HIGH TEMPERATURE HOT CORROSION BEHAVIOR OF TiMOCN-29%Ni AND Cr_3C_2-25% NiCr COATING ON STAINLESS STEEL IN AN AGGRESSIVE ENVIRONMENT

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Abstract

The demand for coatings that can protect the base material from the influence of high temperature corrosion is nowadays increasing. For this reason, new coatings with potential to succeed in aggressive environments of energy, marine, food, etc. industries are being developed. TiMoCN-29% Ni (experimental coating) and Cr_3C_2-25% NiCr coatings were applied to the substrate material 1.4923 (P91) which is used as an effective material for structural components in power equipment. Evaluated coatings were deposited using optimized parameters of HP/HVOF (High Pressure / High Velocity Oxygen Fuel) thermal spraying technology. Resistance study of selected thermally sprayed coatings against high temperature corrosion was conducted in the corrosive environment of 60% V_2O_5 and 40% Na_2SO_4 at the temperature of 750 °C and in the environment of 59% Na_2SO_4, 34.5% KCl and 6.5% NaCl at temperatures of 525 °C and 575 °C. After the corrosion tests, the evaluated coatings were analyzed using optical and scanning electron microscopy (SEM) and subsequently the elemental composition (EDX) of each coating was conducted. Based on the results achieved, the experimental TiMoCN-29% Ni coating by the Japanese company Fujimi was further evaluated using X-ray diffraction. The obtained results prove that not all coatings deposited using HP/HVOF thermal spraying technology can be used as an appropriate protection for functional component surfaces.

Keywords: HP/HVOF, corrosion resistance, hot corrosion

1. INTRODUCTION

The majority of research projects is nowadays focused on standard parameters evaluated by "as sprayed" coatings and also on monitoring of their other physical and physical-mechanical properties, their dependence on temperature, corrosive environments, modes and conditions (like composition of furnace atmosphere etc.) [1]. Corrosion in the presence of molten salts is called high temperature corrosion. The high temperature corrosion process involves the deposition of salts on material surface. At operating temperatures, certain 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 than the individual compounds alone. Material attack introduced by salts formed at the surface must not be always caused by impurities in coal or oil, but takes place in every environment where the penetration of salts to the material surface occurs, e.g. in the marine industry [2].

Several different measures are used in order to deal with high temperature corrosion. However, the majority of them prevents or limits the high temperature corrosion only partially and temporarily. For this reason, the application of protective coatings appears to be the most efficient and economical solution. On the other hand, not every protective coating is suitable for every type of environment, and therefore it is very important to identify which coatings provide desirable protection in a particular environment. All information was gain in the literature [3], [4], [5] and [6].

2. EXPERIMENTAL PROCEDURE

This paper describes high temperature corrosion test based on the influence of corrosive-aggressive salt mixture at 750 °C. The test procedure was as follows. The specimens were firstly polished to the surface roughness of Ra_{max} = 1 µm, then rinsed with alcohol and heated in an oven at 250 °C. Heating is necessary for proper adhesion of the salt layer. For proper simulation of conditions and result comparison, there was chosen salt mixture in proportion of 40% Na_2SO_4 and 60% V_2O_5, which is a eutectic with low melting point of 550 °C. This salt mixture was mixed with alcohol and applied to the surface of evaluated specimens in the amount of (3-5) g/cm^2. This step was followed by drying of applied mixture for 3 h in an oven at 100 °C. Before testing in furnace, the specimens were weighed and the weight was subsequently measured after each cycle. In order to compare the results easily, the number of cycles was set on 50. Each cycle consisted of one hour in the furnace composed of silicon carbide and the subsequent cooling for 20 minutes at room temperature. The test was performed on the coated specimens and steel P91 was used as a base material.

The second high temperature corrosion test was based on the application of certain amount of salt mixture with composition of 59% Na_2SO_4, 34.5% KCl and 6.5% NaCl on the surface of evaluated coatings. The prepared specimens were placed on a ceramic plate in the autoclave. The autoclave had an environment with 30% humidity maintained throughout the test period using a device for humidity generation. Two measurements were performed, each with interval of 168 hours. Moreover, beside different temperatures, all test parameters were identical. The temperature of the first measurement was 525 °C and of the second 575 °C. The specimens were then removed from the autoclave and cold poured using Dentacryl. This procedure prevents from the loss of corrosion products formed at specimen surface during corrosion test. The specimens were afterwards cut and again poured in order to conduct metallographic observation in cross-section. Metallographic evaluation was completed using scanning electron microscope. The exposed specimens were further evaluated using elemental composition change. This evaluation was performed using EDX elemental analysis. Finally, all results were analyzed in terms of coating suitability for testing environment.

