

HIGH TEMPERATURE CORROSION STUDIES OF HVOF SPRAYED COATINGS IN MOLTEN SULPHATE SALTS ENVIRONMENT

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Abstract

The generally applied requirements on lowering of emission production in the field of power industry have led, among others, into the application of low-emission combustion process of coal fired power plants. Besides the emissions reduction, this process has led to an increase of boilers parts corrosion degradation due to the reducing atmosphere in low-emission boilers, responsible for sulphide corrosion and molten salt attack. In such environment, the protection of the exposed surfaces gains importance. Among others, the thermal spraying technology can offer a suitable way of surface corrosion protection. In the present work, the high temperature corrosion behaviour of CoCrAlYTaNiSi and Cr₃C₂-25%NiCr High Pressure/High Velocity Oxygen Fuel (HP/HVOF) sprayed coatings is evaluated and compared to the behaviour of bare structural steel (SPT360) substrate. The specimens were exposed to a molten salt environment, i. e., 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ at 690 °C under cyclic condition, simulating the working environment in low-emission boilers of coal-fired power plants. The thermogravimetric method was used to establish the kinetics of corrosion. X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) techniques were used to analyse the corrosion products and determine the corrosion mechanism. The thermogravimetric measurement shows high oxidation rate of SPT360 steel. Cr₃C₂-25%NiCr coating provides slightly better performance compared to CoCrAlYTaNiSi coating. Based on the obtained results, both coatings were found to have higher corrosion resistance than the SPT360 steel substrate, offering a sufficient surface protection in a given environment.

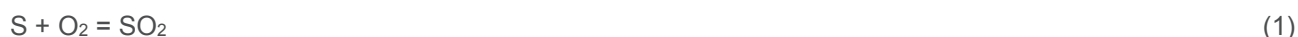
Keywords: High temperature corrosion, low-emission boilers, coal fired boilers, HVOF, thermal spraying, CoCrAlYTaNiSi, Cr₃C₂-25%NiCr

1. INTRODUCTION

High temperature corrosion is an accelerated corrosion that occurs when metals and alloys are covered with thin film of molten salt. This complex salt deposit attacks protective oxide scale formed on the surface of the material. Combination of high temperature with presence of molten salt deposit leads to severe high temperature corrosion as observed e.g. in boilers, gas turbines, internal combustion engines and industrial waste incinerators [1-4]. The 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ corrosion environment is found in coal fired boilers [5, 7-9]. High temperature corrosion of coal fired boilers is caused by burning low grade fuel in combination with low emission combustion process. In order to decrease the amount of nitride oxides (NO_x) emission production, modified low emission combustion process is applied which limits air excess at the burner exhaust area in the furnace chamber. The reducing gas environment results to sulphide corrosion and molten salt attack [4-6].

Due to the depletion of coal resources, low grade fuel with high impurities content is burned. Amounts and characteristic of coal impurities, such as sulphur, sodium, vanadium, and chlorine depends on the location of the coal mine. Sulphur is mainly contained in the coal in the form of iron sulphides, mostly ferrous disulphide

FeS₂. Sulphur can also be found in the form of organics compound combined with original coal constituent part and sulphates. During the combustion process, the ferrous disulphide FeS₂ is mostly decomposed into iron and sulphur oxides. When the combustion occurs in a reducing atmosphere due to the limited air excess, there will be no complete decomposition and ferrous disulphide FeS₂ forms ferrous sulphide FeS. The ferrous sulphide and iron interact and form an eutectic mixture with lower melting point which causes sintering. If the air deficit is too high, there is a high probability that ferrous sulphide will not react with iron. The ferrous sulphide is deposited on the boiler walls and causes sulphide corrosion. Generally, the sulphur is released from ferrous sulphide, reacts with oxygen and sulphur dioxide SO₂ is being produced, that further partially oxidizes to sulphur trioxide SO₃, see equation 1 and 2 [5,6].



High temperature corrosion has two mechanisms: sulphite, which is caused by alkaline sulphates (sodium, potassium) and corrosion caused by complex sulphate compounds Na₃Fe(SO₄)₃ and K₃Fe(SO₄)₃, which are formed by alkaline sulphates and Iron (III) oxide Fe₂O₃ contained in fly ash. The latter corrosion mechanism is more important for coal boilers [6].

