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Abstract

Coatings on low activation steels are required in fusion technology in order to reduce the tritium permeation rate through the steel into the cooling water system by a factor of at least 100. Alumina seems to be a promising coating material. However, an appropriate coating system must also have the potential for self healing since the ceramic alumina scale tends to fail if mechanical stress is applied.

Hot-dip aluminising is an applicable technology to coat ferritic-martensitic steels which consists of two main process steps: Firstly, hot dip aluminising of the steel (700 °C, 30 s) Secondly, transformation of the very hard intermetallic scale Fe_2Al_5 into FeAl and α-Fe(Al) phase during a subsequent heat treatment (1040 °C, 30 min). The pressure chosen for the HIP experiment was 1000, 2000 and 3000 bar. Compared to a heat treatment without superimposed high pressure pores formation due to the Kirkendall effect could be suppressed successfully. The influence of the high pressure on the heat treatment (1040 °C, 30 min) will be discussed in this paper.

Einfluß des HIP - Prozesses auf aluminierte ferritisch-martensitische Stähle

Kurzfassung

Beschichtungen auf niedrigaktivierenden Stählen sollen die Tritiumpermeationsrate (TPR) durch den Stahl hindurch ins Kühlwasser minimieren. Al_2O_3 erweist sich als geeignetes Beschichtungsmaterial und erfüllt die geforderten Kriterien.

Eine Methode zur Beschichtung ferritisch-martensitischer Stähle ist das Hot-Dip-Aluminierverfahren mit anschließender Wärmebehandlung. Nach dem Tauchen in Al (700 °C, 30 s) schließt sich eine Wärmebehandlung an, die der Vergütungsvorschrift für F82H-mod. entspricht (1040°C, 0.5 h / 750°C, 1 h). Dabei wird die spröde intermetallische Phase Fe_2Al_5 in die weniger harte FeAl und α-Fe(Al) Phase umgewandelt. Als Folge unterschiedlicher Diffusionskoeffizienten von Fe und Al bildet sich zudem noch ein Porensaum zwischen der FeAl und α-Fe(Al) Phase aus. Durch die Beaufschlagung von hohen Drücken (1000, 2000, 3000 bar) während der Austenitisierung (1040 °C, 30 min) konnte die Bildung von Poren erfolgreich verhindert werden. Der Einfluß des hohen Drucks auf die Fe-Al-Schichtsystem wird in diesem Bericht vorgestellt.

Content

1. Introduction

In the water cooled lead lithium metal (WCLL) blanket concept the permeation of tritium through the structural material into the cooling water circuit is foreseen to be minimised by the use of suitable coatings which act as tritium permeation barriers (TPB).

It is well known that thin alumina layers can reduce the tritium permeation rate by several orders of magnitude [1-3]. Hence, the development of alumina layers as TPB on reduced activation steels [4] (namely ferritic-martensitic steels) is the main effort.

Hot dip aluminising with subsequent heat treatment seems to be a promising coating method to fulfil the goals required. 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. This heat treatment has to enable the transformation of the brittle Fe_2Al_5 layer formed during the aluminising process on the steel surface into more ductile phases (preferable FeAl and / or α-Fe(Al)). Therefore, the standard heat treatment for steel F82H-mod. is used for transformation of the brittle phase which requires reaustinisation at 1040 °C for 0.5 h and subsequent tempering at 750 °C for 1 h. It could be shown, that the necessary goals can be fulfilled with this heat treatment: transformation of the brittle Fe_2Al_5 layer, complete incorporation of solidified Al into the steel matrix by diffusion [5-7] and formation of a thin alumina layer on top of the coating as a very efficient tritium permeation barrier [2, 8]. During the transformation of the brittle phase Fe_2Al_5 two more ductile layers are formed: an external layer (FeAl) and an internal layer (α-Fe(Al)). The two layers are separated by a band of pores, which was formed due to the Kirkendall effect. The formation of pores should be suppressed by using high pressure during the heat treatment. If no pores would be formed during the process it is likely that the tritium permeation rate can be reduced and the mechanical properties of the system should be improved as well.