3. RESULTS AND DISCUSSION

Weight gain graph for both evaluated coatings in **Figure 1** shows how the evaluated coatings behave in the aggressive environment with high temperature corrosion. TiMoCN-29%Ni coating was completely damaged in the eleventh cycle, and therefore no other results are reported. Carbide coating Cr_3C_2-25%NiCr showed much better resistance to high temperature corrosion in the chosen environment. Based on these results, the carbide coating Cr_3C_2-25%NiCr is more suitable for chosen corrosive environment. These results are also consistent with other experiments performed under the same conditions. Furthermore, SEM photographs and tables with elemental composition using EDX analysis are included.

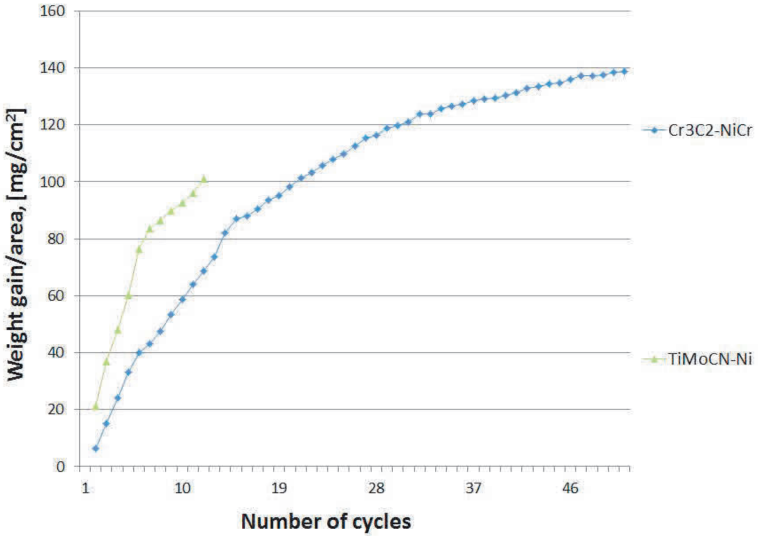
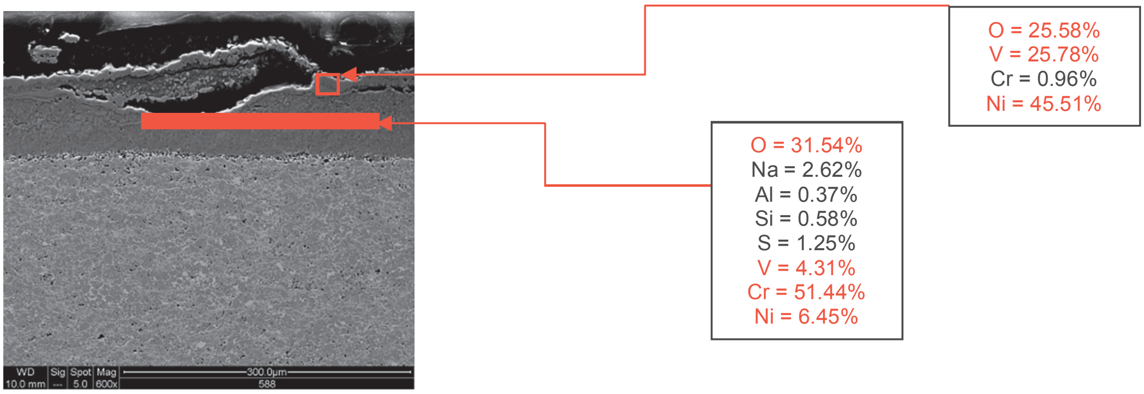


Figure 1 Weight gain/area vs. number of cycles plot for bare and HVOF sprayed P91 steel subjected to molten salt environment (Na_2SO_4 - 60% V_2O_5) for 50 cycles at 750 °C

Figure 2 shows the microstructure of Cr_3C_2-25NiCr coating in cross-section after the exposure to corrosive environment. The photograph apparently shows the mechanism of corrosion damage and proves the disruption of coating from the surface. There was formed an oxide layer which was further degraded by molten salts. For this reason, the coating lost its protective oxide layer and consequently broke progressively from the surface.