Sulphitation:

First, sodium is converted to sodium oxide Na₂O and further reacts with sulphur trioxide SO₃ to form sodium sulphate Na₂SO₄ (equitation 3 and 4). The resulting concentration of sodium sulphate Na₂SO₄ depends on the amount of sodium, because the concentration of sodium sulphate Na₂SO₄ is much smaller than sulphur trioxide SO₃. [4,6].



Sodium sulphate Na₂SO₄ and / or potassium sulphate K₂SO₄ and iron oxide Fe₂O₃ deposited on the thermal apparatus reacts with SO₃ contained in the flue gas and form complex compounds [3-6].

Corrosion caused by complex sulphate compounds:



These complex compounds have a low melting point and react with the iron material of the boiler equipment.



Ferrous sulphide FeS (right side of the equation) reduces to iron oxide Fe₃O₄ to and sulphur trioxide SO₃. Sodium sulphate Na₂SO₄ (equitation 5) repeats the reaction. These complex compounds (equitation 6) 2Na₃Fe(SO₄)₃, K₃Fe(SO₄)₃ and Iron (II) sulphide FeS undergo repeated corrosion process cyclically [6].

2. MOLTEN SALT CORROSION TEST

Cyclic high temperature corrosion test was performed on High Pressure/High Velocity Oxygen Fuel (HP/HVOF) sprayed coatings and bare structural steel (SPT360) substrate. CoCrAlYTaNiSi and Cr₃C₂-25%NiCr coatings were deposited on the chromium-molybdenum steel substrate. The specimens were exposed to a molten salt environment 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ at 690 °C under cyclic condition, simulating the working environment in low-emission boilers of coal fired power plants. Each cycle comprised of 1 h of heating at 690 °C in a silicon carbide furnace followed by 20 min cooling at room temperature

for 50 cycles. For the high temperature test, samples of size 20 x 20 x 5 mm were used. The exposed surface of the tested specimens were polished down to $R_a = 1 \mu\text{m}$. Salt coating deposit of 12% Na_2SO_4 + 82% $\text{Fe}_2(\text{SO}_4)_3$ uniform thickness weighting 3-5 mg/cm^2 was applied with a camel hairbrush on the preheated samples. The specimens were placed to a crucible boats. The resistance of tested specimens to the high temperature corrosion was 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 analyse the corrosion products and determine the corrosion mechanism. Diffractometer D8 Discover (Bruker), SEM EVO MA 15 (Carl Zeiss) and EDS Quantax XFlash 5010 (Bruker) were used for these tasks, respectively. Cross-sections were prepared by standard metallographic procedure using semi-automated Tegramin 25 (Struers) polishing system.

3. RESULTS

3.1. Corrosion kinetic

High temperature corrosion resistance of the tested specimens to the 12% Na_2SO_4 + 82% $\text{Fe}_2(\text{SO}_4)_3$ molten salt environment was determined on the base of thermo-gravimetric method. Weight change measurements were performed after each testing cycle to establish the kinetics of corrosion. Weight gain graph for CoCrAlYTaNiSi and Cr_3C_2 -25%NiCr coatings and bare SPT360 steel substrate after exposure to the corrosion environment is shown in **Figure 1**.

