Behaviour of thermally sprayed coatings exposed to high temperature hot corrosion environment

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Abstract: Thermally sprayed coatings (Cr3C2-CoNiCrAlY, NiCrBSi) were deposited on substrate material Wr.Nr. 1.4923 using HVOF (High Velocity Oxygen Fuel) thermal spraying technology. This substrate material is in nitrided state used as an effective constructional material for components in power equipment. The evaluation of resistance against high temperature corrosion was conducted for both selected thermally sprayed coatings and compared with nitrided stainless steel. All evaluated coatings were cyclically exposed to corrosive-aggressive environment of molten salts mixture with composition of 60% V2O5 and 40% Na2SO4 at the selected temperature of 750 °C. Weight changes of individual samples were measured after every cycle and the results were recorded in the diagram. Furthermore in cooperation with university in Tampere the coatings were tested in corrosive-aggressive environment of molten salts mixture with composition of (59% Na2SO4, 34.5% KCl and 6.5% NaCl) in 30% humidity at the selected temperature of 525 °C and 575 °C. Exposure time of this test was 168 hours. All coatings were analyzed using light and scanning electron microscope (SEM), and also the analysis of elemental composition (EDX) was conducted. Alloys-based coatings showed very similar corrosion mechanism in the selected aggressive environment and the same can be stated about cermet coatings. The obtained results prove that HVOF deposited coatings can replace current surface protection of components in power equipment such as nitriding.

Keywords: high temperature corrosion, HVOF, coatings, thermal spraying

Introduction
Coating properties determine its behavior in operation. The most effective testing is therefore a simulation of real operating conditions. On the other hand, such evaluation method is usually not possible to realize. For this reason, coatings are usually characterized by their physical or mechanical properties. Publications dealing with evaluation of high-temperature behavior are focused on the standard evaluated values observed by "as sprayed" coatings and also on other physical and mechanical properties, their dependence on temperature, corrosive environments, modes and conditions (e.g. composition of furnace atmosphere) [1].

The corrosion in the presence of molten salts is called high temperature corrosion. This corrosion process is based on the deposition of salts on material surface. At operating temperatures, some salts are in liquid state or form complex salt mixtures in the presence of gases containing sulfur. These salt mixtures melt at much lower temperatures in comparison with melting points of their individual components. The sources of salts depositing on material and attacking are not only impurities deposited from coal or oil, but also other environments where salts penetrate to the material surface, e.g. in marine industry. The dissolving of oxides takes place in the salt melt. The principle is following. Molten salts deposit on material surfaces, dissolve protective oxide film and thereby increase the corrosion rate. An example of such mechanism can be sulphate melt. Pure Na2SO4 melts at 884 °C, but in combination with other salts, e.g. NaCl or NiSO4, the melting point of this mixture is lower [2].
High temperature corrosion test was conducted in order to simulate conditions occurring in boilers, refinery furnaces or gas turbines. Residual fuel oils are the most frequently formed substances in these devices. This type of fuel is used due to the exhaustion of refined fuels and mainly for economic reasons. Fuel oils contain sodium, vanadium and sulfur. These elements are in this case regarded as impurities, mainly because of the formation of Na$_2$SO$_4$ (melting point at 884 °C) and V$_2$O$_5$ (melting point at 670° C) during reactions taking place in combustion systems [3], [4] and [5]. These compounds are generally known as ash depositing on the material surfaces and accelerating oxidation (high temperature corrosion). Moreover, vanadium compounds is act as catalysts of oxidation and thus enable oxygen and other gases in the atmosphere to diffuse rapidly to the material surface which consequently creates additional oxidation [6].

Several different types of precautions are being used against high-temperature corrosion. However, most of them prevent from high-temperature corrosion just partially and temporarily. The application of protective coatings seems to be the most efficient and also the most economical solution. On the other hand, not every protective coating is suitable for every type of environment. For this reason, it is crucial to investigate which coatings provide protection in specific environments.