2. Experimental procedure

2.1 Materials

The substrate materials to be aluminised were the fully martensitic steels F82H-mod and MANET II. F82-mod. was produced by JAERI/NKK Corporation Japan. MANET II is taken from the NET-heat (no. 50806) produced by Saarstahl Völklingen, Germany. The chemical composition of the steels is given in table 1. Al used for the melt had an initial purity of 99.5% with the main impurities being Fe and Si. The melt became enriched in the main steel components Fe and Cr with increasing immersion time.

	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%).

2.2 Sample preparation

The materials were delivered as 20 mm thick sheets in a tempered condition. Sheet specimens of 50 x 15 x 1 mm were machined by erosion. 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 a special facility developed in FZK [9]. 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 and HIP process

The heat treatments for all samples were carried out in the HIP 3000 facility, delivered by company Dieffenbacher, Eppingen, Germany. The aluminised samples were cleaned ultrasonically in ethanol, dried and placed in alumina crucibles which were placed in the furnace. The temperatures and times chosen correspond to the instruction for austenisation and tempering for F82H-mod. steel. The samples were HIPped in an argon atmosphere. The conditions for aluminising and heat treatment under pressure were summarised in table 2. The HIP cycle chosen is shown in fig. 1.

sample	steel	Aluminising conditions	Heat treatments	HIP conditions
1	F82H-mod.	700 °C / 30 s	1040 °C / 0.5 h // 750 °C / 1 h	5 bar
2	MANET II	700 °C / 30 s	1040 °C / 0.5 h // 750 °C / 1 h	1000 bar
3	MANET II	700 °C / 30 s	1040 °C / 0.5 h // 750 °C / 1 h	2000 bar
4	F82H-mod.	700 °C / 30 s	1040 °C / 0.5 h // 750 °C / 1 h	3000 bar

Table 2: The conditions for aluminising and heat treatment under pressure.

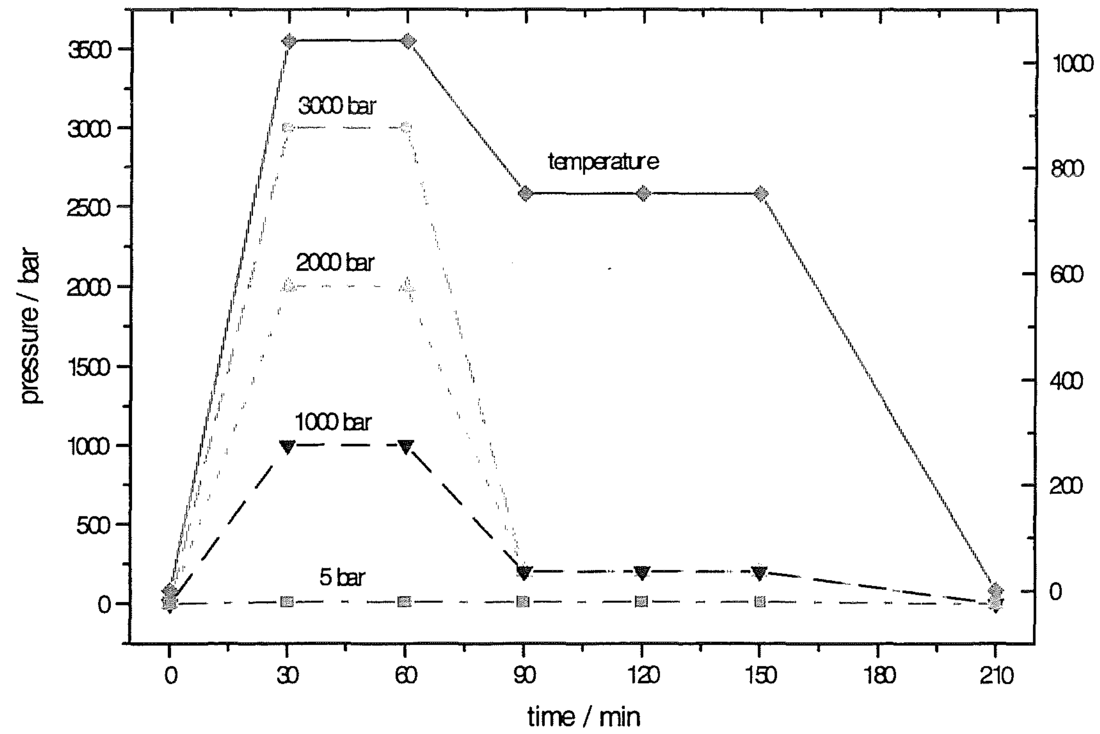

Fig. 1: HIP cycle used for austenisation and tempering of hot dip aluminised steels.

