Investigations on corrosion protective layers in waste incineration plants

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Corrosion in the hot gas area of waste incineration plants is a severe problem that often causes premature damage of components. In general, these components are made of base materials, which are not stable in corrosive conditions (boiler steel). Thermal spraying is an alternative to the most usual process cladding, which has the potential to create cost-efficient protective coatings. Until now, there are still not enough experiences about quality assurance (porosity, oxides) and long run behaviour inside the incineration plants with sprayed coatings.
Since many years, ATZ Entwicklungszentrum is involved in the development and/or advancement of materials, technologies, and applications of thermal spraying for corrosion protection. Currently, pipes, coated with different materials and different technologies are tested by different strategies (corrosion tests under laboratory scale and/or directly in incineration plants).

1 Introduction

Since many years thermal sprayed coatings were tested in corrosive conditions, which are characteristic for waste incineration plants (e.g. /i,ii,iii,iv/). In many cases, the layers show a good resistance under laboratory scale. Thermal sprayed layers often fail under real conditions (investigations directly in waste incineration plants). The reasons are complex. The corrosion resistance of a material is ascertained by many aspects: pre-treatment of the substrate, spray process, spray conditions, layer material, (possible) further treatments after coating, operating conditions in the plants, and other.

2 Corrosion Protection by Thermal Spraying

Thermal spraying is variously applicable for the corrosion protection. Some examples are listed in table 1.

Table 1: corrosion protection by thermal spraying

conditions	layer materials	applications
thermal spray: arc, flame		
1	Al, Zn, AlMg	reinforced concrete, apparatus engineering
thermal spray: HVOF, plasma		
1	stainless steel	apparatus engineering
1 and 4	WC/Co, WC/CoCr	plant engineering
2	MCrAlY, Ni-, Co-base	energy plants, aviation
2 and 4	Cr_3C_2/NiCr	energy plants, turbine construction
2 and 5	NiCr, MCrAlY, Al_2O_3, ZrO_2	engine and turbine construction
3	Ni-, Ti-base, polymer	bio gas and/or sewage plants

[1] corrosion at air / water
[2] hot gas corrosion
[3] biocorrosion
[4] wear
[5] thermal insulation

The choice for a certain spray process and/or layer material depends on the application area and the corrosive stress arising there. Arc spraying and conventional flame spraying are mostly used for cathodic corrosion protection. The sprayed layers (e.g. Al, Zn) are sacrificial anodes for the substrate, whereby the durability of steel beams can be substantially extended /v/. Favoured processes are HVOF and plasma spraying (APS). These processes are preferentially used, if high demands are made on the surface (e.g. against hot gas and/or hot temperature corrosion, biocorrosion). The sprayed resistant layer protects components, which are not stable in these corrosive conditions. Fig. 1 shows an uncoated and a coated structural steel after hot gas corrosion in reducing atmosphere.

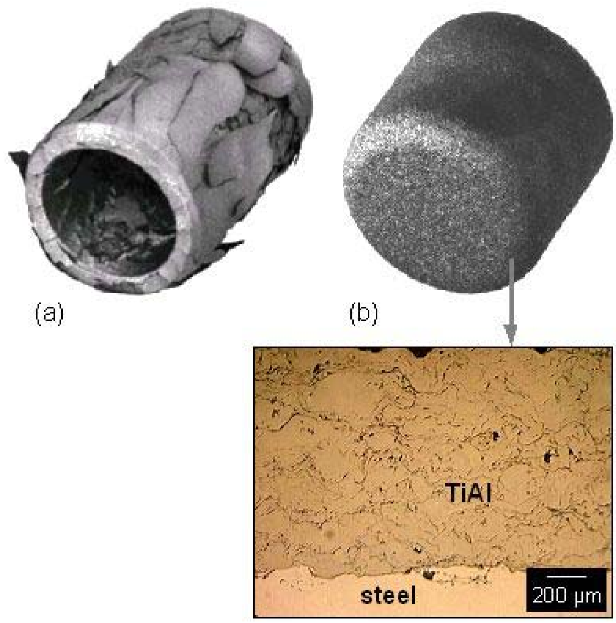


Fig. 1: hot gas corrosion of steel PK925 (X10CrAl18) in reduced atmosphere (Ar-5%H_2-1%H_2S);
(a) non-coated; after 230h at 600°C,
(b) coated with TiAl (APS); after 1000h at 700°C /vi/

In many applications, the surface of a device should be as corrosion as wear resistant. A layer combination is mostly used (metallic intermediate layer against corrosion; ceramic conversion layer against wear). The layer combinations in Fig. 2 (hot gas, 1000°C, 300h) show that the choice of the layer material is an important aspect for the resistance of a substrate. The metallic NiCrAlY-layer is resistant against corrosion, because an oxidation-restraining oxide coating is formed. In contrast, the NiAl-layer is partially destroyed as result of a strong oxidation.

