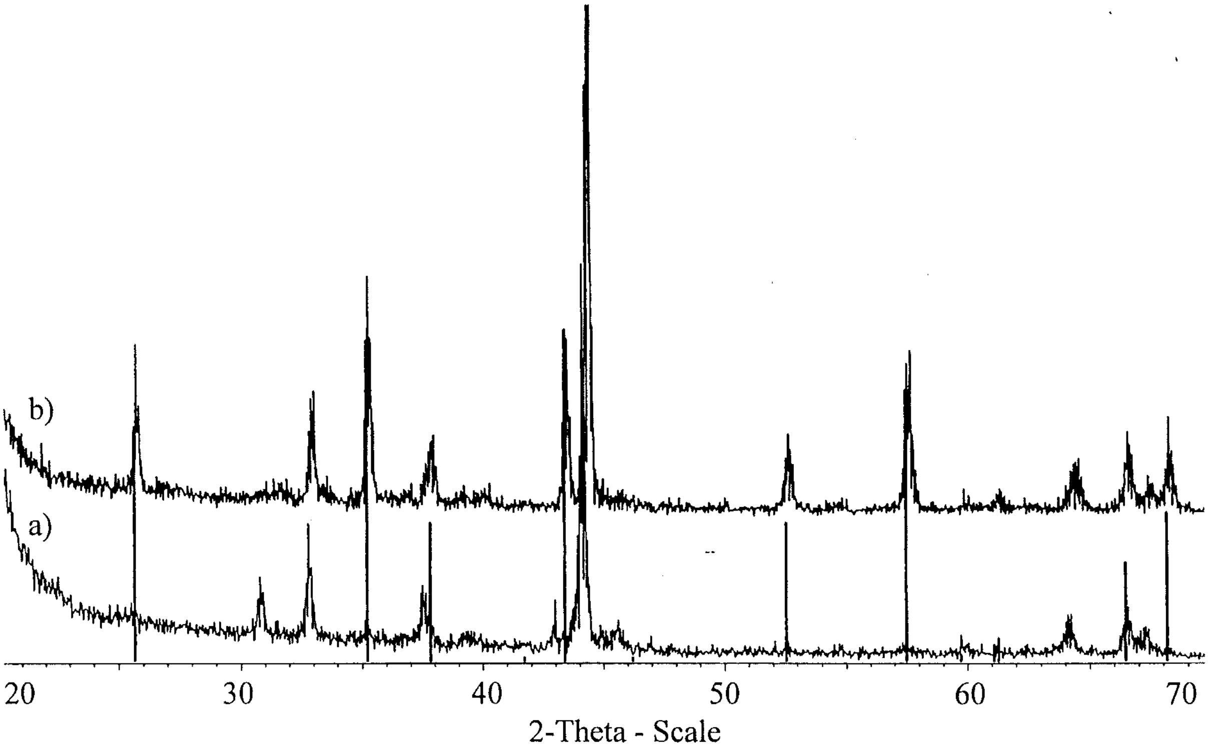

Figure 7: Low angle XRD spectra of aluminised F82H-mod. a) type A b) and type B samples.

3.2.1.3 SEM / EDX

F82H-mod. (sheet specimens)

EDX measurements with accelerator voltages from 10 keV up to 30 keV were carried out on type A and B samples. The results revealed for both samples are in the same range. The high

Al content measured in the near surface area (up to a thickness of circa 0.7 μm) indicates that an oxidation process has occurred which is in agreement with the results obtained with low angle XRD and XPS. Beneath this enriched Al layer, the Al content is found to be reduced.

In contrast to the EDX results, SEM investigations have shown that the morphology of the sample surfaces appears different for type A (1040°C / 0.5 h, 750°C / 1 h) and B (1075°C / 0.5 h, 750°C / 2 h). The surface structure of type A samples is fine-grained and homogeneous at any point on the samples. No cracks or voids and even no corrosion products can be observed all over the samples. The SEM micro graphs of the type A surface is shown in figure 8a-c with different magnifications.

The surface morphology of type B samples is more structured than the surface obtained for type A samples (see figure 8d-f). The scale covers the whole surface homogeneously with a pronounced texture (compare figure 8c with 8f). Additionally, some cracks revealed in the surface scale and corrosion products with a size up to about 50 μm were formed during the heat treatment. EDX point analysis showed that these crystals on top of the surface are mainly composed of Al with a low content of Fe and Cr. From this observation it can be concluded that crack generation took place during quenching from the austenising temperature (1075°C) to room temperature. During the subsequent tempering procedure at 750°C small corrosion products formed on the fresh crack surfaces.

MANET II (pipe specimens)

SEM investigations have shown that the morphology of the sample pipe surfaces appears similar for both types of heat treatment, C (950°C / 2 h, 750°C / 2 h) and D (1075°C / 0.5 h, 750°C / 2 h). The surface was covered by a scale of small corrosion products as to be seen in figure 9a-f. On top of the scale individual crystals have been formed which had a size of 20 to 60 μm. Amount and size of the individual corrosion products increased with higher temperature. EDX analyses have revealed that the surface scale mainly contains Al and smaller concentrations of Fe and Cr. The individual corrosion product on top of this scale are composed of mainly Al and lower amounts of Cr and Fe. It can be seen that the individual crystals are enriched in Cr compared to the scale. Irregular oriented cracks were observed in the surface scale. Cracking of the scale appears more frequent compared to the scale cracking of sample sheets. Also, the cracks appear sharper than on the flat surfaces. Small corrosion products can be seen on the crack flanks.

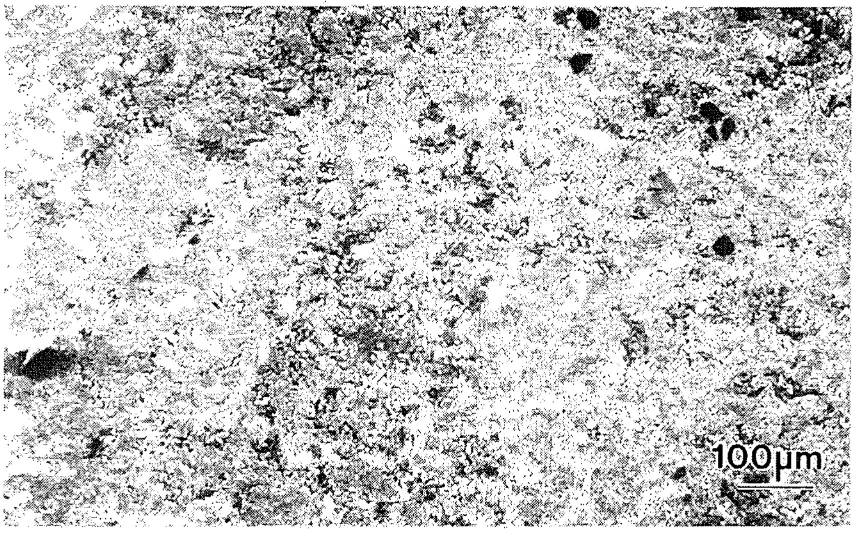

Figure 8a: Surface morphology of a heat treated F82H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h, x 100).

