CORROSION RESISTANCE OF SELECTED HVOF THERMALLY SPRAYED COATINGS

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Abstract

Corrosion resistance of coatings deposited using the HP/HVOF (High Pressure/High Velocity Oxygen Fuel) thermal spraying technology requires high coatings density and a good adhesion to the substrate. The majority of thermally sprayed materials meet the requirements for high corrosion resistance in terms of their composition. However, the porous structure raises doubts about the performance of thermally sprayed coatings in providing sufficient protection to the base material. In fact, corrosion protection is one of the basic coating functions. Anyway, in comparison with wear resistance research, an insufficient attention is paid to the issue of component protection against corrosion attack using the HVOF sprayed coatings. This paper summarizes the results of immersion corrosion tests performed on six selected corrosion resistant coatings, which are compared with the Wr.Nr. 1.4923 nitrided stainless steel. The following coatings were tested: two based cermet coatings (Cr_3C_2-NiCr, Cr_3C_2-CoNiCrAlY), three alloy based coatings (CoCrWC - Stellite 6, NiCrBSi, and NiCrMo - Hastelloy C-276) and one experimental coating (TiMoCN-29%Ni). These coatings were selected as good candidates for the use in corrosive aggressive environments. Steel Wr.Nr. 1.0421 was used as the base material. Corrosion experiment was performed in 5% solution of H_2SO_4 (further H_2SO_4). The evaluation of corrosion attack was made before and after corrosion tests on surface and in coating cross-section after metallographic grinding using an optical microscope (OM).

Keywords: HP/HVOF, corrosion resistance, immersion corrosion test, coating

1. INTRODUCTION

Corrosion resistance is currently one of the major parameters determining the choice of suitable material or coating in corrosion engineering. Consequently, the highest priority is put on the determination of corrosion mechanisms in particular corrosion processes which lead to the degradation of materials or coatings while exposed to corrosive aggressive environments [1]. To protect components operating in corrosive aggressive environments, new corrosion resistant materials are being developed and at the same time new surface treatments for this aggressive environment are being created. HP/HVOF (High Pressure / High Velocity Oxygen Fuel) thermally sprayed coatings are one of the main possibilities in this area.

This paper deals with the corrosion resistance evaluation of coatings deposited by thermal spraying using immersion tests. Based on the immersion tests, we are able to evaluate the extent of corrosion damage depending on the testing period (specimen exposure to the corrosive environments) as well as on other factors which may influence the corrosion process. In the case of cyclic tests, the samples are dried and re-immersed in an aggressive environment. Furthermore, other devices can be used during the test to make the measurements easier. Immersion tests are capable of generating data to indicate the resistance of the material that is subjected to immersion in a specific aggressive environment in industrial sector. It is also important to mention that if the material is exposed to corrosive environment e.g. 24 h in real applications the laboratory testing should take 240 h. This condition is applied in order to improve the corrosion resistance predication of evaluated materials. Furthermore, certain negative aspects leading to problems in industrial applications are usually intensified during the tests. It can be achieved by the increase in pressure, salt concentration and temperature or solution acidity. The corrosion tests should be repeated several times in order to verify an acceptable level of reproducibility [2]. Immersion test is the most reliable method for verifying whether a material can withstand an aggressive environment. Furthermore, this test is a very economical way to identify the most suitable material for component protection against the aggressive environment [2]. Studies dealing with this issue are reported in the literature [3], [4]. This work includes a modified immersion test for all chosen surface treatments. The test procedure is described in chapter Experiment. Within this modified procedure, parameters were further changed according to the test purpose and the aggressiveness of environment. Immersion tests were performed in aggressive environment of H_2SO_4.

2. EXPERIMENTAL PROCEDURE

Five commercially available powders were used to prepare the samples. These powders were Amperit 588.074 (Cr_3C_2-25%NiCr) with particle size distribution for HVOF (-45+15 mm), Amperit 594.074 (Cr_3C_2-25%CoNiCrAlY) with particle size distribution for HVOF (-45+15 mm), M-484.33 (CoCrWC) with particle size distribution for HVOF (-53+20 mm), M-341.33 (Alloy C-276) with particle size distribution for HVOF (-53+20 mm), M-771.33 (NiCrBSi) with particle size distribution for HVOF (-53+20 mm) and one experimental powder labeled T10 (TiMoCN-29%Ni). All coatings were deposited using the HP/HVOF (High Pressure/High Velocity Oxygen Fuel) technology with JP-5000 torch from the TAFA Incorporated company. Already optimized spray parameters were used for the preparation of each coating. The Wr.Nr. 1.4923 (X22) nitrided stainless steel was used as a competing surface treatment technology.