**Experiment**

Two commercially available powders were used for sample preparation. These powders were Amperit 594.074 (Cr3C2-25%CoNiCrAlY) with a particle size distribution (-45+15 mm) and M-771.33 (NiCrBSi) with a particle size distribution (-53+20 mm). Nitrided steel commonly used to protect functional surfaces against this type of corrosion environment was chosen for comparison with evaluated coatings.

All coatings were deposited by HP/HVOF (High Pressure/High Velocity Oxygen Fuel) technology with JP-5000 torch from the company TAFA Incorporated. Already optimized spray parameters were used for each coating. Coatings were deposited on substrate material Wr.Nr. 1.4923 which is in nitrided state used as an effective constructional material for components in power equipment.

The preliminary tests were conducted with cooperation with University of Tampere. One of the commonly used method of testing high temperature corrosion is deposition of solution of salts on the surface of tested samples with following measurements of weight losses after heat required exposition. The test conditions were as follows. Known quantity of salt compound was deposited on the surface of samples (the composition of salt solution was 59% Na$_2$SO$_4$, 34.5% KCl a 6.5% NaCl). The samples with corresponding salts were inserted in to the autoclave with 30% humidity. The tests took 168 hours and were conducted at 525 and 575 °C. After the exposition to the salt environment the samples were removed from autoclave and weighted and afterwards mounted for further SEM and EDX analysis.

This article also describes high temperature corrosion testing based on applying of corrosion-aggressive salt mixture at 750 °C. This testing was more accurately aimed to test specific environment conditions than the previous one. The testing was conducted in company VZÚ Plzeň. The test procedure was as follows. First, the specimens were polished to the surface roughness (Ra) maximally 1μm. Second, the specimens rinsed with alcohol and heated at 250 °C in an oven. This heating was necessary for proper adhesion of salt layer. Third, the salt mixture in proportions of 40% Na$_2$SO$_4$ and 60% V$_2$O$_5$ (eutectic mixture with low melting point at 550 °C) was chosen to simulate the conditions properly and to achieve comparable results with publications [7], [8], [9] and [10]. This salt mixture was mixed with alcohol and applied to the surface of evaluated specimen in amount of (3-5) g/cm$^2$. Finally, the applied mixture was dried for 3h in an oven at 100 °C. Before the testing, the specimens were weighed and the weight was measured after each cycle. Number of cycles was 50 in order to
compare easily with results achieved in foreign research. Each cycle consisted of 1h in silicon carbide furnace and of subsequent cooling for 20 minutes at ambient temperature. Measurements were performed on coated and on nitrided specimen.

Results and discussion

Coating NiCrBSi showed expected results. First set of photographs deals with SEM analysis of coating NiCrBSi exposed to 59% Na$_2$SO$_4$, 34.5% KCl a 6.5% NaCl environment at 525 °C and 575 °C. Figure 1 presents the microstructure of samples before and after exposition. This results show that there was growing oxide layer. The oxide layer is much thicker on samples tested at 575°C even if the difference is only 50 °C. The oxide layer is much clearly visible in Figure 2 where is also possible to observe loosen splat in area of corrosion buildup.

![Fig. 1 Coating NiCrBSi (left – as sprayed, middle – 525 °C, right – 575 °C).](image1)

![Fig. 2 Coating NiCrBSi (exposition 575 °C).](image2)

Figure 3 shows the microstructure of NiCrBSi coating in cross section after the exposure to corrosive environment of 40% Na$_2$SO$_4$ and 60% V$_2$O$_5$. This coating exhibited very aggressive corrosion attack and it was almost dissolved in to the buildup of corrosion products (Figure 3). Both the thin oxide layer and the coating were damaged. Based on the achieved results, this coating is not suitable for this type of corrosive environment.

