



ORIGINAL RESEARCH ARTICLE

Fireside Corrosion Behavior of Thermally Sprayed Coatings for Waste-to-Energy Power Plant Applications

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This study investigates the fireside corrosion behavior of four (Ni-22Cr, Ni-25Cr, Co-25Cr, and NiCo-25Cr) coatings, which were applied using twin wire arc spray technique and subjected to simulated waste-burning environments (a gas composition containing HCl, SO₂, CO₂, N₂, H₂O, balance N₂, plus a salt deposit of 50wt.% KCl + 50wt.% K₂SO₄). The coatings deposited on a conventional base steel alloy (E-250) were tested under these conditions at 550 °C for 500 h in a laboratory-scale atmosphere controlled furnace. After the fireside exposure, the samples were studied using optical microscopy, SEM-EDX, and XRD to deduce coatings performance and possible corrosion mechanisms. The results indicated that all coatings, except Ni-22Cr, outperformed the E-250 steel. The Ni-22Cr and NiCo-25Cr coatings showed similar pitting corrosion behavior with more prominent corrosion pits on Ni-22Cr coating's surface. The Co-25Cr coating showed slightly improved performance to the above two coatings, which can be attributed to the ability of Co to resist corrosion attack under these conditions. Overall, the Ni-25Cr coating composition was conclusively found to be most effective.

Keywords electron microscopy, fireside corrosion, modeling and simulation, thermal spray, waste to energy, wire arc spray

1. Introduction

Waste-to-energy (WtE) power plants and waste incinerators are on the rise in the UK and globally using agriculture waste, typically biomass as a main source of fuel. These plants have been accepted globally to generate power, preserve fossil fuels, reduce landfill use and its related land and water contamination, and produce an eco-friendly environment by reducing the amount of greenhouse gases (N_xO and CO₂) produced (Ref 1). Considering the Paris Agreement, carbon emissions should be reduced to net zero by around the mid-century. WtE power plants have proved to be part of this solution, and data showed a significant reduction (5.2%) in greenhouse gases during 2022 in the UK (Ref 2, 3) from their use. However, during combustion, the high level of chlorine (Cl₂), alkali metals, and moisture content in biomass ash deposits are found to be particularly destructive, trigger high-temperature corrosion of heat exchanger (HX) components in WtE power plants, which ultimately reduces the overall performance of the plant and results in expensive replacement, maintenance, unplanned shutdowns, and outage expense (Ref 4, 5). These deposits are mostly composed of alkali chlorides (KCl/NaCl) and sulfates (K₂SO₄/Na₂SO₄) and accumulate on HX tubes which are

heavily corroded at elevated temperatures contributing to fouling and high-temperature corrosion problems. The high-temperature corrosion of metallic materials, caused by chlorine, is highly detrimental in many applications, particularly municipal solid waste (MSW) incinerators, where HCl is generated from combustion of PVC (Ref 6, 7). In these incinerators, the flue gas typically contains oxygen about ~ 5-10 vol% and HCl concentration ranging from ~ 25 to 1000 vppm (in biomass) and ~ 250-1300 vppm (in MSW materials). Research indicates that chlorine often prevents the development of a protective oxide, leading to accelerated corrosion attack in oxidizing environments (Ref 8). The resulting condensed and volatile reaction products contribute to complex corrosion mechanisms in the presence of chlorine and oxygen. The corrosion behavior becomes more intricate as the alloying elements increase in the materials making it challenging to determine the exact role of each alloying element (Ref 8-10).

In heat exchangers, steam side oxidation affects the inner surfaces, while gas- and deposit-induced corrosion impact the outer surfaces. The high-temperature corrosion of these internal and external surfaces is known as steam side oxidation and fireside corrosion, respectively (Ref 11-13), and are depicted schematically in Fig. 1.

To mitigate fireside corrosion and increase the service life of heat exchanger tubes, protective coatings deposited via thermal spraying are widely used and studied (Ref 10, 14). The effectiveness of these coatings is primarily determined by the coating material choice, its application using spraying technology, and the adequacy of the quality assurance policies used in its manufacture.

Various thermal spraying technologies exist, including plasma spray, high velocity oxy-fuel (HVOF), and arc spray (AS), among others. Arc spray is the most widely used technique in boiler applications, offering high deposition efficiency which enables the rapid application of thicker coatings, making it ideal for applications requiring heavy-duty

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corrosion protection (Ref 15-17). Furthermore, with the correct surface preparation, AS can achieve excellent adhesion. AS process also uses less expensive consumables (wires instead of powders) (Ref 18). From the material standpoint, Ni- and Co-based alloys are dominant in combating corrosion for solid waste-fuel burning environments, over a range of temperatures (Ref 9, 19). Nevertheless, as temperatures increase, the corrosion conditions in waste-burning power plants become more aggressive; one sees higher fireside corrosion rates, increased steam temperatures and higher steam pressures.

To address these challenges, alloys based on Ni, Co, and Cr, deposited by arc spraying, have been studied, Ni-22Cr-, Ni-25Cr-, Co-25Cr-, and NiCo-25Cr-based chemistries. The corrosion resistance of the different coating compositions were investigated under simulated biomass exposure conditions at 550 °C for 500 h, with and without molten salts to simulate a waste-burning combustion environment. Results include the measurement of total weight change kinetics, the measure of metal loss, and the characterization of corrosion products, including phase, microstructure, composition, and the penetration of corrosive elements.

2. Experimental Section

2.1 Sample Preparation

In this study, four different cored wires Ni-22Cr, Ni-25Cr, Co-25Cr, and NiCo-25Cr were used to deposit coatings,

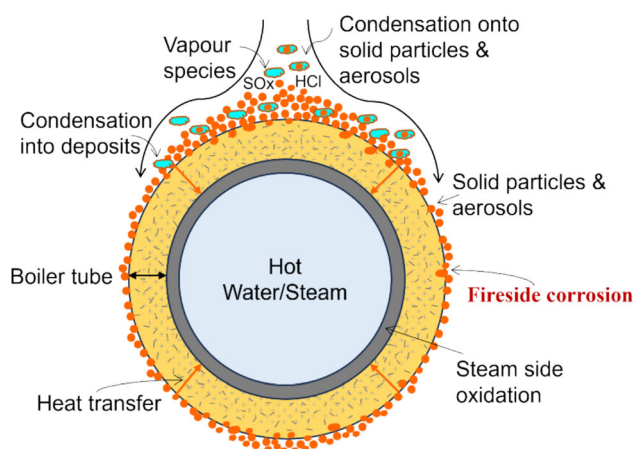


Fig. 1 Schematic presenting corrosion attack on a boiler tube

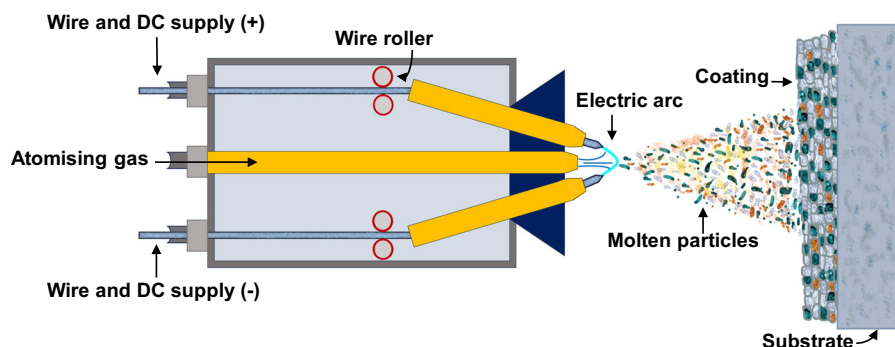


Fig. 2 Schematic illustration of twin wire arc spray coating mechanism

through a twin wire arc spray (TWAS), as illustrated in Fig. 2. This technique can generate a composite layer with tailored chemical, mechanical, and thermal properties by integrating the various materials. The coatings were applied onto a grit-blasted E-250 substrate, which is a steel grade that could be used in different engineering applications due to ease of fabrication, as specified in Table 1. The coated plates were initially prepared as flat sheets measuring 150 mm x 150 mm, and approximately 6 mm thick.

