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Comparison of microstructure and formation of intermetallic phases on F82H-mod. and MANET II

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Abstract

This paper describes investigations on the formation and transformation of aluminde phases on F82H-mod. steel and for comparison on MANET II, as reference materials. In order to achieve the desired mechanical properties of both steels, a fully martensitic microstructure has to be adjusted by a special heat-treatment. For the improvement of the microstructure of the Al based permeation barrier, a heat treatment after hot dip aluminising is necessary as well. To meet both requirements, heat treatments at different temperatures (700°C/100 h or 1075°C/0.5 h for MANET II and F82H-mod.) were performed for comparison after hot dipping, followed by a subsequent annealing at 750°C for 2 h. At the highest temperature, the perfectly adhering aluminide scale can be subdivided into an upper FeAl phase, an intermediate band of pores and a lower part of α-Fe(Al) solid solution phase. Differences in microstructure and phase composition between MANET II and F82H-mod. are described by microanalytical techniques.

1. Introduction

In the water cooled liquid metal breeder concept, the breeder material Pb–17Li is pumped with extremely low velocity through the channels. Therefore, the tritium partial pressure is significantly high in Pb–17Li in which the tritium solubility is low. To reduce the diffusion of tritium through the structural material into the cooling water circuit, a tritium permeation barrier on the steel is necessary for economic and safety reasons. It is known that thin alumina scales have the ability to reduce the T permeation rate by several orders of magnitude [1]. A layer consisting of AlFe phase or α-Fe(Al) solid solution should be able to fulfil this demand [2,3] and additionally would have good mechanical properties. Several methods have been developed to produce such scale systems on martensitic 8–10%Cr steels [4–8]. The hard and brittle intermetallic Al_5Fe_2 layer formed on the structural material e.g. by hot dip aluminising process can be transformed into a softer phase by subsequent heat treatment.

In this paper the Al_5Fe_2 layer formed by hot dip aluminising on two different low activation steels, F82H-mod. and MANET II, is described, as well as the influence of temperature and time on the subsequent heat-treatment of the transformation of this phase. Additionally, the consequence is discussed, if a heat treatment below the Ac_{1b} temperature of the steels is sufficient for a complete phase transformation in reasonable time or if higher temperatures are necessary. If higher temperatures are required, the substrate–coating system has to undergo a complete reausteniteing and tempering process to reproduce the mechanical properties of the steel substrates.

2. Experimental procedure

The chemical composition of the materials to be aluminised is given in Table 1. The cleaned sheets (50 × 15 × 1.5 mm) were degreased in acetone and finally cleaned in an ultrasonic ethanol bath. Afterwards, the whole austeniting and tempering process was carried out. Hence, the MANET II samples were heat treated under vacuum at 1075°C for 30 min and at 750°C for 2 h and the F82H-mod. sheets were heat treated at 1040°C

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

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	V	Nb	W	Ta	Fe
MANET II	0.10	0.18	0.76	0.004	0.005	10.37	0.65	0.58	0.21	0.16	–	–	Bal.
F82H-mod.	0.09	0.11	0.16	0.002	0.002	7.7	–	–	0.16	–	1.95	0.02	Bal.

for 30 min and at 750°C for 1 h, respectively. In order to improve the wetability of the steel surfaces with the Al melt the specimens were dipped into a saturated solution of KCl, NaCl and Na_3AlF_6 (ratio 5:4:1) in water and dried prior to aluminising. For the immersion process an Al melt of 99.5% purity has been used.

Aluminising has been carried out by using the facility described in [9]. The facility is connected gas tight to the bottom side of a glove box filled with reducing Ar–5%H_2 mixture to prevent oxidation of the Al melt. The sample sheets were dipped into the 700°C hot Al melt. After 10–30 s of exposure the dipped samples were pulled out and cooled down in the glove box by natural cooling.

In order to investigate the transformation behaviour of the brittle intermetallic Al_5Fe_2 phase formed during the aluminising procedure several heat-treatments were performed. The particular conditions are summarised in Table 2.

The temperatures chosen play an important role in view of the mechanical properties of the structural materials. 700°C is far below Ac_{1b} temperature (Ac_{1b} of MANET II: 775°C [10]; Ac_{1b} of F82H-mod. 835°C [11]). If higher temperatures are required for the transformation of the intermetallic Al_5Fe_2 phase, the whole system has to be austenitised completely and tempered again. These conditions differ little for the two steels. For better comparison aluminised F82H-mod. specimens were heat-treated using the prescription for MANET II.