The Wr.Nr. 1.0421 (DIN 11 523) construct steel was used as the base material. The substrate surface was degreased and grit blasted before spraying. Brown corundum F22 of grain size (0.8 to 1.0) mm was used as the abrasive medium. Before coating deposition, all specimens were blasted in order to achieve a proper adhesion of the coating on the substrate material. The coating thickness was in the range of 250-400 µm.

2.1. Corrosion test

Reported corrosion test was developed in co-operation of the Thermal Spraying Department and the Laboratory of Chemistry within the company of Výzkumný a zkušební ústav Plzeň. This test enables to evaluate all surface treatments and wide range of materials in any aggressive environment (corrosion). Regarding the evaluation of thermally sprayed coatings, the coating selection was primarily assessed, which is also associated with the proper choice of spraying parameters. Wr.Nr. 1.0421 appears to be the most suitable substrate material. This material has lower corrosion resistance which is suitable for the identification of open porosity in the corrosion test. The specified dimensions of the test specimen were Ø25 mm × 5 mm. It is also appropriate to test three specimens of each coating in order to ensure the accuracy of results. Deposited coating specimens were embedded using the EpoFix Kit embedding system from the Struers Company. This kit contains the Hardener and the EpoFix Resin. After 48 h hardening in air the specimens were removed from the embedding dishes and were further grinded using a sandpaper of grain size 220. Specimens were cut with a laboratory saw to the same height (13 mm). This dimension must be identical for all the evaluated specimens to be of the same volume. Then the specimens were grinded and polished. It is also very important that both the grinding and polishing processes should be conducted without a polishing head, which means that each specimen must be prepared in a manual mode. It was also essential to avoid the grinding of the entire coating. Ideally, the surface should be modified in the way that as little as possible should be removed. After that, the surfaces of all the evaluated specimens were photographed to compare the changes in their microstructure. A next set of samples was also prepared to take photos of cross sections of coatings. After taking OM and SEM photographs prior to the tests, the Lukopren S 8280 silicone sealant was applied around the diameter. After the vulcanization 3 mm/24 h, the measurement of the area that would be subjected to the corrosion attack during the test was performed. This measurement was performed using the AM 7000 USB microscope. All specimens were afterwards placed into a drying cabinet for two hours and into the Scheibler desiccator for the next one hour. Each specimen was weighed three times using Sartorius 1602 MP and one value was calculated. One reference sample composed of dentacryl and Lukopren was added and also weighed three times. The reference sample is used to verify that both Lukopren and dentacryl do not show any changes during testing. Before the evaluated specimens were placed into the corrosive environment, the upper edge of the container was coated with silicone grease and covered in order to achieve relatively unaffected test conditions. After all specimens had been placed into the measuring beakers the acid level was marked on the beakers in order to see whether evaporation of a corrosive environment would occur. If evaporation takes place, the breaker must be periodically re-filled. Time and temperature of the room where corrosion testing took place were recorded during the test. Evaluated specimens were removed from the container after first 24 hours. All specimens were firstly removed from the corrosive environment. Subsequent rinsing was very important. Each specimen was rinsed in a bath of distilled water, then rinsed using a squeeze bottle and again in distilled water. All specimens were placed into a drying box oven at 100 °C for 2 h, which is time needed for complete drying. All the evaluated specimens were then removed from the oven and left 1 h in the Schleibler desiccator. Weighing to determine weight loss or gain of individual coatings followed. The reference sample was always weighed first to check if there was any change in the value. Acceptable scale deviation of reference sample before immersing into the corrosive environment is ± 0.0005 g. The specimens were re-immersed into the corrosive environment after the measurements. After re-immersing, the level marks were checked and missing medium was filled up to the level mark where it was necessary. This procedure has been repeated until visible damage on the coating appeared. This was very different and therefore also cycles of individual coatings varied in terms of time. Mostly used intervals according to scientific literature are 0 h, 24 h, 72 h, 144 h and 240 h. After the corrosion tests had been completed the sealant (Lukopren S 8280) was removed from the specimen using a knife or another sharp object (razor). Further, the specimen had to be rinsed using a degreaser (Jar), wiped with cotton wool, rinsed with pure alcohol and dried with compressed air. After this cleaning the specimens were evaluated using SEM or OM on the coating surface. Further, the specimens were cut with a laboratory cutter and alcohol was used as cooling liquid to prevent corrosion. Cut specimens were water poured again based on the above mentioned procedure followed by metallographic preparation. Finally, all tested specimens were evaluated using SEM or OM in cross sections.