Post spraying, these plates were cut into square specimens, each measuring $\sim 15 \times \sim 15$ mm with an overall thickness of ~ 6 mm.

2.2 Fireside Corrosion Exposure Conditions

Given the complex operating conditions for boilers in WtE power plants, a well-controlled, laboratory-scale, high temperature corrosion test was designed and conducted to understand the effects of variables such as time, temperature, gas phase, and deposit chemistries on the corrosion process. An alumina-lined vertical tube furnace (Fig. 3) was used to carry-out the fireside corrosion tests in a controlled atmosphere for 500 h exposure.

Samples were ultrasonically cleaned in acetone, followed by isopropanol alcohol (IPA), for 20 minutes each, before applying the salt deposits (Ref 20). Dimensional metrology of all cleaned samples was performed using digital microscopy ($\pm 1 \mu\text{m}$ resolution) before exposure. A deposit mixture (KCl + K_2SO_4 in a 50:50 wt.%) was prepared in IPA and applied using the pipette method, as shown in Fig. 4, to achieve an approximate 25 mg/cm² coverage. The samples were then placed on a hot plate at 100 °C for 10 minutes to ensure the complete evaporation of the IPA. All the samples (see Table 2) were placed in individual alumina crucibles and then set into the furnace at 550 °C. Temperature and gas composition were controlled, with gases supplied via mass flow controllers to achieve a specific gas composition, as specified in Table 3. Each test cycle involved multiple salt applications, reapplying the salt deposit every 100 h of sample exposure. This setup aimed to simulate real waste firing conditions, accelerating fireside corrosion processes through higher deposit deposition fluxes. Deposit-free (bare) samples were also exposed to set a baseline for assessing the corrosion damage, using dimensional metrology (Ref 21). The weight of each sample was monitored, before and after each cycle, to assess the sample's performance and detect spalling.

Table 1 Nominal composition of E-250 steel grade

Commercial name	C	Mn	P	S	Fe
E-250 (wt.%)	0.14-0.20	0.60-0.90	≤ 0.04	≤ 0.05	Bal.

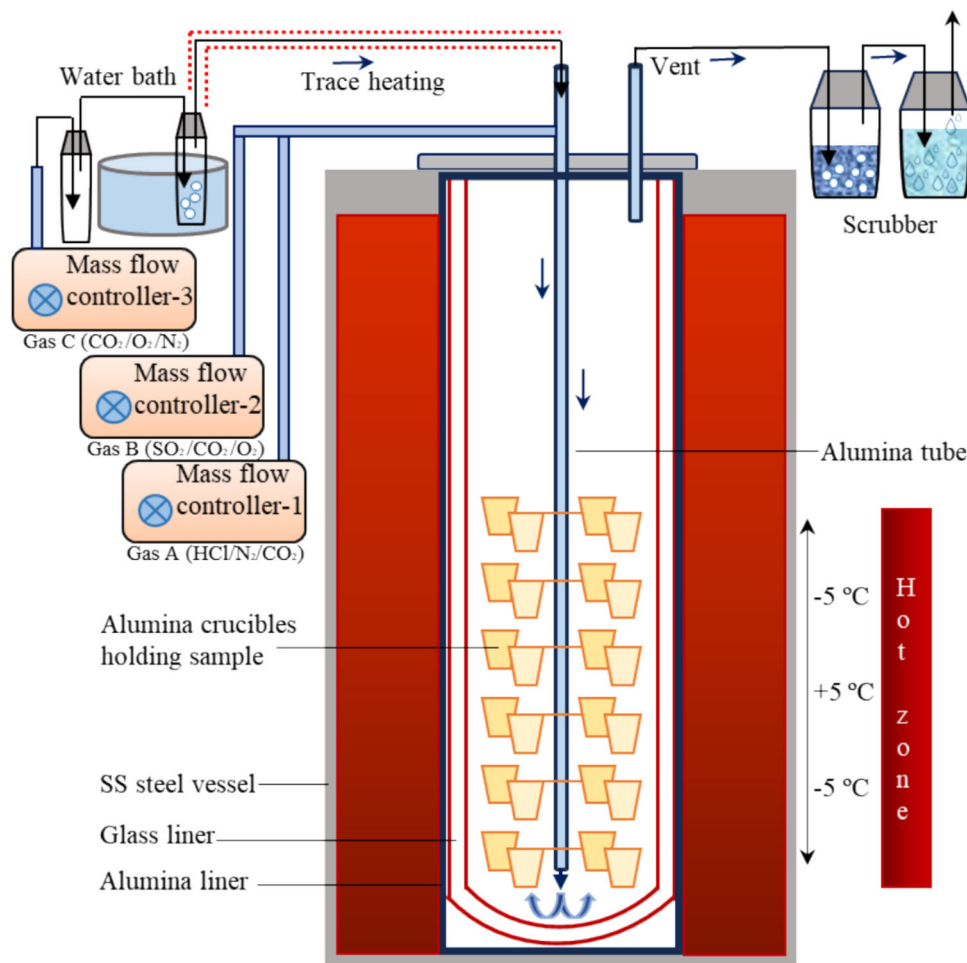


Fig. 3 Schematic of fireside corrosion rig

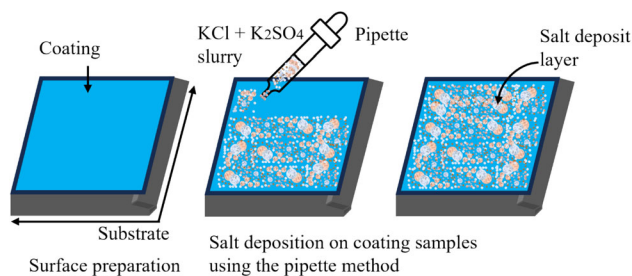


Fig. 4 The illustration represents the application of salt deposit mixture on coating sample using the pipette method

2.3 Pre and Post-Corrosion Characterization

Characterization after 500 h exposure included multiple analytical techniques to analyze corrosion products, microstructures, and coatings loss. The coatings' cross-sectional

microstructures were examined using TESCAN VEGA3 scanning electron microscopy (SEM) equipped with a backscattered electron (BSE) detector, operating at an accelerating voltage of 20 kV (Ref 20). Elemental composition for scale growth process analysis was performed using energy-dispersive x-ray spectroscopy (EDX) maps. The phase identification of the coatings was conducted using x-ray diffraction (XRD) with Cu K α radiation (wavelength: 1.54 Å) at an applied voltage of 40 kV. Coating thickness was measured with digital microscopy (Keyence VHX-7000). For XRD analysis, the sample size was 15 × 15 mm, while those for SEM-EDX, and dimensional metrology (DM) characterization were further sectioned, cold-mounted in low shrinkage epoxy resin, polished up to 1 μm diamond suspension in an oil-based system, and coated with 10 nm of gold for increased conductivity for SEM.

Dimensional metrology was applied to generate probabilistic models of coating damage for each exposed sample. Twenty-four data points were collected around the border of

Table 2 Details of sample identification codes alongside exposure time and temperature used for fireside exposure

Code	Coatings	Salt	Exposure time, h	Temperature, °C
1a	Ni-22Cr	No Salt	500	550
1b	Ni-22Cr	KCl-K ₂ SO ₄		
2a	Ni-25Cr	No Salt		
2b	Ni-25Cr	KCl-K ₂ SO ₄		
3a	Co-25Cr	No Salt		
3b	Co-25Cr	KCl-K ₂ SO ₄		
4a	NiCo-25Cr	No Salt		
4b	NiCo-25Cr	KCl-K ₂ SO ₄		

Table 3 Nominal gas composition used to simulate WtE environment

Gas Composition	CO ₂	O ₂	H ₂ O	SO ₂	HCl	N ₂
	13%.vol	4.0%.vol	13%.vol	200 vppm	400 vppm	Bal.

exposed coating samples using a microscope. Thickness measurements were taken along the border of metal loss. These readings were compared to pre-exposure data to evaluate coating performance.

