Comparison of high temperature corrosion resistance of NiCr-based coatings applied by High Velocity Oxygen Fuel and Twin Arc Spray processes

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Abstract
High temperature corrosion in a molten sodium sulfate salt environment is a serious problem of coal-fired boiler components. The promising possibility for surface protection is to apply thermally sprayed coatings. However, the key to success is to choose the optimal material and the proper spraying technology for a given application. Therefore, this study is aimed at a comparison of the high temperature behaviour of two protecting NiCr-based coatings sprayed by different technologies on 1.4903 (W.nr.) chrome-molybdenum steel. NiCrMoWFe was deposited by High Velocity Oxygen Fuel technology (HVOF). Twin wire arc spray technology (TWAS) was used to deposit multi-layered “multicoat” consisting of NiCrMoNbTa and NiCrTi with ceramic overlay Armaguard coated by brush. Chrome-molybdenum steel 1.7715 (W.nr.) commonly used in coal-fired boiler was also exposed to the high temperature corrosion test to evaluate the potential benefit of the coating. Coated as well as the uncoated specimens were exposed to the molten salt environment 18% Na₂SO₄ and 82% Fe₃(SO₄)₃ at 690 °C under cyclic condition. The thermogravimetric approach was used to determine kinetics of corrosion. The X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) techniques were used to analyze the corrosion products and determine the corrosion mechanism. The results of high temperature corrosion resistance show that NiCrMoWFe coated by HVOF and multicoat sprayed by TWAS was comparable.

1 Introduction
High temperature corrosion is accelerated corrosion that occurs when metals and alloys are covered with a thin film of molten salt. High temperature corrosion of coal-fired boilers is caused by burning low grade fuel in combination with the low emission combustion process. Low grade fuel contains a high amount of impurities such as sulphur, sodium, vanadium, chlorine, and incombustible material which produce ash during combustion. Fly ash can deposit on boiler components and forms the molten salt film. This complex salt deposit attacks the protective oxide scale formed on the surface of the material which leads to severe high temperature corrosion [1, 2, 3, and 4].

Thermal sprayed coatings are applied to the surface of coal-fired boiler components to allow them to function under extreme conditions and extend their service life. Protective coating serves as an effective diffusion barrier between the corrosion environment and substrate material to provide corrosion and oxidation resistance. The coating reacts with the environment and produces the protective oxide scale which should result in surface passivation [5, 6 and 7].

The objective of this work is to compare two thermal coating technologies to apply such coatings. High Pressure/High Velocity Oxygen Fuel (HP/HVOF) and Twin Arc spray technology (TWAS). HVOF technology allows applying coatings with low porosity (about 1%) and low oxide particles content with no significant thermal influence and mechanical alterations of the substrate material. On the other hand, TWAS technology is intended for on-site coating/repairs and lower financial costs.
2 High temperature corrosion test

A high temperature corrosion test was performed on Ni-based coatings deposited by HP/HVOF and TWAS technology as well as uncoated steels samples. NiCrMoWFe coating was deposited by HVOF technology. Twin wire arc spray technology was used to deposit Multicoat NiCrMoNbTa and NiCrTi coatings with Armaguard (ceramic overlay coated by brush). All of these coatings were deposited on high temperature corrosion resistant chrome-molybdenum steel 1.4903 (W.nr.). Uncoated chrome-molybdenum steel 1.7715 (W.nr.) commonly used in coal-fired boiler and chrome-molybdenum steel 1.4903 were included in the high temperature corrosion test for comparison.

The specimens were exposed to a molten salt environment 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ at 690 °C under cyclic condition, simulating the working environment in low-emission boilers of coal-fired power plants. For the high temperature test, samples of size 20 x 20 x 5 mm were used. The exposed surface of the tested specimens was polished down to Ra = 1 µm. Salt deposit (3-5 mg/cm$^2$) of 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ with uniform thickness was applied with a brush on the preheated samples. Then the specimens were placed to ceramic crucible. Each cycle of the test included 1 hour of heating at 690°C in a furnace followed by 20 min cooling at room temperature for 50 cycles. Weight change measurements were performed after each testing cycle to determine the kinetics of corrosion. The samples were weighted with the ceramic crucible.

The results of the high temperature corrosion test were evaluated using the thermogravimetric method to determine the kinetics of corrosion products. X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) techniques were used to analyze the corrosion products and determine the corrosion mechanism [8].

3 Results

3.1 Corrosion kinetic

The weight gain versus the number of cycles plots for tested specimens is shown in Figure 1. The first 10 testing cycles of the test were not displayed in the weight gain graph because the corrosion behavior of the samples was affected by the formation of the passivation oxide layer and the stabilization of the whole test.

![Figure 1](image_url)

Figure 1. Weight gain versus the number of test cycles graph for tested samples after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

Weight gains that were observed during the high temperature corrosion test were caused by the formation of corrosion products. Therefore, the best corrosion resistance shows the sample with the smallest weight gain. Both NiCr based coatings show similar behavior during the test. Although uncoated steel 1.4903 shows the smallest weight gain during the entire period of the test, peeling of the scale was observed during the test (Figure 2 c). The uncoated steel 1.7715 showed significant weight gain and extensive peeling (Figure 2 d). The weight gain of the both uncoated steel wasn’t affected by peeling of the scale (Figure 2 a, b), because of all parts of the scale were captured in the crucible and were weighted with the samples.
Figure 2. Macrophotography of tested samples after exposure to 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

3.2 SEM and EDS cross-section analysis

SEM and EDS techniques were used to analyze the corrosion products and determine the corrosion mechanism. SEM and EDS micrograph in Figure 3-6 depict the cross-section of coated and uncoated samples after exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ molten salt environment.

