

HIGH TEMPERATURE HOT CORROSION BEHAVIOR OF SELECTED THERMALLY SPRAYED COATINGS ON X22 STAINLESS STEEL IN AN AGGRESSIVE ENVIRONMENT AT 750 °C

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Abstract

Cr₃C₂-NiCr, Cr₃C₂-CoNiCrAlY, TiMoCN-Ni (experimental coating), Stellite 6, NiCrBSi and Hastelloy C-276 coatings were deposited on substrate material Wr.Nr. 1.4923 (X22) which is in nitrided state used as an effective constructional material for components in power equipment. All evaluated coatings were deposited using HVOF (High Velocity Oxygen Fuel) thermal spraying technology. The evaluation of resistance against high temperature corrosion was conducted for all selected thermally sprayed coatings. Furthermore, corrosion resistance comparative study between coating surface protection and nitrided stainless steel X22 was also carried out. All evaluated coatings were exposed to corrosive-aggressive environment in the form of molten salts mixture with composition of 60% V₂O₅ and 40% Na₂(SO)₄ at the selected temperature of 750 °C. Further, all coatings were exposed to cyclic conditions. Each cycle included one hour long exposure of evaluated coatings with salts mixture layer on the surface at 750 °C in a silicon carbide furnace. 20 minutes cooling in air followed the exposure period. Weight changes of individual samples were measured after every cycle and the results were recorded in the diagram.

After the corrosion tests, all coatings were analyzed using scanning electron microscope (SEM), and also the analysis of elemental composition (EDAX) 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: HP / HVOF, hot corrosion, corrosion resistance, aggressive corrosive environments

1. 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 [2].

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 $\text{Na}_2(\text{SO})_4$ melts at 884 °C, but in combination with other salts, e.g. NaCl or $\text{Ni}(\text{SO})_4$, 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 $\text{Na}_2(\text{SO})_4$ (melting point at 884 °C) and V_2O_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 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.

2. EXPERIMENTAL PROCEDURE

As it was already mentioned, five commercially available powders were used for sample preparation. These powders were Amperit 588.074 ($\text{Cr}_3\text{C}_2\text{-NiCr}$) with a particle size distribution suitable for HVOF (-45+15 μm), Amperit 594.074 ($\text{Cr}_3\text{C}_2\text{-25\%CoNiCrAlY}$) with a particle size distribution suitable for HVOF (-45+15 μm), M-484.33 (CoCrWC) with a particle size distribution suitable for HVOF (-53+20 μm), M-341.33 (Alloy-276) with a particle size distribution suitable for HVOF (-53+20 μm), M-771.33 (NiCrBSi) with a particle size distribution suitable for HVOF (-53+20 μm) and one experimental powder labeled T10 (TiMoCN-Ni). 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 (X22) which is in nitrided state used as an effective constructional material for components in power equipment.

This article describes high temperature corrosion testing based on applying of corrosion-aggressive salt mixture at 750 °C. The testing conducted in company VZÚ Plzeň. The test procedure was as follows. First, the specimens were polished to the surface roughness (R_a) max. 1 μm . 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% $\text{Na}_2(\text{SO})_4$ and 60% V_2O_5 (an 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.

3. RESULTS AND DISCUSSION

3.1. Corrosion protection and durability of thermally sprayed coatings

The graph of weight gains of individual evaluated coatings in **Fig. 1** shows how coatings behaved in aggressive environment of high temperature corrosion. Coatings marked as 771 and T10 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 both carbide coatings and the lowest weight gain was exhibited by alloy based coatings marked 341 (Hastelloy C-276) and 484 (Stellite 6). The obtained results proved that the best performance in selected corrosive environment exhibit alloy based coatings and the worst exhibited the nitrided surface treatment. These results are consistent with other experiments already conducted under the same conditions. Furthermore, the paper includes also photographs made by SEM with tables describing elemental composition determined using EDAX analysis. **Fig. 2** presents the microstructure of the $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ in cross section after the exposure to corrosive environment. 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. 3** presents the microstructure of the $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating in cross section after the exposure to corrosive environment. The photograph shows evident mechanism of corrosion damage where the disruption of coating processed from the surface similarly as previous $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ carbide coating. Oxide layer was formed and reacted with molten salts resulting in corrosive attack on the coating.