Cross sections were prepared to study the coating thickness and adherence after aluminising and subsequent heat-treatment, respectively. Analytical investigations were carried out using optical microscopy, SEM/EDX and EPMA. The microhardness was measured by Vickers hardness testing (HV0.05).

Table 2
Conditions of the heat-treatments after aluminising

Steel	Hot dip aluminised	Heat treated
MANET II	700°C/30 s	700°C/30 h in air
MANET II	700°C/30 s	700°C/100 h in air
MANET II	700°C/10 s	1075°C/0.5 h in Ar and 750°C/2 h in Ar
F82H-mod.	700°C/30 s	700°C/30 h in air
F82H-mod.	700°C/30 s	700°C/100 h in air
F82H-mod.	700°C/10 s	1075°C/0.5 h in Ar and 750°C/2 h in Ar

3. Results

3.1. Aluminised specimens

After hot dip aluminising both steels, MANET II and F82H-mod., were homogeneously covered by solidified Al. Not even some uncovered areas remained on the surface of the sheets. Cross sectional examinations have shown the same structure of coating for both steels. There is an external layer on top and an internal one beneath which is adjacent to the steel matrix. EPMA investigation have shown that the composition of the external layer corresponds to pure Al.

The internal layer mainly exists of the brittle compound Al_5Fe_2. The composition found with SEM/EDX point analyses are 70–72 at.% Al, 26–28 at.% Fe and circa 2 at.% Cr. The chromium content in the internal layer on the substrate MANET II is slightly higher than on F82H-mod. which corresponds well to the composition of these steels. In the transition zone between the internal and external layer a small band of the compound Al_3Fe could be detected. The precipitates in the solidified Al layer were also found to be crystals of Al_3Fe.

The thickness of the intermetallic layer composed of Al_5Fe_2 and Al_3Fe was determined to be 40 μm on MANET II and 26 μm on F82H-mod., respectively. The microhardness obtained for Al_5Fe_2 phase on both steels is around 1100 HV0.05.

3.2. Aluminised and subsequent heat-treated specimens

Hot dip aluminised samples were heat-treated at 700°C with varying times in order to transform the brittle intermetallic Al_5Fe_2 phase into a softer compound.

The following observations correspond to both base materials, MANET II and F82H-mod., and will be described in detail. During the heat treatment, the solidified Al overlayer was completely incorporated into the steel substrate by diffusion. Metallographical examination showed the formation of many pores in the intermetallic layer. Perpendicular and some horizontal cracks were observed. The perpendicular crack growth starts at the surface and ends somewhere in the intermetallic layer. Beneath the porous external layer which varies strongly in thickness another layer was observed. The

Table 3
Thicknesses of the different phases on the hot dip aluminised and subsequent heat-treated F82H-mod. and MANET II specimens

Heat-treatment	F82H-mod.		MANET II	
	AlFe	α-Fe(Al)	AlFe	α-Fe(Al)
700°/30 h	8 µm	8 µm	9 µm	8 µm
700°/100 h	16 µm	13 µm	21 µm	15 µm

interface between these two intermetallics forms a sharp boundary. By increasing heating time, the thickness of this layer is increased. Some small pores have formed at the interface internal layer to the substrate.

With EPMA the different phases formed were analysed. The external layer mainly consists of about 70 at.% Al, 28 at.% Fe and circa 2 at.% Cr, which corresponds to Al_5Fe_2 phase in the Al–Fe phase diagram [12]. The analyses of the next phase beneath Al_5Fe_2 resulted in 66 at.% Al, 28 at.% Fe and about 2 at.% Cr. This composition corresponds well with the Al_2Fe phase. In the following a small plateau is indicated at about 48 at.% Al before the concentration of Al steadily decreases down to zero. The concentration measured are 48–22 at.% Al, 46–66 at.% Fe and 4–10 at.% Cr corresponds to AlFe phase, 9–0 at.% Al, 80–88 at.% Fe and 10–11 at.% Cr to α-Fe(Al). Hence, the transformation of Al_5Fe_2 phase during heat-treatment into other softer phases has occurred but is still not finished.

All phases described were observed on each sample independent of heating time or base material. Only the thickness of the different phases formed varies. The values measured of AlFe and α-Fe(Al) phase and the thickness of all layers on the F82H-mod. and MANET II specimens are summarised in Table 3. The microhardness indicated for the external layer consisting of Al_5Fe_2 and Al_2Fe phases is between 810 and 860 HV0.05.