3. Results and Discussion

3.1 Characterization of as-Deposited Coatings

The morphologies of as-deposited coatings (Ni-22Cr, Ni-25Cr, Co-25Cr, NiCo-25Cr) are shown in Fig. 5. Original coatings had irregular lamellar structures. Ni-22Cr, and Ni-25Cr coatings had similar composition except additional percentage of Fe and Cr in coating 2. It is worth noting that the Mo content was 2-4% in the coatings, which was less than the added Mo proportion (5-9%). One possible explanation was that fine Mo particles in the wires were easy to be carried away by the gas flow during thermal spraying, resulting in the lower Mo content in the deposited coatings (Ref 22). In all four coatings, the dispersion of alloying elements was uniform inside the coatings. However, the porosity level appeared to differ. The Co-25Cr, and NiCo-25Cr coatings exhibited higher porosity compared to the other two coatings, which could facilitate the ingress of corrosive deposits and gases, potentially reducing their corrosion resistance under fireside conditions. The average thickness measured through Keyence microscopy at 24 random positions in the cross-section images is 550 ± 2 , 580 ± 2 , 600 ± 2 , and 300 ± 2 μm for Ni-22Cr, Ni-25Cr, Co-25Cr, and NiCo-25Cr, respectively.

3.2 Mass Change Data

Figure 6 illustrates the mass change data of all four coatings covered with KCl and K₂SO₄ (1b, 2b, 3b, 4b) and bare samples (1a, 2a, 3a, 4a) at 550 °C for 500 h.

All four bare coating samples exhibited very little mass change compared to samples covered with corrosive salt deposits. The mass change data for sample 1b, covered with KCl and K₂SO₄ exhibit very little mass change. 4b showed the

highest mass loss value of ~ 190 mg/cm² after 500 h of exposure. However, 2b and 3b showed a very similar trend of mass change values. It was also evident that cycling of corrosion testing resulted in loosening oxide scales eventually spalling off from the substrate surface (E-250) as shown in irregular mass change data trends in Fig. 6. Spalling of an oxide layer suggested an acceleration in the corrosion process as evidenced in the downward trend for coated samples with corrosive salts.

3.3 Optical Image Analysis

All four coatings were observed under the optical microscope after fireside corrosion exposure test. Images presented in Fig. 7 and 8 show that all salt deposit coating samples, and bare samples (exposed to the gas phase only), sustained little damage to the surface of the samples. However, the surface of 2a and 2b samples showed less degradation compared to the other three coatings. The metal loss of both 2b and 3b showed a similar morphology at the gas-deposit interface, whereas 1b and 4b showed a consistent internal layer, suggesting internal damage around the specimen.

At 550 °C, a fine layer of corrosion products is formed on the surface of coatings 1b, 3b, and 4b. Coating 1b and 4b also exhibit typical pitting corrosion behavior, where the outer corrosion boundaries are marked by metal loss and the internal pits indicate the extent of sound metal loss. The degradation mechanisms at 550 °C are characterized by the gradual spalling of the oxide layers from the coating surfaces, resulting in irregular mass changes, as plotted in Fig. 6. Spalling of an oxide layer accelerates the corrosion process as evidenced in the curves; however, after the formation of a new layer, the mass change rate starts decreasing again.

3.4 Dimensional Metrology

The dimensional metrology analysis can be used to quantify the corrosion resistance of different coating materials by providing metal loss statistical distributions for each coating. The coating loss/probability plot (Fig. 9) demonstrates the

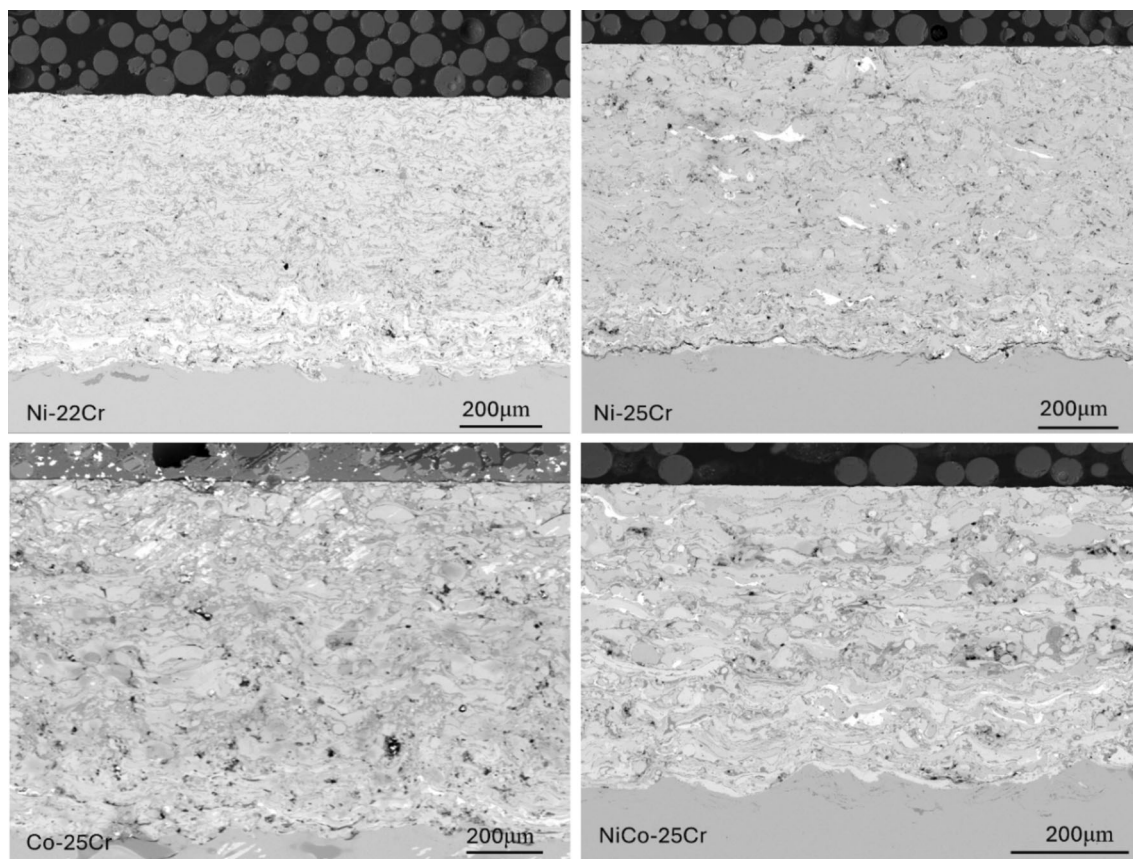


Fig. 5 Morphology of coatings: Ni-22Cr, Ni-25Cr, Co-25Cr, NiCo-25Cr

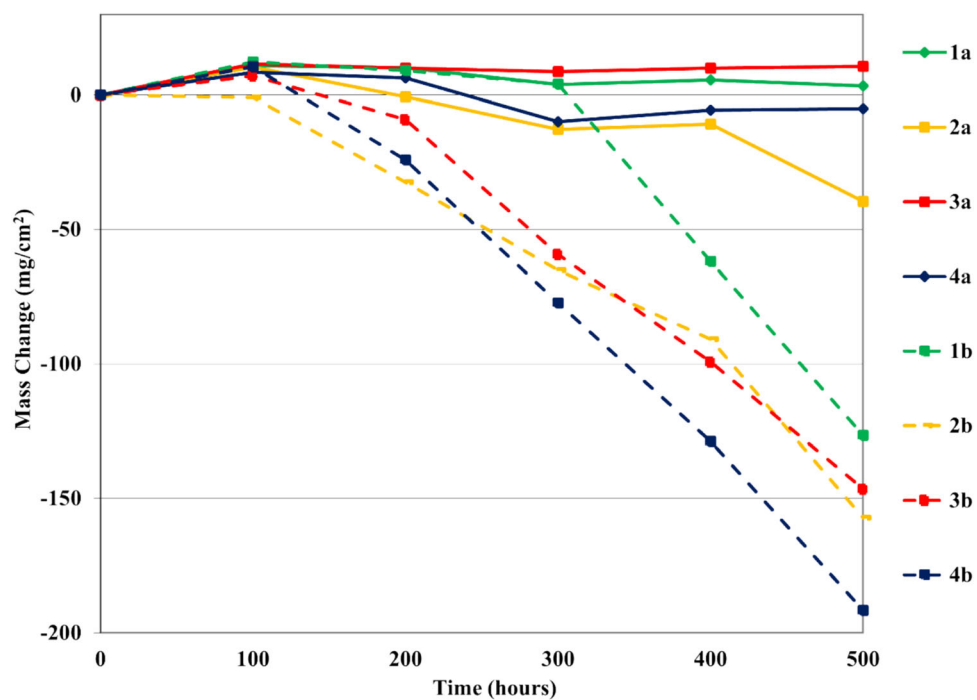


Fig. 6 Mass change data of bare (solid lines) and salt-deposited (dashed lines) samples exposed to WtE boilers environment at 550 °C for 500 h

