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Coating behaviour for materials of industrial waste incinerators and heat exchangers in high temperature corrosive atmospheres

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Abstract. — A coating obtained by flame spraying (Ni-Al) and an aluminizing type (Sermaloy J) were tested in laboratory and in industrial waste incinerator (substrate: AISI 310S steel). In laboratory tests, the studied parameters were: HCl-content (1 and 3% vol. in air + 0.1% vol. SO₂), temperature (600 and 800 °C) and thermal cycling between 800 and 400 °C. The increasing of the temperature and HCl-content, and also thermal cycling lead to a degradation of the non coated steel and Ni-Al coated specimen behaviours; as for Sermaloy J, only temperature raising seems to have a detrimental effect (first batch). For the field tests, the specimens were exposed at about 600 °C in flue gases containing about 0.4% vol. HCl and flying ashes (sodium chloride and sulfate); the corrosion phenomena are more closed to molten salts interactions than to gaseous corrosion: Ni-Al behaves better compared with Sermaloy J and the non coated steel which are much more attacked than in laboratory. However, Sermaloy J and Ni-Al can lead to a real protection of a steel substrate but the manufacturing conditions have a great influence on the behaviour of the coated specimens.

1. Introduction.

Metallic materials are often severely attacked in the high temperature (600-800 °C) corrosive atmospheres encountered in industrial waste incinerators especially when the chlorine content in the waste is high. A thermodynamical study was carried out [1-3] and showed that, among all oxides forming on high temperature alloys, alumina presents the largest domain of stability in oxichlorinating and oxisulfidizing atmospheres. However, because alumina forming alloys are not a good solution in the 600-800 °C intermediate temperature range, an aluminium rich coating could be a promising way to reduce the alteration of the materials. So, a joint research programme has been undertaken in that field by CEA, BERTIN and GEREP.

Four coatings used particularly in aeronautical industry and whose implementation could be technically compatible with the construction of industrial incinerators, were selected: Ni-Al (oxyacetylene gun and wire, 20wt% Al; porosity about 8-10%), NiCrAlY (atmospheric spraying gun and powder; wt%: 22Cr-10Al-1Y; porosity about 5%), Al₂O₃ (with 1wt% SiO₂; porosity about 8%) on NiCoCrAlY underlayer (wt%: 17.5Cr-2.5Co-5.5Al-0.5Y, both atmospheric spraying gun and powder) and Sermaloy J (30wt% Al, aluminizing type coating with diffusion treatment between 900 and 1050 °C [4, 5]; the suppliers were Turbomeca for the three first coatings and Heurchrome for the last one. AISI 310S type steel (7 RE 10 supplied by Sandvik, with 1.28wt% Si and 0.1Ce), was chosen as substrate because of its good mechanical properties in the 600-800 °C temperature range, and also for its cost.

In a first step, laboratory screening tests were carried out on all the materials. Two coatings revealed a poor behaviour at 800 °C: complete destruction of NiCrAlY (coating thickness: 480-550 μm) and scaling of Al_2O_3 (alumina thickness: 400-560 μm); so, they were given up for the continuation of the study.

As for the two other coatings (Ni-Al and Sermaloy J), their behaviour and the substrate one were characterized in laboratory tests and during exposure in the GEREP incinerator. The results obtained are presented in this paper.

2. Experimental.

2.1 EXPERIMENTAL DEVICES. — For laboratory tests, carried out by CEA, the Coralline rig was used; it is composed of eight independant test sections (open circuit) where the specimens (only one type of material per test section) are leached by the gas.

As for the GEREP incinerator, it burns chlorinated liquid wastes (average Cl-content: about 7wt%). The specimens were located between the postcombustion chamber and the off-gas neutralization system.

2.2 OPERATING CONDITIONS. — For each laboratory tests, the exposure duration was 500 hours and the total flow rate was 15 l.h⁻¹ (at 20 °C) under atmospheric pressure. The studied parameters were (see Tab. I): HCl-content (1 and 3% vol. in air + 0,1% vol. SO_2), temperature (600 and 800 °C) and thermal cycling (hold temperature: 800 °C; for one hour per day down to 400 °C). For the field tests, the specimens were exposed at about 600 °C during 800 hours and under a flue gas rate of 35 000 Nm³h⁻¹ containing about 0.4% vol. HCl and flying ashes mainly constituted of sodium chloride and sulfate, as shown by analysis.

2.3 MATERIALS PREPARATION AND CHARACTERIZATION. — The non coated steel was ground with SiC 600 paper while the coated specimens were just cleaned with solvent; weight and dimensions were measured.