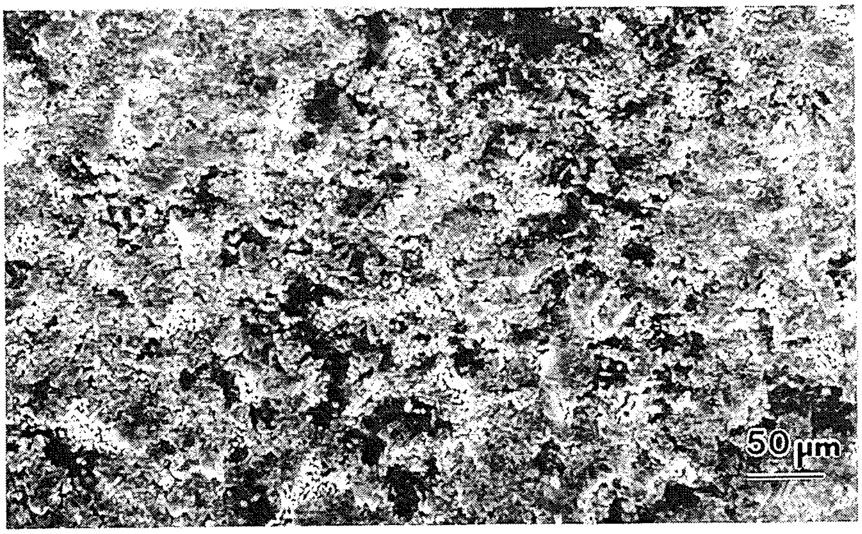

Figure 8b: Surface morphology of a heat treated F82H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h, x 200).

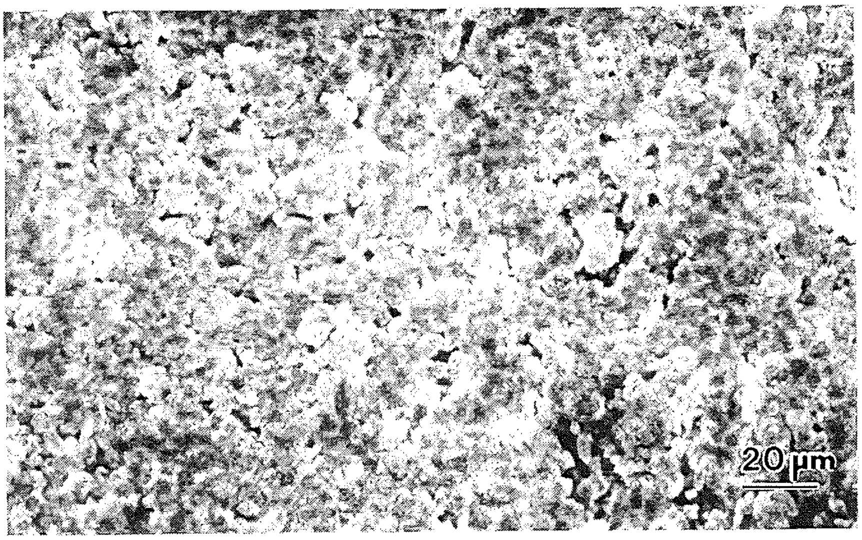

Figure 8c: Surface morphology of a heat treated F28H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h, x 500).

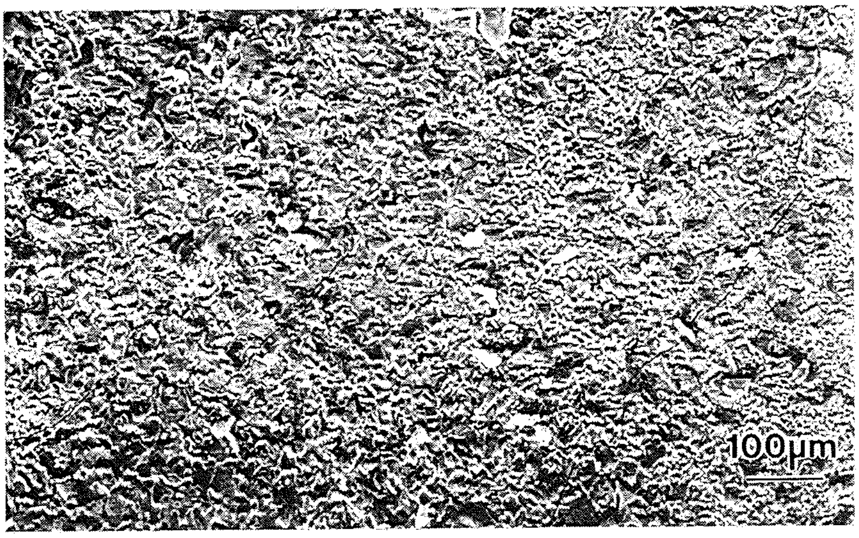

Figure 8d: Surface morphology of a heat treated F82H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h, x 100).

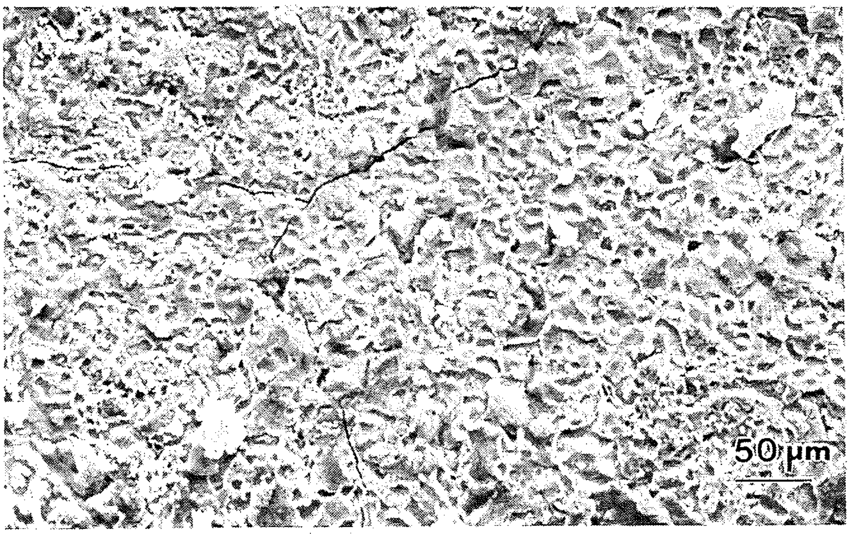

Figure 8e: Surface morphology of a heat treated F82H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h, x 200).