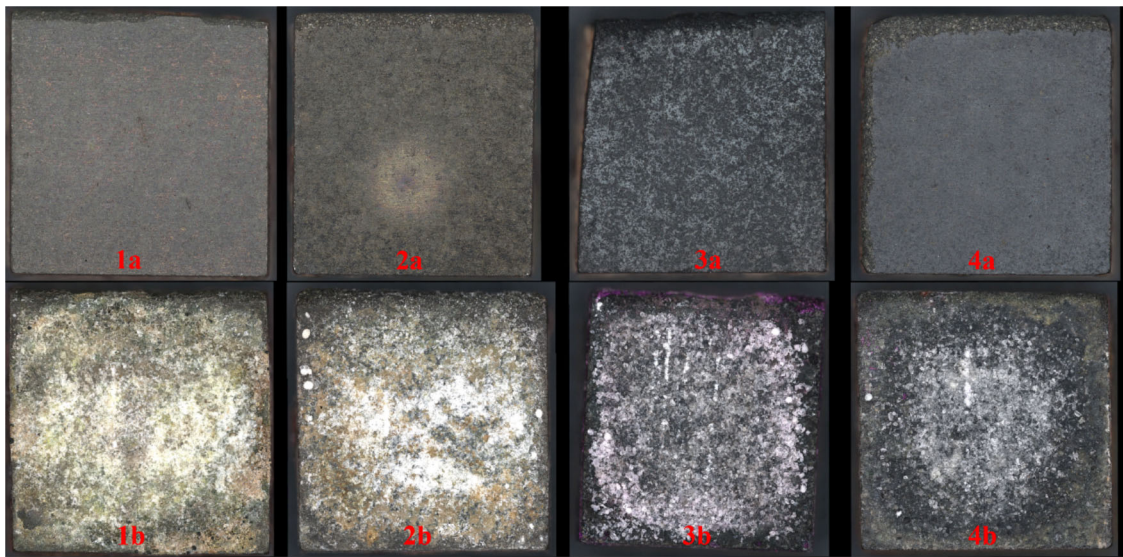


Fig. 7 Optical microscopy images from the surface of bare and salt-deposited samples exposed to WtE environment at 550 °C for 500 h

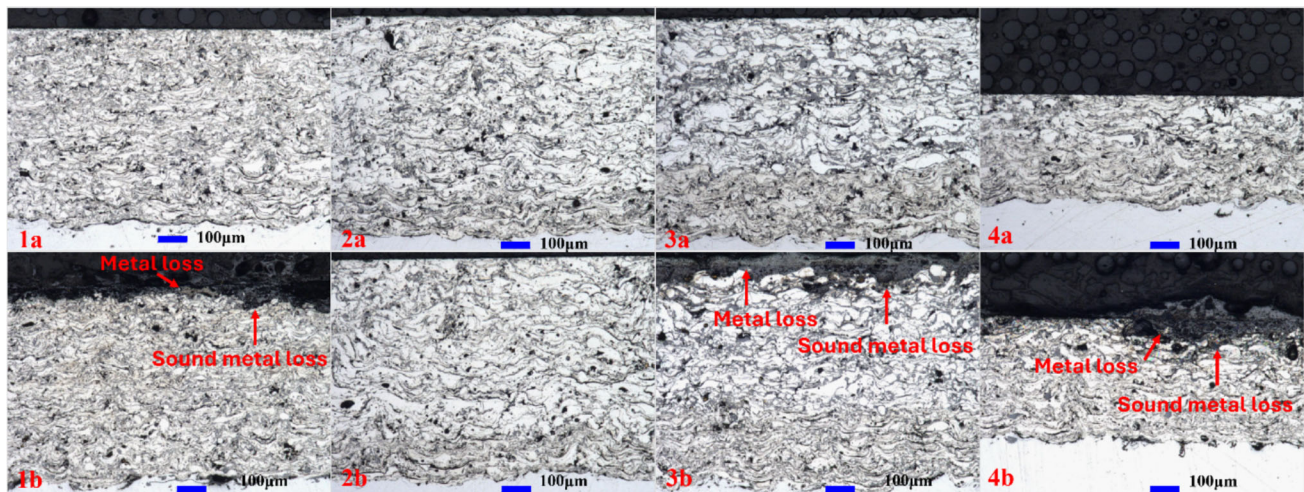


Fig. 8 Optical microscopy images of cross sections of bare and salt-deposited samples exposed to WtE environment at 550 °C for 500 h

extent and risk of damage observed on exposed coated specimens.

Figure 9 depicts the distribution of corrosion damage for bare coating samples (1a, 2a, 3a, 4a), and salted coating samples (1b, 2b, 3b, 4b) exposed to simulated solid waste combustion gases at 550 °C. It is observed that coating 2b experienced significantly less corrosion damage compared to coatings 1b, 3b, and 4b after 500 h of exposure. However, the median coating loss for coating 2b was approximately $\sim 48 \mu\text{m}$, while the median coating loss for coating 1b was notably higher ($\sim 92 \mu\text{m}$). The greatest median coating loss was recorded for coatings 3b and 4b at $\sim 124 \mu\text{m}$.

3.5 SEM-EDX Analysis

SEM-EDX analysis was conducted on two bare coating samples (Fig. 10, 11) and four salt-deposited coating samples (Fig. 12, 13, 14, 15) to evaluate the effect of corrosive salt deposited on coatings performance. It was observed that potassium was concentrated in outer regions of the oxide scale

in all four salt-deposited coating, indicating that K did not diffuse through the oxide scale. The simultaneous absence of Cl_2 in these regions suggests that Cl_2 is no longer present as potassium chloride. It is believed that KCl released Cl_2 , which subsequently reacted with hydrogen in the environment to form HCl, and is evaporated.

The EDX analysis on Ni-22Cr coating, Fig. 12 presents a BSE image and EDX maps for the Ni-22Cr coating. A dense deposit layer was noticed on the surface of the coating. The EDX maps revealed that the outer layer of scale is likely to be a nickel oxide rich non-protective oxide, with only minimal Cr presence. In contrast, the inner layer had a significantly thick chromium oxide. Additionally, chlorine penetration is observed near the coating–substrate interface. Oxygen is found to form a layered structure in the outer regions and is present throughout the cross section. It is also observed that potassium is dispersed across the entire outer surface and concentrates above the chromia layer, sulfur is also present in the same region likely to be in the form of potassium sulfate (Ref 23, 24), (one of the deposits).