All materials were characterized before and after test by cross-section optical micrographic examination. Analysis were performed by SEM/EDS or electron microprobe and X-ray diffraction. Before test, the Ni-Al coating seemed well adherent to the substrate and did not present cracks. Besides, a cold-worked zone was observed on the steel side near the coating interface, probably due to the sand-blasting carried out before coating operation. The thickness of Ni-Al was not regular because of manual operation (Fig. 1) and especially for the second batch for which the deposit was thinner and more porous on edges: 340-650 μm for the first batch and, for the second one, 330-570 μm on large sides and less than 200 μm on the edges. As for Sermaloy J, almost the same features and very regular thicknesses were observed for the two batches; the coating can be divided in 3 main zones (Figs. 2 and 3): external zone (irregular profile, maximal thickness 40 μm ; wt% 22.5Al-6.7Cr-15.6Ni-49.5Fe), intermediate zone (about 15 μm ; Ni-Al rich barrier, wt%: 26.6Al-2.2Cr-57.5Ni-11.3Fe) and internal zone (about 55 μm ; wt%: 2.0Al-28.2Cr-11.6Ni-52.1Fe).

3. Results of tests.

Table I reports the main micrographic measurements for all the tests, in terms of maximal thickness loss of sound metal per side.

Fig. 1. — Cross section optical micrograph of a Ni-Al coated specimen before test (C = coating, S = substrate).

Fig. 2.

Fig. 3.

Fig. 2. — Cross section optical micrograph of a Sermaloy J coated specimen before test (electrolytic attack; C = coating, S = substrate).

Fig. 3. — X-image of aluminium (electron microprobe) showing the diffusion zones of Sermaloy J coating on steel before test (1 = external zone; 2 = intermediate zone; 3 = internal zone; S = substrate).

3.1 NON COATED STEEL. — In the laboratory tests, at 600 °C, the steel suffers only a slight attack and is covered by a chromia layer. On the other hand, the corrosion at 800 °C is characterized by a general attack with an underlying Cr-depleted zone and the formation of numerous cavities (Fig. 4); oxides mixtures (Cr_2O_3 , NiO, $(\text{Cr, Fe})_2\text{O}_3$) and also NiCl_2 are covering the surface. Under thermal cycling, the loss of sound metal is split up in general attack (400 μm) and intergranular penetration underneath (Fig. 5). In the field tests, the steel undergoes only an intergranular attack with grain loosening (Fig. 6).

For the tests at 800 °C, sigma phase is observed in the grains and at the grain boundaries; the same phenomenon is also observed with the coated specimens.

3.2 Ni-Al COATING. — This coating does not seem to be attacked in all the tests and is covered by an alumina layer. However, a quite important scaling occurs with the second batch but, in the non scaled areas, oxides are present at the substrate interface and an intergranular attack, whose depth depends on experimental conditions (see Tab. I) is observed in the steel (Figs. 7, 8 and 9).

Table I. — *Results of metallographic measurements.*

Material	Batch n°	Lab. (*) or field (**) test	HCl ⁻ content (% vol)	Temp. (°C)	Maximal loss of sound metal per side (μm)	
Non coated steel	1	lab.	1	600	Coating	Substrate
	1	lab.	1	800	—	5
	1	lab.	1	800/400	—	160
	1	lab.	3	800	—	570
	1	field	0, 4	800	—	430
	1	field	0, 4	600	—	490
Ni – Al coating	1	lab.	1	600	0	0
	1	lab.	1	800	0	30 – 50
	2	lab.	1	800/400	0(***) (1)	80
	2	lab.	3	800	0(***) (2)	250 – 500
	2	lab.	3	800	0(***) (1)	120
	2	field	0.4	600	0(***) (2)	640
Sermaloy J coating	1	lab.	1	600	60	0
	1	lab.	1	800	0(***)	0
	2	lab.	1	800/400	0	0
	2	lab.	3	800	0	0
	2	field	0.4	600	100 (1)	130
	2	field	0.4	600	100 (2)	370

(*) 500 hours.

(**) 800 hours.

(***) partial scaling.

(1) areas where the coating is adhering and complete.

(2) scaled areas and edges.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 4. — Cross section optical micrograph of a non coated steel specimen after laboratory test at 800 °C (constant) with 1% HCl.

Fig. 5. — Cross section optical micrograph of a non coated steel specimen after laboratory test with thermal cycling.

Fig. 6. — Cross section optical micrograph of a non coated steel specimen after field test at 600 °C.

3.3 SERMALOY J COATING. — As for the Sermaloy J coating, at 600 °C, the external zone is covered with an irregular alumina layer but presents cavities and suffers an internal oxidation (Fig. 10), mainly of Fe concentrated along the grain boundaries, with an Al-depletion in the grains. At 800 °C, a partial scaling of the external zone is observed (Figs. 11 and 12) and an electron microprobe examination reveals that aluminium diffuses, on one hand, from the external zone to form an alumina layer on the surface and, on the other hand, from the intermediate zone towards the substrate where the Al-content is twice as high as before test. In the field tests, in some areas, the coating has completely disappeared and, where it is still present, it undergoes a general attack with cavities (Fig. 13) which, in some cases, penetrate the substrate.

Fig. 7.

Fig. 8.

Fig. 7. — Cross section optical micrograph of a NiAl coated specimen after laboratory test with thermal cycling (middle of large side; C = coating, S = substrate).

Fig. 8. — Cross section optical micrograph of a NiAl coated specimen after laboratory test with thermal cycling (edge; C = coating, S = substrate).