3. RESULTS

The graph in **Figure 1** and **Figure 2** shows the weight losses for all the evaluated surface treatments in an aggressive environment of H_2SO_4 at room temperature. For better clarity, the results of weight losses in H_2SO_4 were divided into two graphs. **Figure 1** clearly shows that the lowest corrosion resistance of all four evaluated coatings exhibited the TiMoCN-29% Ni coating. Cr_3C_2-25%NiCr, Stellite 6 and Hastelloy C-276 coatings showed the highest corrosion resistance of all evaluated coatings, see **Figure 1**. The remaining four types of surface treatments exhibited the lowest corrosion resistance according to their high corrosion losses and gains, see **Figure 2**. Sulphuric acid is a very aggressive substance, which is used very often in many industry sectors. For this reason it is very important to find a surface treatment that will be resistant to aggressive environment for as long as necessary in operation. Cr_3C_2-25%NiCr was the first evaluated coating. **Figure 3a** shows how the aggressive environment of sulphuric acid aqueous solution affected the coating. NiCr matrix was etched and based on **Figure 1**, corrosion products were most likely formed between splats in the coating, which increased its weight. These corrosion products initially prevented further penetration of aggressive environment, but gradually spread deeper and probably also dissolved in the environment, see **Figure 1**. The second evaluated coating - Hastelloy C-276 - most likely showed a very similar corrosion mechanism, see **Figure 3b**. Corrosive environment penetrated into the depth of about 150 µm, which was less than at Cr_3C_2-25%NiCr. This is also demonstrated on the graph in **Figure 1**, where the weight changes were not so significant for the Hastelloy C-276 coating. Based on these results the Hastelloy C-276 coating is more resistant to aggressive environment of sulphuric acid aqueous solution in comparison with the Cr_3C_2-25%NiCr coating. The Stellite 6 coating showed the best corrosion resistance of all the evaluated surface treatments, see **Figure 4a**. The graph in **Figure 1** shows that there were most likely formed corrosion products preventing further penetration of corrosion into the coating. Based on the weight change description, weight initially increased, but the increase stopped during the test and showed relatively constant values. Based on **Figure 4b**, TiMoCN-29%Ni exhibited similar corrosion mechanism in the first half of tests. However, the penetration of corrosive environment to the base material led to a rapid start of coating and substrate degradation, which resulted in weight losses in the second half of the test, see **Figure 1**. The Cr_3C_2-25%CoNiCrAlY coating sustained a very similar corrosion damage comparing with the TiMoCN-29%Ni coating. The corrosion test for this coating had to be interrupted one cycle earlier due to widespread degradation, see **Figure 5a**. This was also proved by the graph in **Figure 2**. NiCrBSi behaved differently in an aggressive environment of H_2SO_4 aqueous solution in comparison with other evaluated coatings. This coating acted as an anodic protection of the substrate material. **Figure 5b** apparently shows a gradual dissolution of the coating down to the substrate. The graph in **Figure 2** shows that the coating reacted with an aggressive environment resulting in creation of corrosion products on the surface which gradually dissolved into the environment together with the coating during the first part of the test. In the second part of the test, the substrate material melted into the corrosive environment. According to presented results, see **Figure 5b** and **Figure 2**, this coating is not suitable for protection of components in an environment of H_2SO_4. Nitrided stainless steel behaved very unstably in this aggressive environment and in comparison with the other evaluated surface treatments it is very inadequate for protecting functional parts operating in this particular corrosive environment. Nitrided stainless steel showed uniform corrosion (etching) over the entire exposed surface, see **Figure 6a** and **Figure 6b**. According to the graph in **Figure 2**, gradual dissolution of the material over the entire surface that was exposed to corrosive environment probably occurred for both nitride stainless steel with and without surface activation using TiH.

