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Investigations of corrosion protective layers in thermal energy plants

Abstract

Corrosion in the hot flue gas area of energy plants is a severe problem that often causes premature damage of components, e.g. boiler steels are mostly not stable in corrosive conditions in waste incineration plants. Thermal spraying is an alternative coating technology 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, adhesion) 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 are used is variously applications for corrosion protection (table 1). 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 are sacrificial anodes for the substrate, whereby the durability of steel beams can be substantially extended /1/. Favoured processes are HVOF and plasma spraying. These processes are preferentially used, if high demands are made on the surface (e.g. against hot gas and/or hot temperature corrosion, bio-corrosion). The sprayed resistant layer

protects components, which are not stable in these corrosive conditions.
In the last years, thermal sprayed layers are more and more tested and used in thermal energy plants like waste incineration plant (e.g. /2-5/). In many cases, the coatings show good or very good stability under laboratory scale but fail often under industrial conditions. 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, further treatments after coating, operating conditions in the plants et al..
The ATZ Entwicklungszentrum is engaged in the development of corrosion protection layers for thermal energy plants such as waste incineration plants and/or biomass power plant and biological plants such as biogas fermentation. The thermal spraying processes HVOF and plasma spraying as coating technology and nickel base alloys and/or layer combinations as layer materials are favoured. In biological units polymer coatings are also of interest.
This article contained first results of thermal sprayed corrosion protective layers for waste incineration plants.

Table 1: corrosion protection by thermal spraying (some samples)

conditions	layer materials	applications
arc spraying; flame spraying		
1	Al, Zn, AlMg	reinforced concrete, apparatus engineering
HVOF; plasma spraying		
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 and/or water [2] hot gas corrosion [3] bio-corrosion
[4] wear [5] thermal insulation

2. Corrosion Protection in Waste Incineration Plants

In waste incineration plants components are exposed aggressive and corrosive atmosphere of high temperature. Under the operation conditions with usual fuels the heat exchanger surfaces suffer increasingly a dynamic reduction of their life time due to corrosion processes /6/ (Fig. 1).

Fig. 1: salt melt corrosion on blank superheater /7/

At present the coatings are mainly realized with cladding. During these process the coating layers receive a deep interaction with the base material. One result of the cladding process is the permeation of iron from the substrate into the layer. The increase of the iron content in the layer can reduces the corrosion protection effect. Due to corrosion it can finally come to an emaciation of the layer and to a damage of the components within a short time /7/.
Although an optimal cladding-layer has a long durability (more than 20.000 hours of operation), these process 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 /8/.
The choice has to consider the different corrosive components in the atmosphere in waste incineration plants. Nickel base alloy are favourite, in particular alloy 625. Beside nickel (protection against chlorides), the elements chrome (protection against sulphates) and molybdenum (protection against chlorides) possess a great importance for the corrosion protection.
Despite the advantages of thermal spraying compared to cladding process, the present results are not yet completely satisfying. Mostly thermal sprayed layers on the frontwall often flaked off and the substrate is attacked. On the other side coatings on the superheater are in many cases stable and give a good corrosion resistance. The reasons are versatile, for example pre-treatment of the tubes, repair or new coating, the tube and/or the flue gas temperature, the chemism of the atmosphere (more details in /9/).

3. Investigations of Thermal Sprayed Layers

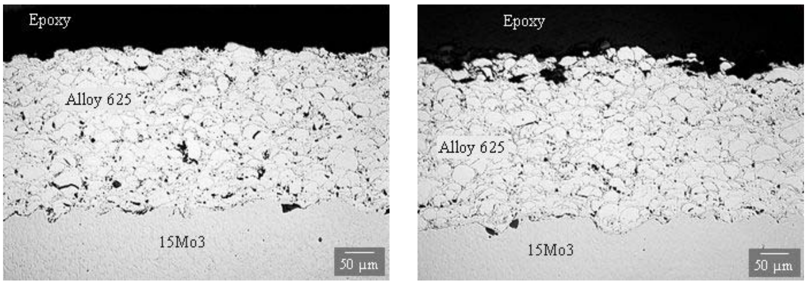
For a good corrosion resistant layer some thermal spraying technologies and many different layer materials (mostly nickel base alloys) are investigated. In this article first results are represented. The nickel base alloy “Alloy 625” and the thermal spray process kerosene-HVOF was used.

