ISHOC 2014

International Symposium on High-temperature Oxidation and Corrosion 2014



Abstracts

23-27 June 2014
Hakodate, Hokkaido Japan

Organiser
The Iron and Steel Institute of Japan

Co-Organiser
Japan Society of Corrosion Engineering

Coatings for Oxycombustion - Supercritical Steam Boilers Components

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1. INTRODUCTION

The need to produce energy more efficiently and with a reduced environmental impact, has become evident. This leads to increasingly extreme conditions imposing more demanding performances on materials, such as higher temperatures and pressures, and more corrosive atmospheres. An alternative to facilitate CO_2 capture is the use of oxygen instead of air for combustion (oxycombustion) of any fuel in the boiler of steam power plants. As the nitrogen presence on the combustion atmosphere is almost zero, the NO_x emissions are drastically reduced and it is then possible to separate and capture practically 100 % of the produced CO_2 [1]. However, oxycombustion atmospheres are much higher in CO_2, SO_2 and water vapor and under this atmosphere corrosion rates are expected to be higher, moreover when supercritical steam conditions are required, and the components are exposed to temperatures higher than 600º C. In fact, some boiler components, such as the superheater tubes, are exposed to both steam and fireside corrosion at these high temperatures, and ferritic steels corrode at very fast rates under both atmospheres. Unless materials with lower thermal conductivity and higher cost are used (austenitic steels and Ni base alloys), protective coatings will be needed. A number of new coatings, applied by techniques capable of depositing said coatings both on the inner and outer surfaces of heat exchanger tubes, such as slurry application and HVOF, are being studied within the EC project POEMA [2].

Aluminide slurry coatings are already known to be very stable both under steam and fire-side corrosion at 650º C [3]. However degradation occurs by Al interdiffusion which may have two negative effects: 1) it causes Al depletion at the surface, resulting in an Al content lower than the critical value required to maintain a stable protective alumina layer and 2) it causes the precipitation of AlN, depleting the steel from N and possibly affecting the mechanical properties of the material after long term. Moreover, these coatings exhibit through-thickness cracks due to thermal expansion coefficient mistmatch between the iron aluminide phases, in particular Fe_2Al_5, and the substrate (Figure 1). In order to reduce diffusion and to avoid the presence of cracks, new Ni and Cr modified aluminide coatings have been produced on P92 by non-line-of-sight hybrid processes. In addition, an Al modified stainless steel coating has been deposited by HVOF. It is a hard, alumina former coating to be used on the external surfaces of the tubes on which erosion by ashes is an issue.

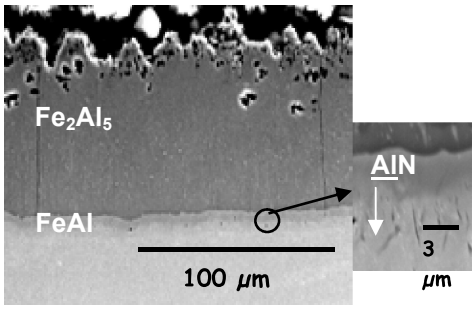


Fig. 1: Slurry aluminide coating on P92

The microstructure of the new coatings will be shown. In addition, extensive laboratory testing of these coatings is on-going, both under oxycombustion model atmospheres with and without ash erosion, as well as under pure steam at 650º C and the preliminary results will be presented. Finally, results obtained with selected coatings in a pilot oxycombustion boiler operated by CIUDEN in Leon, Spain will also be shown. Results indicate that some of the tested coatings exhibit very stable behavior under both atmospheres at 650º C.

2. EXPERIMENTAL

2.1 Substrate

Samples coupons (20x10x3 mm) were machined from tubular sections of P92 (C: 0.1, Mn: 0.5, Si: 0.03, Cr: 8.8, Ni: 0.06, Mo: 0.4, W: 1.8, V: 0.20, S: 0.006, N: 0.046 Fe: bal., wt. %,) obtained from Vallourec Mannesmann

2.2 Coatings

Slurry aluminide: The Al slurry is a CrVI free water base proprietary composition containing only inorganic compounds. Prior to coating, the samples surface was ground (Struers 120) and solvent degreased. The Al slurry was applied by

spraying and the coated samples were subjected to a diffusion heat treatment performed under argon flow at 700º C for 10 h.