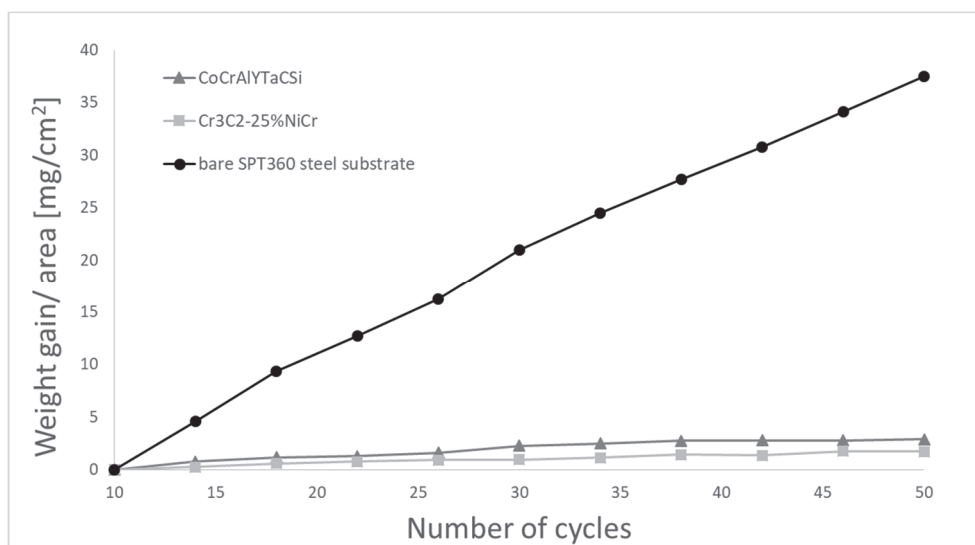


Figure 1 Weight gain versus the number of test cycles graph for CoCrAlYTaNiSi and Cr_3C_2 -25%NiCr coatings and and bare SPT360 steel substrate after the exposure to the 12% Na_2SO_4 + 82% $\text{Fe}_2(\text{SO}_4)_3$ corrosion environment

The first 10 testing cycles of the high temperature corrosion test are not recorded in the weight gain graph because the corrosion behaviour of the samples was affected by the formation of the passivation oxide layer and the test stabilization. Weight gains that were observed during the high temperature corrosion test were caused by the formation of corrosion products. The best corrosion resistance was shown by the sample with the smallest oxidation rate. The bare SPT360 steel substrate showed a significant weight gain. The oxidation was substantial throughout the entire high temperature corrosion test. Against it, the HP/HVOF sprayed coatings showed insignificant weight gain and resisted to the corrosive environment throughout the whole testing period. Cr_3C_2 -25%NiCr coating shown slightly smaller weight gain and thus provide better protection against high temperature corrosion than CoCrAlYTaNiSi coating.

3.2. SEM and EDS cross-section analysis

SEM and EDS techniques were used to analyse the corrosion products and determine the corrosion mechanism. The results of SEM and EDS analysis for CoCrAlYTaNiCr coatings and bare SPT360 steel substrate in the cross section area after the exposure to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ aggressive corrosion environment are shown in the **Figures 2-4**.

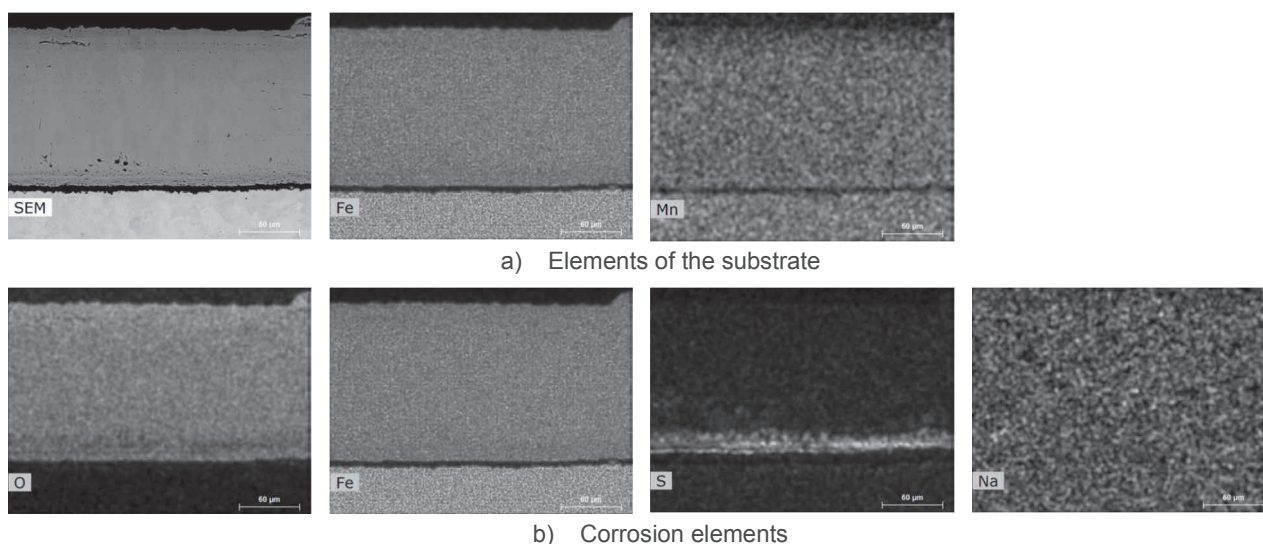


Figure 2 SEM photograph and EDS map of cross-section bare SPT360 steel substrate after the exposure to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ corrosion environment a) Elements of the substrate b) Corrosion elements