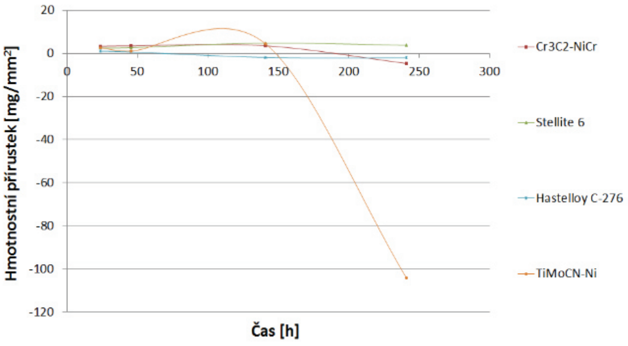


Figure 1 Weight losses of evaluated surface treatments during immersion corrosion tests in H_2SO_4 at room temperature

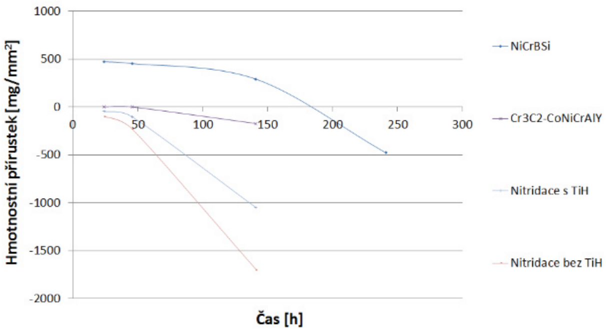
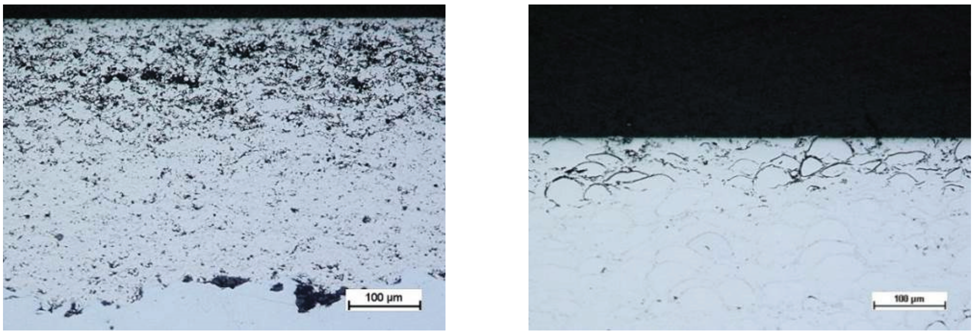
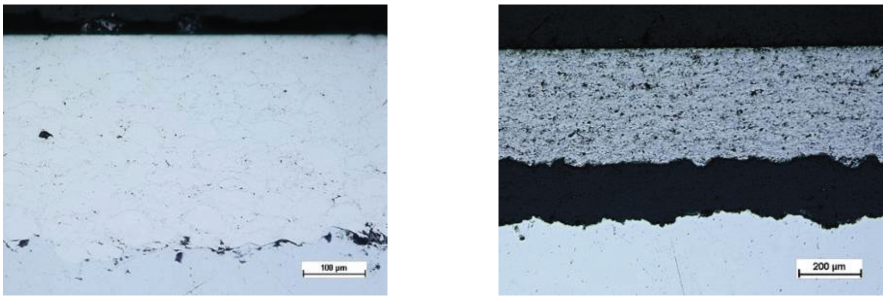


Figure 2 Weight losses of evaluated surface treatments during immersion corrosion tests in H_2SO_4 at room temperature



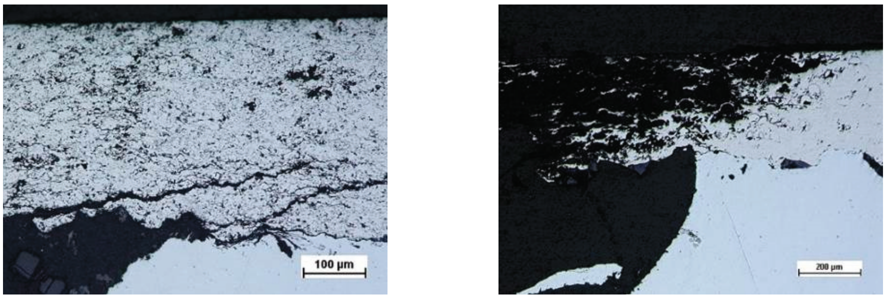
a)
b)

Figure 3 a) Cross-section of Cr_3C_2-25%NiCr coating after the exposure to H_2SO_4 and **b)** cross-section of Hastelloy C-276 coating after the exposure to H_2SO_4