Table 2: some elements of the E-filter ash; in [g/kg]

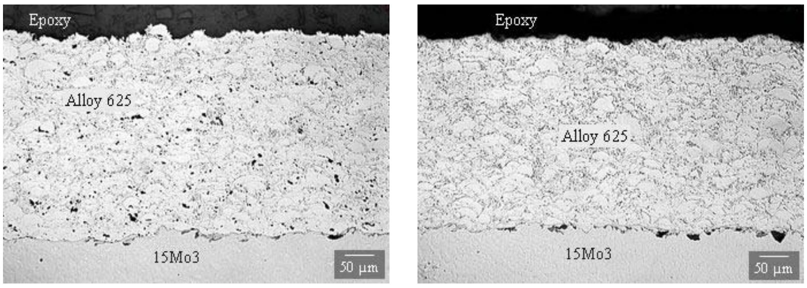
chlorine	sulfur (SO_3)	sodium	potassium
244	158	144	134

calcium	zinc	lead	copper
78,5	42,3	14,1	2,6

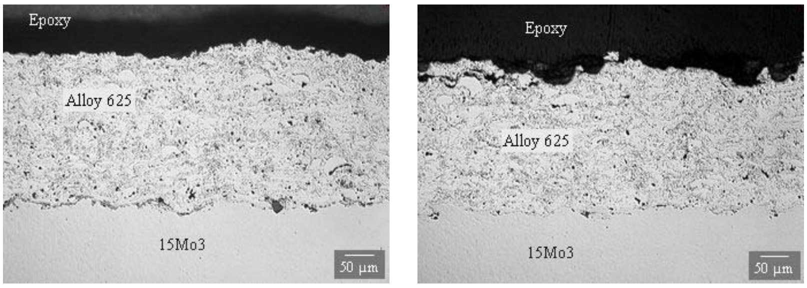
First laboratory tests were accomplished in order to examine the influence of the spray parameters on the layer. In the following investigations the fuel liquid kerosene was varied. Oxygen and hydrogen remained constant. The coated tube were treated in a muffle furnace at 430°C (no corrosive atmosphere; only air). The corrosive medium was E-filter ash of an incineration plant, in which the pipes were embedded on one side. The quantities of the most important components of ash are specified in table 2. The sprayed tubes were analyzed every 300h, a sample was taken and the ash replaced.



(a), (b) spray parameter kerosene 6 l/h

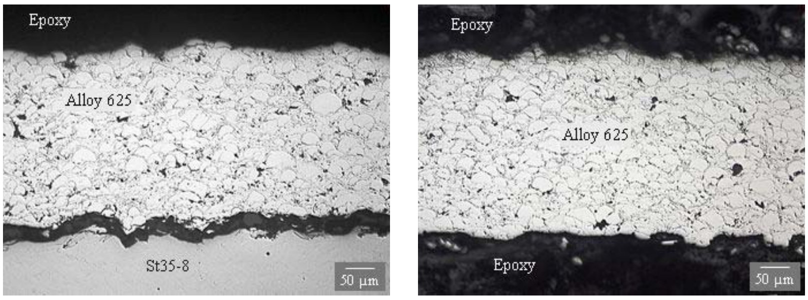


(c), (d) spray parameter kerosene 10 l/h

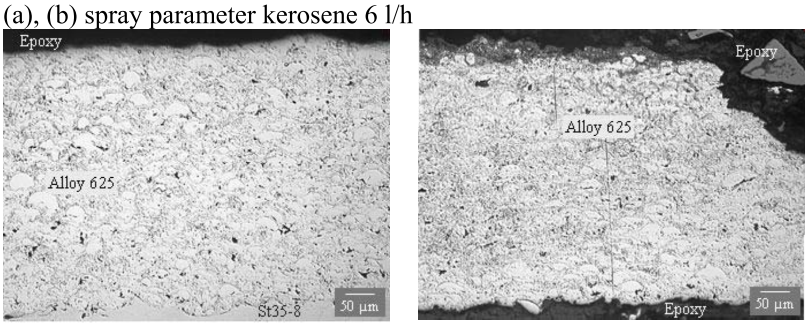


(e), (f) spray parameter kerosene 14 l/h

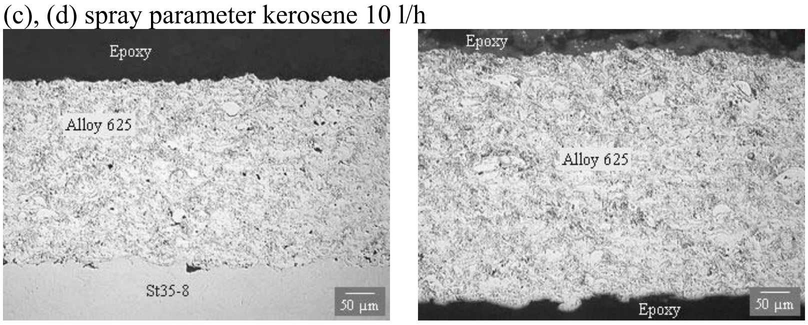
Fig. 2: Alloy 625 (coated by kerosene-HVOF); initial state *(left)*, after 900h in the laboratory test *(right)*