Fig. 9. — Cross section optical micrograph of a NiAl coated specimen after field test at 600 °C (C = coating, S = substrate).

Fig. 10.

Fig. 11.

Fig. 10. — Cross section optical micrograph of a Sermaloy J coated specimen after laboratory test at 600 °C with 1% HCl (C = coating, S = substrate).

Fig. 11. — Cross section optical micrograph of a Sermaloy J coated specimen after laboratory test at 800 °C (constant) with 1% HCl: external zone present (C = coating, S = substrate).

Fig. 12.

Fig. 13.

Fig. 12. — Cross section optical micrograph of a Sermaloy J coated specimen after laboratory test at 800 °C (constant) with 1% HCl: external zone scaled (C = internal zone of the coating, S = substrate).

Fig. 13. — Cross section optical micrograph of a Sermaloy J coated specimen after laboratory test at 600 °C (C = coating, S = substrate).

4. Discussion.

4.1 INFLUENCE OF TEMPERATURE. — The important increase (factor 30) of the corrosion rate of non coated steel can be attributed to the very important increase of the metallic chlorides vapor pressure between 600 and 800 °C [2,6-8]. This phenomenon has already been observed with other alloys [1].

For Ni-Al coated specimens, the increase from 600 to 800 °C induces a slight internal attack at the steel-coating interface, probably due to the relatively high porosity of the layer.

As for Sermaloy J coating, it seems that the temperature raising from 600 to 800 °C has increased the scaling of the external zone and this phenomenon can perhaps be related to the diffusion of aluminium detailed in 3.3.

4.2 INFLUENCE OF THERMAL CYCLING. — The comparison of the results obtained with non coated steel clearly shows the detrimental effect of thermal cycling at 800 °C (factor 3) [3].

For Ni-Al coated specimens, the important scaling observed during the test can be either attributed to the effect of mechanical stress induced by thermal cycling or to the poor quality of the coating delivered for the second batch. However, in the still adhering areas, the attack observed at the coating interface is also higher after thermal cycling. So, this phenomenon which results from the porosity of the coating, would have led sooner or later to a scaling in presence of thermal cycling.

Finally, the very good behaviour of Sermaloy J after thermal cycling (no attack) can certainly be related to the quality of the alumina layer covering the external interface and also to the bonding of the coating on the steel by a diffusion zone.

4.3 INFLUENCE OF HCl-CONTENT. — The comparison of the tests carried out with 1 and 3% HCl, demonstrates the influence of this parameter on the corrosion rate of the non coated 310S steel. This is in accordance with previous observations [1], which showed that the corrosion of various alloys by HCl containing gases was often controlled by the diffusion of HCl to the interface.

For Ni-Al coated specimens, an important scaling is observed in the 3% HCl test. As discussed previously, this phenomenon can be attributed to the poor quality of the coating or to the attack at the steel-coating interface resulting from the porosity, which can lead to a scaling.

The Sermaloy J is not corroded at 800 °C with 3% HCl, which clearly demonstrates the improvement that can be obtained with this coating even in this very aggressive environment.

4.4 COMPARISON OF LABORATORY TESTS WITH FIELD TEST. — As pointed out by the important quantities of ashes surrounding the specimens, the corrosion conditions are completely different in the two types of tests, even if the chloride contents of the atmospheres are of the same order of magnitude. So, in the field test, the corrosion phenomena are more close to molten salts interactions than to gaseous corrosion. In that case, the important porosity of Ni-Al is not so detrimental than in laboratory tests. In fact, no sulfate or chloride have been found in the coating and this is probably the reason for the better behaviour of Ni-Al in field tests compared with the other materials.

The corrosion suffered by the Sermaloy J coating seems to show that the thin layer of alumina is not sufficient to resist the fluxing resulting from the presence of chlorides and sulfates [5].

As for the steel behaviour, its corrosion rate is much higher in the field test (factor 100) and it seems to demonstrate that the chromia layer formed at the surface is much more easily dissolved in molten salts than an alumina type layer.

5. Conclusion.

This study has shown that Al-rich coatings, such as Sermaloy J and Ni-Al, can lead to a real protection of a steel substrate, in oxichlorinating atmospheres and also in presence of molten sulfates and chlorides. However, this study has also pointed out the important influence of

the manufacturing conditions on the behaviour of the coated specimens (unperfect reproducibility between batches, irregular thickness due to manual operation, porosity of Ni-Al).

If in clean atmosphere laboratory tests, SO_2 has no noticeable influence in the corrosion process compared with HCl [7], on the contrary, sulfur oxides, leading to formation of sulfates in presence of alkaline compounds (field tests), can lead to very different phenomena [5, 9]. So, taking into account the promising results obtained with Ni-Al and Sermaloy J, the study should be extended with a particular attention paid to the following parameters: optimization of the coating processes (automatic operation, decrease in the Ni-Al porosity by powder spraying and surface remelting, evaluation of pack cementation for aluminizing) [5], behaviour in gas-molten salts environments, technical and economical comparisons of coatings to high temperature alloys.

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