

CORROSION BEHAVIOR OF SELECTED HVOF THERMALLY SPRAYED COATINGS IN AGGRESSIVE ENVIRONMENTS

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Abstract

Corrosion resistant coatings must exhibit high density (low porosity), good adhesion to the substrate and of course low penetration of oxides. This paper deals with corrosion resistance comparison of six corrosion resistant coatings, which are frequently used in power plants. The comparison of following coatings is described: two cermet coatings Cr₃C₂-NiCr and Cr₃C₂-CoNiCrAlY, one experimental coating TiMoCN-Ni, and three alloy based coatings CoCrWC (Stellite 6), Hastelloy C-276 and NiCrBSi. Each of these six coatings was evaluated using immersion corrosion tests in two selected corrosive aggressive environments. Aqueous solution of 5% H₂(SO)₄ and artificial seawater were selected as corrosive aggressive environments. All coatings were deposited on W.Nr. 1.0553 carbon steel using thermal spraying technology HP/HVOF (High Pressure/High Velocity Oxygen Fuel). Carbon steel was used as the base material mainly to determine if the open porosity of evaluated coatings does not pose a problem in terms of components surface protection. Evaluation of coating corrosion attack was performed on the surface and in the cross-section of coatings. The evaluation was made before and after corrosion tests using optical and scanning electron microscopy. Furthermore, the amount of corrosion products was examined using mass weight loss/gain during the whole measurement. The corrosion behavior for all investigated coatings was very different. Cr₃C₂-NiCr cermet coating and alloy based Stellite 6 and Hastelloy C-276 exhibited the highest corrosion resistance in both selected aggressive environments.

Keywords: HP / HVOF, corrosion, corrosion resistance, aggressive corrosive environments, porosity

1. INTRODUCTION

The coatings formed by thermal spraying technology operate under different conditions (e.g. corrosive environments, different types of wear etc.) and also provide a wide range of functions (e.g. biocompatible coatings, thermal barriers etc.). Thermal spraying technology enables to create coatings based on metals, ceramics and polymers [1]. HP/HVOF belongs to the most effective thermal spraying technologies for deposition of coatings, and primarily also for deposition of cermets based coatings. This technology takes advantage of two factors. These factors are high-speed deposition and specific temperature for application of coatings with characteristic structure and properties [2]. Thermally sprayed coatings deposited by HP/HVOF have very low porosity and excellent adhesion to the substrate material, and therefore also good corrosion resistance. The thermal spraying technologies provide a great potential in terms of protection for devices and their components operating in aggressive environment [3]. However, open porosity can occur by some coatings deposited using HP/HVOF, which poses a big problem for their subsequent use in aggressive corrosive environment. It is very important to create a coating that would not have open porosity and will be able to protect components in aggressive corrosive environments. To obtain such coating, the general knowledge about the thermal spraying technology, coating and application possibilities are necessary [4]. Corrosion resistance of Cr₃C₂-NiCr coating is highly dependent on the type of technology (HVOF vs. Plasma), construction of the spray equipment and on spraying parameters [5]. It is very important to be aware of all

factors that need to be considered to choose the coating properly. The basic factors are coating material, deposition technology and spray parameters. This paper evaluates six selected coatings that are being used in aggressive environments. The selected coatings are two cermet coatings $\text{Cr}_3\text{C}_2\text{-NiCr}$ and $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$, one experimental coating TiMoCN-Ni and three alloy based coatings CoCrWC (Stellite 6), NiCoCrMoWFe (Hastelloy C-276) and NiCrBSi .

$\text{Cr}_3\text{C}_2\text{-NiCr}$ cermet coating deposited by HP/HVOF is used in a wide range of industrial applications such as gas turbines, automotive industry, manufacturing techniques and many others. The coating should exhibit less than 1.5 % porosity. This very low porosity is crucial property in terms of corrosion protection of components. Furthermore, this coating is characterized by high resistance against high temperature corrosion due to the formation of nickel and chromium oxides, and nickel-chromium spinel [6].

In comparison with $\text{Cr}_3\text{C}_2\text{-NiCr}$, there are not so many technical publications of $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$, but it has been proven that this coating provides excellent erosion and wears protection, even at temperatures approaching 1000 °C. Furthermore, it was found out that the coating has better oxidation resistance than the $\text{Cr}_3\text{C}_2\text{-NiCr}$. It is used nowadays for furnaces and turbines components operating at high temperatures [7].