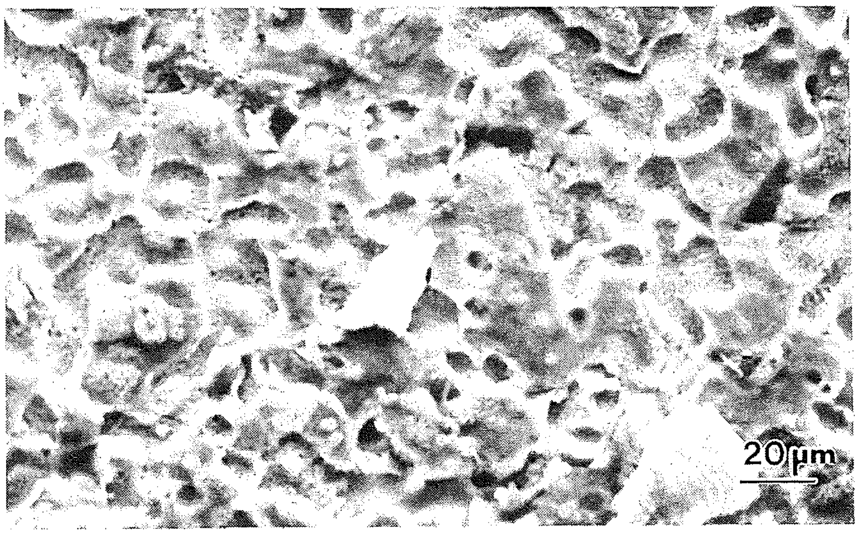

Figure 8f: Surface morphology of a heat treated F28H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h, x 500).

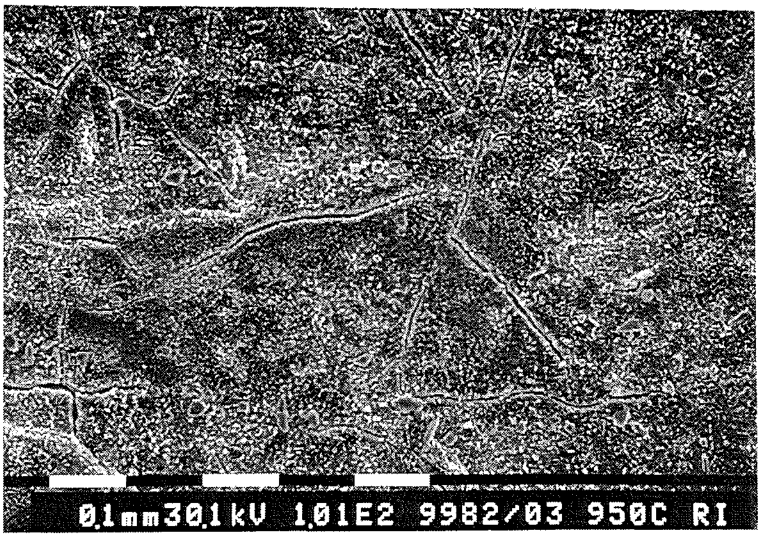

Figure 9a: Surface morphology of a heat treated MANET II sample pipe (type C: 950°C / 2 h, 750°C / 2 h, inside wall, x 100).

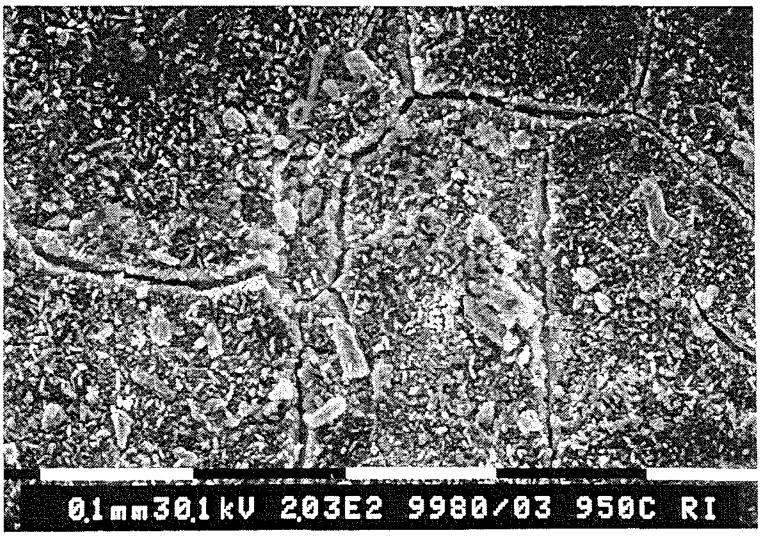

Figure 9b: Surface morphology of a heat treated MANET II sample pipe (type C: 950°C / 2 h, 750°C / 2 h, inside wall, x 200).

Figure 9c: Surface morphology of a heat treated MANET II sample pipe (type C: 950°C / 2 h, 750°C / 2 h, inside wall, x 500).

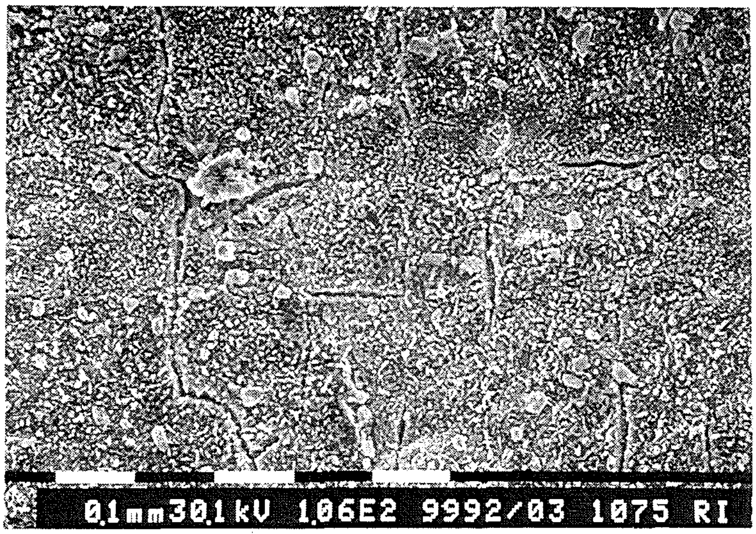

Figure 9d: Surface morphology of a heat treated MANET II sample pipe (type D: 1075°C / 0.5 h, 750°C / 2 h, inside wall, x 100).

