Development of new Protective Coatings for Extremely Corrosive High Temperature Environments

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Introduction

In many industrial gasification and combustion processes highly corrosive conditions are encountered that make high demands on metallic components of the used materials. Examples are plants for the incineration of waste, special refuses, bio mass, sludge etc. These charges contain high quantities of chlorine and sulphur compounds as well as heavy metals, that have a strong corrosive effect based on attacks from gaseous species and saline melts. Fig. 1 shows the mechanism of chlorine corrosion. To limit the extent of the corrosive attack many plants are operated at relatively low temperatures, although an operation at higher temperatures would be desirable from an economic point of view, especially in waste incineration plants with regards to an improved degree of efficiency. Additionally certain process temperatures shall not fall below specific limits to comply with legal requirements of emission protection. The methods for protection against corrosion used so far like galvanic nickel-plating, build-up welding or thermal spraying of nickel based materials or the use of compound tubes (high-alloyed tube casing on ferritic heat exchanger tube) do not allow a significant increase of the process temperature above 400°C. In the field of waste incineration the demand on reliable, powerful capacity for incineration will raise due to the prohibition of the disposal of untreated waste, in force since July 2005 in Germany. Therefore the requirements for an efficient concept of corrosion protection that enable higher process temperatures combined with extended lifetime are growing.

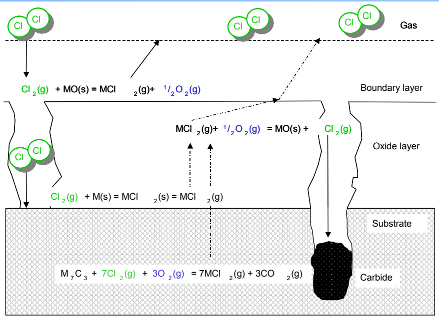


Fig. 1: Mechanism of Chlorine-Corrosion

Approach

A significant increase of the temperatures of the tube wall in heat exchangers that are exposed to aggressive process media is possible only by the application of new concepts for protection. The combination of thermally sprayed coatings (APS, HVOF) with an additional sealing with nano-scaled SiO_2/B_2O_3-partikels by means of the sol-gel-procedure offers the potential for a significant enhancement of corrosion resistance.

As spray coating materials are used:
- $TiAl_{48.9}$ (intermetallic phase)
- $Ni_{75.6}Cr_{19.2}Si_{5.2}$ (alloy)

Thermodynamic calculations for the intermetallic phase TiAl showed that in a temperature range of 400-800°C Titania is dissolved only partially in melts of chlorides from lead and zinc. Data from the literature confirm that intermetallic phases with high aluminium contents exhibit a high potential of resistance.

A more conventional way is followed in form of a NiCrSi-alloy. This approach is supported by observations in the literature that an optimised combination of the alloying elements Ni, Cr and Si have good prospects for enhanced corrosion resistance.

Coatings

Fig. 2 shows TiAl spray coatings that have been applied by means of APS-(**A**tmospheric **P**lasma **S**pray) and HVOF-procedure (**H**igh **V**elocity **O**xygen **F**uel) onto the respective substrate materials. The open porous structure of the spray coating is noticeable.

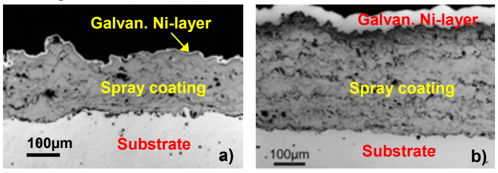
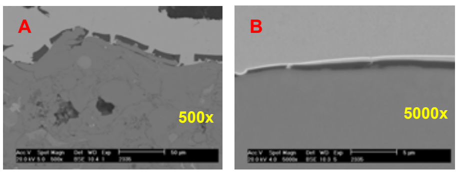


Fig. 2: TiAl-Spray coatings

a) APS on 1.7335 (Fe-1Cr-0,4Mo)
b) HVOF on 1.4749 (Fe-28Cr)

For the sealing of the pores nanoparticles were applied by means of sol-gel method and thermally treated to remove the organic parts and subsequently sintering to a gas-tight layer. SEM images of the different regions (A and B) of the coatings and the sealing are given in fig. 3.