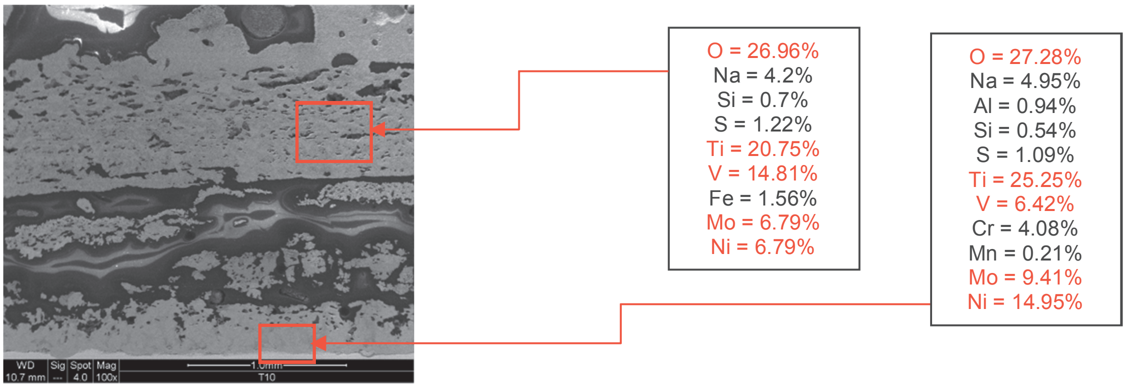
Figure 3 shows the microstructure of TiMoCN-29% Ni in cross-section after the exposure to corrosive environment. The photograph presents the mechanism of corrosion damage and shows total destruction of coating, probably caused by high temperature. New phases and oxides with higher volume were most probably created and this change destroyed the coating. Based on the obtained results, this coating is not suitable for high temperature applications.



O = 25.58%
V = 25.78%
Cr = 0.96%
Ni = 45.51%

O = 31.54%
Na = 2.62%
Al = 0.37%
Si = 0.58%
S = 1.25%
V = 4.31%
Cr = 51.44%
Ni = 6.45%

Figure 2 Cr_3C_2-25%NiCr coating after the exposure to corrosive environment of molten salts Na_2SO_4 - 60% V_2O_5 after 50 cycles at 750 °C



O = 26.96%
Na = 4.2%
Si = 0.7%
S = 1.22%
Ti = 20.75%
V = 14.81%
Fe = 1.56%
Mo = 6.79%
Ni = 6.79%

O = 27.28%
Na = 4.95%
Al = 0.94%
Si = 0.54%
S = 1.09%
Ti = 25.25%
V = 6.42%
Cr = 4.08%
Mn = 0.21%
Mo = 9.41%
Ni = 14.95%

Figure 3 TiMoCN-29%Ni coating after the exposure to corrosive environment of molten salts Na_2SO_4 - 60% V_2O_5 after 50 cycles at 750 °C

Cr_3C_2-25% NiCr carbide coating exhibited relatively good anti-corrosion properties during the second test of high temperature corrosion at the exposure temperature of 525 °C, evident from **Figure 4**. However, at the exposure temperature of 575 °C, the coating exhibited very rapid reduction in thickness, meaning significant degradation. The corrosion attacked matrix and individual carbides delaminated from the coating surface. It is very interesting that the corrosion attack is not so significant at the exposure temperature of 525 °C in comparison with 575 °C, however, the temperature increase is only 50 °C; see **Figure 4** and **Figure 5**. No evaluations have been made yet to clarify this coating behavior. For this reason, it would be appropriate to continue in this research.

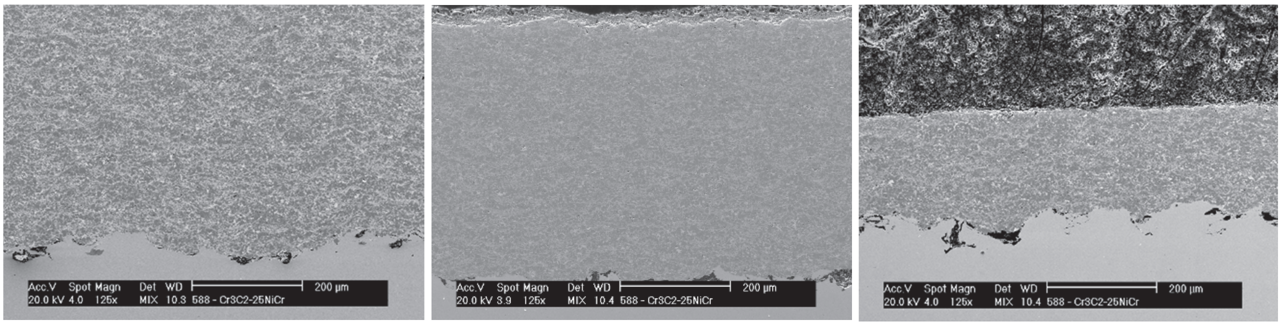


Figure 4 Cr_3C_2-25% NiCr coating left before the exposure, in the middle after the exposure at 525 °C and right at 575 °C