Ni Aluminide: this coating was applied in two steps: 1) Ni was initially deposited by electroless deposition from a $NiSO_4$, $(NH_4)_3C_6H_5O_7$ and $NaH_2PO_2{\cdot}H_2O$ solution at 50 ºC followed by a heat treatment at 600ºC for 10 hours and 2) the sample was subsequently aluminized by means of applying an Al slurry followed by a diffusion heat treatment at 700º C for 10 h.

Cr Aluminide**:** this coating was also applied in two steps: 1) Cr was initially deposited by a chromium based proprietary slurry followed by a diffusion heat treatment at 1050 ºC for 5 h and 2) the sample was later aluminized by means of applying an Al slurry followed by a diffusion heat treatment at 1035º C for 35 min.

Table I: Composition of the HS Alloy Powder.

	Fe	Cr	Mo	W	C	Mn	Si	B
wt %.	balance	< 20	< 5	< 10	< 2	< 5	< 2	< 5

Al modified stainless steel: a nano scale hard steel (HS) alloy powder (Table I) was mixed with Al (8 wt. %) and sprayed by means of a Sulzer Metco Diamond Jet Hybrid HVOF unit (A-3120) mounted on a 6 axes robot (ABB) and fed by a twin rotation powder feeder. Before coating, the specimens were grit blasted and degreased.

2.2 Laboratory Testing

2.2.1 Steam oxidation: uncoated substrates were ground (Struers 120) prior to testing. The schematics of the closed loop laboratory rig employed at INTA are shown elsewhere [4]. Prior to testing, laboratory air is displaced from the specimen chamber by means of N_2 which is kept flowing while heating up to the test temperature (approximately at a rate of 600º C/h). Once the test temperature has been reached, the N_2 flow is stopped and pure steam is introduced at a linear velocity of 7 cm/s. To carry out weight measurements or to remove samples, the furnace is cooled to about 300º C under N_2 atmosphere and the specimens are subsequently removed. The reheat cycle is also carried out under N_2 atmosphere.

2.2.2 Fire-Side Corrosion: the test was performed using an experimental especially designed rig with four independent lines for H_2O, SO_2, O_2, N_2 and CO_2 feeding a tubular reactor placed in a furnace. The gas composition is shown in Table II. The samples were placed in alumina crucibles and exposed to the flowing gaseous atmosphere at atmospheric pressure and 650ºC. The exhaust gas was neutralized by bubbling it through alkaline solutions. The test begins by flowing nitrogen for 1 h while the furnace is heating up to the test temperature. Once the test temperature is reached, the nitrogen is closed and the corrosive gases and water are introduced at a linear velocity of 7 cm/s. Every 7 days the test is stopped to weight the specimens by cutting the corrosive gas mixture and turning the furnace off. Cooling to room temperature takes 2 h.

Table II: Composition of the oxyfuel atmospheer for the Fire-Side Corrosion Test

	CO_2	H_2O	N_2	O_2	SO_2
Vol.%	70	30	7	2	1

2.2.3 Pilot Plant Testing: the test was carried out in a fluidized bed combustion boiler burning coal and operating in oxycombustion conditions in CIUDEN´s pilot plant (Leon, Spain). Reheat tubes were coated and tested at plant conditions. The tubes were exposed to 20 days at 650º C. Special attention was focused into corrosion due to gases and fly ash.

2.3 Characterization.

The oxidized specimens were characterized by light optical microscopy (Leica MEF 4) and field emission scanning electron microscopy (FESEM) employing a JEOL JSM 840 system equipped with an energy dispersive X-ray spectrometer (EDS) KEVEX MICROANALYST 8000 with a RÖNTEC signal processor.

3. RESULTS AND DISCUSSION

New Coatings

Two new modified diffusion aluminide coatings have been deposited employing combinations of different processes, in all cases capable of being applied to both internal and external surfaces of heat exchanger tubes.

The first coating was obtained in four steps: 1) first applying 25 μm de Ni(P) by means of electroless deposition from a P containing precursor, 2) a diffusion heat treatment at 600º C, 3) application of an Al slurry and 4) a final heat

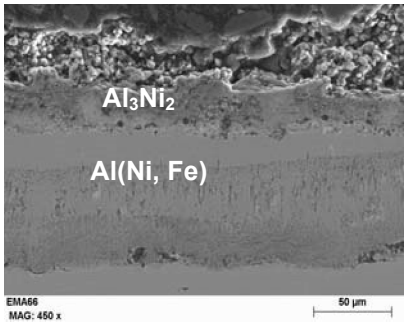


Fig. 2. Ni aluminide coating on P92

treatment at 700º C. As a result, a coating comprising distinct zones was obtained as shownin Fig. 2. According to the XRD pattern as well as EDS analysis, the other layer is composed of Ni_2Al_3 and AlP, whereas the internal zone corresponds to Al (Ni,Fe). Ni aluminides are less brittle than Fe aluminides and accordingly, no cracks are observed in this coating which exhibits an Al content of 65-70 wt. % near the surface.