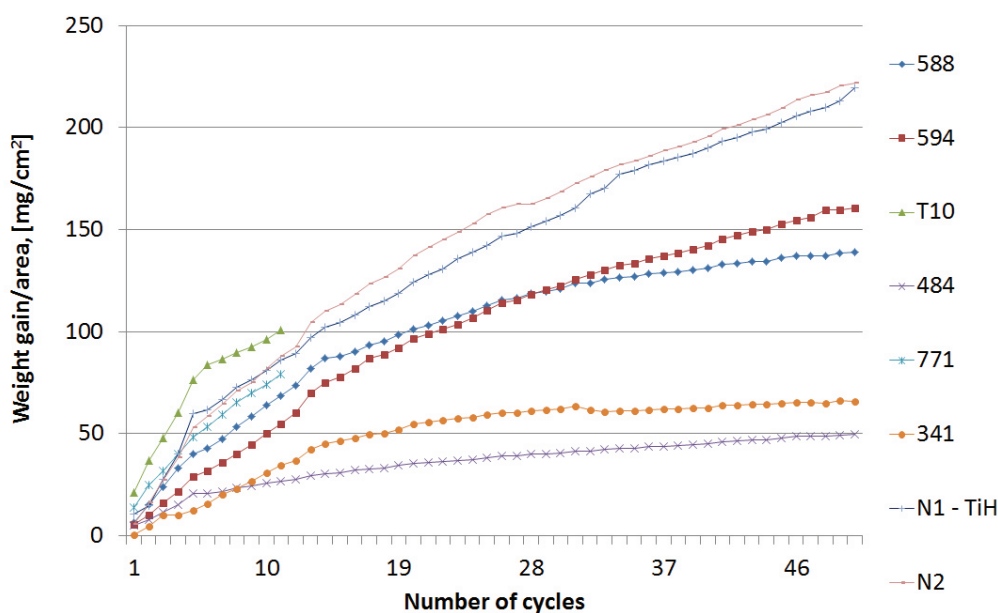


Fig. 1 Weight gain/area vs. number of cycles plot for the bare and HVOF spray coated X22 steel subjected to molten salt environment ($\text{Na}_2(\text{SO})_4$ - 60% V_2O_5) at 750 °C for 50 cycles

Fig. 4 shows the microstructure of TiMoCN-Ni coating in cross section after the exposure to corrosive environment. The photograph evidently shows the corrosion damage mechanism resulting in total coating destruction, most likely caused by high temperature. There were most probably created new phases and oxides with higher volume and this change resulted in coating destruction. It proved that this coating is not suitable for high temperature applications. **Fig. 5** presents the microstructure of Stellite 6 coating in cross section after the exposure to corrosive environment. The photograph apparently shows the mechanism of corrosion damage based on the formation of oxides on coating surface. These oxides reacted with salt mixture resulting in attack of individual splats on the coating surface. However, the corrosion attack on this coating is

negligible. **Fig. 6** presents the microstructure of Hastelloy C-276 coating in cross section after the exposure to corrosive environment. The photograph shows the same mechanism of corrosion damage as Stellite 6 coating. It can be said that these coatings exhibit very similar corrosion mechanism. **Fig. 7** shows the microstructure of NiCrBSi coating in cross section after the exposure to corrosive environment. This coating exhibited very aggressive attack. 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. 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.

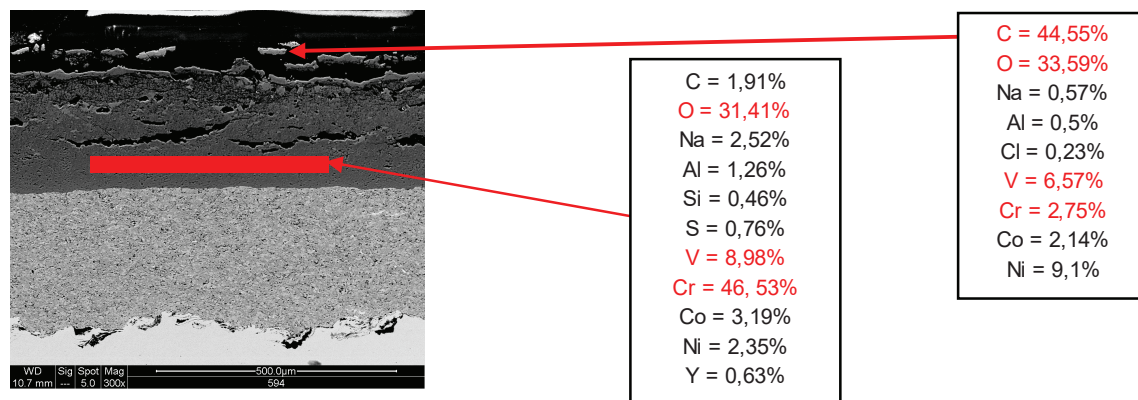


Fig. 2 $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO}_4) - 60\%\text{V}_2\text{O}_5$ after 50 cycles