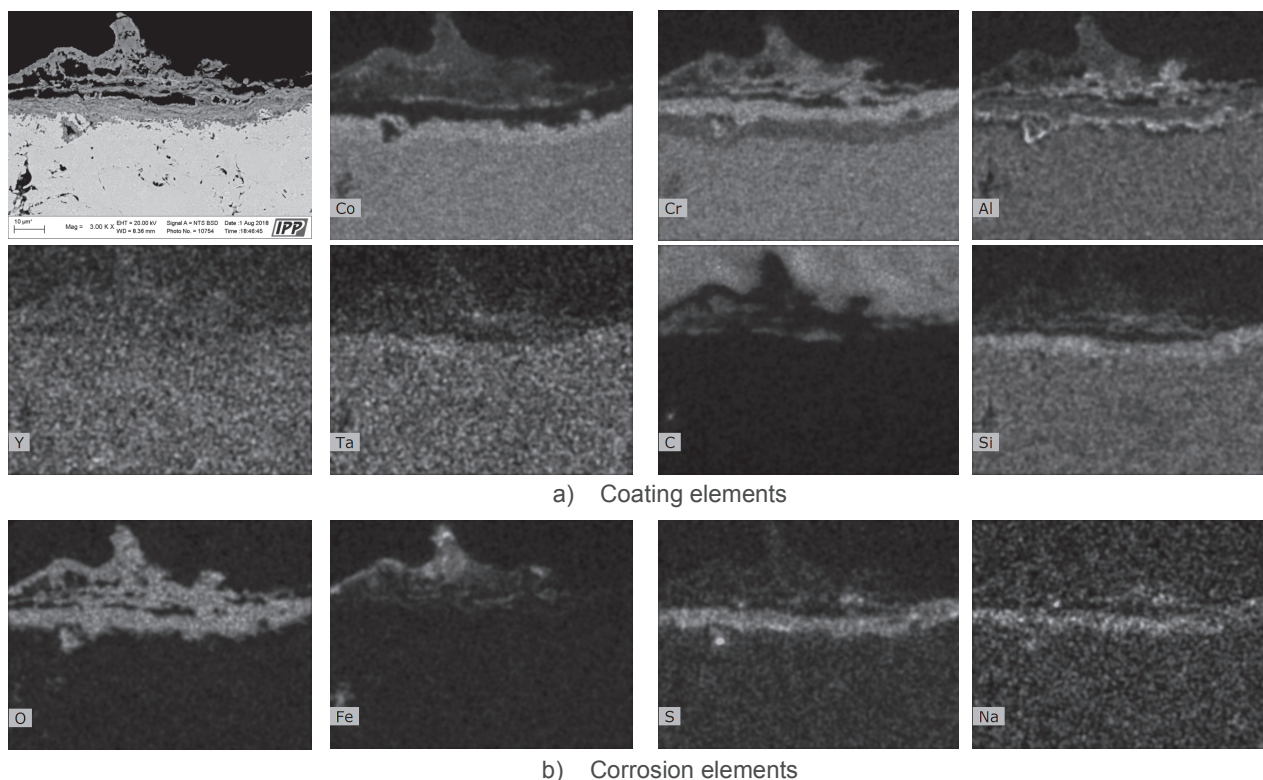


Figure 3 SEM photograph and EDS map of cross-section CoCrAlYTaNiCr coating after the exposure to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ corrosion environment a) Elements of the substrate b) Corrosion elements

The EDS analysis of bare SPT360 steel substrate (**Figure 2**) shows rather thick and delaminating the Fe and O rich scale, i.e. presence of iron oxides. The sulphur occurred in high concentration at the interface of the scale and the substrate. Corrosion attack of the CoCrAlYTaNiSi coating is very uniform and the oxide layer is very thin. The EDS mapping results (**Figure 3**) show that all elements are evenly distributed in the coating structure with a greater concentration of Cr, Co, Al and Si at the corrosion layer and coating surface. According to EDS analysis for Cr₃C₂-25% NiCr coating, iron occurs on the surface of the corrosion layer, see **Figure 4**. At the interface of corrosion layer and coating surface is nickel depleted region. Sulphur occurred in a high concentration at the bottom of the oxide layer.