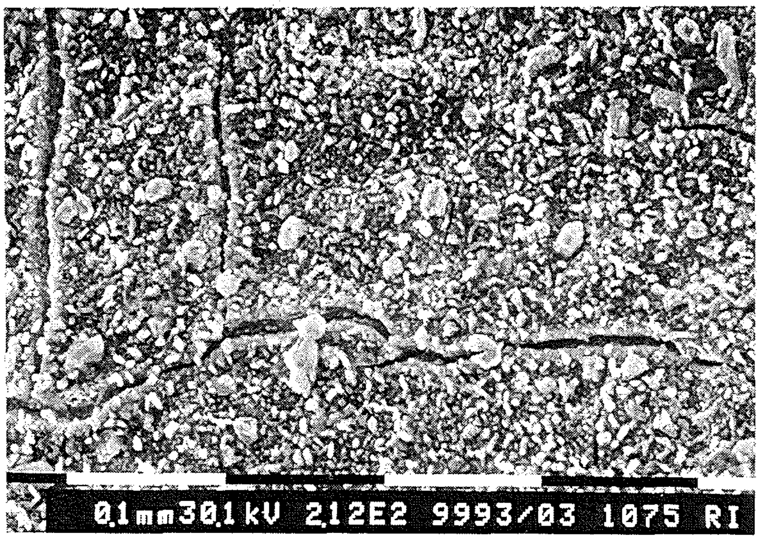

Figure 9e: Surface morphology of a heat treated MANET II sample pipe (type D: 1075°C / 0.5 h, 750°C / 2 h, inside wall, x 200).

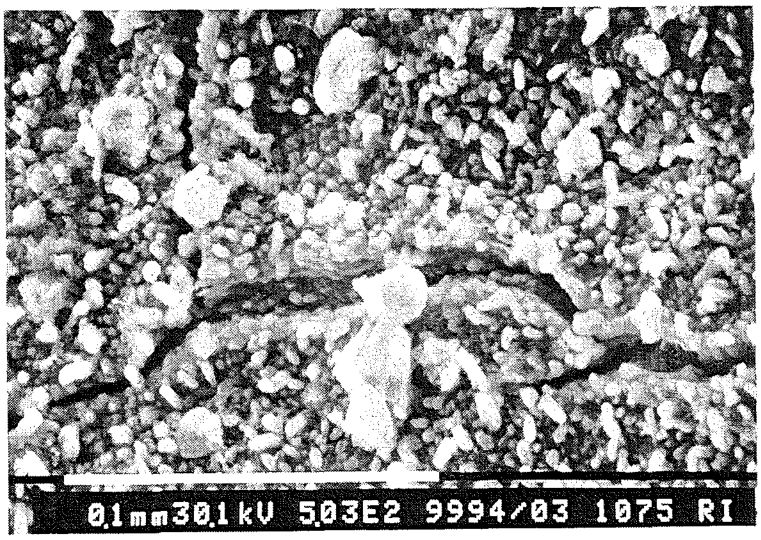

Figure 9f: Surface morphology of a heat treated MANET II sample pipe (type D: 1075°C / 0.5 h, 750°C / 2 h, inside wall, x 500).

3.2.2 Metallographical examination

F82H-mod. (sheet specimens)

Cross sectional views of the scale after heat treatment are shown for type A samples (1040°C / 0.5 h + 750°C / 1 h) in figure 10a and b and for type B samples (1075°C / 0.5 h + 750°C / 2 h) in figure 10c and d at various magnifications. Independent of the heat treatment the samples look similar concerning the layers formed, the adherence and the structure of the substrate. In the following the results of the metallographical examination will be discussed for type A and B.

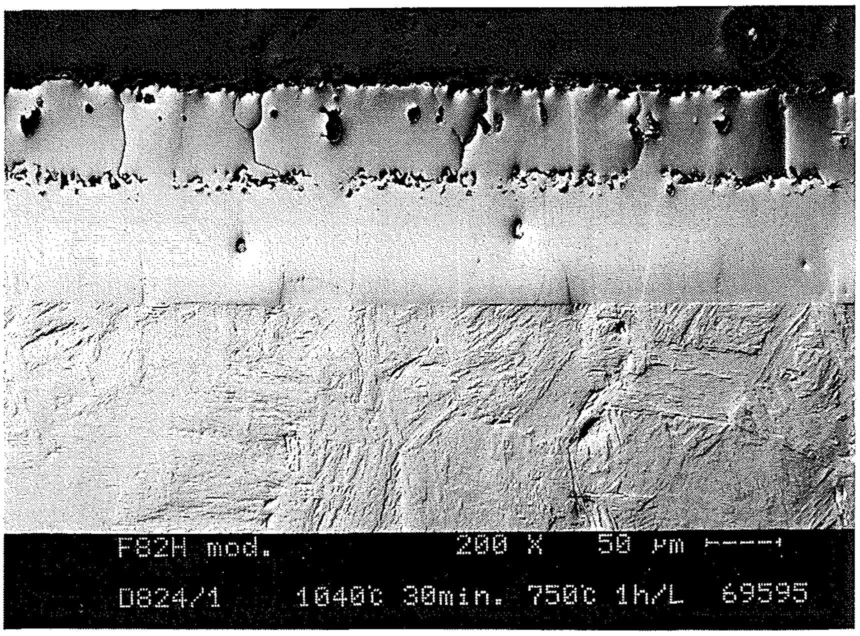

Figure 10a: Cross section of a heat treated F82H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h, x 200).

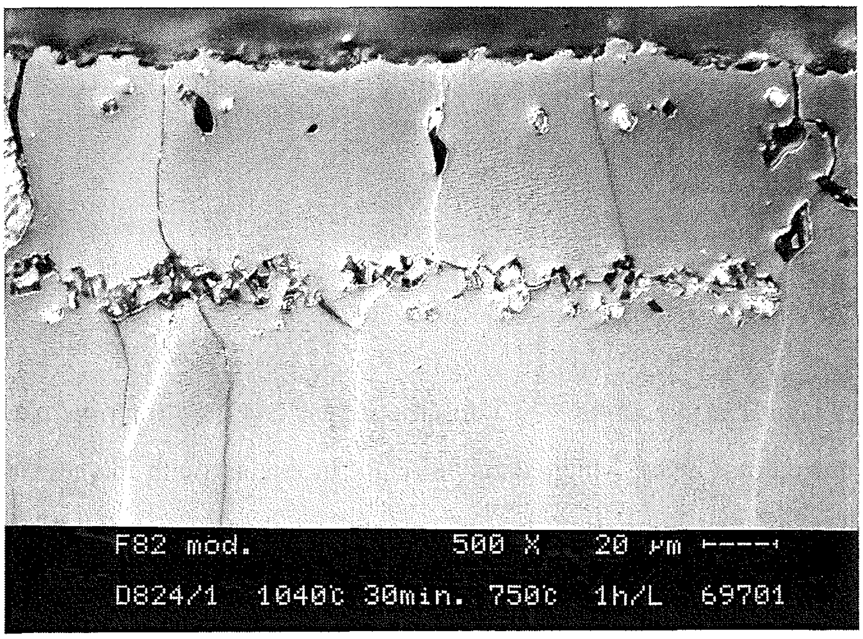

Figure 10b: Cross section of a heat treated F82H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h, x 500).