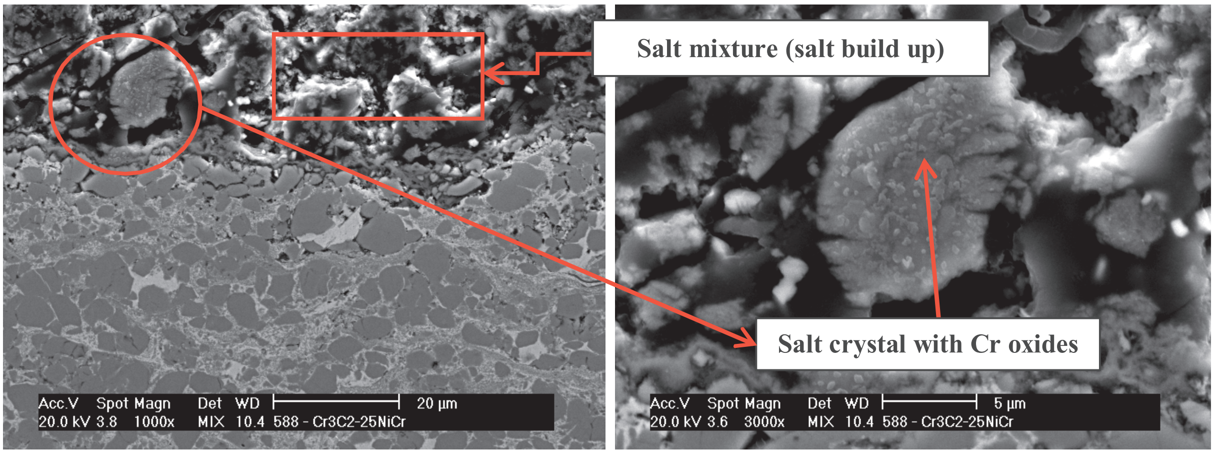


Figure 5 Cr_3C_2-25% NiCr coating after the exposure at 575 °C

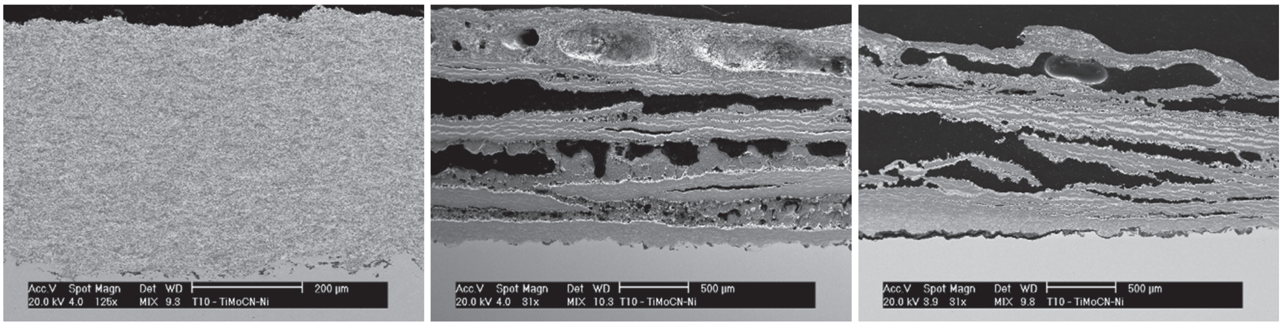


Figure 6 TiMoCN-29% Ni coating left before the exposure, in the middle after the exposure at 525 °C and right at 575 °C