After the molten salt corrosion, a continuous oxide scale was formed on the surface of NiCrMoWFe coating (Figure 3). The oxide scale consists mainly of chromium and molybdenum. A chromium depletion area can be seen below the surface of the coating. Also, small amounts of tungsten and iron are observed in the volume of scale and nickel on the top of the oxide scale. The substrate steel seems to be unaffected. Please note that molybdenum and sulfur peaks in EDS spectrum overlap, so they could not be distinguished.

Figure 3. SEM photograph and EDS map of the cross-section of HP/HVOF sprayed NiCrMoWFe coating after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

The cross-sectional analysis SEM/EDS of Multicoat sample after exposure to the molten salt environment is shown in Figure 4. Armaguard - ceramic overlay coating is mainly formed by zirconium and silicone oxides. The oxide protective scale is not formed. A thin area of iron is observed on the top of Armaguard overlay coating and interface of the upper coating NiCrTi, which came from corrosion environment. The oxides contained in the upper coating NiCrTi were mostly
formed during TWAS process. NiCrMoNbTa lower coating and substrate steel seem to be unaffected.

The oxide scale on uncoated steel 1.4903 consists mainly of chromium with a small amount of vanadium and manganese, see Figure 5. On the interface of oxide scale and steel, there is an area rich in chromium. A thin chromium depletion area can be seen underneath. On the top of steel, under the oxide scale, is the higher content of silicone. Again, molybdenum and sulfur overlapped. It can be assumed that the thin area on the interface of the oxide layer and the substrate is sulfur because of the content of molybdenum in steel 1.4903 is just about 1%.

Figure 4. SEM photograph and EDS map of the cross-section of TWAS sprayed Multicoat after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

Figure a) Elements of the coating

Figure b) Elements of corrosive environment

Figure a) Elements of the substrate
b) Elements of corrosive environment

Figure 5. SEM photograph and EDS map of the cross-section of uncoated steel 1.4903 after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

The SEM micrograph (Figure 6) for high temperature corroded steel 1.7715 reveals the thick delaminating oxide scale formed mainly by iron. It can be seen a thin layer of the silicon on the top of the oxide scale. Also, there can be observed a small amount of chromium in the upper part of the oxide scale.

a) Elements of the substrate

b) Elements of corrosive environment

Figure 6. SEM photograph and EDS map of cross-section of uncoated steel 1.7715 after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ corrosion environment

3.2 XRD Analysis

Table 1. XRD results for tested samples after the exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$

| Sample             | Majority phases      | Minority phases  |
|--------------------|----------------------|------------------|
| NiCrMoWFe Multicoat| NiO, Cr$_2$O$_3$, NiCr$_2$O$_4$, Fe$_2$O$_3$, ZrO$_2$, SiO$_2$| FeMoO$_4$, NiMoO$_4$, Fe$_2$O$_3$, Cr$_2$O$_3$, Y$_2$O$_3$|
| Uncoated steel 1.7715 | Fe$_2$O$_4$, Fe$_3$O$_4$ | - |
| Uncoated steel 1.4903 | Fe$_2$O$_4$, Fe$_3$O$_4$ | Na$_2$SO$_4$ |

The XRD results for the coated and uncoated samples after exposure to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ molten salt environment are reported in Table 1. NiCrMoWFe coating was found to have
the nickel and chromium oxides and spinel NiCr$_2$O$_4$ as the majority phase. FeMoO$_4$, NiMoO$_4$, Fe$_2$O$_3$ was observed as minority phase. The XRD analysis results of Multicoat indicate that the scale is mainly consisting iron, zirconium, and silicon oxides. Also, there can be seen yttrium oxide. The oxide scale of each uncoated steel is mainly formed by iron. The residual amount of corrosion environment was found in the case of steel 1.4903.

3 Conclusion
In the current investigation are compared NiCr-based coatings applied by two different types of thermal spray technologies. The specimens were exposed to the 12% Na$_2$SO$_4$ + 82% Fe$_2$(SO$_4$)$_3$ molten salt environment at 690 °C under cyclic condition, simulating the working environment in low-emission boilers of coal-fired power plants.

NiCrMoWFe HP/HVOF sprayed coating shows high corrosion resistance in the given environment. The passivation oxide scale formed by NiO, Cr$_2$O$_3$, NiCr$_2$O$_4$ contributed to the corrosion resistance and have shown the tendency to act as a diffusion barrier to the oxidizing species. Multicoat applied using by TWAS technology also shows high corrosion resistance due to protective ceramic overlay Armaguard. Outer ceramic overlay was mainly formed by zirconium and silicone. Although uncoated steel 1.4903 shows the smallest weight gain during the high temperature test. On the surface of 1.4903 steel was created thick oxide scale mainly by iron with tendency to peel. Uncoated steel 1.7715 suffered severe corrosion attack. Intensive peeling was observed during the high temperature corrosion test. The results show a high oxidation rate during exposure to the corrosion environment and the presence of large amounts of iron oxides.

Both protective coating showed high corrosion resistance during test. Results of High temperature corrosion test showed that the specially designed Multicoat applied with TAWS technology can fully replace more expensive HP/HVOF NiCrMoWFe coating in case of coal fired boiler protection.

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