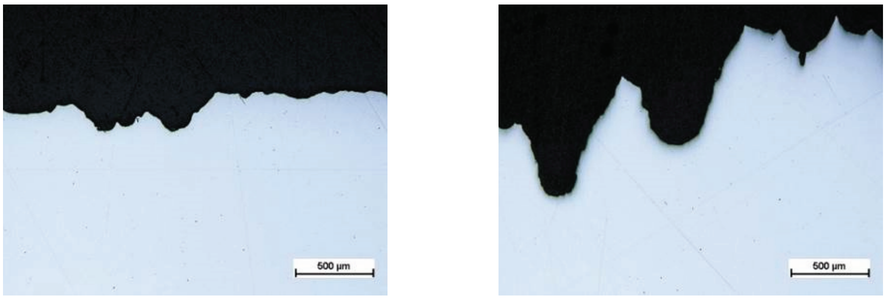
a) b)

Figure 4 a) Cross-section of Stellite 6 coating after the exposure to H_2SO_4 and **b)** cross-section of TiMoCN-29%Ni coating after the exposure to H_2SO_4



a) b)

Figure 5 a) Cross-section of Cr_3C_2-25%CoNiCrAlY coating after the exposure to H_2SO_4 and **b)** cross-section of NiCrBSi coating after the exposure to H_2SO_4



a) b)

Figure 6 a) Cross-section of nitrided stainless steel with TiH surface activation after the exposure to H_2SO_4 and **b)** cross-section of nitrided stainless steel without TiH surface activation after the exposure to H_2SO_4

4. DISCUSSION

Sulphuric acid is an aggressive substance, which is used very often in many industry sectors. For this reason, it is very important to find a surface treatment that will be resistant in this aggressive environment for as long as necessary for operation. The Cr_3C_2-25%NiCr coating exhibited etching of matrix to the depth of about 200µm, see **Figure 3**. When we consider this result and the graph of weight gains and losses in **Figure 1**, we can derive the probable corrosion mechanism. In the first phase of corrosion attack, the acid reacted with coating and focused mainly on the NiCr matrix. The reactions resulted in formation of corrosion products, which generally have higher weight. It was not possible to remove the corrosion products due to their position, which consequently influenced the weight. Next corrosion testing led to more massive dissolving of the coating (mostly matrix NiCr) and next measuring showed a weight loss. The Hastelloy C-276 and the Stellite 6 alloy coatings exhibited the best resistance to sulphuric acids of all the evaluated surface treatments. The Hastelloy

C-276 coating showed some penetration of corrosive environment mainly along splat borders to the depth of 100 μm. However, the penetration of corrosive environment stopped in this depth and corrosion products worked as diffusion barrier which prevented further penetration of aggressive environment to the base material. It can evidently be seen on the graph in **Figure 1**. Stellite 6 coating exhibited very similar mechanism, but with a negligible intensity. For this reason, this coating is very suitable for the use as protection of functional components in sulphuric acid. TiMoCN-29%Ni and C_2-25%CoNiCrAlY coatings exhibited similar corrosion mechanism, but the acid penetration was very rapid and relatively high porosity could not prevent this phenomenon. It is possible that adjustment of their spraying parameters can help to achieve a lower porosity and the coatings could be used as protection of components in the environment of H_2SO_4. The last evaluated NiCrBSi coating is absolutely unsuitable for the use in this corrosive environment, because the acid attacked the coating from the surface resulting in a complete dissolution into the corrosive medium. Nitrided stainless steel behaved very unstably in this aggressive environment and that is why it is very inappropriate for the protection of functional areas in this type of corrosive environment. Nitrided stainless steel exhibited uniform corrosion (etching) over the entire exposed surface, see **Figure 6a** and **Figure 6b**. According to the graph in **Figure 2**, gradual dissolution of material from the entire surface exposed to the corrosive environment probably occurred for the nitrided specimens both with and without surface activation using TiH.

5. CONCLUSION

The results of immersion test in H_2SO_4 at room temperature show that the Hastelloy C-276 and the Stellite 6 alloy based coatings exhibited the best resistance. The Cr_3C_2-25%NiCr carbide based coating also offers a satisfactory protection in this environment. The NiCrBSi coating exhibiting dissolution is completely unsuitable for this type of environment. The TiMoCN-29%Ni and the Cr_3C_2-25%CoNiCrAlY coatings are extremely unsuitable for this aggressive environment due to a high degree of porosity in microstructures after spraying.

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