![Fig. 3 NiCrBSi coating after the exposure at the temperature of 750°C in corrosive environment of molten salts 40% Na$_2$SO$_4$ – 60% V$_2$O$_5$ after 50 cycles.](image3)
Carbide coating $\text{Cr}_3\text{C}_2-25\%\text{CoNiCrAlY}$ did behave completely differently than the alloy coating. During the exposition to 59% $\text{Na}_2\text{SO}_4$, 34.5% $\text{KCl}$ a 6.5% $\text{NaCl}$ environment and temperature 525 °C the coating exhibited only uneven formation of oxide layer with no damage to coating as is documented in Figure 4. This figure also presents the exposition at 575 °C and the situation there is completely different. The coating exhibited huge grow of corrosion products buildup and reduction of its thickness (almost half of original thickness) which is easily observable from Figure 4 (left and right photograph – before and after exposition). Figure 5 presents the mechanism of corrosion. The mechanism is based on corrosion of coating matrix and following chipping of individual carbides. This mechanism starts from the surface of coating and continues deeper to the interface with substrate material. Figure 6 presents the microstructure of the $\text{Cr}_3\text{C}_2-\text{CoNiCrAlY}$ in cross section after the exposure to corrosive environment of 40% $\text{Na}_2\text{SO}_4$ and 60% $\text{V}_2\text{O}_5$. The photograph shows evident mechanism of corrosion damage and the disruption proceeding from coating surface. The oxide layer formed on the coating was degraded by molten salts. Consequently, the coating lost its oxide layer and degraded from the surface.

Fig. 4 $\text{Cr}_3\text{C}_2-25\%\text{CoNiCrAlY}$ coating (left – as sprayed, middle – 525 °C, right – 575 °C).

Fig. 5 $\text{Cr}_3\text{C}_2-25\%\text{CoNiCrAlY}$ coating detail (exposition 525 °C). Possible to see corrosion of matrix and loosen carbides.

Fig. 6 $\text{Cr}_3\text{C}_2-\text{CoNiCrAlY}$ coating after the exposure at the temperature of 750°C in corrosive environment of molten salts 40% $\text{Na}_2\text{SO}_4$ – 60% $\text{V}_2\text{O}_5$ after 50 cycles
Figure 8 shows cross sections of nitrided steel with and without surface activation using TiH prior to the nitriding. The nitrided layer did not manage protect the underlying material from corrosive attack.

![Cross sections of nitrided steel](image)

**Remnants of nitrided layer**

**Completely corroded without any signs of nitrided layer**

*Fig. 8 Nitrided steels after the exposure at the temperature of 750°C in corrosive environment of molten salts 40% Na₂SO₄ – 60% V₂O₅ after 50 cycles*

The following graph of weight gains of individual evaluated coatings in Figure 9 shows how coatings behaved in aggressive environment of high temperature corrosion. Coating NiCrBSi exhibited in the 11th cycle total destruction and therefore no further results are included in this paper. The graph shows that nitride surface treatment exhibited the highest weight gain. Further, high weight gain show carbide coating. The obtained results proved that the worst performance in selected corrosive environment exhibit the nitrided surface treatment. The NiCrBSi is also not recommended for such environment because it was completely destroyed only in first 11 cycles of testing. The carbide coating provides better results but it is still not sufficient to be considered as anticorrosion protection for use in this corrosion environments. These results are consistent with other experiments already conducted under the same conditions.

![Weight gain/area vs. number of cycles plot](image)

*Fig. 9 Weight gain/area vs. number of cycles plot for the bare and HVOF spray coated steel subjected to molten salt environment 40% Na₂SO₄ – 60% V₂O₅ at 750 °C for 50 cycles.*
**Conclusion**

The tests results proved that with increasing temperature the coating corrosion resistance decreases drastically. Carbide coating proved the assumption that corrosion degradation of carbide coatings is mainly based on mechanism of deterioration of coating matrix with following loss of carbides. Based on the obtained results, both coatings and nitride layer performed poorly in protection of base material against corrosive environment of salts mixture 40% Na₂SO₄ – 60% V₂O₅. The worst performance showed NiCrBSi coating which was destructed in only 11 cycles and then the nitrided layer. Furthermore, it was proved that the thermally sprayed coatings performed many times better than nitriding as protection of component functional areas in this type of corrosive environment. Further research will be done in this area with focus on coatings with high potential to protect the substrate even in such corrosion aggressive environment. The main focus will be aimed at alloy base coating.

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**References**

References must be numbered in square brackets (e.g. [1]), in the order of appearance in the text. The list of references should be included at the end of the text.