2.5 Analytical examination

Metallographical examination was carried out to study the influence of high pressure to the coating thickness, adherence after aluminising and subsequent heat treatment and the quality of the layers. EPMA line scans were performed on polished cross sections of the specimens HIPped at 5, 1000, 2000 and 3000 bar resp. in order to get information about the phases formed and their thickness. The micro hardness was measured by Vickers hardness testing (HV0.05).

3. Results

3.1 Metallographical examination

Metallographical cross section of the aluminised and subsequent heat treated F82H-mod. sample after HIPping is shown in fig. 2. Two layers can be identified on the steel surface: an internal layer namely α-Fe(Al) with a thickness of about 80 μm and an external layer (FeAl) of circa 60 μm thickness. The thickness of the internal layer is found to be dependent of the heat treatment chosen. On the other hand, the thickness of the external layer is dependent on the amount of solidified Al which adhered on the surface after the hot dip aluminising process [7]. These two layers are separated by a porous band which is clearly seen in the specimen heat treated under low pressure (5 bar) (fig. 2). The sample surface appears to be rather rough. In the external layer, near to the sample surface, a few pores were formed as well. Additionally, perpendicular cracks starting from the surface along grain boundaries are observed. In most cases they were stopped in the porous zone, sometimes also in the middle of the layer. A crack growth into the internal layer was never observed.

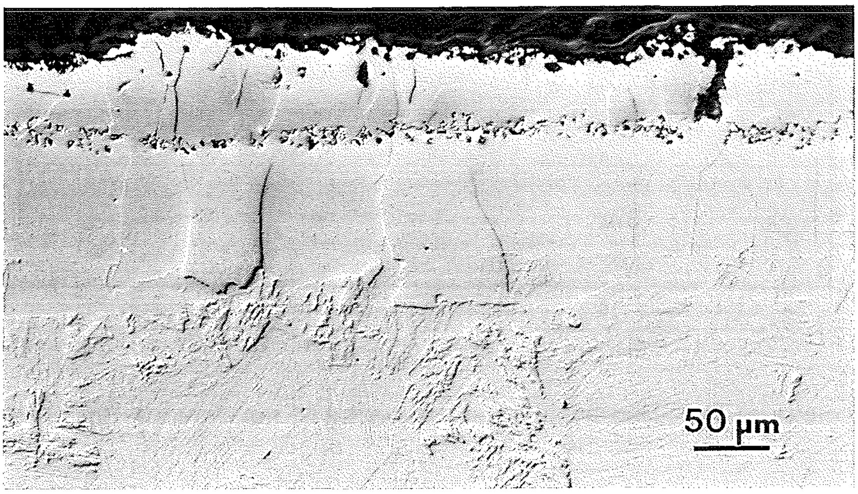

Fig. 2: Polished cross section of hot dip aluminised F82H-mod. sample after heat treatment (1040 °C / 30 min, 750 °C / 1 h) under 5 bar.

In fig. 3 a, b and c the metallographical cross sections of hot dip aluminised specimens HIPped at 1000, 2000 and 3000 bar are shown. The observations made on different HIP treated samples are comparable. Hence in the following, the examinations will be discussed without distinction between these three samples.