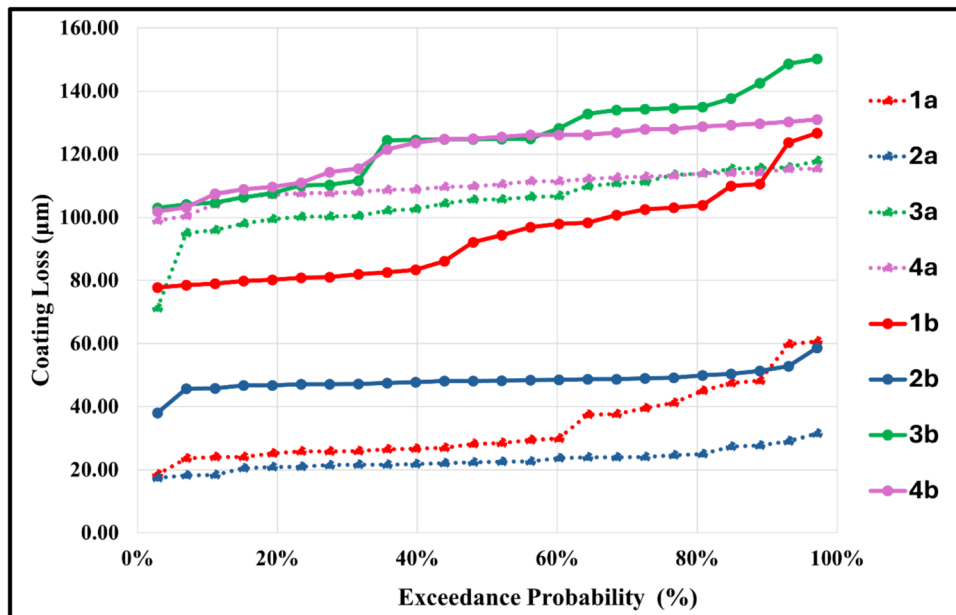


Fig. 9 Coating loss distribution of bare and salt-deposited samples exposed to WtE environment at 550 °C for 500 h

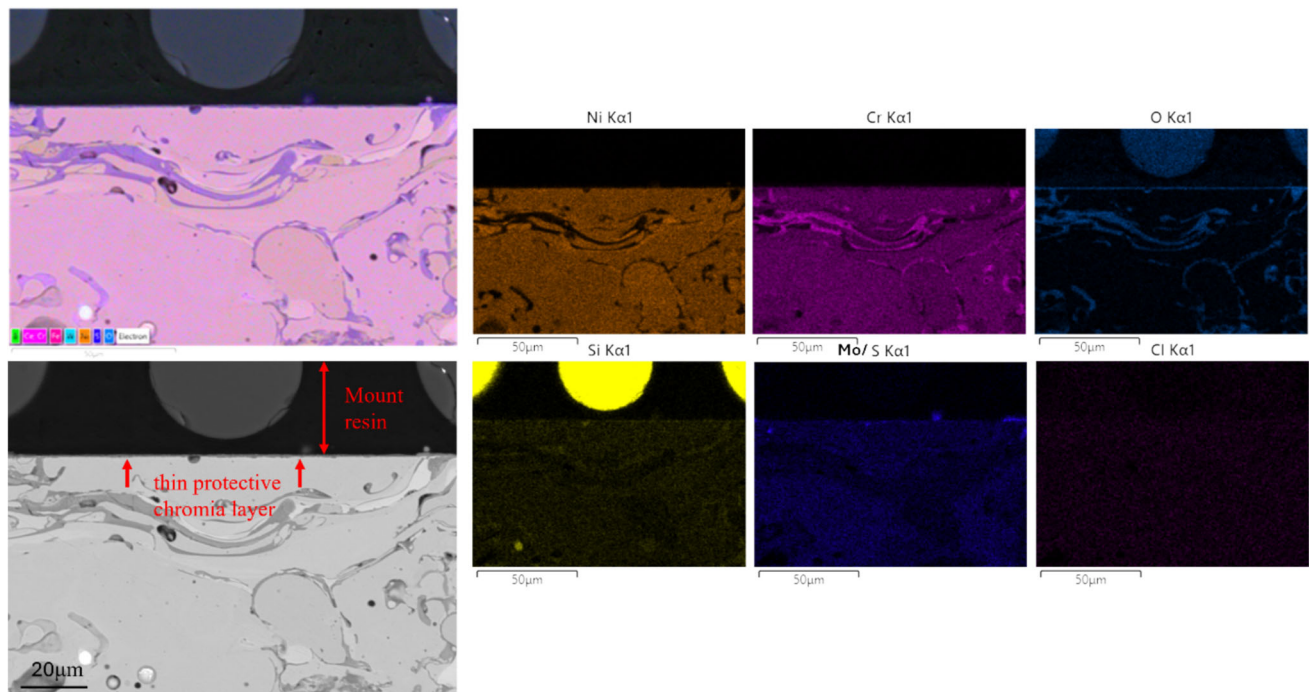


Fig. 10 BSE image and EDX maps on bare Ni-25Cr coating exposed to gaseous atmosphere at 550 °C after 500 h exposure

Another phenomenon noticed in all coatings (Fig. 12, 13, 14, 15) is the formation of metal chloride complexes, which may have facilitated the formation of Ni and Co oxides in the coatings at the gas-scale interface (Ref 23, 25). This process is typically associated with the formation of pits (which can be seen in (Fig. 12, 15), and potassium and nickel-rich areas. The pits in these two coatings may indicate that the corrosion process is in its early stage. Additionally, regions rich in Ni, Co, K, O, and S have been observed, this possibly due to the formation of alkali metal tri-sulfates, as documented in the literature (Ref 23). These regions also show a depletion of Ni

(Fig. 12, 15) and Co (Fig. 14) relative to the bulk coatings, corresponding to areas of internal corrosion.

In Fig. 13, when looking in greater detail at the internal corrosion regions, it is evident that these regions are characterized by grain boundaries. The EDX maps in Fig. 12 reveal that these internal layers of Cr formed bonds with O at various boundaries, leading to the formation of protective oxides and depletion of Ni in these regions. Additionally, it appears that there are some traces of Cl just below the surface of the coating.

Ni-oxide and Co-oxide were observed in the corrosion scale (in Fig. 12, 14, 15). However, EDX analyses detected chlorine

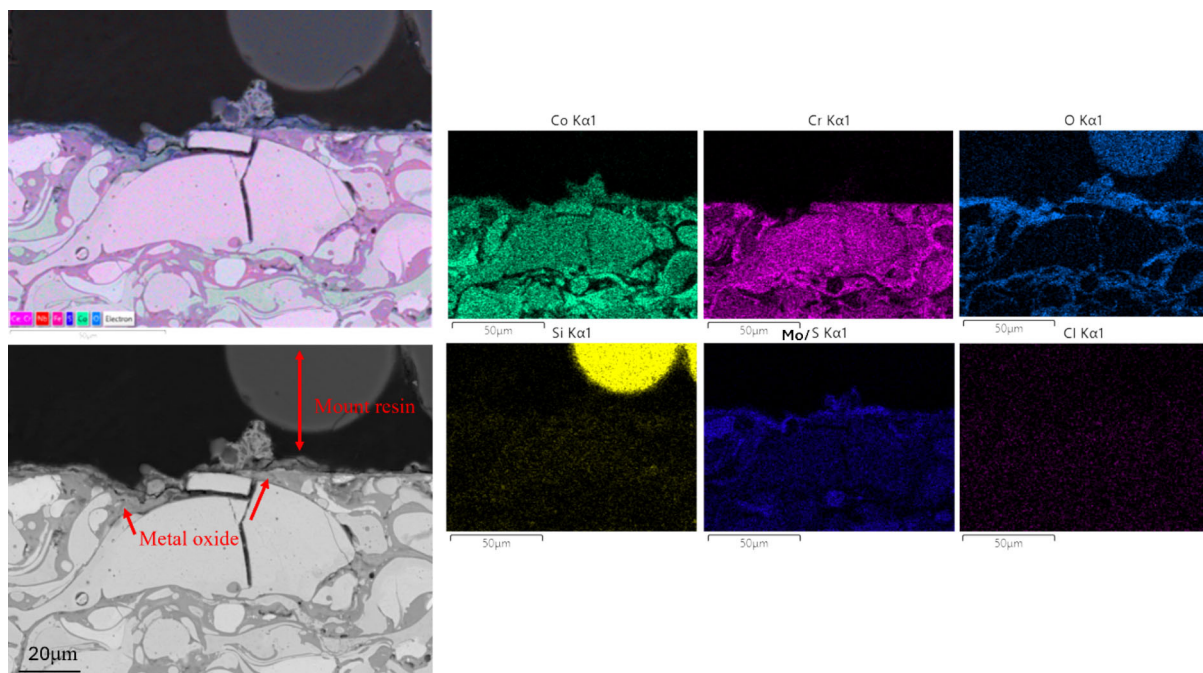


Fig. 11 BSE image and EDX maps on bare Co-25Cr coating exposed to gaseous atmosphere at 550 °C after 500 h exposure