Experimental TiMoCN-Ni coating seems to be promising for the use in certain parts of devices operating under aggressive conditions. This coating is supplied by the Japanese company Fujimi, and due to the high content of Ti, it could be expected to be resistant in corrosive environment.

Stellite 6 (CoCrWC) was chosen as an example of alloy based coatings. Stellite alloys are characterized by high hardness, toughness and typically exhibit excellent anti-corrosion properties. Due to the content of Co and Cr, the coating can be used for devices operating at high temperatures. These alloys behave at high temperatures as a diffusion barrier for the degradation media. This behavior is caused by the formation of chromium oxide on the borders of splats rich in Co, and by the formation of surface oxides, particularly cobalt and chromium together with cobalt-chromium and nickel-chromium spinels [8].

NiCrMo (Hastelloy) based coatings exhibit excellent corrosion protection. It is very important to consider that the corrosion resistance of coatings is connected with spraying parameters. It was found out that corrosion resistance is increasing with reduction of unmelted particles proportion in the coating. The boundaries between splats, which create the coating, are especially susceptible to the corrosion due to the presence of oxides [9].

NiCrBSi coating exhibits excellent corrosion resistance due to the selective oxidation occurring along splats boundaries rich in nickel and cobalt which form chromium and silicon oxides (Cr_2O_3 and SiO_2). These oxides block passages in the pores, and thereby allow the coating to improve resistance to penetration and diffusion of corrosive media. Moreover, very low porosity and structure of flat splats in the coating also contributes to the development of resistance to high temperature corrosion at elevated temperatures [8].

In all these six described coatings were tested by immersion corrosion tests in two suitably selected corrosive aggressive 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).

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. Structural steel W.Nr. 1.0533 (DIN 11 523) of $\text{Ø}25 \times 5 \text{mm}$ dimension was used as substrate material for proper verification of protective properties (the existence of open porosity) in corrosive aggressive environments. It

was used as substrate material for all evaluated coatings. These samples were cold mounted using the EpoFix Struers set. Mounted samples were metallographically polished. Subsequently, the photos of microstructures on surface and in cross section of all evaluated coating were made before corrosion tests using optical and scanning electron microscopy. Capillary test was performed and showed the necessity to use sealing protection around the samples circumference and on their surfaces. Silicone sealant Lukopren S 8280th was used as suitable alternative for sealing treatment. Surface measurement (using light microscopy) of the area exposed to corrosive attack was made after the vulcanization (3mm/24h) of the sealant. All samples were afterwards three times measured on the scale with accuracy of 0.0001g. Reference sample was added to the evaluated samples into the corrosive environment to verify the accuracy of sample mass measurements after the first and the subsequent weighing during the corrosion testing. The first weighing of samples was performed after 24h. Samples were first washed in deionized water bath and subsequently by washing bottle before every weighing. After this procedure, the samples were placed in the box dryer to dry at 100 °C for 3h. After 3 hours necessary for adequate drying, the samples were removed from the kiln and placed for 1h into Schleibler exicator. Finally, it was followed by weighing to determine weight loss or gain for each evaluated coating. The reference sample was always measured as first. The reference sample changed its weight with an acceptable tolerance of ± 0.0005 g. All evaluated samples were measured three times. After the measurements, the samples were immersed back into the corrosive environment. Resulting microstructure evaluation using optical and scanning electron microscopy was performed on all samples after the corrosion testing was completed.

Aqueous solution of 5 % $H_2(SO)_4$ with 150ml volume was selected as aggressive corrosive environment. The second environment was artificial seawater of the same volume and with chemical composition summarized in **Table 1**. First corrosion tests were conducted at room temperature.

Table 1 Chemical composition of artificial seawater

| Artificial seawater | | | |
|--|---------------------|---|---------------------|
| Salt | Concentration [g/l] | Salt | Concentration [g/l] |
| NaCl | 24.54 | NaHCO ₃ | 0.2 |
| MgCl ₂ x 6H ₂ O | 11.1 | KBr | 0.1 |
| Na ₂ SO ₄ | 4.09 | H ₃ BO ₃ | 0.03 |
| CaCl ₂ | 1.16 | SrCl ₂ x H ₂ O | 0.04 |
| KCl | 0.69 | NaF | 0.003 |

