Karl-Winnacker-Institut

High Temperature Materials

Development of Coatings against Metal Dusting Attack

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Introduction

"Metal Dusting" is a catastrophic form of high-temperature corrosion generally ocurring for reducing and strongly carburizing atmospheres with carbon activities greater than one (a_c>1) in the temperature range from 400 °C to 700 °C. The corrosion attack leads to a powder composed of graphite and fine metal particles as the reaction product. Metal dusting is a serious problem for several industries such as petrochemical plants, coal gasification plants, heat treating industries and there is a strong demand for a technical solution. The aim of this work is the development of metal dusting resistant coatings for industrially important high-temperature alloys. Two different coating methods are applied: diffusion and overlay coatings. The diffusion coatings consist of Al, Ti, Si plus Cr as a diffusion barrier and the overlay coatings are produced by HVOF and consist of TiAl. Five different materials have been selected as substrates (**table 1).** The carburizing-reducing test atmosphere consists of a mixture of CO, H_2 and H_2O, with carbon activities greater than one. An industrial atmosphere consisting of CO - CO_2 - H_2 - N_2 - CH_4 - H_2S and HCl has been tested as well.

Table 1: Composition of the steels

Alloy	%C	%Si	%Cr	%Al	%Mn	%Mo	%P	%S	%Ni
X18CrN28	0,15-0,20	1	26-29	-	1	-	0,045	0,03	-
X10CrAl18	0,12	0,70-1,40	17-19	0,70-1,20	1	-	0,04	0,03	-
10CrMo9 10	0,08-0,15	0,5	2-2,5	-	0,40-0,70	0,90-1,20	0,030	0,025	-
Alloy 800	0,12	1,00	19-23	0,15-0,60	2	-	0,03	0,02	30,0-34,0
Alloy P91	0,08-0,12	0,20-0,50	8,0-9,5	<0,040	0,30-0,60	0,85-1,05	0,02	0,01	<0,40

Concept

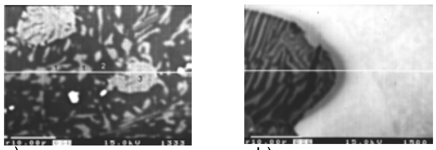
Since the materials tested in this project are different in composition, the process parameters for the diffusion coatings will be different. Because of this, the best coating to protect each material will not be the same. The experimental concept is as follows:

1) Development of new coating systems based upon Ti, Si, Cr and/or Al containing phases
2) Application of these coatings by several techniques (HVOF and diffusion techniques)
3) Isothermal testing within the temperature range of 400 through 700 °C in flowing gas mixtures (H_2, CO and H_2O). Variation of process (test) parameters like gas composition and temperature to adjust exactly defined carbon activities.
4) Study of corrosion kinetics and quantitative determination of corrosion attack under these conditions.
6) Testing of optimized system under real conditions.

Materials

Substrate
- 10CrMo9 10
- X10CrAl18
- X18CrN28
- Alloy 800
- Alloy P91

Coating
- TiAl (HVOF)
- Al,Si,Cr, Ti (Diffusion process)
- Al-Cr, Al-Ti, Al-Si, Al-Si-Ti (Codiffusion process)



a) b)

Fig. 2: EPMA-Analysis of the aluminide coating on X10CrAl18.
a) Different phases inside the coating:
1.- Cr-Al intermetallic
2.- Fe-Al intermetallic
3.- Cr-carbide,
b) Zone between the coating and the substrate with decreasing aluminium content.

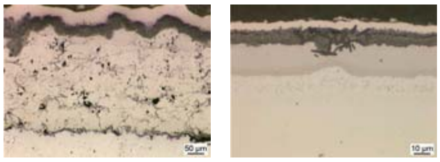


Fig. 3. Formation of a Ti- and Al-rich oxide scale on top of the coating after exposure under metal dusting conditions at 700 °C. Left: -TiAl HVOF coating on alloy 10CrAl18. Right: Ti-Al codiffusion coating on Alloy 800.

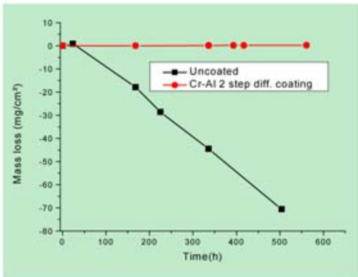


Fig. 4: Mass change measurements for alloy 10CrMo9 10 without coating and with a Cr-Al 2 step diffusion coating.

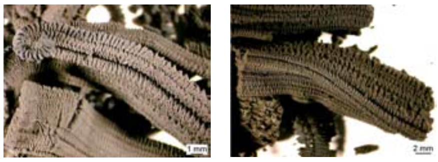


Fig. 5: Coke deposits on Alloy P91 after exposure under metal dusting conditions at 620°C.

Experimental

Two different coating methods have been applied: diffusion and thermal spray coatings. The diffusion coatings were produced by the pack cementation method" and consist of Al, Ti, Si plus Cr as a diffusion barrier. An example of Microprobe analysis of an Al-diff. coating is shown in Fig. 2. The overlay coatings based on the intermetallic -TiAl phase were produced by HVOF.

