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Scale structure of aluminised Manet steel after HIP treatment

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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. A technology is introduced here to form a ductile Al enriched surface scale on Manet II steel (Fe-10.3%Cr) with an alumina overlayer. This technology consists of two main process steps. Hot dip aluminising has been performed at 700°C for 30 s in order to introduce Al to the near surface zone. The very hard intermetallic scale Fe_2Al_5 which forms during the immersion process gets completely transformed into $FeAl_2$, FeAl and α-Fe(Al) phases during a subsequent hot isostatic press (HIP) process step at high pressure at 1040°C for 30 min. The pressures chosen for the HIPing were 1000 and 2000 bar. Without HIPing pores form due to the Kirkendall effect. The influence of the high pressure on the heat treatment (1040°C, 30 min) will be discussed in this paper.

1. Introduction

In the water cooled lead lithium (WCLL) metal 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 a major technological effort.

Hot dip aluminising with subsequent heat treatment seems to be a promising coating method to fulfil the required goals. In order to optimise the coating structure with respect to the demands of a tritium permeation barrier, a suitable heat treatment must be carried out after aluminising. The heat treatment, which transforms the brittle Fe_2Al_5 layer on the steel surface (which is formed during the aluminising process) into more ductile phases, is the standard heat treatment of reaustinisation at 1040°C for 0.5 h and subsequent tempering at 750°C for 1 h.

The necessary goals which are fulfilled with this heat treatment include the 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]. However, during the transformation of the brittle Fe_2Al_5 phase 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 are formed due to the Kirkendall effect. The formation of pores should be suppressed by using high pressure during the heat treatment. If no pores are formed during the heat treatment it is likely that the tritium permeation rate can be reduced and the mechanical properties of the system should be improved as well. The effect of hot isostatic press (HIP)ing during heat treatment was examined here.

2. Experimental

2.1. Materials

The basic material to be aluminised was the ferritic–martensitic steel Manet II. Its development was performed in FZK under the task low activation alloys

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[4]. Manet II NET-heat No. 50806 was produced by Saarstahl Völklingen, Germany with the following nominal composition (wt%): C 0.10, Si 0.18, Mn 0.76, Cr 10.37, Ni 0.65, Mo 0.58, V 0.21, Nb 0.16 and Fe balance. Al used for the aluminising melt had an initial purity of 99.5%, with the main impurities being Fe and Si. The melt became enriched in Fe and Cr with increasing immersion time. Degreased Manet II steel sheets ($50\times15\times2$ mm^3) were dipped into a flux (solution of KCl, NaCl and Na_3AlF_6 (ratio 5:4:1) in water) and dried before aluminising.

2.2. Aluminising process

Aluminising was carried out by using a special facility developed at FZK [9]. A glove box features a gas tight connection to a heated alumina crucible. As working atmosphere Ar–5%H_2 was used to avoid oxidation of the Al melt. 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 convection.

2.3. Heat treatment and HIP process

The heat treatments were carried out in the HIP 3000 facility, provided by Dieffenbacher, Eppingen, Germany. The aluminised samples were cleaned ultrasonically in ethanol, dried and placed in alumina crucibles, which were placed in the HIP furnace. The temperatures and times chosen correspond to austenisation and tempering for F82H-model steel. The samples were HIPed in an argon atmosphere. HIPing occurred at 1040°C for 30 min at 1000 and 2000 bar. The subsequent austenisating process (750°C, 1 h) was carried out without superimposed pressure.