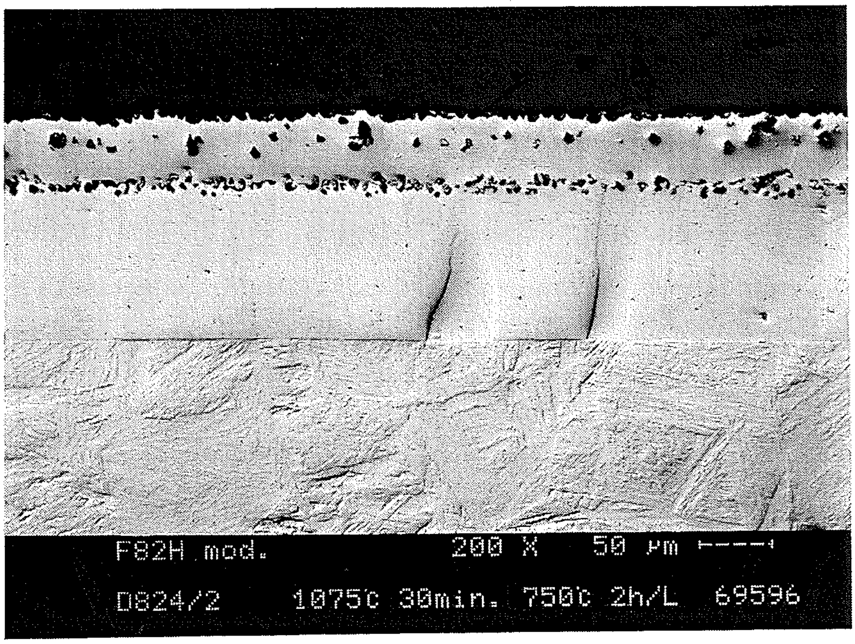

Figure 10c: Cross section of a heat treated F82H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h, x 200).

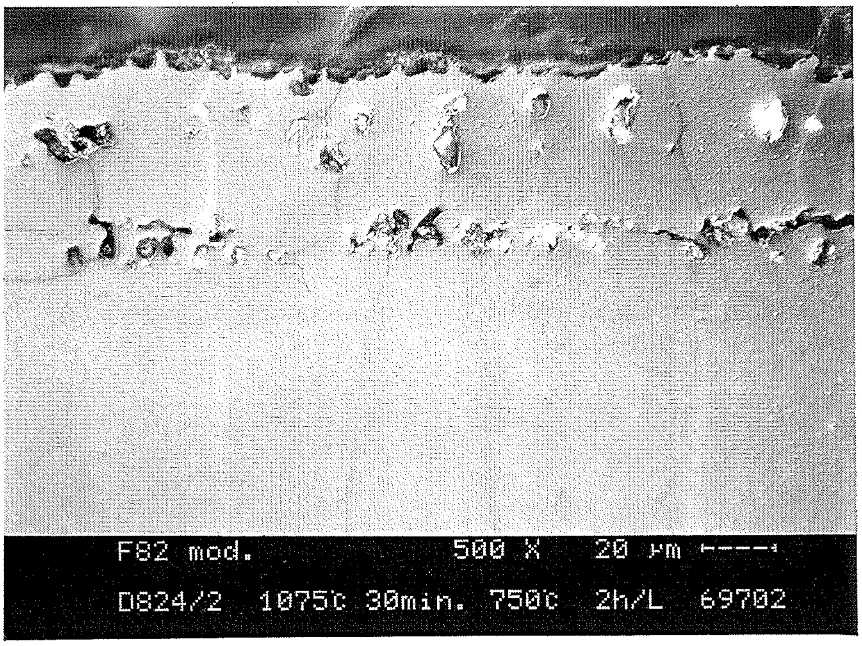

Figure 10d: Cross section of a heat treated F82H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h, x 500).

In general, the layer can be subdivided into an external layer, an intermediate band of high porosity and an internal layer, which stands directly in contact with the substrate. The interface to the substrate beneath the internal layer is indicated as a sharp boundary. The sample surface appears to be rather rough. In the external layer, near to the sample surface, a few pores were formed. Additionally, cracks starting from the surface are observed. In the most times they were stopped in the porous zone, in some seldom cases also in the middle of the layer. A crack growth in to the internal layer was never recognised. The structure of the layer is characterised by grains oriented perpendicular to the surface. Small needles like precipitations can be observed in the internal layer which are homogeneously distributed. The grain structure beneath the layer has the typical appearance of martensitic substrate.

The thickness of the external layer is dependent on the amount of solidified Al which adheres on the surface after the hot dip aluminising process. On the other hand, the thickness of the internal layer dependent on time and temperature used for the heat treatment. Type A samples result in an internal layer with 70 µm in thickness, type B samples reveal a 90 µm thick layer. The equal values are obtained on MANET sheets treated in the same manner (aluminised and heat treated). This indicates that the diffusion process to form the internal layer is independent on the ferritic steel used as base material.

MANET II (pipe specimens)

The structure of the layers on MANET II pipes is similar after both heat treatments, type C (950°C / 2 h, 750°C / 2 h) and D (1075°C / 0.5 h, 750°C / 2 h). Cross sectional views of the layers of heat treated sample pipes are given in figure 11a-d respectively for the outside and inside pipe wall. No significant changes of the scale structures can be observed compared to the structures of the F82H-mod. sheet specimens. The total scale thickness defined as the distance between the scale-substrate interface and the exterior surface of the coating was measured to be around 100 and 125 µm respectively, for type C and D samples. Scale cracks could be observed which generated at the surfaces and propagated through the external layer of the scale, as can be seen for instance in figure 11b for an inside pipe wall. Sometimes those cracks

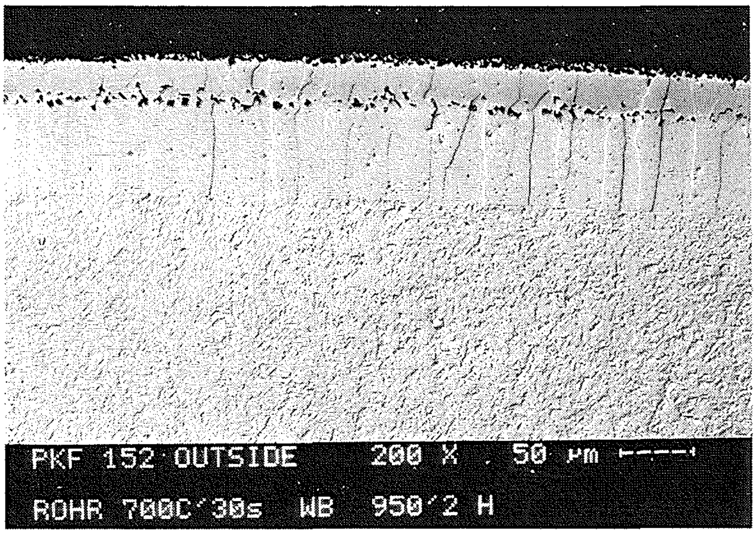

Figure 11a: Cross section of a heat treated MANET II sample pipe (type C: 950°C / 2 h, 750°C / 2 h, outside wall, x 200).