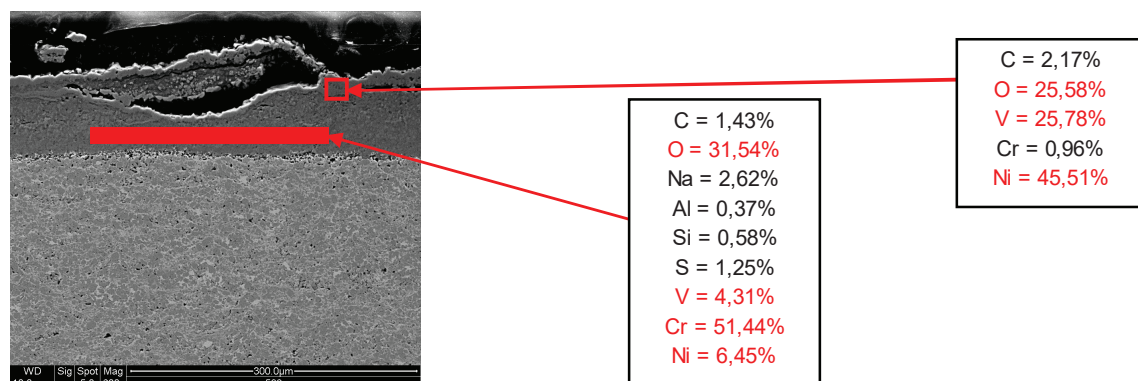


Fig. 3 $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO}_4) - 60\%\text{V}_2\text{O}_5$ after 50 cycles

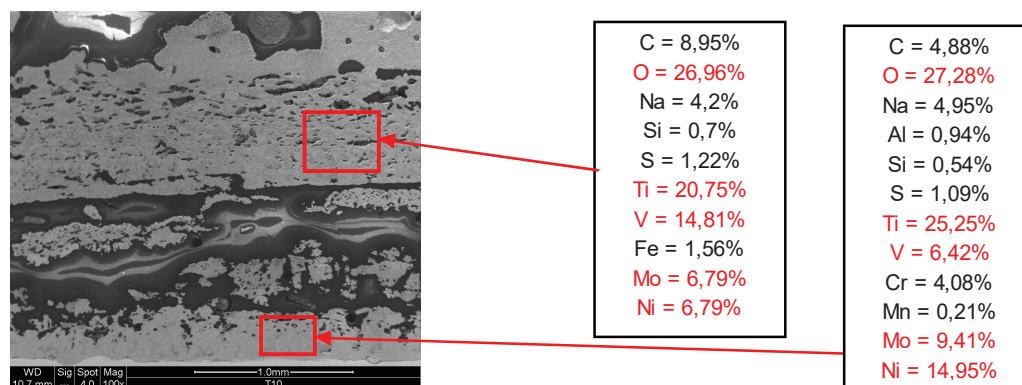


Fig. 4 TiMoCN-Ni coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO}_4) - 60\%\text{V}_2\text{O}_5$ after 50 cycles

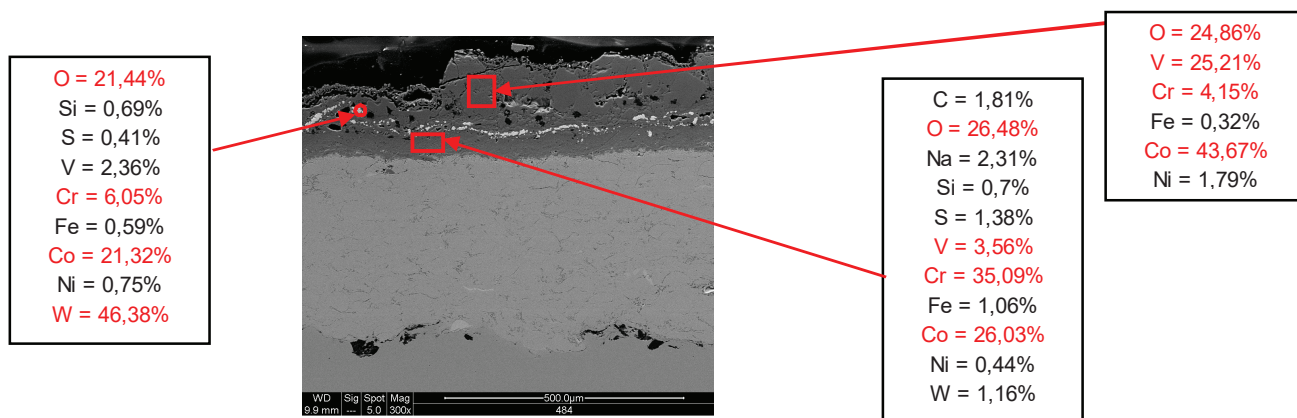


Fig. 5 Stellite 6 (CoCrW) coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO})_4$ - 60% V_2O_5 after 50 cycles