3. RESULTS AND DISCUSSION

3.1 Microstructure of coatings

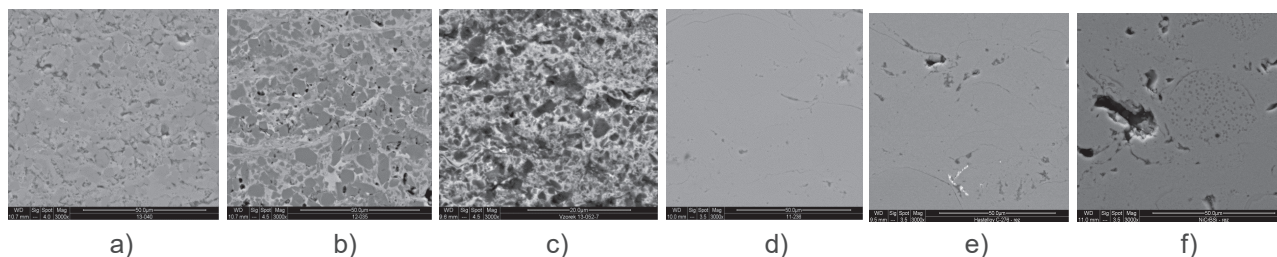


Fig. 1 SEM pictures of coatings in cross sections, from the left is $Cr_3C_2-CoNiCrAlY$, Cr_3C_2-NiCr , $TiMoCN-Ti$, Stellite 6, Hastelloy C-276, NiCrBSi before corrosion tests at 3000x magnification.

Different structures of all evaluated HVOF sprayed coatings can be seen in the photos in **Fig. 1**. Cr₃C₂-CoNiCrAlY and TiMoCN-Ni coatings have the highest porosity according to SEM photos. These coatings contain networks of pores and unmelted particles having influence on the corrosion protection properties of individual coatings.

3.2 Corrosion protection and durability of thermally sprayed coatings

Corrosion resistance of coatings and surface protection using HP/HVOF sprayed coatings is strongly dependent on the appropriate spraying parameters for individual coating and on corrosive environment in which the coating works. For better clarity, the results of mass loss in 5 % H₂(SO)₄ environment are divided into two graphs. **Fig. 2b** shows that NiCrBSi and TiMoCN-Ni coatings exhibited the lowest protection to the substrate and the lowest corrosion resistance in 5% H₂(SO)₄. On the contrary, Cr₃C₂-NiCr coating exhibited the smallest corrosion attack and the highest protection to the substrate in 5 % H₂(SO)₄. The results in the graphs are with accuracy ±0.001g. Coatings corrosion behavior was different in artificial seawater in comparison with 5 % H₂(SO)₄. TiMoCN-Ni exhibited the biggest corrosive attack and the lowest protection to the substrate in artificial seawater. Other coatings exhibited very similar behavior; see the diagram in **Fig. 3**. Based on the results below, the corrosion of all evaluated coatings was stronger in H₂(SO)₄ aggressive environment compared with artificial seawater. This difference in corrosion behavior increased with increasing time of exposure. However, if we consider only the aspect of the protection to the substrate material, the lowest protection in both aggressive environments exhibited Cr₃C₂-CoNiCrAlY due to very high porosity, see **Fig. 1a**.

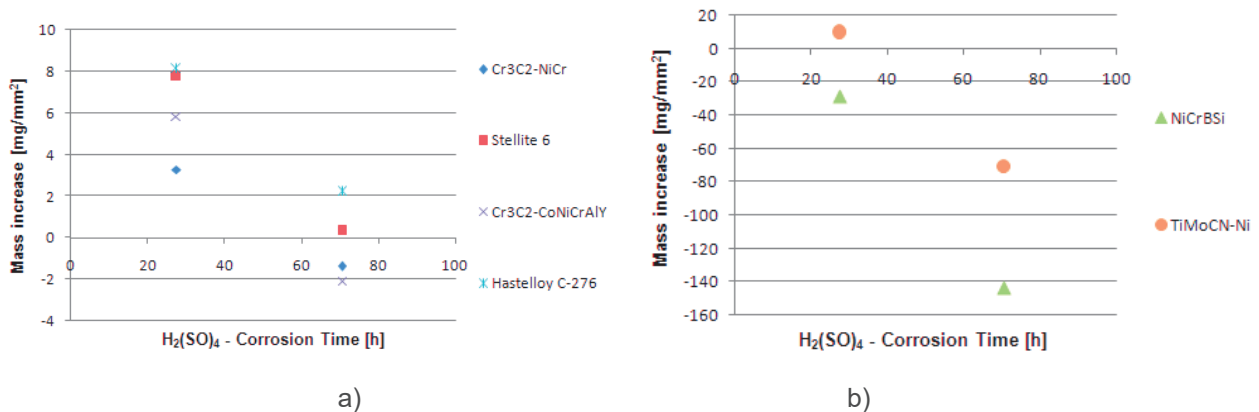


Fig. 2 Mass gains of coatings after immersion corrosion testing in 5 % H₂(SO)₄ at room temperature