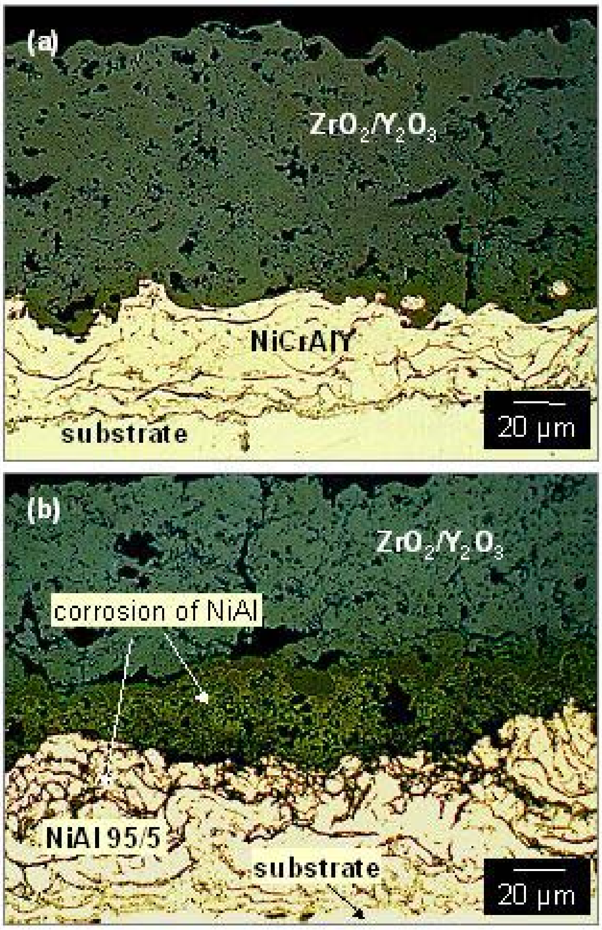


Fig. 2: hot gas test (1000°C, 300h, air);
(a) intermediate layer NiCrAlY, conversion layer ZrO_2/Y_2O_3 (APS)
(b) intermediate layer NiAl, conversion layer ZrO_2/Y_2O_3 (APS)

3 Corrosion Protection in Waste Incineration Plants

In thermal plants (e.g. waste incineration plants) components are exposed aggressive and corrosive atmospheres of high temperatures. Under the operation conditions with usual fuels the heat exchanger surfaces (e.g. 15Mo3) suffer increasingly a dynamic reduction of their life time due to corrosion processes /vii/ (Fig. 3).

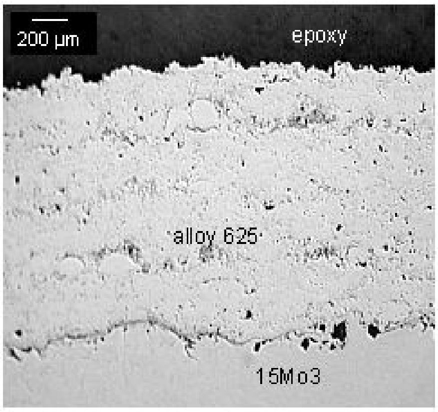
Fig. 3: salt melt corrosion on blank superheater /viii/

At present the coatings are mainly realized with cladding. The coating layers receive a deep connection with the base material during the cladding process. As result of the cladding process, Iron permeates from the substrate into the layer. The increase of the iron content in the layer reduces the corrosion protection effect. Due to corrosion processes it can finally come to an emaciation of the layer and to a damage of the components within a short time /viii/.

Although an optimal cladding-layer has a long durability (more than 20.000 hours of operation), these processes require a high financial input. An alternative process is the thermal spraying. Advantages of this procedure are adhesion mechanisms, which minimize the mixing up of substrate and layer material. The adhesion of thermal sprayed layers are primarily realized by mechanical interlocking, Van der Waals-forces and/or micro welding, whereby the corrosion protection effect is not impaired by the base material.