(a), (b) spray parameter kerosene 6 l/h



(c), (d) spray parameter kerosene 10 l/h



(e), (f) spray parameter kerosene 14 l/h

Fig 3: Alloy 625 (coated by kerosene-HVOF) after 200h in waste incineration plant (wind side); *left* – tube sheet temperature 350°C; *right* – tube sheet temperature 430°C

In fig. 2 micrographs of the coated tubes in the initial state and after 900h are represented. The influence of the spray parameters can be recognized clearly. The higher the kerosene content the higher is the temperature in the burning chamber of the spray gun. Thus the particles of the layer material are more strongly melted and the oxide content in the layer is increased, which has an explicitly influence on the corrosion behaviour of the coatings. The "cold" coating (6 l/h kerosene) shows first flakings and at the "hot" layer (14 l/h kerosene) are pittings after 900h. In opposite the coating sprayed with 10 l/h kerosene don't show any changes.

In order to compare these results with industrial conditions so called material probes are coated with the same layers and examined in an incineration plant. In this area the flue gas temperature lay between 680 and 740°C. The probes was cooled by air. Due to this kind of cooling different sheet temperature are measured. Two samples of every probe were taken. The sheet temperatures lays around 350°C and 430°C. The results are represented in fig. 3.

The results of the lab tests were confirmed in terms of corrosion resistance dependency on the spray parameters. The "cold" layer (with 6 l/h kerosene) was flaked off after 200h. This points on a insufficient adhesion between layer and substrat and/or to high tensions in the layer. Beside the spray parameters the tube sheet temperature have also an influence of the layer stability. With higher sheet temperatures (fig. 3, right column) all layers flaked off and showed local corrosive attacks. In this case the layer isn't stable at tube sheet temperatures higher than 400°C.

An important result of the investigations is the influence of the oxide content in the thermal sprayed layer. In many discussions it was said that the oxides represent weak points of the coatings. Therefore its content must be low for a good corrosion resistance. The investigations clarify that a low oxide content don't show necessarily the best result. There is evidence that in the corrosive environment of a waste incineration plant a higher oxide content is advantageous for a better adhesion between layer and substrat. But, if the oxide content is to high a stronger corrosive attack is observed (see fig. 2e and f). In the presented case the optimum lies in a middle kerosene content.

On the other side the results under industrial conditions aren't satisfying because the most layers already failed after only 200h. Therefore continuative investigations are necessary. Possible ways are the use of layer combinations and the subsequently sealing of the layer.

4. Summary

The accomplished investigations showed that:

- alloy 625 is chemically stable (no corrosion of the alloy);
- if the oxide content is to low, the layer flacked off (spray conditions “to cold”; insufficiently adhesion);
- if the oxide content is too high, the layer shows pittings (spray conditions “to hot”);
- at using HVOF, the layer porosity is negligibly (no layer failure due to porosity ascertainable);
- complete failure of the layer at tube sheet temperature 430°C (HVOF-sprayed alloy 625 seems unsuitable in interaction with a high flue gas temperature).

Further investigations are concentrated on layer combinations (combinations of different materials and/or spray technologies) and post-treatment of the sprayed coatings. In addition finer powders are to be tested.

4. References

/1/ M. Knepper; in Proceedings Thermal Spray Conference, Düsseldorf (1999); 106 ff.

/2/ C. Schroer, M. Spiegel, H.-J. Grabke; in „Werkstoffwoche `98 – Band III; Symposium 3 / Symposium 7 (A. Kranzmann, U. Gramberg); Wiley-VCH (1999); 251 ff.

/3/ M. Spiegel; Materials & Corrosion 50 (1999); 373 ff.

/4/ K. Yamada, Y. Tomono, J. Morimoto, Y. Sasaki, A. Ohmon; Vacuum 65 (2002), 533 ff.

/5/ K. Hidaka, K. Tanaka, S. Nishimura, K. Kawarada; in Proceedings of ITSC’95, Kobe, Japan (1995); 609 ff.

/6/ W. Spiegel; „Berichte aus Wassergüte- und Abfallwirtschaft“, TU München 162 (2001); 345 ff.

/7/ W. Spiegel, T. Herzog, W. Müller, W. Schmidl; „Praxisnahe Unterstützung der Betreiber bei der Optimierung und nachhaltigen Nutzung der bayrischen MV-Anlagen“; Endbericht L21, LfU 11/2002

/8/ S. C. Cha, P. Wölpert; Advanced Engin. Mat. 5 (2003); 213-217

/9/ P. Crimmann, D. Bendix, M. Faulstich; in Proceedings of ITSC ’05, Basel (2005); 1463 ff. (CD-ROM)