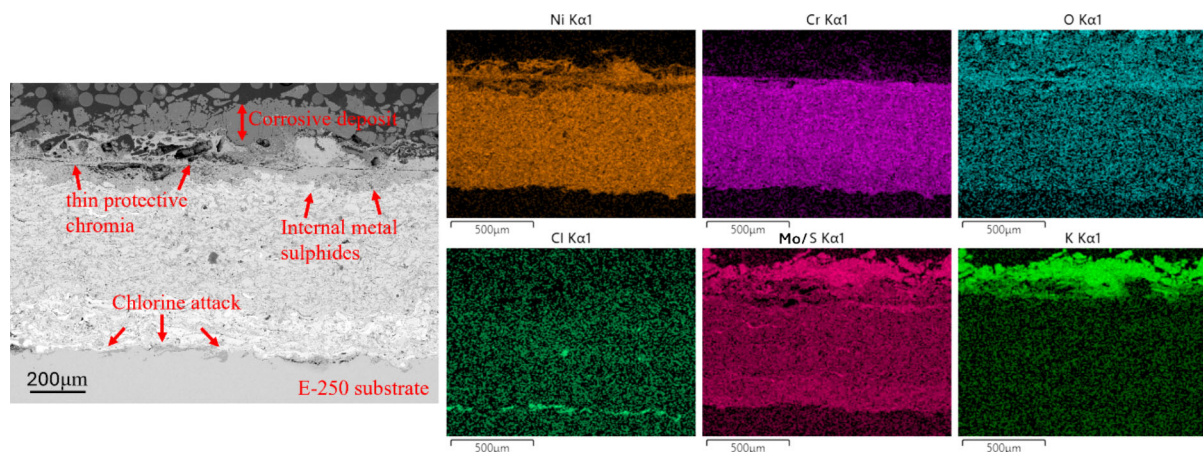


Fig. 12 BSE image and EDX maps on salt-deposited Ni-22Cr coating exposed to WtE environment at 550 °C after 500 h exposure

penetration in all coatings, suggesting the formation of nickel chloride and cobalt chloride, which eventually converted to oxides. At given conditions, a well-adherent corrosion scale can be seen in Ni-22Cr, Co-25Cr, and NiCo-25Cr coatings which mainly consist of Ni-oxide (Fig. 12, 13, 14, 15) and Co-oxide (Fig. 14), with minimal chlorine content. The surface morphology of these scales can be noticed in EDX maps presented in Fig. 12, 14, and 15. In Fig. 13, the EDX analysis confirmed the formation of chromia and silica, on the outer layer and grain boundaries of Ni-25Cr coating, indicating the development of slowly growing protective oxide (Cr_2O_3 & SiO_2) scales. These protective scales prevented further Cl penetration into the coating making the system more corrosion resistant at 550 °C under specific waste-burning conditions.

Figure 14 presents the BSE image and EDX maps of the salt-deposited cobalt-based coating (Co-25Cr). The BSE image corroborates observations from OM images (Fig. 3b, 8) indicating that deposits remain on the surface of the coating.

According to EDX maps very little Co is being depleted from the outer regions, indicating the formation of cobalt oxide along with the presence of a very thin protective chromia layer on the surface. However, Cl has also been found in these regions as well, which suggests that Cl may have reacted with Co to form Co-Cl complex, which subsequently reacted with oxygen to produce cobalt rich oxides.

In certain regions of Fig. 12, 14, and 15, the formation of volatile metal oxide has been observed in the upper layer at metal-oxide interface. These metal oxides are produced as volatile metal chlorides evaporate, diffuse outward, and subsequently convert into oxides in areas with greater oxygen partial pressure.

In general, Ni-22Cr coating (Fig. 12) had a higher pitting corrosion effect across its surface due to chlorine attack, in comparison to Co-25Cr, and NiCo-25Cr coatings (Fig. 14, 15). EDX maps of the NiCo-25Cr coating (Fig. 15) showed some regions of high chlorine concentration. This indicates that

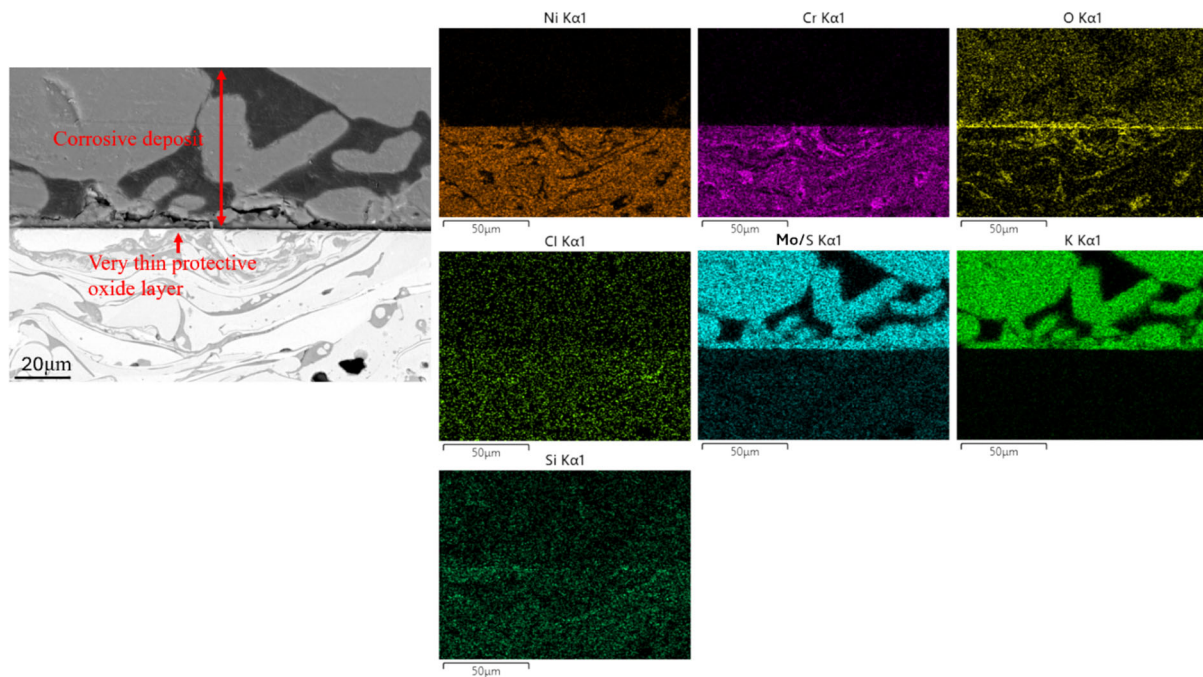


Fig. 13 BSE image and EDX maps on salt-deposited Ni-25Cr coating exposed to WtE environment at 550 °C after 500 h exposure