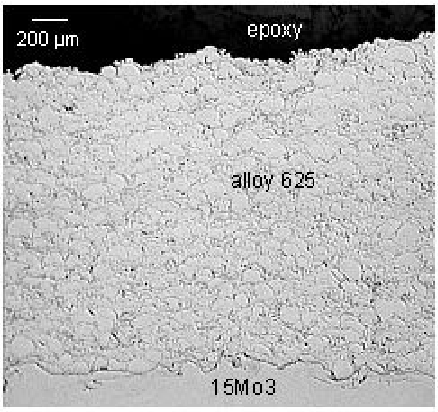
Important conditions for an optimal corrosion protection are the adhesion and the leak tightness of the layer. An open porosity should be avoided. HVOF sprayed layers are more dense and have less oxide embeddings than plasma sprayed layers /ix/.
The choice has to consider the different corrosive components in the atmosphere in waste incineration plants. Nickel base alloy (examples in Fig. 4)are favourite, in particular alloy 625. Beside nickel

(against chlorides), the elements chrome (against sulphates) and/or molybdenum (against chlorides) possess a great importance for the corrosion protection.



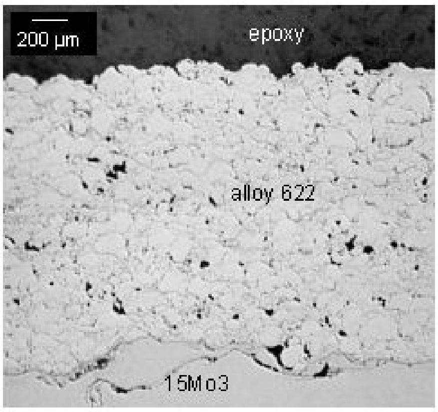
(a)

alloy 625
HVOF
(DJ - Sulzer Metco)



(b)

alloy 625
kerosin-HVOF
(CJS - Thermico)



(c)

alloy 622
kerosin-HVOF
(CJS - Thermico)

Fig. 4: Nickel base alloys, sprayed by different HVOF processes

Despite the advantages of thermal spraying compared to cladding process, the present results are not yet completely satisfying. Two examples are specified in the following, which make clear the complexity within the waste incineration plants. A layer from the nickel-based alloy Inconel 625 was produced by HVOF on boiler steel 15Mo3 in both cases. The layers were analyzed after 7.500 hours of operation.

Positive results were particularly obtained within the range of the superheaters. Fig. 5 shows the cutout of a pre-superheater tube coated with Inconel 625 by HVOF. The salt-ash-deposit on the surface did not led to a corrosive attack (see the micrographs in Fig. 5). These results show that the HVOF process can create a dense layer and that the nickel-based alloy Inconel 625 can protect the boiler steels.