A Cr enriched aluminide was also deposited by first enriching P92 with Cr by slurry application, followed by aluminization also by means of a slurry at 1000º C. Cr was added as the surface Al content was expected to be lower than that of the original aluminide coating showed in Fig. 1 due to higher diffusion degree caused by the higher heat treatment temperature. It is known than the critical amount of Al required to maintaining a protective alumina scale is related to the Cr content, the higher the Cr the lower the critical Al content. The microstructure of the coating shown in Fig. 3 is, as expected, different as only FeAl was observed by XRD instead of Fe_2Al_5. At the surface the content of Al is 15 wt. % and that of Cr 10 wt. %. Two zones are observed separated by Kirkendall porosity, below which, the Al content slowly decreases to 2 wt. %, at about 200 μm from the surface at the interface with the substrate. A heat treatment at 1000º C will cause a change in the microstructure of the P92 affecting its mechanical properties. However in the case of the heat exchanger tubes, these can be re-heat treated to obtain the required ferritic-martensitic microstructure or alternatively, the coating process may be undertaken prior to the final tempering-annealing alloy treatment [5].

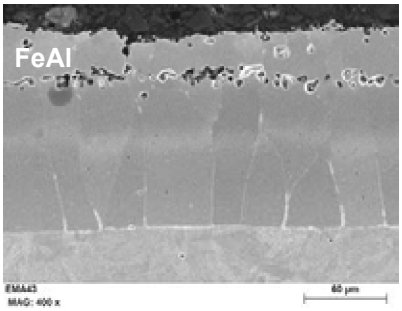


Fig. 3. Cr enriched aluminide coating on P92

The third coating was deposited by HVOF from a powder obtained by mixing a commercial HS powder with 8 wt. % Al. Although the commercial powder ir rich in Cr (18 wt. %), prior testing under steam at 650º C [6] had shown that a protective Cr rich scale did not form, and for this reason Al was added. The as deposited microstructure exhibits a non-uniform dispersion of Al particles within the coating as shown in Fig. 4 and a global Al content of 5 wt. %. The Vickers microhardness of this coating was reduced from 1000 to 750 when Al was added, but the modified coating was still considered as hard enough.

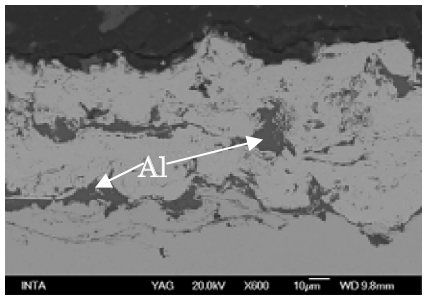


Fig. 4. Al enriched HS coating on P92

Steam Oxidation Testing

Testing of the three new coatings together with uncoated P92 and the reference pure aluminide coating has begun under 100 % atmospheric, flowing steam. The preliminary results indicate that all coatings are protective in comparison with uncoated P92 after 1000 h as shown in Fig. 5. In particular, the Cr aluminide coating has exhibited an excellent behavior confirmed by the microstructure of the sample taken after 1000 h which is exactly the same as the initial coating. In contrast with the behavior of the pure aluminide coating which as mentioned earlier exhibits a high degree of Al inwards diffusion. Both the NiAl and Al modified HS coatings shown higher weigh gains but tending to stabilized. The microstructure of the NiAl after 1000 h shown some degree of oxidation in the internal layers of the coating, likely due to defects present in the original coating microstructure. The HVOF deposited Al modified HS is very rough formed a protective Al oxide and the higher increase in weight may be simply due to the higher specific surface.