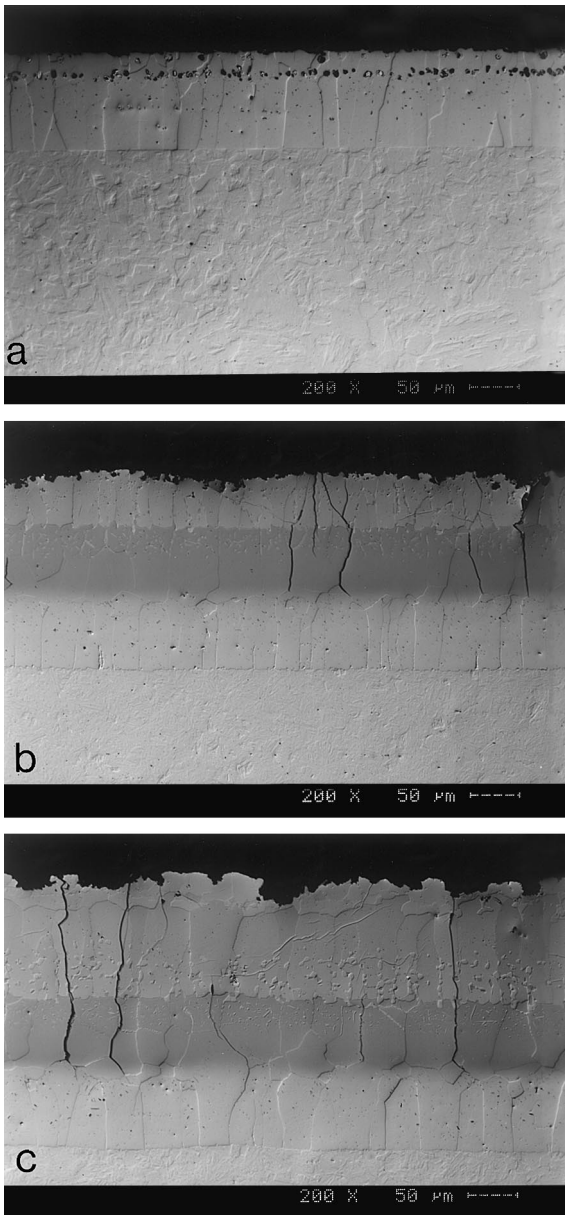

Fig. 1. Cross-sections of hot dip aluminised Manet II sample sheets after heat treatment (1040°C/30 min, 750°C/1 h) under: (a) 1 bar; (b) 1000 bar; (c) 2000 bar.

3. Results

3.1. Metallographical examination

Fig. 1(a) shows a cross-section of an aluminised Manet II specimen which was heat treated without superimposed pressure as a reference. 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) about 25 μm thick. The thickness of the internal layer was found to be dependent on the heat treatment chosen, while the thickness of the external layer was dependent on the amount of solidified Al which adhered to the surface after the hot dip aluminising process [7]. These two layers were separated by a porous band. The sample surface appeared to be rather rough. In the external layer, near to the sample surface, a few pores were formed as well. Additionally, cracks starting from the surface were observed. In most cases they arrested in the porous zone, and sometimes in the middle of the layer. Crack growth into the internal layer was never observed.

Metallographical cross-sections of the aluminised and HIPed Manet II samples are shown in Fig. 1(b) (1000 bar) and (c) (2000 bar). The observations made on the samples HIPed at different pressures were similar. Hence in the following, the examinations will be discussed together for these two samples. A three-layered scale (1000 bar) and a four-layered scale (2000 bar) were observed on the steel surfaces. The thickness of the internal layer (α-Fe(Al)) was around 80 μm and the layer in the middle (FeAl) was about 60 μm thick. In the case of sample 1 (1000 bar) a new external layer ($FeAl_2$) appeared with a variable thickness from 30 to 60 μm which is responsible for the non-uniformity of the total thickness. In the case of sample 2 (2000 bar) two new layers were observed. The thickness of the external layer (Fe_2Al_5) varied between 0 and 30 μm, the layer beneath ($FeAl_2$) had a maximum thickness of 90 μm.

It is notable that pores were not observed in the over layer system after HIPing either in between the FeAl and α-Fe(Al) layers or in the upper region of the FeAl layer. All layers seem to be homogeneous without any defects. Cracks starting from the external layer were always arrested and grew no further than the FeAl zone. Crack growth into the internal layer was never observed.

3.2. EDX line scans

Energy dispersive X-ray (EDX) line scan of sample 1 is shown in Fig. 2(a). The brittle Fe_2Al_5 phase formed during the hot dip aluminising had completely transformed after heat treatment into three new compounds. The external layer consists of the $FeAl_2$ phase having an Al content of 66–67 at.%. Just beneath the $FeAl_2$, a region of FeAl phase was found. The concentration profiles for Fe, Al and Cr show a sharp change from the $FeAl_2$ phase to FeAl which reflects the missing compounds between 54 and 66 at.% Al in the Fe–Al phase diagram. According to the binary Fe–Al phase diagram [10] the FeAl phase is stable between 29 and 54 at.% Al at 1040°C. The thickness of the zone which corresponds to the intermediate layer in the metallographical cross-section is around 60 μm. Beneath the FeAl phase 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 of the surface their concentration increases up to the matrix composition.

In the EDX line scan of sample 2 the FeAl and α-Fe(Al) phases are identified as well (Fig. 2(b)). The thickness of the layers and their composition look similar to those in sample 1. This is in agreement with the metallographical examinations. In addition to the two FeAl and α-Fe(Al) layers, two other phases can be seen on top having an Al content of around 70 and 66–67 at.%, respectively. These correspond to Fe_2Al_5 and $FeAl_2$ phases determined from the binary Fe–Al phase diagram.

The measured spectra, thickness and number of the layers are in agreement with the results of the metallographical examinations.