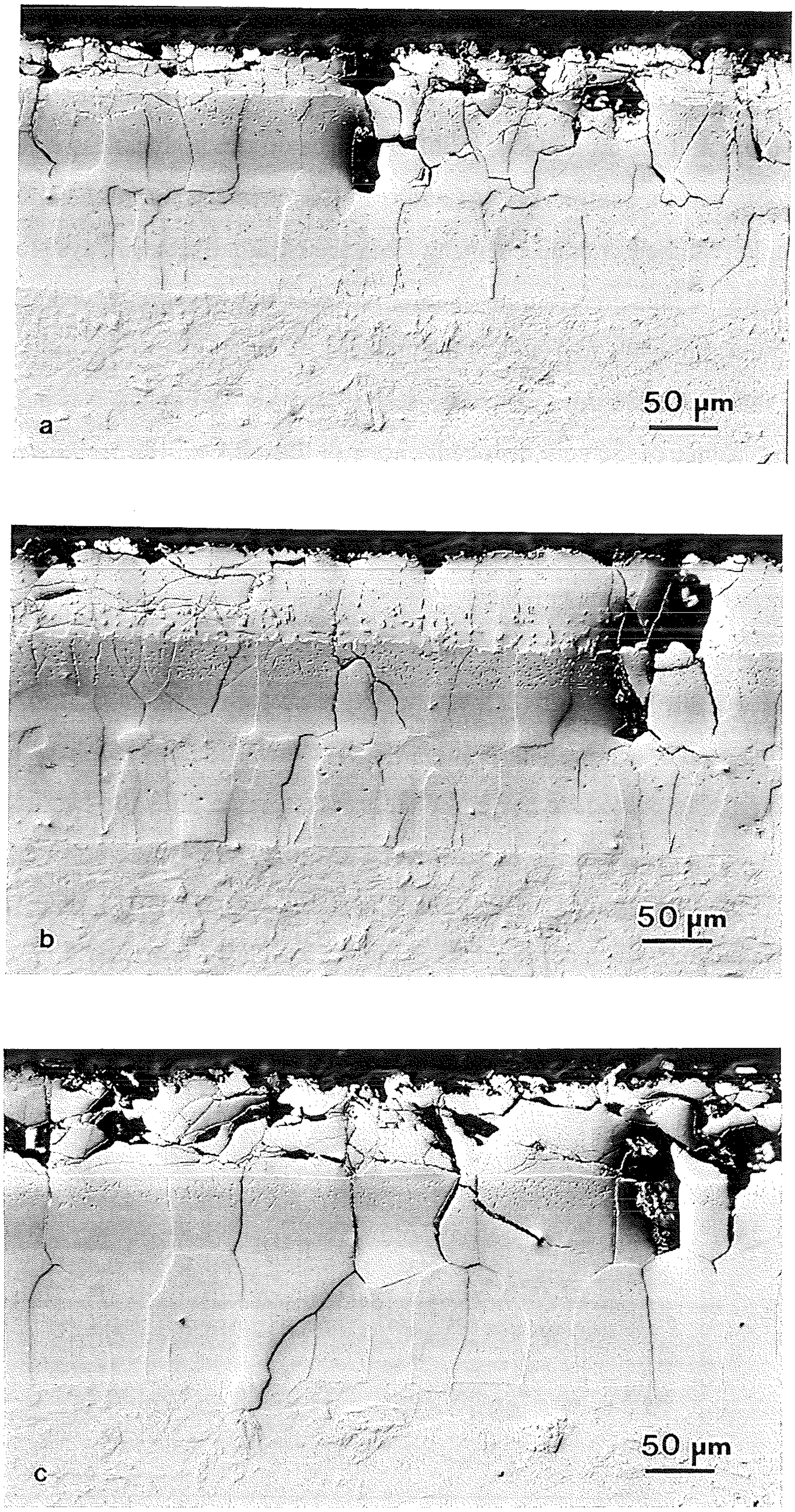

Fig. 3: Polished cross sections of hot dip aluminised F82H-mod. sample sheets after heat treatment (1040 °C / 30 min, 750 °C / 1 h) under a) 1000 bar, b) 2000 bar and c) 3000 bar.

The samples 2, 3 and 4, HIPped at 1000, 2000 and 3000 bar, showed one additional scale on top, compared to sample 1, HIPped at 5 bar. The thickness of the internal layer (α-Fe(Al)) is around 80 µm and the middle layer (FeAl) is circa 60 µm in thickness which corresponds to the values obtained for sample 1. FeAl and α-Fe(Al) layers seem to be homogeneous without any defects. Perpendicular cracks starting from the external layer always stopped at the latest in the FeAl zone. Crack growth into the internal layer was never observed. The new appearing external layer (mainly $FeAl_2$) shows a thickness of circa 35 µm (sample 2), about 60 µm (sample 3) and around 80 µm (sample 4), resp. Many vertical cracks and defects are observed in this layer because of the very brittle character of this phase.

Remarkable is that pores can not be recognised in any HIPped sample in the over layer system after the high pressure treatment neither in between the FeAl and α-Fe(Al) layers nor in the upper region of the FeAl layer.