Figure 11b: Cross section of a heat treated MANET II sample pipe (type C: 950°C / 2 h, 750°C / 2 h, inside wall, x 200).

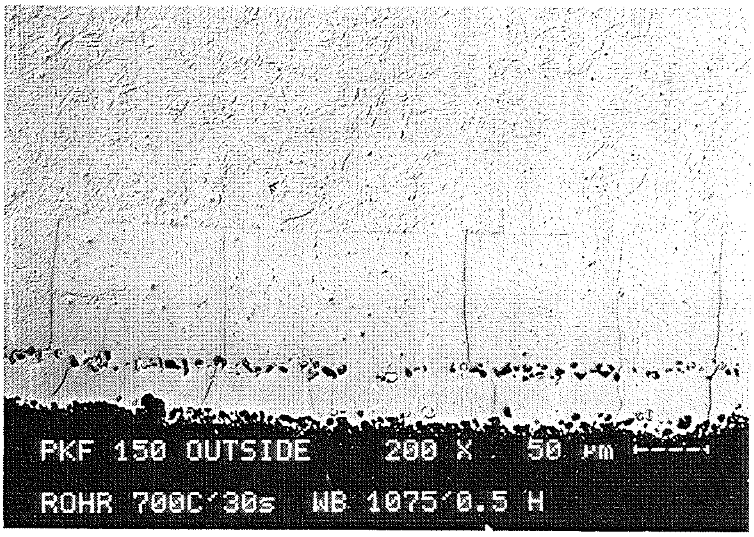

Figure 11c: Cross section of a heat treated MANET II sample pipe (type D: 1075°C / 0.5 h, 750°C / 2 h, outside wall, x 200).

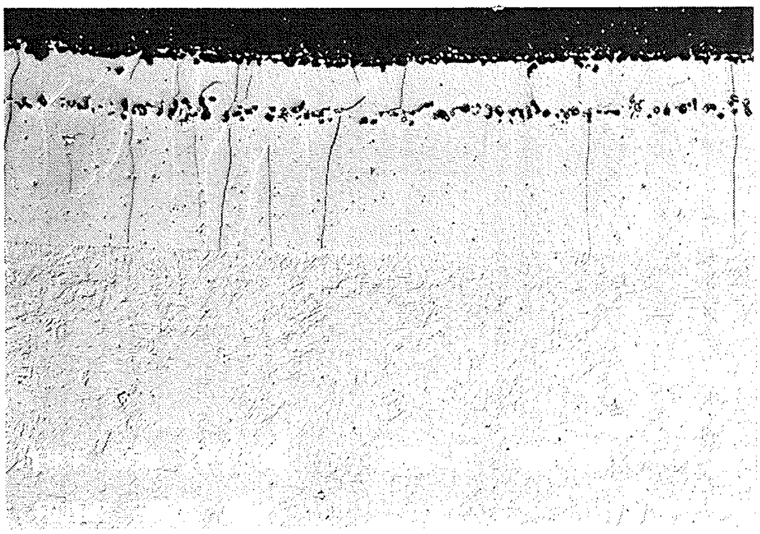

Figure 11d: Cross section of a heat treated MANET II sample pipe (type D: 1075°C / 0.5 h, 750°C / 2 h, inside wall, x 200).

stopped in the external layer but more often they stopped in the intermediate zone of high porosity. Crack propagation across the internal layer were never observed either in the pipe or sheet specimens.

3.2.3 Analytical examination

F82H-mod. (sheet specimens)

EPMA line scans were performed on polished cross sections of type A and B samples. The results are shown in figure 12a and b. The compositions found for the different layers are identical for both heat treatments A and B. Therefore, the results obtained will be discussed without differentiation between type A and B samples in the following. It can be seen that the intermetallic Fe_2Al_5 phase has completely transformed after the heat treatment. On top there is a high concentration of Al and O which indicates the formation of an alumina layer (see figure 12b). Just beneath the surface a zone of FeAl phase is recognised. According to the binary Fe-Al phase diagram (which has been used here rather then the ternary Fe-Cr-Al phase diagram) this phase is stable between 29-54 at% Al at 1040°C and 30-54.5 at% at 1075°C, respectively. As already mentioned above, the extension of this zone, the external layer, is dependent of the amount of solidified Al which remained on the surface after the hot-dip aluminising process.

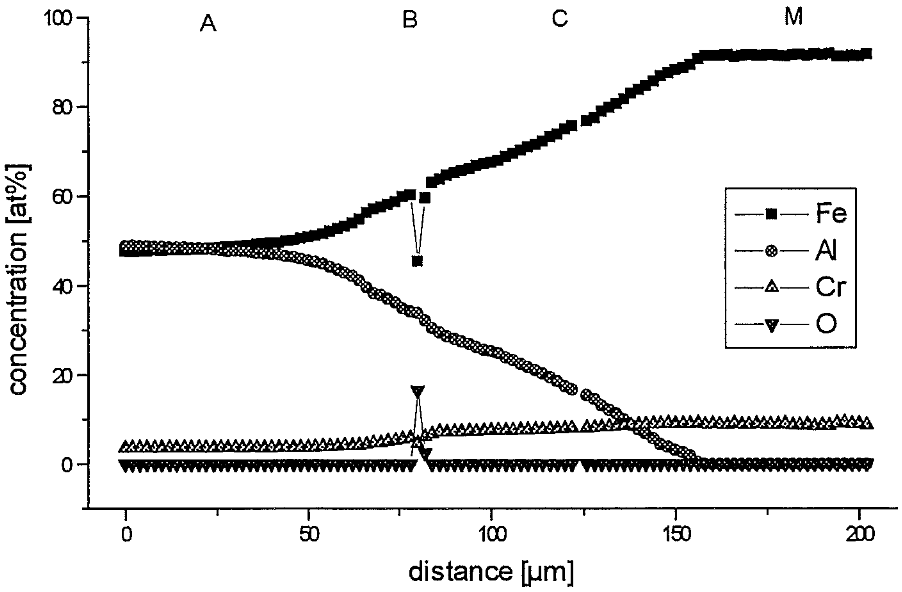

Figure 12a: EPMA line scan of a heat treated F82H-mod. sample sheet (type A: 1040°C / 0.5 h, 750°C / 1 h)., A...FeAl, B...band of pores, C...α-Fe(Al), M...matrix.