A: - nanocoatings (6-8 µm thick)
- numerous defects
- no closed layer
- no nanocoating residue below delaminated layers

B: - nanocoating (100-700 nm thick)
- only few defects
- almost closed layer

Fig. 3: REM images of TiAl-APS coatings sealed with a SiO_2/B_2O_3-nanocoating

The applied sealing in fig. 3 is not perfect and possesses several defects. However an improvement in corrosion resistance was already noticeable (see section exposure). SEM images of improved nanocoatings are given in fig. 4. There almost closed layers with only few defects were obtained which additionally showed a good infiltration into pores and cracks. It is expected that sealing of HVOF-coatings should be even better due to the much smoother surface on these coatings. Metallographic examinations and exposure testing is in progress.

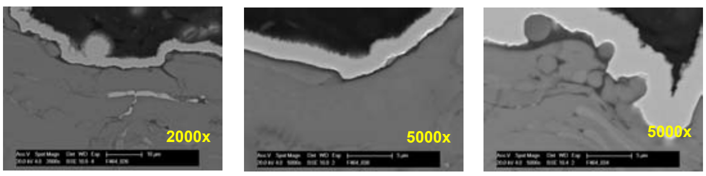


Fig. 4: REM images of TiAl-APS coatings sealed with an improved SiO_2/B_2O_3-nanocoating

Exposures

Samples were exposed to a humid (*10% H_2O*) atmosphere (*94,75 vol-% N_2, 5 vol-% O_2, 0,25 vol-% HCl*) at 600°C for 288 h. The salt mixture, that simulates the deposits of the process were chosen that way (SO_3/Cl^- ratio: 2.3, 15 wt-%) that a severe corrosive attack is enabled (fig. 5).

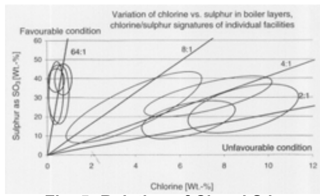


Fig. 5: Relation of Cl and S in deposits of different waste incineration plants (W. Spiegel 2001)

While strong intergranular corrosion is observed at uncoated samples (fig. 6) the corrosive attack at spray-coated (fig. 7a) and even more pronounced at additionally sealed samples is considerably weaker (fig. 7b). The protective effect of the nanosealing is also clearly visible in fig. 8.

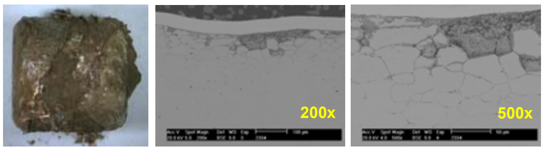


Fig. 6: 1.4749 without coating

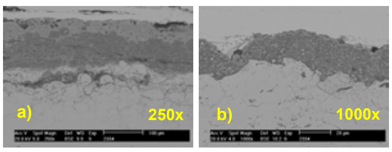


Fig. 7: 1.4749 with
a) HVOF-NiCrSi-coating
b) additional SiO_2/B_2O_3-Nanocoating

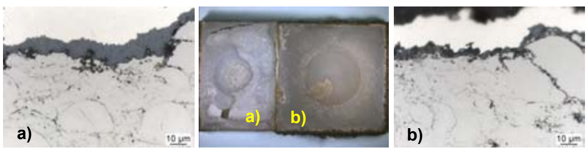


Fig. 8
a) 1.7337 with HVOF-TiAl-coating
b) additional SIO_2/B_2O_3-Nanocoating

Summary and perspective

Upon exposure under simulated conditions of waste incineration uncoated specimens exhibit massive corrosive attack. Spray coatings offer an improved resistance that can be enhanced significantly by additional sealing with nano-coatings. Improvements of the nanocoatings concerning composition and coating process to yield closed layers with no or only few defects are in progress and first improved sealings are currently exposed to simulated waste incineration environ-ments.