3.2 EPMA line scans

EPMA line scan of sample 1 is shown in fig. 4. The brittle Fe_2Al_5 phase formed during the hot dip aluminising procedure has completely transformed after the heat treatment. Just beneath the surface a region of the existence of FeAl phase can be recognised. According to the binary Fe-Al phase diagram [10] this phase is stable between 29-54 at% Al at 1040°C. The thickness of the zone which corresponds to the external layer is around 60 µm.

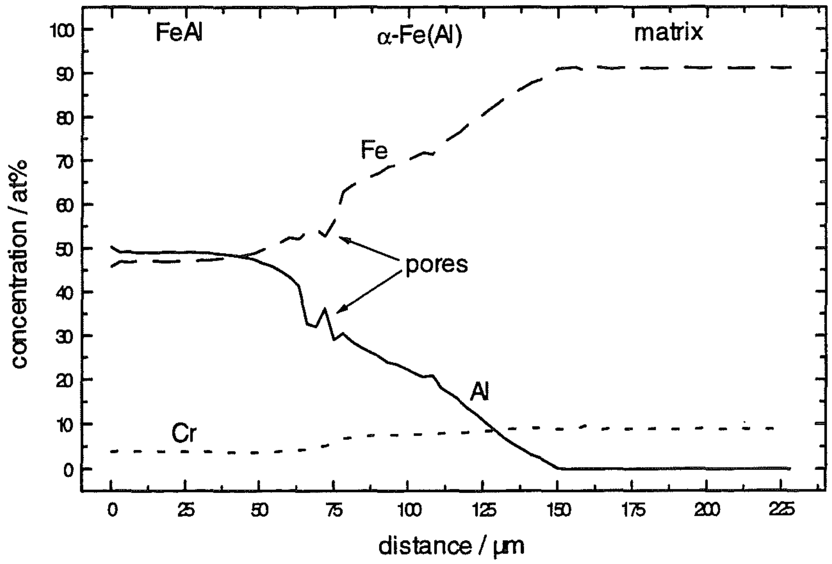

Fig. 4: EPMA line scans of hot dip aluminised F82H-mod. sample sheets after heat treatment (1040 °C / 30 min, 750 °C / 1 h) under 5 bar.