Coated and uncoated specimens were isothermally tested under metal dusting conditions (25%CO-73%H_2-2%H_2O) for different periods of time at 400, 620 and 700 °C. At 620 °C a typical industrial atmosphere was used as well.

The samples were ultrasonically cleaned in ethanol and acetone and weighed before inserting into the furnace. After each exposure, the samples were brushed for coke removal (if present) and weighed to register the mass change. Measurements of the thickness of the specimens were carried out as well. At the end of the test the samples were cross-sectioned for metallographic examination.

Results

An example of the results at 620 °C is shown in Fig. 1. All coatings had generally a good behaviour under metal dusting conditions. This is due to the protective oxide scale that can be developed on top of the coatings under metal dusting conditions (Fig. 3). The Al-diff. coating was applied on all samples and tested at all temperatures showing good results. Fig. 4 shows the mass change measurements of Alloy 10CrMo9 10 for the uncoated and Al-coated material. Ti-Al codiff. coating was applied on alloy 800 showing a very good behaviour as well and at 620 °C, this coating was also applied on alloy 10CrMo9 10 and on alloy P91 showing metal dusting except for the alloy 10CrMo9 10 under standard atmosphere. The codiffusion coating consisting of Si and Al showed good results as well except for the alloys P91 and 10CrMo9 10 on which metal dusting took place at 620 °C. However, the incubation time was prolonged from 5 h for the uncoated materials to 1176 h for the coated materials. The coating consisting of three different elements: Ti, Al and Si developed with the pack cementation method as well was only applied on alloy 800 and alloy P91 and tested at 620 °C and neither metal dusting nor coke deposition was observed during the exposure. The uncoated samples showed metal dusting with different incubation times and coke deposition took place. The coke deposits are different in size and shape. An example can be seen in Fig. 5.

Conclusions

The application of a coating to a material is a very complex process and each material needs different parameters to get the optimum coating so that the application process will be different each time.

Chromium acts as a barrier against the aluminium diffusion. Thus, the alloy 10CrMo9 10, which has the lowest chromium content, has been further enriched with chromium before the aluminizing process to prevent depletion of aluminum by inward diffusion into the substrate.

The test results obtained so far indicate:

- Al-diffusion coatings were protective for all alloys at all temperatures and no coke deposition or metal dusting occurred.
- Ti-Al-codiffusion coatings showed good results for Alloy 800 and coke deposition or metal dusting did not take place.
- Si-Al-codiffusion coatings showed good results for all temperatures and all alloys except for Alloy P91 and 10CrMo9 10 which showed some coke deposition.
- Ti-Si-Al-codiffusion coating was applied on Alloy 800 and alloy P91 and tested at 620 °C for 672 h and no metal dusting was observed.
- TiAl-coating applied by the HVOF technique was protective for alloy X10CrAl18 at all temperatures.

620 °C					Diffusion Coatings					Overlay Coat.
Alloy	atmosphere	Type of attack*	Without coating	Cr-Al-2step diff.coating	Al-diffusion coating	Al-Si co-diffusion	Al-Si-Ti co-diffusion	Ti-Al co-diffusion	Ti-diffusion coating	HVOF TiAl
Test duration			1681 h	1681 h	1681 h	1849 h	1345 h	672 h	1345 h	1681 h
10CrMo9 10	standard	MD	2	0	-	(1513 h) 2	-	0	-	-
(1.7380)		CF	2	0	-	(1513 h) 1	-	0	-	-
10CrMo9 10	industrial	MD	2	0	-	(1513 h) 1	-	2	-	-
(1.7380)		CF	2	0	-	(1513 h) 1	-	1	-	-
Alloy P91	standard	MD	2	-	(1009 h) 0	1	0	1	-	-
(1.4903)		CF	2	-	(1009 h) 0	1	0	1	-	-
Alloy P91	industrial	MD	2	-	(1009 h) 0	1	0	2	-	-
(1.4903)		CF	2	-	(1009 h) 0	1	0	1	-	-
X10CrAl18	standard	MD	0	-	0	0	-	-	-	0
(1.4742)		CF	1	-	0	0	-	-	-	0
X10CrAl18	industrial	MD	1	-	(1176 h) 0	0	-	-	-	0
(1.4742)		CF	1	-	(1176 h) 0	0	-	-	-	0
Alloy 800	standard	MD	2	-	0	(1345 h) 0	0	0	-	-
(1.4876)		CF	2	-	0	(1345 h) 0	0	0	-	-
Alloy 800	industrial	MD	1	-	0	(1345 h) 0	0	0	0	-
(1.4876)		CF	2	-	0	(1345 h) 0	0	0	1	-
X18CrN28	standard	MD	0	-	0	0	-	-	-	-
(1.4749)		CF	1	-	0	0	-	-	-	-
X18CrN28	industrial	MD	0	-	(1176 h) 0	0	-	-	-	-
(1.4749)		CF	0	-	(1176 h) 0	0	-	-	-	-

Fig. 1. Classification of the attack for the alloys tested at 620 °C. Abbreviations: MD: metal dusting, CF: coke formation, 2: heavily attacked, 1: slightly attacked, 0: no attack.