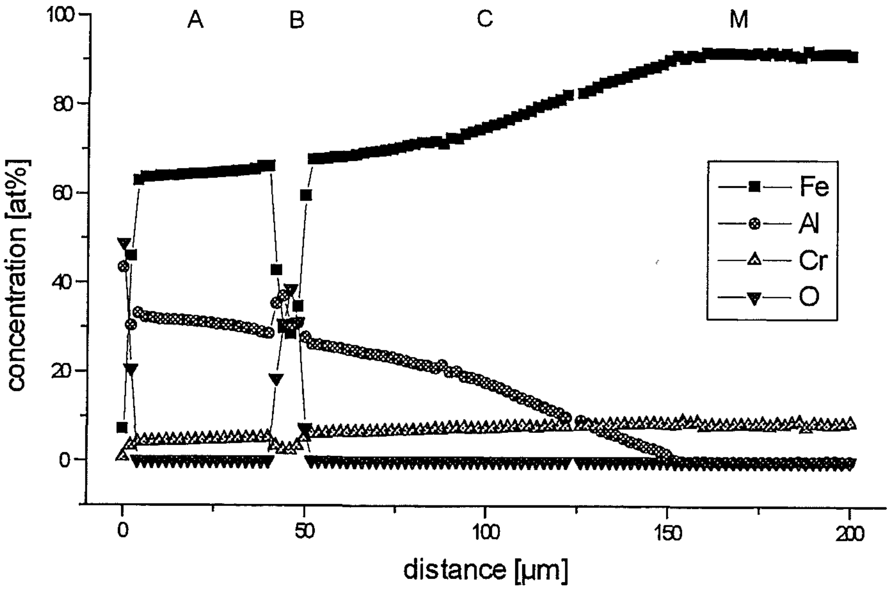

Figure 12b: EPMA line scan of a heat treated F82H-mod. sample sheet (type B: 1075°C / 0.5 h, 750°C / 2 h)., A...FeAl, B...band of pores, C...α-Fe(Al), M...matrix.

The strong scatter of the concentration gradients beneath the FeAl phase results from interactions of the electron beam with pores of the intermediate layer. A correct quantitative analysis is not possible there. For the internal layer the Al concentration decreases more rapidly than for the external layer. Within 70 µm (type A) and 90 µm (type B) respectively, the Al concentration decreases from 30 to 0 at%. The content of Fe and Cr show the opposite trend. The composition revealed corresponds to the compound α-Fe(Al) according to the binary phase diagram.

Therefore both types of heat treatments, A and B, are suitable to transform the brittle Fe_2Al_5 compound into softer, more ductile phases (FeAl and α-Fe(Al)). The same results were obtained for aluminised MANET sheets subsequently heat treated like type A and B samples.

MANET II (pipe specimens)

No EPMA line scans on aluminised MANET pipes were performed. Therefore, results revealed on MANET sheets after heat treatment D will be presented in the following. In figure 13 the line scan is plotted. The Al content decreases continuously from around 45 at% on the surface down to zero in the steel. Fe and Cr content show the opposite trend. The values measured indicated the formation of AlFe phase in the external and α-Fe(Al) in the internal layer. Hence, the intermetallic Fe_2Al_5 phase has transformed completely into softer phases.

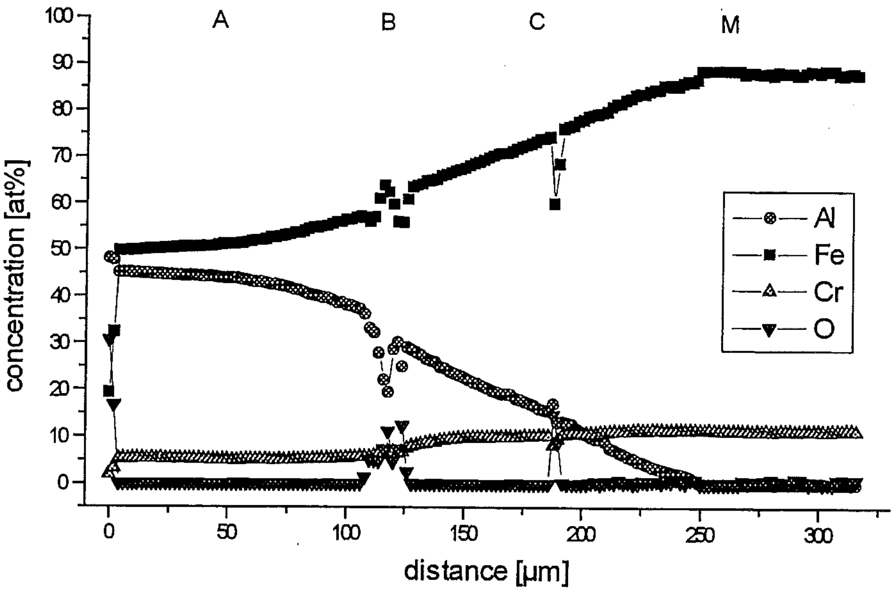

Figure 13: EPMA line scan of a heat treated MANET II sheet (type D: 1075°C / 0.5 h, 750°C / 2 h). A...FeAl, B...band of pores, C...α-Fe(Al), M...matrix.

3.2.4 Vickers micro hardness

F82H-mod. (sheet specimens)

The observations made for type A and B are the same. Hence, the results obtained for both kind of samples will be discussed together in the following. The transformation of the brittle Fe_2Al_5 phase into softer, more ductile phases can be observed by micro hardness measurements. The values revealed are summarised in table 3.

	Type A / HV 0.05 1040°C / 0.5 h, 750°C / 1 h	Type B / HV 0.05 1075°C / 0.5 h, 750°C / 2 h
external layer FeAl	290 - 372	225 - 296
internal layer α-Fe(Al)	321 (beneath band of pores) 242 202 (interface coating/steel)	309 (beneath band of pores) 292 192 (interface coating/steel)
substrate F82H-mod.	230 - 250	235 - 250

Table 3: Results of micro hardness measurements (HV 0.05) on type A and B samples.

The micro hardness obtained for FeAl (external layer) stays constantly over the whole area. This corresponds with the EDX measurements which showed a uniform composition of Fe and Al in this region. In the internal layer the Al content changes from around 30 to 0 at%. This fact can also be observed with changing micro hardness values in this layer: with decreasing Al content the micro hardness decreases as well. The hardness of the substrate remained unchanged compared to the virgin material.

MANET II (pipe specimens)

The results obtained for type C and D samples are listed in table 4. The micro hardness values measured on the external layer are uniform over the whole layer. In the internal layer the hardness shows a gradient: a decrease from outside to the inside can be observed. The hardness of the substrate MANET stayed uneffected after the heat treatments. The results are in agreement with measurements revealed on type A and B samples.