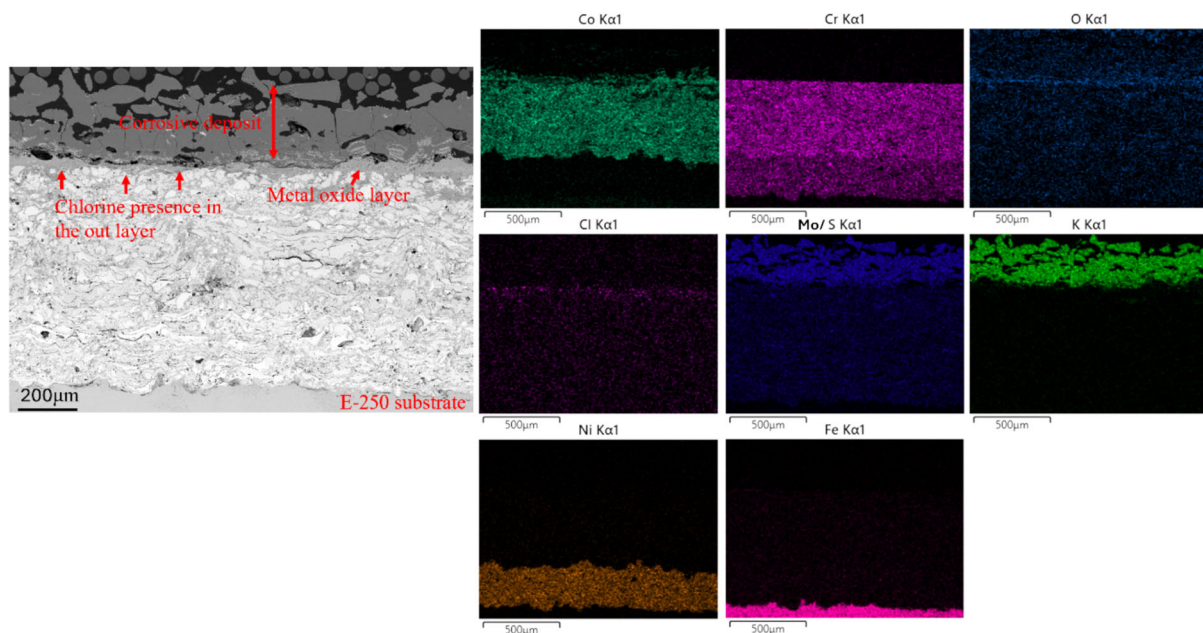


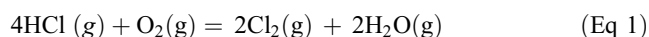
Fig. 14 BSE image and EDX maps on salt-deposited Co-25Cr coating exposed to WtE environment at 550 °C after 500 h exposure

chlorine has migrated from the deposits to the coating surface. Above this region, the presence of Ni, Co, and O indicates the conversion of nickel chloride and cobalt chloride into oxides due to thermodynamic more stable scales in high partial pressure of oxygen. Additionally, EDX maps confirmed that all coatings have a thick layer of K_2SO_4 as a deposit.

3.6 Analysis of Corrosion Products

Chlorine is the primary aggressive element in corrosion, particularly during short exposure periods. Although the equilibrium described in Eq 1 is build up by a slow rate in

the gas phase, the presence of metal oxides catalyses the reaction. In an oxidizing environment, chlorine is produced from HCl (Ref 26) through the following reaction:



The partial pressure of oxygen and chlorine determines the thermodynamic stability of metal oxides and chlorides at a specific temperature. The equilibrium conditions for the atmospheres containing 4 vol.% O_2 and 400 vppm HCl are indicated in Fig. 13(a), (b), and (c), which presents thermodynamic phase stability curves for different systems Ni- O_2 - Cl_2 ,

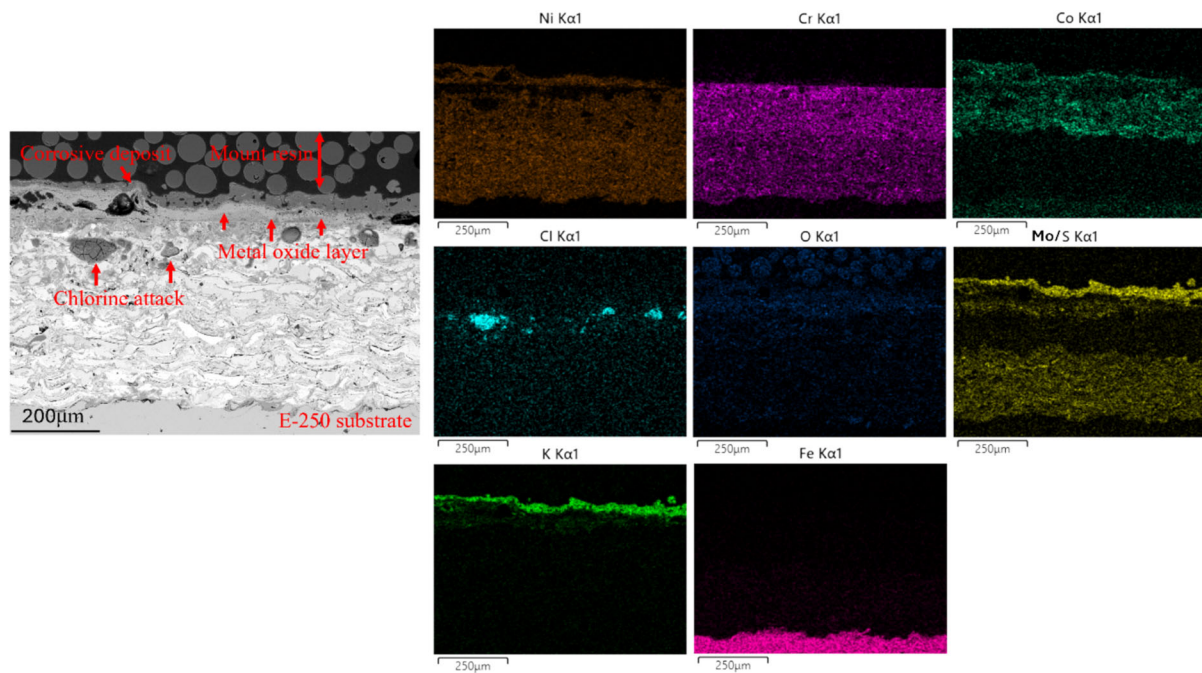
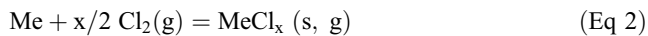


Fig. 15 BSE image and EDX maps on salt-deposited NiCo-25Cr coating exposed to WtE environment at 550 °C after 500 h exposure

Cr-O₂-Cl₂, and Co-O₂-Cl₂ at 550 °C. Under the given experimental atmospheric conditions, oxides are thermodynamically stable phases. However, at the metal-oxide interface, the partial pressure of oxygen decreases leading to the stabilization of metal chlorides (Ref 26, 27). Depending on the specific metal elements, various volatile compounds (solid and gaseous chlorides) may form at this interface, as described in Eq 2 (Fig. 16).



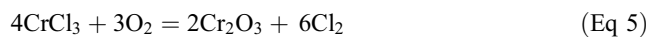
A difference of Gibbs free energy of formation for various divalent chlorides are compared at 600 °C, and CrCl₂ has the most negative value, followed by CoCl₂ and NiCl₂ (CrCl₂—286.0 kJ/mol; CoCl₂—220.0 kJ/mol; NiCl₂—174.0 kJ/mol). These findings suggest that nickel should behave less reactively than cobalt and chromium (Ref 28-30). The resulting solid chlorides have a high equilibrium vapor pressure $P_v(\text{Me}_x\text{Cl}_y)$ and undergo continuous evaporation as described by:



Regarding phase analysis by XRD, Fig. 17(A) and (B) shows displacement of the phase analysis of the coating surfaces after fireside corrosion exposure. On the outermost surface of coatings 1, 2, and 4(1a, 2a, 4a), characteristic peaks of Ni-oxide at 37.2°, 43.3°, and 75.3° were clearly detected, indicating that Ni-oxides were the main corrosion substance on these coatings. In contrast, the XRD pattern of coating 3 (3a) differs from other three coatings, showing cobalt oxide characteristics peaks at 22.7°, 33.4°, 36.9°, 48.7°, and 65.7°. It is important to note that although despite the use of mixed alkali metal salts as corrosive agents in fireside corrosion experiment, the primary corrosion products were oxides.

3.7 Corrosion Resistance Nature of Coating

Since SEM-EDX, XRD, and dimensional metrology can only assess coating performance before and after fireside corrosion exposure, the actual corrosion mechanism and the extent of corrosion resistance can only be inferred. Fireside corrosion primarily originates from the penetration of corrosive elements and the adherence of molten deposits, against which coatings provide a protection barrier. Protection is achieved through the growth of dense oxide layers, including Cr₂O₃, NiO, and CoO. According to Kawahara (Ref 31), the degree of deposit penetration decreases in the order of Fe₂O₃ > Cr₂O₃ > SiO₂. Additionally, it was observed that both coating thickness reduction and the penetration depth of molten salts decreased with increasing Cr content. Therefore, reinforcing the surface of fireside tubes with multiple oxides in the coating helps to mitigate corrosion caused by the penetration of molten deposits and corrosive gases.