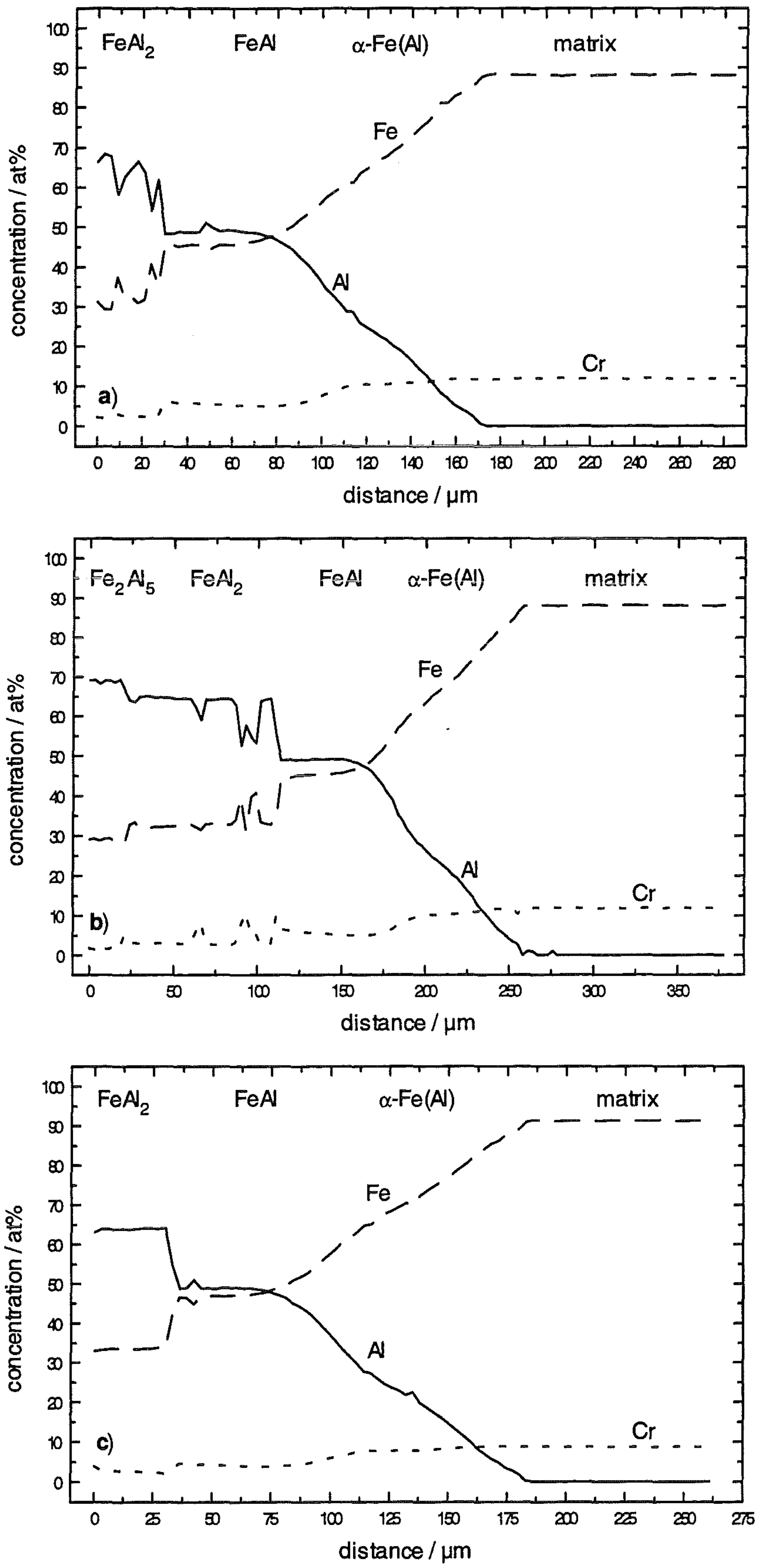

Fig. 5: EPMA line scans of hot dip aluminised F82H-mod. sample sheets after heat treatment (1040 °C / 30 min, 750 °C / 1 h) and HIPping under a) 1000 bar, b) 2000 bar and c) 3000 bar.

The strong change of the concentration gradients of Fe and Al after the FeAl phase results from the interactions of the electron beam within the band of pores. Beneath the pores the Al concentration decreases from 30 to 0 at%. This composition corresponds to α-Fe(Al). The steel elements Fe and Cr show the opposite trend. Within 80 μm their amount raises up to the matrix composition.

In the line scans of sample 2, 3 and 4 (see fig. 5 a, b, c) the phases FeAl and α-Fe(Al) are analysed as well. The thickness of the layers and their composition looks identical to sample 1. This is in agreement with the metallographical examinations. Additionally to the two phases FeAl and α-Fe(Al) a new external layer was formed. In sample 2 and 4 the Al content in this layer is in the range of 66 to 67 at%, which corresponds to a $FeAl_2$ phase determined from the binary Fe-Al phase diagram. Furthermore the phase Fe_2Al_5 can be detected besides $FeAl_2$ in the upper region of sample 3. The concentration profiles of Fe, Al and Cr from phase $FeAl_2$ to FeAl are very steep between 54 and 66 at% Al in the Fe-Al phase diagram. The measured spectra are in full agreement with the results of the metallograhical examinations. The thickness and number of the layers are identically for both methods.

For better comparison the Al concentrations measured on samples 1, 2, 3 and 4 versus thickness of the phases are presented in one diagram (see Fig. 6).