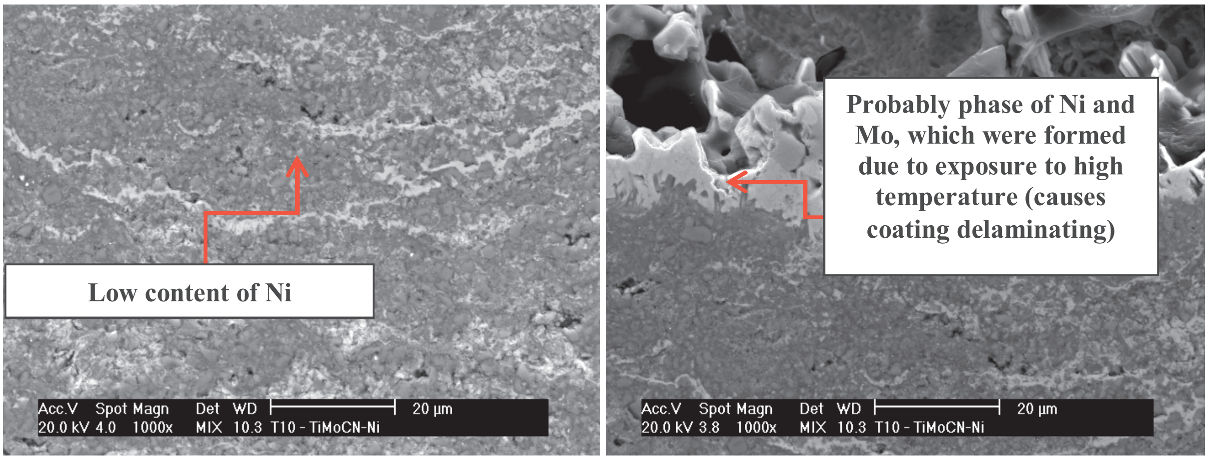


Figure 7 TiMoCN-29%Ni coating after the exposure at 525 °C

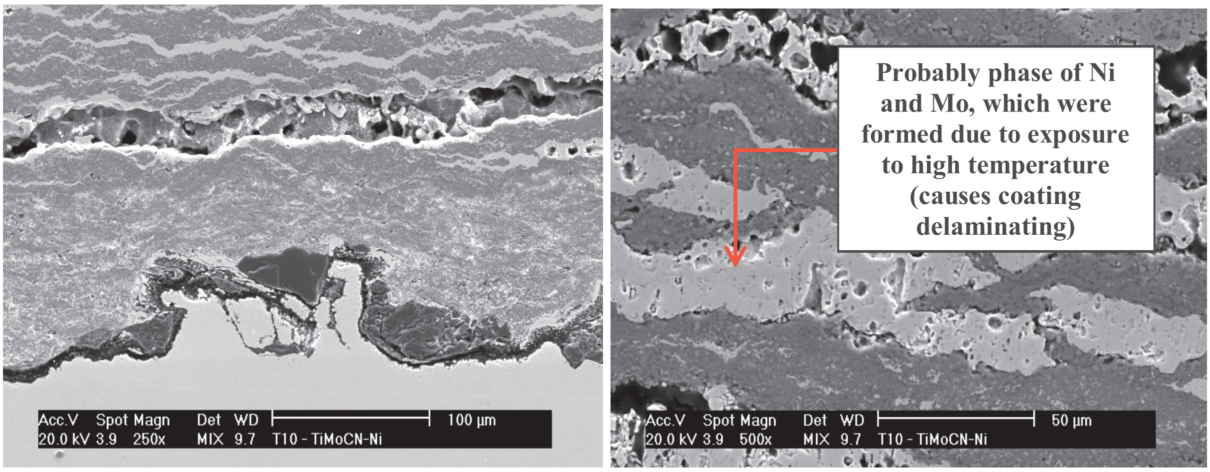


Figure 8 TiMoCN-29%Ni coating after the exposure at 575 °C

The second evaluated coating was experimental coating TiMoCN-29% Ni. The evaluation of high temperature corrosion proved that this coating is absolutely unsuitable for high temperatures. This conclusion is based on the results on **Figure 6**, **Figure 7** and **Figure 8**. The results show that higher temperatures lead to total coating destruction which is most probably caused by the formation of new phases between splats. In this case, the formation of Mo and Ni phases with larger volume resulted in the increase of internal stresses and consequent relaxation in form of coating delaminating. This phenomenon was observed at both selected exposure temperature. The coating evaluation using diffraction phase analysis was performed after the corrosion tests.

4. CONCLUSION

- Based on the conducted experiments, suitably selected coatings deposited using HVOF thermal spraying technology can work as a successful protection of functional surfaces which operate at high temperatures in corrosive-aggressive environment.
- It was proven that the ability of coating to protect the substrate material decreases with increasing environment temperature.
- The first high temperature corrosion test showed that TiMoCN-29% Ni coating is not suitable for high temperature applications in this type of corrosive environment. This result was confirmed also after the second high temperature corrosion test.
- The corrosion mechanism involving the degradation of matrix and subsequent release of carbides from the coating surface was observed by Cr_3C_2-25% NiCr coating. It was found that this type of degradation by carbide coatings is strongly dependent on the exposure temperature. The obtained results clearly prove that with a small increase of temperature by 50 °C the degradation corrosion rate of this coating dramatically increases.
- Cr_3C_2-25% NiCr coating exhibited improved protection against high temperature corrosion in comparison with TiMoCN-29% Ni coating.
- It was found that the experimental coating TiMoCN-29% Ni is totally unsuitable in applications to protect functional surfaces of components which are subject to high temperature corrosion.

ACKNOWLEDGEMENTS

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