3.3. Aluminised and subsequent oxidised specimens

The metallographic cross sections of aluminised MANET II and F82H-mod. specimens after heat treatment at 1075°C for 0.5 h is shown in Fig. 1a and (b). The thickness in total is about 250 µm for MANET II and 125 µm for F82H-mod., respectively. For both materials an internal and external layer could be observed. The internal layer on MANET II is 125 µm thick and on F82H-mod. 105 µm. The external layer is indicated to be 100 µm for MANET II and only 10 µm for F82H-mod. In the case of MANET II the porous band has a thickness of around 25 µm, in the case of F82H-mod. the thickness is circa 10 µm. In the upper region of the external layer on the MANET II specimens some pores could be observed. The surface is rather inhomogeneous and rough. Not so on the F82H-mod. specimens: the surface seems to be quite smooth and no pores have formed in the external layer.

EPMA results of MANET II specimens are shown in Fig. 2. The Al content decreases continuously from around 55 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 Al_5Fe_2 phase has transformed completely into softer phases.

The composition of the F82H-mod. sample is given in Fig. 3. The Al content lowers from 45 at.% down to zero in the steel. The internal and external layer consists of α-Fe(Al) phase. In this case, Al_5Fe_2 phase has completely changed only into one phase. The formation of AlFe could not be identified.

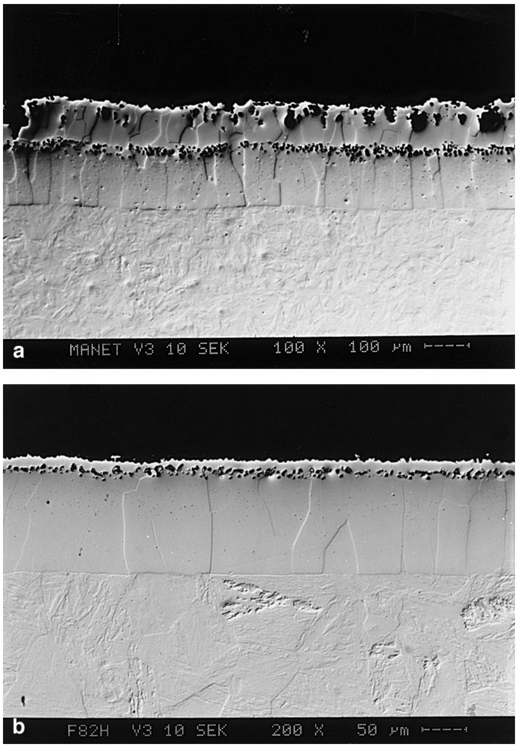

Fig. 1. Cross section of aluminised (a) MANET II and (b) F82H-mod. samples, heat-treated at 1075°C for 0.5 h.

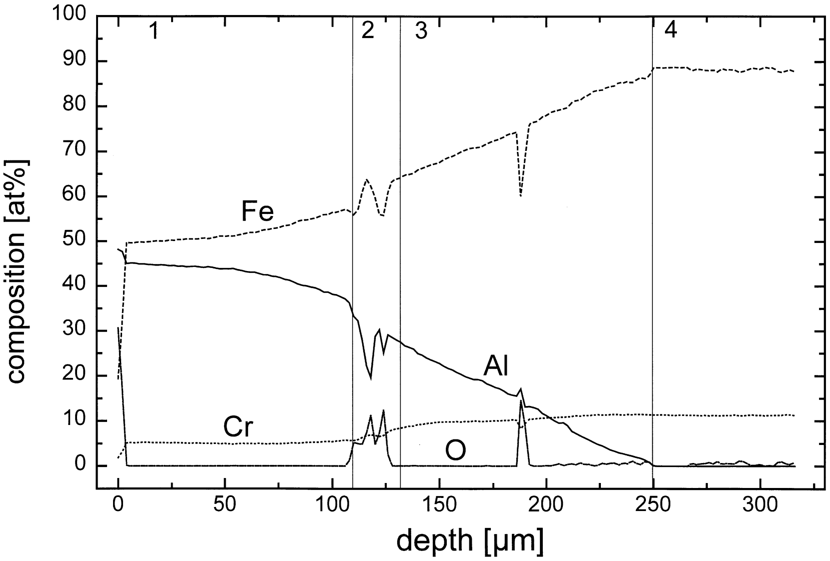

Fig. 2. EPMA line scan of aluminised MANET II sample, heat-treated at 1075°C for 0.5 h: (1) external layer AlFe phase, (2) porous band, (3) internal layer α-Fe(Al), (4) steel.