	Type C / HV 0.05 950°C / 2 h, 750°C / 2 h	Type D / HV 0.05 1075°C / 0.5 h, 750°C / 2 h
external layer FeAl	275 - 340	270 - 315
internal layer α-Fe(Al)	325 (beneath band of pores) 240 215 (interface coating/steel)	335 (beneath band of pores) 290 200 (interface coating/steel)
substrate MANET	220 - 250	235 - 270

Table 4: Results of micro hardness measurements (HV 0.05) on type C and D samples.

The investigations have shown that there is no difference in the results for sheet and pipe specimens. However, it is obvious that both the total porosity and the average area of one pore increase with temperature.

4. Preliminary tests

4.1 Compatibility with Pb-17Li

Hot dip aluminised and subsequent oxidised MANET samples were exposed to flowing Pb-17Li alloy in the PICOLO loop at 450°C up to 10,000 h. The flow velocity of the liquid alloy was about 0.3 m/s. The samples were taken out of the corrosion loop after exposure times of 1000, 2000, 3000, ..., 10,000 h. The post analyses of each sample revealed that no corrosion attack of the alloy has occurred. The compositions and structures of the surface and the layers did not change also after an exposure time of 10,000 h. Therefore, the layers exhibited a protecting action against liquid metal corrosion. The layers also could withstand a number of temperature changes between 450°C and room temperature [7-9].

4.2 Compatibility with water

Exposure of hot dip aluminised and subsequent heat treated samples in water are under investigation by ENEA Casaccia, Italy. The experiment is still running and hence, no results are available by now.

4.3 Permeation measurements

Hot dip aluminised MANET discs were subsequently heat treated for 15 h or 30 h at 750°C or 10 h or 30 h at 950°C in air, respectively. The permeation measurements for all specimens were carried out by JRC Ispra, Italy. The reduction in deuterium permeation rate of up to three orders of magnitude were achieved for aluminised samples which underwent a heat treatment of 30 h at 950 °C [10]. In case of the heat treatment at 750°C for 15 h, the maximum reduction in permeation rate was measured to be around 260 times at 470°C and 1000 at 300°C for aluminised samples [11].

Permeation measurements on aluminised and heat treated (type D) MANET samples were made in Brasimone, ENEA; Italy. Preliminary tests show that the results obtained for these samples [12] are not as good as the results revealed on samples after longer heat periods [10].

5. Compatibility with ITER test module preparation

A detailed description of the fabrication of the ITER test Module (ITM) is given in the Design Description Document (DDD) for the WCLL Blanket Module (2nd draft, 21 September 1997).

Until now, it is not clear, when the austenising and tempering procedure of the steel will be performed. Hence, in the following two routes will be presented for the TPB fabrication:

The first route considers the production of the TPB as a part of the module fabrication: the sequences of the module fabrication include the different phases of the TPB production. In this case, the tubes hot dip aluminised on the inside or the outside will be inserted in their positioning grids. After the segment box is closed the assembly will be completed by a thermal treatment for stress relief, temperature and duration are tbd. Probably the austenisation and tempering steps for the steel has to be performed (1075°C, 0.5 h / 750 °C, 2 h which corresponds to the heat treatments type B and D respectively, described in this report). Fortunately, the coating procedure presented in this report has considered that the whole TPB production is compatible with the heat treatments required for the steel.

The second route thinks about that the hot dip aluminised and heat treated tubes are inserted into the module during the assembly phase, which separates the heat treatments needed to prepare the TPB from those typical of the production of the module, which are not completely defined at the moment. Any way, a heat treatment after the final fabrication of the segment box is required. Therefore, the TPB should be stable to stay at 700-750°C for some hours without any change of the micro structure. In this report it could be shown, that the heat treatment of 750°C / 2 h on aluminised and oxidised samples had not effect on the micro structure of the coating.

Hot dip aluminising technique with a subsequent oxidation process is compatible with the different heat treatments required independent of the fabrication chosen for the ITER test module fabrication (route one or two). The different heat treatments needed for the steel optimisation were taken already into account by the development of the optimised coating procedure.

6. Summary

The investigations have shown that the hot dip aluminising technique is a suitable method to form an intermetallic layer by a controlled manner into the surface near zone of martensitic steels like MANET and F82H-mod. For both sample geometries, sheet and tube samples, a very brittle intermetallic compound Fe_2Al_5 was formed mainly by inward diffusion of Al into the steel during the immersion process. On top of this intermetallic layer an overlayer of solidified Al melt exists.

In order to get an alumina layer on top of the surface as tritium permeation barrier (TPB) and to transform the brittle Fe_2Al_5 compound into a softer phase a heat treatment above A_{c1} temperature of the steels has to be performed. It was found that the structures of the layers formed are very similar independent of the heat treatment and the structure material chosen (F82H-mod.: type A and B; MANET: type C or D). The layers formed can be subdivided into three different zones: an external layer of FeAl, an intermediate porous band and an internal layer existing of α-Fe(Al). The formation of the pores took place at the FeAl and α-Fe(Al) interface for the different diffusion coefficients of Al and Fe in the α-Fe(Al) zone. The thickness of the internal layers formed is dependent of the temperature of the heat treatment: the higher the temperature the thicker the layer.

The **formation of an alumina scale** on top of the external layer was proved with different analytical methods. Heat treatment type B is sufficient to build the α-Al_2O_3 phase, type A treated samples just formed different alumina phases.

The requirement of the **capability of self-healing** of the alumina layer in case of cracking or spalling off is not investigated in total. However, the thermodynamic calculations done under the assumption of an oxygen saturated environment revealed that self-healing should occur [13, 14]. The Al content in the FeAl layer is sufficient. The kinetics of the process remains to be proven by experiments.

Another important demand to the layer is the **corrosion resistance in Pb-17Li** at high temperature. It was shown that alumina layer withstands the flowing alloy up to 10,000 h at 450°C without any corrosion attack.

The **corrosion experiment in water** with aluminised samples is still running, therefore, no data are available at the moment. But the first results are expected to be at hand in the beginning of next year.

The **reduction in deuterium permeation rate** of up to three orders of magnitude were achieved for aluminised samples which underwent a heat treatment of 30 h at 950 °C. These results corresponds to the requirements. For lower temperatures and / or shorter times chosen for the heat treatment the permeation rate factor decreases down to smaller values.

Both proposed **ITER test module fabrication processes** are compatible with the hot dip aluminising technique with a subsequent oxidation process. The heat treatments needed for the optimisation of the TPB are the same which are necessary for the structural material. Hence, the two processes are compatible with each other.

It could be shown that hot dip aluminising is a suitable technique to produce TBP on tubes for the inside and the outside. The layers are compatible with Pb-17Li, the PRF is sufficiently high and the process is compatible with the ITM geometry and the fabrication sequence.

Acknowledgement

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