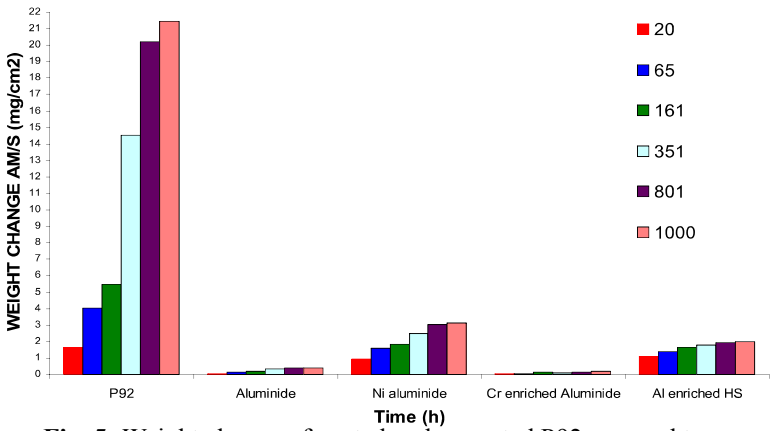


Fig. 5: Weight change of coated and uncoated P92 exposed to flowing steam at 650º

Fire-Side Oxycombustion Testing

Similar results have been obtained for up to 300 h at 650ºC under this atmosphere with very low weight gains of the

coated specimens as compared to uncoated P92 as shown in figure 6. The test will be completed after 1500 h of exposure.

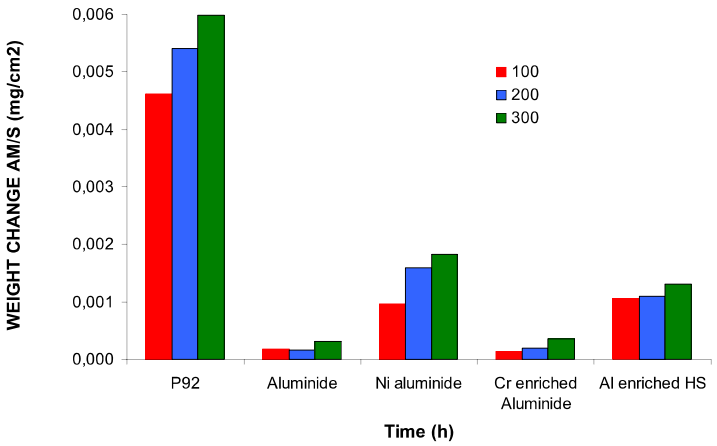
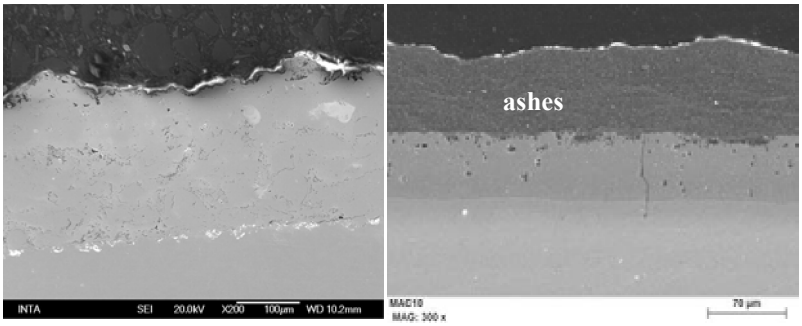


Fig. 6: Weight change of coated and uncoated P92 exposed to an oxycombustion atmosphere at 650º

Pilot Plant Testing

Although still for a short duration (480 h) both the reference aluminide coating as well as the Al modified HS were applied to the external surfaces of reheater P92 tubes and exposed to a real coal oxycombustion atmosphere in a pilot boiler at 650º C. Both coatings appeared unaffected as shown in figure 7a and b respectively. Ashes deposited on these coatings do not appear to significantly react with both materials as shown for instance in figure 7a in the case of the aluminide coating.



a) b)

Fig. 7. Coatings applied on reheater P92 tubes and exposed to a coal oxycombustion atmosphere at 650º C for 480 h: a) Al enriched HS HVOF deposited coating and b) slurry aluminide

4. CONCLUSION

New coatings have been developed for superheater tubes. Both Cr and Ni aluminides can be applied in the internal as well as external surfaces of the tubes. The preliminary test results indicate that in particular the Cr aluminide coating may represent an improvement over the pure aluminide coating as it does not exhibit cracks and degradation by diffusion is significantly slow. Both the pure aluminide and the Al modified HS coating were tested in a pilot oxycombustion boiler for 480 h at 650 º C and no degradation was observed even after deposition of ashes on the surface of the coatings. The HVOF deposited AL modified hard steel is a candidate to be used in erosion prone zones.

Acknowledgements

The authors are grateful for the support by the Spanish Ministry of Economy and Competitiveness for financial support (ENE2011-29203-C02-01) as well as the EC (POEMA, G.A. No.: 310436). We also acknowledge ENDESA for supporting the pilot plant tests at CIUDEN and all members of the Metallic Materials Area at INTA for technical support.

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