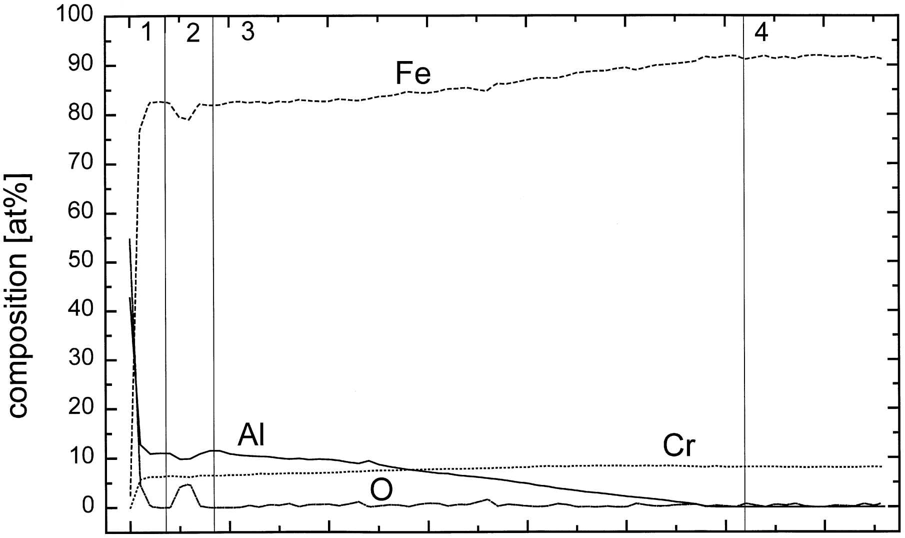

Fig. 3. EPMA line scan of aluminised F82H-mod. sample, heat-treated at 1075°C for 0.5 h: (1) external layer α-Fe(Al) phase, (2) porous band, (3) internal layer α-Fe(Al) phase, (4) steel.

The microhardnesses obtained for these two phases are in the range of 260 HV0.05. For the base materials values around 260 HV0.05 for MANET II and 212 HV0.05 were measured.

4. Discussion and conclusions

F82H-mod. and MANET II could be completely coated by hot dip aluminising. The composition of

Al_5Fe_2 formed on both steels during hot dip aluminising was identical whereas the thickness of the intermetallic layer itself varies dependent of the substrate. The different chromium content of the two steels could influence the diffusion behaviour of Fe and Al. Due to this fact, the intermetallic layer formed on F82H-mod. is around 26 μm, a little smaller than the 40 μm thick layer on MANET II. The microhardness obtained for Al_5Fe_2 phase on both steels is in good agreement with that of other authors [13,14].

Solidified Al diffused completely into the steel after heat treatment at 700°C. Hence, the thickness of the Al_5Fe_2 layer is dependent on the thickness of the Al overlayer after the hot dipping process. Afterwards the transformation of the phase Al_5Fe_2 starts at the layer–steel interface. The formation of all phases with smaller Al content than Al_5Fe_2 of the Al–Fe phase diagram could be detected: Al_2Fe, AlFe and α-Fe(Al). The transition of Al_5Fe_2 into AlFe and α-Fe(Al) phases might be slightly faster on MANET II compared to F82H-mod. due to the difference in the composition of the two steels. The growth rate of the transformed zones on MANET II follows a slightly subparabolic growth rate [15].

During high temperature oxidation of the aluminised steel sheets, a complete transformation of the intermetallic Al_5Fe_2 compound occurred. In the case of MANET II two phases, AlFe and α-Fe(Al), were formed. In the case of F82H-mod. only α-Fe(Al) could be detected. The coating on MANET II is double in thickness (250 μm) compared to the coating on F82H-mod. (125 μm). The aluminised heat-treated MANET II specimens show an inhomogenous porous structure in the upper region of the external layer and a broad band of pores between the thick internal and external layer. Compared to the MANET II, results from the outcome for F82H-mod. samples are very promising.

The formation of slightly different contents of the compounds during hot dip aluminising and heat-treatment on the two steels is responsible for the different diffusion behaviour of Al, Fe and Cr.

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