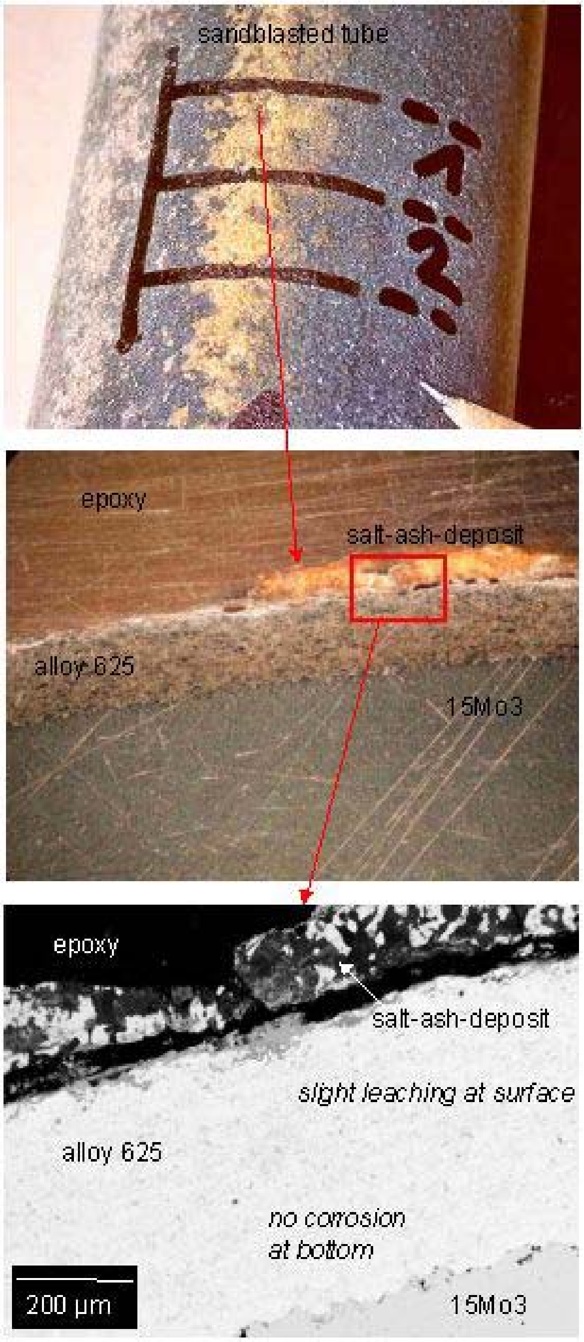
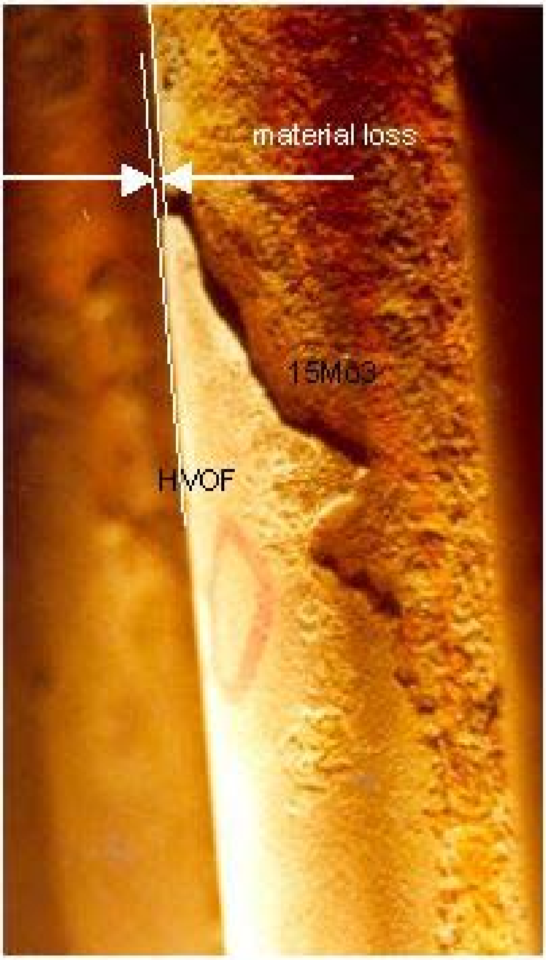


Fig. 5: pre-superheater (coated with alloy 625 - HVOF) after 7.500 hours of operation (conditions: 385°C/40bar steam; 400-500°C fluegas), /x/

Fig. 6 shows a cutout of a frontwall coated with Inconel 625 by the HVOF process. In contrast to the superheater the frontwall-layer is flaked off, whereby the substrate is attacked.



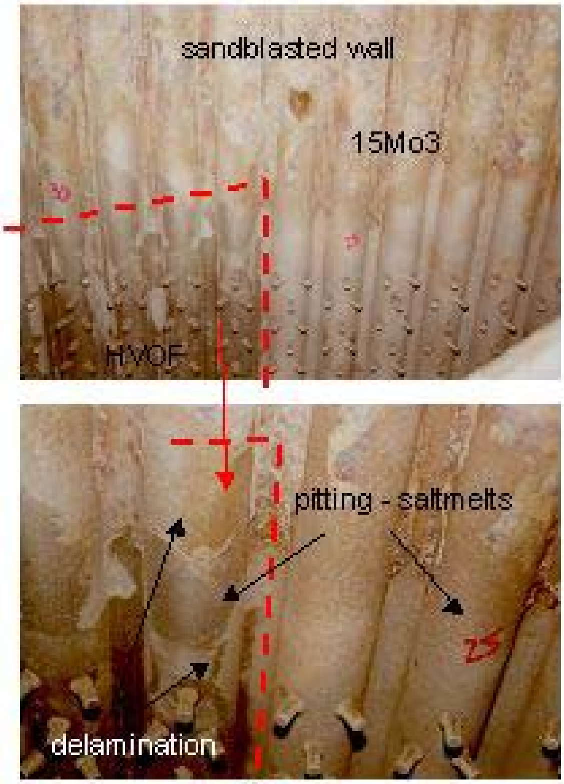


Fig. 6: frontwall (coated with alloy 625 - HVOF) after 7.500 hours of operation (conditions: 240°C/40bar steam; 850°C fluegas), /x/