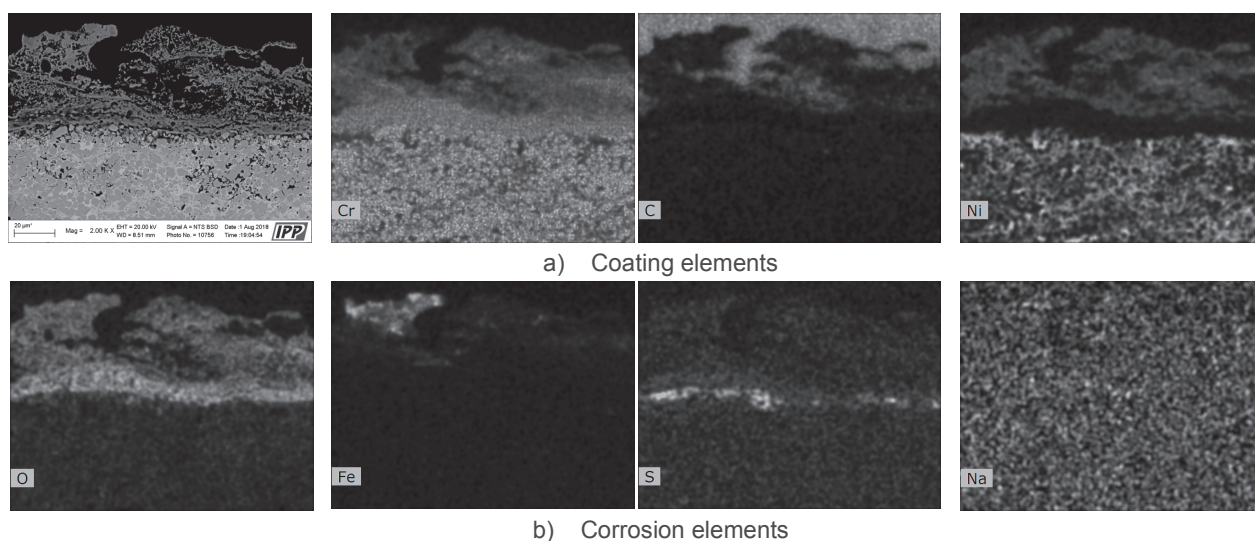


Figure 4 SEM photograph and EDS map of cross-section Cr₃C₂-25%NiCr coating after the exposure to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ corrosion environment a) Elements of the substrate b) Corrosion elements

3.3. XRD analysis

Results of XRD analysis of CoCrAlYTaNiSi and Cr₃C₂-25%NiCr coatings and SPT360 steel substrate after exposure to the molten salt environment 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ are given in **Table 1**. The XRD analysis was performed on the surface of the high temperature corrosion tested specimens gently cleaned from the corrosive medium. The X-ray diffraction pattern of the specimens after exposure is shown in **Figure 5**.

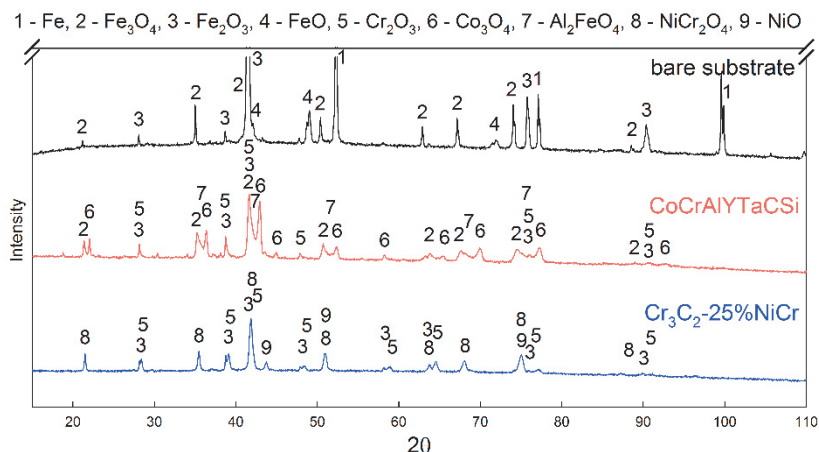


Figure 5 XRD results of CoCrAlYTaNiSi and Cr₃C₂-25%NiCr coatings and bare SPT360 steel substrate after the exposure to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ corrosion environment

Table 1 XRD results for CoCrAlYTaNiSi and Cr₃C₂-25%NiCr coatings and bare SPT360 steel substrate after exposure to the molten salt environment