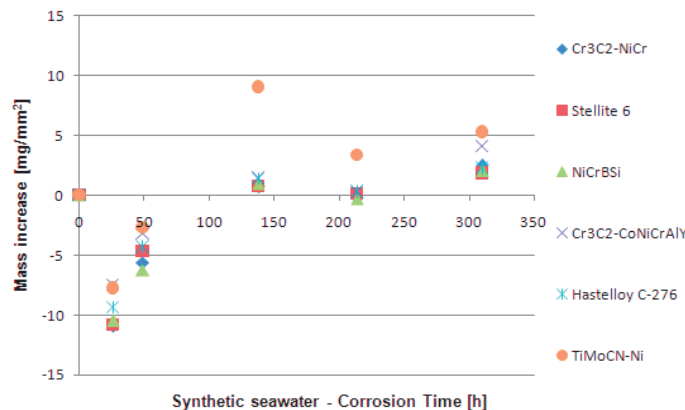


Fig. 3 Mass gains of coatings after immersion corrosion testing in artificial seawater at room temperature

The best corrosion protection to the substrate in 5% solution of $H_2(SO)_4$ out of the cermet coatings exhibited Cr_3C_2-NiCr . **Fig. 4a** shows the cross section of the coating before the test in 5 % solution of $H_2(SO)_4$, and **Fig. 4b** shows the cross section of this coating after the immersion corrosion test. $Cr_3C_2-CoNiCrAlY$ showed the worst corrosion protection out of all three evaluated cermet coatings. **Fig. 4c** shows the cross section of the coating before the test in 5 % solution of $H_2(SO)_4$ and **Fig. 4d** shows the cross section of $Cr_3C_2-CoNiCrAlY$ after the immersion corrosion test. The pictures show that the penetration of corrosive media to the substrate and the damaged adhesion between the coating and the substrate material were most likely caused by high open porosity of $Cr_3C_2-CoNiCrAlY$. Stellite 6 coating exhibited the best corrosion protection to the substrate in 5 % solution of $H_2(SO)_4$ out of alloy coatings. **Fig. 4e** shows cross section of Stellite 6 before the test in a 5 % solution of $H_2(SO)_4$, and **Fig. 4f** shows the cross section of Stellite 6 coating after immersion corrosion testing. NiCrBSi exhibited the worst corrosion protection out of three evaluated alloy based coatings. **Fig. 4g** presents cross section of the coating prior to the test in 5 % solution of $H_2(SO)_4$ and **Fig. 4h** shows cross section of NiCrBSi coating after immersion corrosion testing. The pictures indicate that there probably occurred reaction between NiCrBSi a 5 % solution of $H_2(SO)_4$ and gradual dissolution of the coating without any attack on the substrate material. This statement is supported by the results of the weight gain measurement, see **Fig. 2b**.

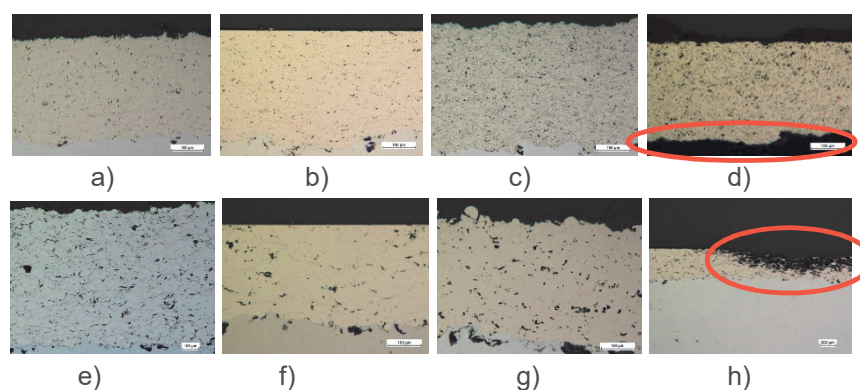


Fig. 4 Photos of evaluated coatings in cross section before and after corrosion testing in aqueous solution of 5 % $H_2(SO)_4$, where a) Cr_3C_2-NiCr coating before testing, b) is Cr_3C_2-NiCr coating after corrosion testing, c) $Cr_3C_2-CoNiCrAlY$ coating before testing, d) $Cr_3C_2-CoNiCrAlY$ coating after corrosion tests, e) Stellite 6 coating before testing, f) Stellite 6 coating after corrosion tests, g) NiCrBSi coating before testing, h) NiCrBSi coating after corrosion tests