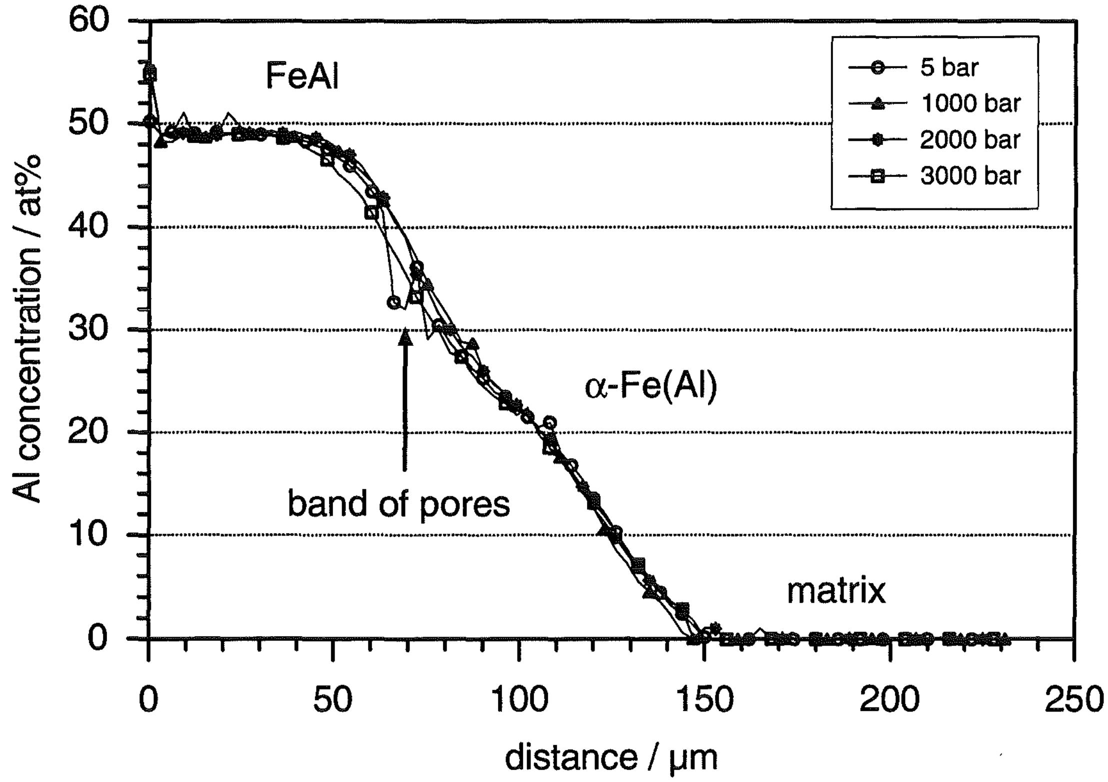

Fig. 6: Comparison of the Al concentration versus distance obtained for ample 1, 2, 3 and 4.

3.3 Vickers micro hardness testing

In general it was found, that with decreasing Al content the micro hardness value decreased in all Fe-Al phases measured. The micro hardness values obtained for the different phases on sample 1, 2, 3 and 4 are presented in Fig. 7.

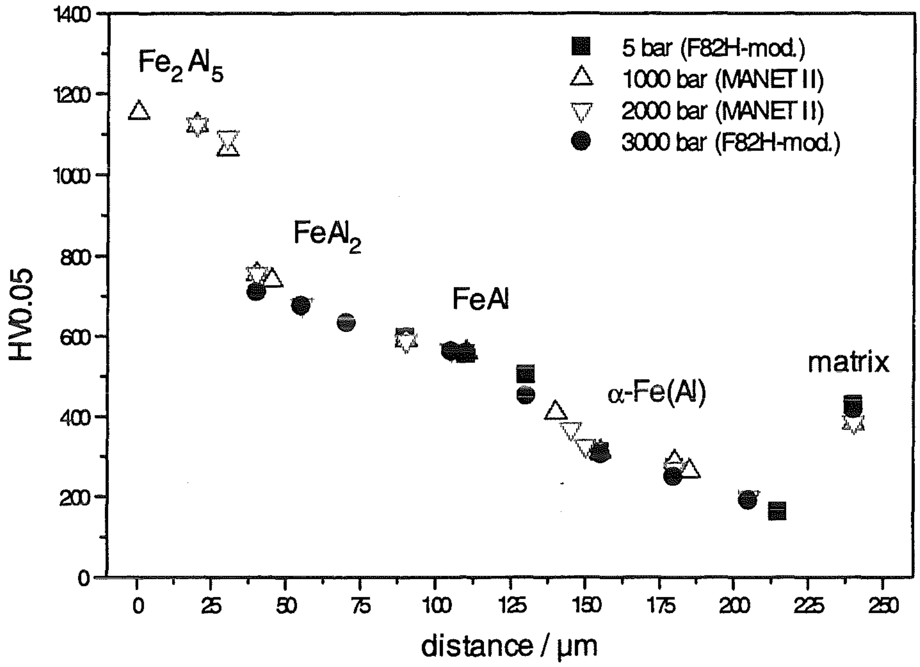

Fig. 7: Micro hardness measurements through the layers on samples 1, 2, 3 and 4.