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 Fe–Al phases on sample 1 and 2 are comparable. Therefore, the results will be discussed without differentiation between the two samples. The micro hardness values determined for $FeAl_2$ (+Fe_2Al_5) lie between 1150 and 700 HV0.05. The micro hardness profile of the FeAl phase showed a reduction from about 600 to 400 HV0.05 with increasing depth. The hardness of the α-Fe(Al) phase decreased from 310 to 190 HV0.05 along the depth. All results reflect the change in scale composition across the depth. The base metal Manet II had an average micro hardness value of 384 HV0.05 in sample 1 and 386 HV0.05 in sample 2.

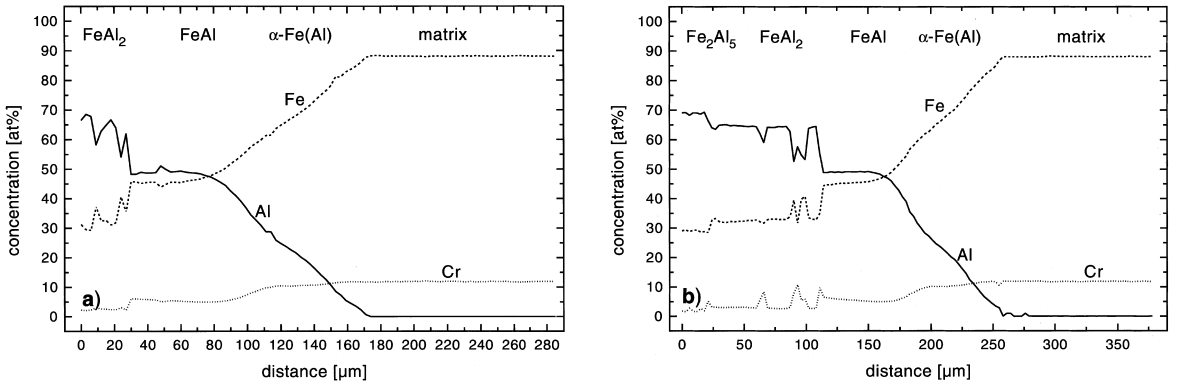

Fig. 2. EDX line scans of hot dip aluminised Manet II sample sheets after heat treatment (1040°C/30 min, 750°C/1 h) under: (a) 1000 bar; (b) 2000 bar.

4. Discussion

Comparing the HIPed sample 1 (1000 bar) with sample 2 (2000 bar) and the reference (unHIPed) sample indicates that applied pressure during heat treatment suppresses the formation of pores. At the high pressure the brittle Fe_2Al_5 phase was not completely transformed into the ductile phases FeAl and α-Fe(Al). In the case of sample 1 the brittle phase $FeAl_2$ was formed. In the case of sample 2 there is still some residual Fe_2Al_5 phase.

The reason for the presence of the brittle phases is not yet known. It is obvious that the transformation rate of Fe_2Al_5 into the phases FeAl and α-Fe(Al) gets slower with increasing pressure. One reason could be that the diffusion coefficients of Fe and Al are lower at higher pressure and/or the stability of the compounds is strongly dependent on pressure. Unfortunately no Fe–Al phase diagram as a function of pressure exists.

The micro hardness values achieved for α-Fe(Al) phase are in good agreement with results published previously [5,7,11]. Hence, the pressure apparently has no influence on the microstructure of the α-Fe(Al) phase. In contrast to this, the values obtained on FeAl (400–600 HV0.05) and Manet II steel (around 385 HV0.05) are higher than values measured previously [5,7] of 200–300 HV0.05 for FeAl and 235–270 HV0.05 for Manet II after the same heat treatment. However, there seems to be no influence of pressure, because both 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 HIPed samples. Therefore, the difference seems to be an effect of cooling rate. Normally, the specimens are quenched after heat treating at 1040°C before tempering [5,7]. In the HIP apparatus quenching is not possible. The temperature was lowered from 1040°C to 750°C without cooling down to ambient temperature. So this must be the reason for the different micro hardness values obtained. It is well known that the hardness values of FeAl and Manet II steel are strongly affected by the cooling rate [11]. Whereas the hardness value of α-Fe(Al) is less sensitive to the cooling rate.

5. Conclusions and outlook

The influence of the HIP process on hot dip aluminised specimens is significant. Two effects were observed on HIPed samples:

- Pore formation was suppressed.
- Fe_2Al_5 was not completely transformed into the ductile phases FeAl and α-Fe(Al).

The absence of the pores could have a positive influence on the reduction of the permeation rate. Hence, permeation measurements of HIPed samples should be performed. Further investigation with varying HIP times, temperature and pressure should be carried out for better understanding the influence of the pressure on phase transformation in the Fe–Al system.

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