The best corrosion protection to the substrate in artificial seawater out of cermet coatings showed again Cr_3C_2-NiCr . **Fig. 5a** shows cross section of the coating before the test in artificial seawater and **Fig. 5b** shows the cross section after the immersion corrosion test. $Cr_3C_2-CoNiCrAlY$ coating exhibited again the worst corrosion protection out of three evaluated cermet coatings. **Fig. 5c** shows cross section of the coating before the corrosion test in artificial seawater and in **Fig. 5d** shows cross section of $Cr_3C_2-CoNiCrAlY$ coating after immersion corrosion test. The pictures apparently show that the penetration of corrosive media to the substrate and the damaged adhesion between the coating and the substrate material were most likely caused by high open porosity of $Cr_3C_2-CoNiCrAlY$. **Fig. 5e** also shows selective corrosion of this coating, but it could be just corrosion products of the substrate material washed up through the open porosity.

The best corrosion protection to the substrate in artificial seawater out of alloy based coatings exhibited Hastelloy C-276. **Fig. 5f** shows cross section of Hastelloy C-276 coating before the test in artificial seawater and **Fig. 5g** shows the cross section of Hastelloy C-276 coating after immersion corrosion testing. NiCrBSi coating exhibited the worst corrosion protection out of all three evaluated alloy based coatings. **Fig. 5h** shows cross section of the coating before the test in artificial seawater and **Fig. 5i** shows cross section of NiCrBSi coating after immersion corrosion testing. The photo **Fig. 5j** shows that selective corrosion probably occurred

by this coating, but it could be just corrosion products of the substrate material washed up through the open porosity.

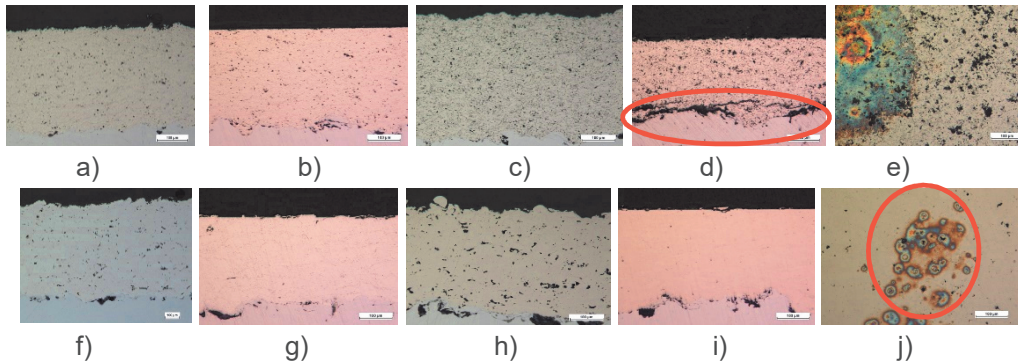


Fig. 5 Photos of evaluated coatings in cross section before and after corrosion testing in artificial seawater, where a) $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating before testing, b) is $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating after corrosion testing, c) $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ coating before testing, d) $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ coating after corrosion tests, e) Stellite 6 coating before testing, f) Stellite 6 coating after corrosion tests, g) NiCrBSi coating before testing, h) NiCrBSi coating after corrosion tests.

CONCLUSION

1. Based on the expectations, it was confirmed that alloy coatings generally exhibit better corrosion protection to the substrate than cermet coatings. This fact is probably connected with lower porosity in comparison with cermet coatings.
2. $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating showed the best behavior of all evaluated cermet coatings in aggressive environment of 5 % $\text{H}_2(\text{SO})_4$ solution, both in terms of corrosion protection to the substrate material and of coating resistance against corrosion attack. This coating exhibited the same results in corrosive environment of artificial seawater. $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ showed the worst behavior in terms of substrate material corrosion protection in both corrosive environments. It was caused by high porosity of this coating. In my opinion, it is possible to reduce this high porosity by the choice of another spraying parameters
3. Stellite 6 exhibited the highest resistance in 5 % solution of $\text{H}_2(\text{SO})_4$ out of all alloy based coatings and Hastelloy C- 276 in artificial seawater. NiCrBSi exhibited the worst behavior in both environments.

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