The micro hardness values obtained for the phases FeAl and α-Fe(Al) on samples 1, 2, 3 and 4 are comparable. Therefore, the results will be discussed without differentiation between the four samples for these two phases in the following. Thereafter, the micro hardness values achieved for $FeAl_2$ and Fe_2Al_5 in samples 2, 3 and 4 will be presented.

The micro hardness of FeAl phase is reduced from about 600 to 400 HV0.05 with increasing depth. The hardness of α-Fe(Al) phase decreases from 310 to 190 HV0.05 along the depth.

The micro hardness value of $FeAl_2$ is in the order of 700 HV0.05 (sample 4) and 750 HV0.05 (samples 2 and 3), resp. All results reflect the change in scale composition across the depth.

The basic material F82H-mod. obtained the average micro hardness value of 420 HV0.05 on samples 1 and 4, the average micro hardness resulted for samples 2 and 3 (basic material MANET II) is circa 400 HV0.05.

4. Discussion

The comparison of sample 1 (5 bar) with the HIPped samples 2, 3 and 4 (1000, 2000 and 3000 bar) shows distinct differences: the absence of the band of pores in the HIPped samples and the presence of a new brittle phase. Probably the formation of pores was suppressed by high pressure.

The reason for the presence of the $FeAl_2$ and Fe_2Al_5 phases is not clear yet. It is obvious that the transformation rate of Fe_2Al_5 into the phases FeAl and α-Fe(Al) is slower at higher pressures than at 5 bar. The explanation could be that the diffusion coefficients of Fe and Al are lower at high pressure and / or the stability of the compounds is strongly dependent of pressure. Unfortunately no Fe-Al phase diagram is available as a function of temperature and pressure.

The micro hardness values achieved for α-Fe(Al) phase are in good agreement with results published before [5, 7, 11]. Hence, the pressure has no influence on the micro structure of α-Fe(Al) phase. In contrary to this, the values obtained for FeAl phase (400 – 600 HV0.05) and F82H-mod. steel (420 HV0.05) are higher than the data measured previously which have shown hardness values of 200 – 300 HV0.05 for FeAl, 230 – 250 HV0.05 for F82H-mod. and 220 – 240 HV0.05 for MANET II after the same heat treatment as described in this paper [5, 7] but with cooling to ambient temperature between austenisation and tempering steps. Hence, there seems to be no influence of pressure, because all samples show these higher values. In [11, 12] specimens were investigated after a heat treatment at 1040 °C for 30 min without tempering (750 °C, 1 h). The micro hardness values obtained on these samples are in good agreement with the values measured on the HIPped samples.

The dependence of cooling rate and tempering time on the micro hardness values of different ferritic-martensitic steels was well investigated by Schirra et al. [13]. After the austenisation process (1040 °C, 30 min) it is required to cool the steel under the M_f-temperature (M_f martensite finish) to be sure that a complete transformation into the martensitic structure has occurred. In the case of F82H-mod and MANET II M_f temperature is around 230 °C. If the subsequent tempering process should have an effect on the hardness values of the steel, it has to be ensured, that the austenisation procedure was successful, i. e. the martensitic structure was formed. Even long time of tempering could not influence the hardness if the austenisation was not completed [13].

In our experiment the heating cycle was different to the typical heat treatment for this steel: after 1040 °C, 30 min the samples were not cooled down under M_f temperature but only to 750 °C. Hence, the martensitic structure was not reached and the subsequent tempering process was without any effect on the hardness. Our data are in full agreement with the with the results described in [13].

5. Conclusions and outlook

There exists a significant influence of the HIP process of hot dip aluminised specimens on the microstructure. Two effects were observed on the HIPped samples:

- The formation of pores were suppressed successfully.
- Fe_2Al_5 was not completely transformed into the ductile phases FeAl and α-Fe(Al), but an additional brittle phase $FeAl_2$ with partly remains of Fe_2Al_5 was identified.

The absence of the pores could have a positive influence on the reduction of the permeation rate. Hence, permeation measurements of HIPped samples have to be done. Further investigation with varying holding times during the HIP process are strongly required for better understanding of the influence of the pressure on the Fe-Al system.

In the next series of experiments the HIP cycle has to be changed to ensure a cooling down from austenisation temperature under M_f before tempering. A fully transformation of the whole steel into the martensitic structure should therefore be assured.

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