Sample	Majority phases	Minority phases
CoCrAlYTaNiSi	Al ₂ FeO ₄ , Co ₃ O ₄ , Fe ₃ O ₄	Fe ₂ O ₃ , Cr ₂ O ₃ , Na ₂ SO ₄ , FeSO ₄ 4H ₂ O
Cr ₃ C ₂ -25%NiCr	NiCr ₂ O ₄ , Cr ₂ O ₃ , Fe ₂ O ₃	NiO
Bare SPT360 steel	Fe, Fe ₃ O ₄ , Fe ₂ O ₃	FeO

4. DISCUSSION

The aim of the present work was to evaluate and compare the high temperature corrosion resistance of CoCrAlYTaNiSi and Cr₃C₂-25%NiCr High Pressure/High Velocity Oxygen Fuel (HP/HVOF) sprayed coatings and bare SPT360 steel substrate. All specimens were exposed to a molten salt environment 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ at the temperature 690 °C under cyclic condition.

High temperature corrosion resistance of the tested specimens was determined by the thermo-gravimetric method. The method was established on the base of the kinetics of corrosion products. The corrosion behaviour of the first 10 testing cycles was affected by the formation of passivation oxide layer and the stabilization of the whole test. The coatings have shown the tendency to act as a diffusion barrier to the corrosive medium and successfully have retained its continuous contact with the substrate steel. The bare SPT360 steel substrate showed a high weight gain. The best high temperature corrosion resistance to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ environment showed Cr₃C₂-25%NiCr coating, which had the smallest weight gains during the test. CoCrAlYTaNiSi coating shown slightly higher weight gain, nevertheless this coating showed high temperature corrosion resistance throughout the whole testing period too.

The XRD result shows the presence mainly of Fe₃O₄, Fe₂O₃ in the oxidized SPT360 steel substrate. The EDS analysis confirmed the presence of such upper oxide layer. The presence of large amount of the iron oxides with uniform distribution in the scale indicates no protective layer formation. The high concentration of the sulphur at the interface of the scale and substrate confirmed severe corrosion attack by 12% Na₂SO₄ 82% Fe₂(SO₄)₃ molten salt environment.

The corrosion attack of the CoCrAlYTaNiSi coating is very uniform. The EDS mapping results show that all elements are evenly distributed in the coating structure with a greater concentration of Cr, Co, Al and Si at the interface of corrosion layer and coating surface. According to the occurrence of oxygen can be concluded that these elements formed a corrosion barrier on the surface of the coating which prevented the action of the corrosive environment. The Fe and S possibly come from the molten salt environment which, diffuse towards the coating.

The oxide scale of Cr₃C₂-25%NiCr coating is mainly composed of nickel-chromium oxides NiCr₂O₄ and chromium oxide Cr₂O₃. The greatest concentration of these oxides is found at the interface of the coating and the corrosion layer, which is evident from EDS mapping. In general, the presence of Cr₂O₃ oxide prevents oxidation of the coating. Cr₂O₃ works as a blocking barrier which prevents diffusion of corrosive environment to the inner matrix of alloys. The presence of Fe₂O₃ has been attributed to diffusion of corrosion environment. The Ni depleted region has formed at the interface of the coating surface and the oxide layer, meanwhile the NiO is primarily on the surface of the oxide layer.

5. CONCLUSION

This study investigated and compared the high temperature corrosion behaviour of CoCrAlYTaNiSi and Cr₃C₂-25%NiCr HP/HVOF sprayed coatings and bare SPT360 steel substrate. The specimens were exposed to the 12% Na₂SO₄ + 82% Fe₂(SO₄)₃ molten salt environment at 690 °C under cyclic condition, simulating the working

environment in low-emission boilers of coal fired power plants. All specimens were evaluated using thermogravimetric method to determine the kinetics of the corrosion. To analyse of the corrosion products and determine the corrosion mechanism, X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) techniques were used.

The bare SPT360 steel substrate suffered severe corrosion attack. The results of analyses show high oxidation rate during exposure to the corrosion environment and presence of large amounts of the iron oxides. HP/HVOF sprayed coatings were found to have great high temperature corrosion resistance. The chromium rich oxide scale contributed to the improved high temperature corrosion resistance and the coatings have shown the tendency to act as diffusion barrier to the oxidizing species. Cr₃C₂-25%NiCr coating showed slightly better resistance to molten salt environment than CoCrAlYTaCSi coating.

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