The reasons of the different behaviour of the same coating in different range of a boiler are versatile. The probably most important aspect results from the coating process. The coating of the frontwall took place directly in the boiler (repair coating). The necessary pre-treatment of the substrate (e.g. sand blasting) can't be accomplished (or only insufficiently). In addition, there are serious quality differences in the layer, due to the geometry of the frontwall. The coated layer in the covings between the individual evaporator tubes is very porous and therefore insufficiently dense (overspray). The results are an increasingly infiltration and flaking of the layer and finally a corrosive attack of the steel substrate.

In contrast, the superheater tubes were coated in a spray chamber. Thereby a suitable pre-treatment of the substrate is possible. In addition, the negative effects of the overspray are widely avoided by the free geometry of the construction unit.

An other aspect is the chemism of the atmosphere. The fluegas is loaded with gaseous chlorides (HCl and metal chlorides). Chloride is more stable than sultates at higher fluegas temperatures. An insufficient sulphating of the metal chloride in the fluegas (SO_2/SO_3-amount is to low) leads to a deposition of chlorides on the substrate surface /xi/. The aggressive metal chlorides remains stable and penetrate, infiltrate and/or destroy (high temperature chlorine corrosion) the layer. The fluegas temperature is decreasing on the way to the superheater. It comes to a faster sulphating of the metal chlorides, because sulfate is more stable at lower fluegas temperatures. Alloy 625 is substantially more stable opposite to the sulphates.

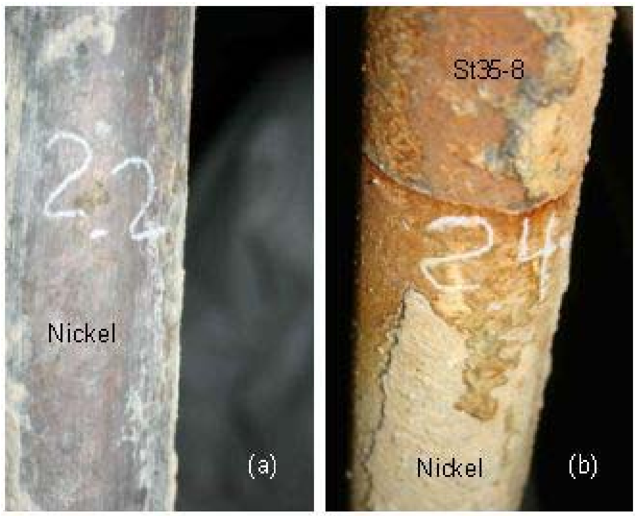


Fig. 7: evaporator tubes (coated with nickel - HVOF) after 4.100 hours of operation (conditions: 285°C/80bar steam; ;

(a) sealed with ceramic precursor
(b) non-sealed

Besides the modifications of the spray processes and/or the choice of the coating material, the corrosion protection can be improved by further treatments. Nowadays a sealing of the sprayed layer is often used. Fig. 7 shows boiler tubes (material: carbon steel St35-8) coated with nickel (HVOF) after 4.100 hours in operation. The left tube was sealed with a ceramic precursor. This layer compound is more stable than the simple nickel coating on right.

4 Summary

Thermal spraying is characterised by high flexibility and mobility. It represents a suitable alternative for the production of corrosion protective layers compared to chemical and/or electro-chemical deposition as well as cladding. However there is still the necessary for investigation, because thermal sprayed layers partly fail in waste incineration plants. Some successes face some disappointments.

If a thermal sprayed layer fails, then the reasons are mostly an insufficient adhesion as well as an insufficient leak tightness of the layer. Possibilities for the improvement of the layer quality are e.g. the optimizing of the thermal spray process: stronger acceleration of the particles and use of finer powders for a more adhesive and dense layer, lower kinetic energy for decrease the oxide content. In addition the further treatment by sealing shows first positive results, so this surface modification is strengthened examined in the future.

5 References

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