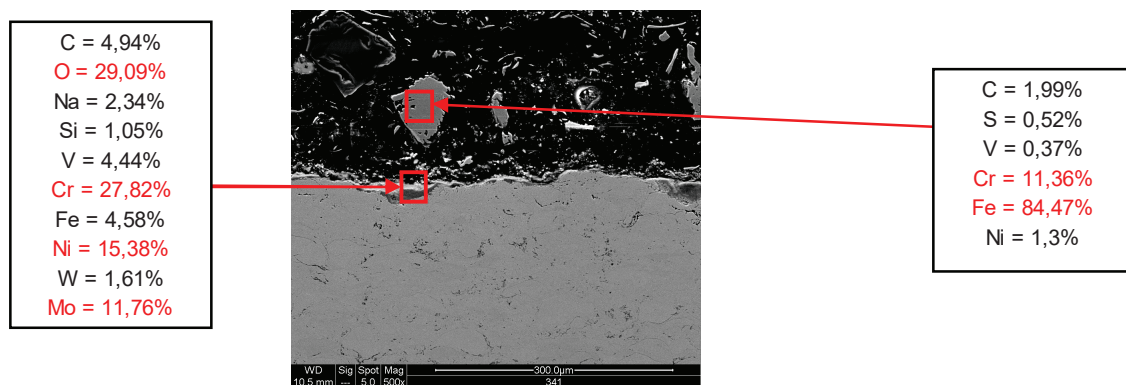


Fig. 6 Hastelloy C-276 (NiCrMoW) coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO})_4$ - 60% V_2O_5 after 50 cycles

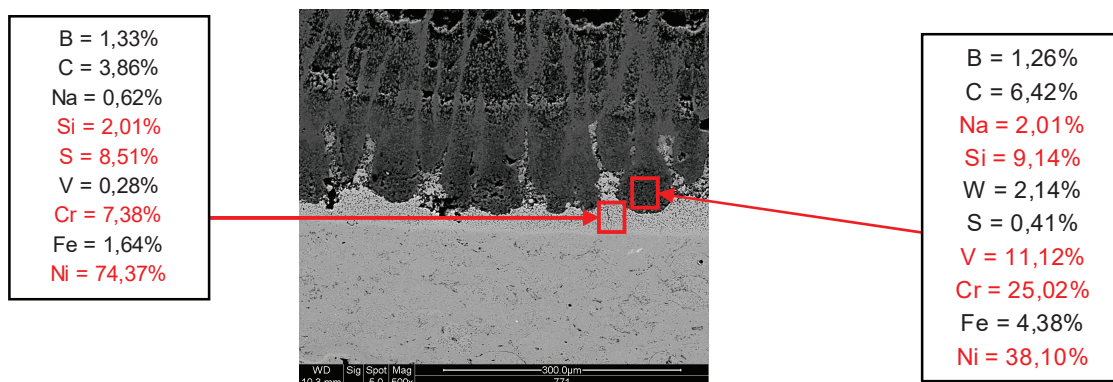


Fig. 7 NiCrBSi coating after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO})_4$ - 60% V_2O_5 after 50 cycles

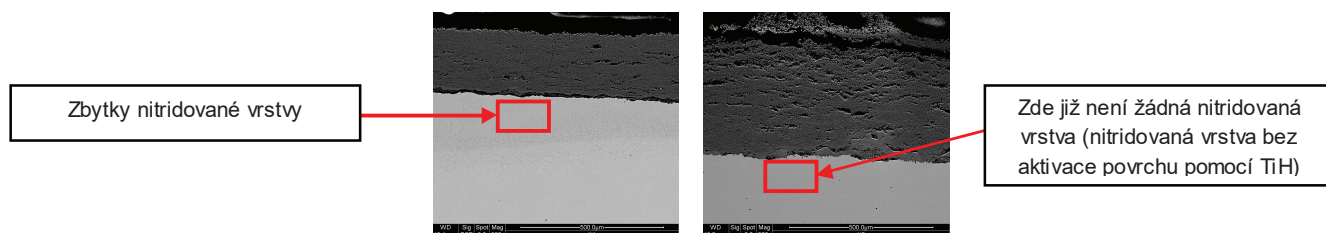


Fig. 8 Nitrided steels after the exposure at the temperature of 750°C in corrosive environment of molten salts $\text{Na}_2(\text{SO})_4$ - 60% V_2O_5 after 50 cycles

4. CONCLUSION

- 1) Based on the obtained results, alloy based coatings Hastelloy C-276 and Stellite 6 performed the best in protection of base material against corrosive environment of salts mixture $\text{Na}_2(\text{SO})_4$ - 60% V_2O_5
- 2) The worst performance showed T10 and NiCrBSi coatings which are therefore not suitable for high temperature applications in this type of corrosive environment.
- 3) 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.

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