However, the continuous penetration of Cl-containing corrosive species leads to the gradual conversion of Cr₂O₃ into chlorides, as described in Eq 4. The accumulation of molten salts on the coating surface generates additional Cl₂, which accelerates the corrosion process. Moreover, Cl₂ is also produced through the oxidation of chlorides, as summarized in Eq 5. These reactions promote the formation of cracks and defects due to the oxidation and chlorination of coating elements, leading to corrosion layer formation and coating thickness loss. Although the coating does not fully prevent corrosion, it effectively mitigates the corrosion process by making a protective barrier film.

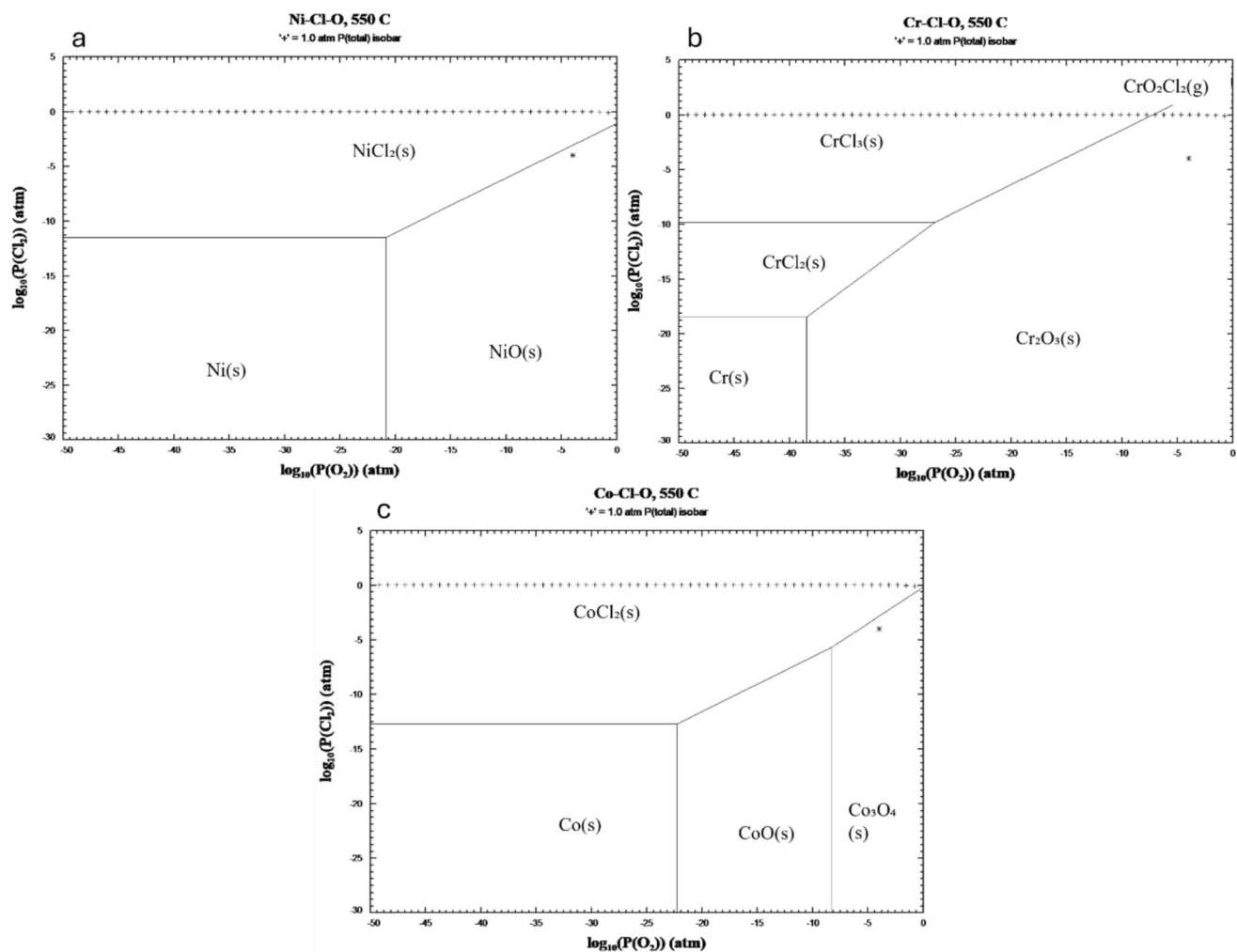


Fig. 16 Thermodynamic stability diagrams of Ni-O₂-Cl₂, Cr-O₂-Cl₂, and Co-O₂-Cl₂ at 550 °C

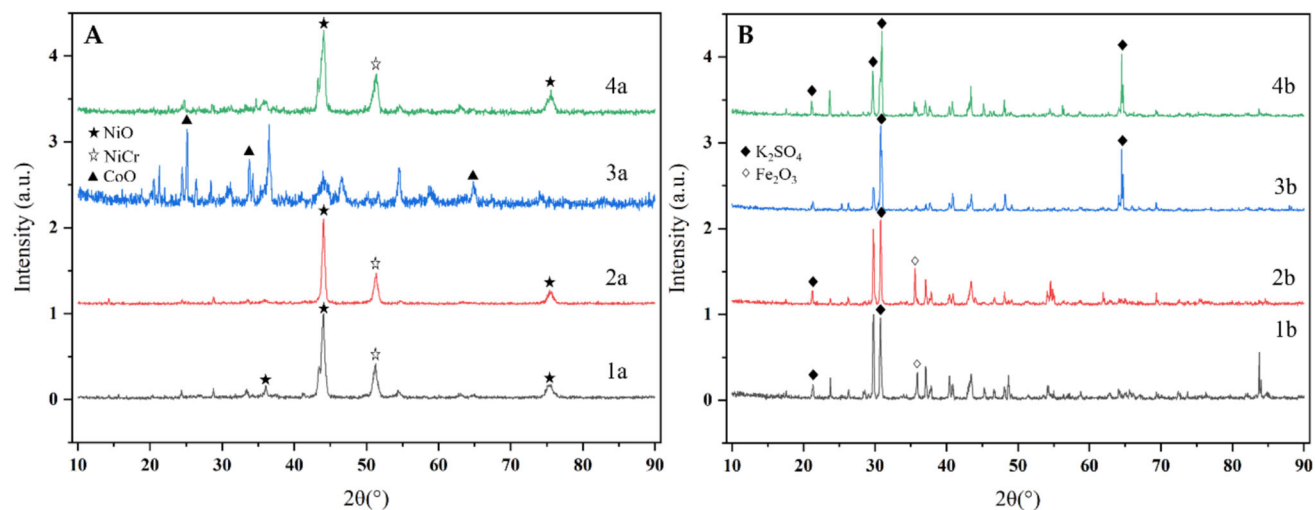


Fig. 17 XRD analysis of Ni-22Cr, Ni-25Cr, Co-25Cr, and NiCo-25Cr coating samples exposed to corrosive gases simulate WtE boilers fireside corrosion conditions at 550C for 500 h: (A) bare samples; (B) covered with salt deposits (KCl- K₂SO₄)

4. Conclusion

This study has investigated the fireside corrosion behavior of four distinct coatings (Ni-22Cr, Ni-25Cr, Co-25Cr, and NiCo-25Cr) applied on an E-250 steel substrate using the TWAS technique. All coating were exposed to simulated waste-burning conditions at 550 °C for 500 h using a deposit re-coat method. The deposits used in this study were composed of KCl and K₂SO₄. The coating samples were analyzed using optical microscopy, dimensional metrology, SEM, EDX, and XRD. Additionally, some thermodynamic calculations were performed to evaluate the mixed scales and corrosive deposits formation under specific conditions. The results reported indicate that all four different combinations experienced distinct corrosion behaviors, leading to varying levels of internal corrosion attack.

- Ni-22Cr, Co-25Cr, and Ni-25CrCo coatings were unable to prevent the diffusion of corrosive elements (Cl, S) through the coating thickness of approx. 500 microns at 550 °C.
- From SEM-EDX analyses, it has been noted that Ni-22Cr, Co-25Cr, and NiCo-25Cr coatings exhibited internal corrosion along the surface. Few areas in Ni-22Cr coating were characterized by depletion of Ni and both Ni, Co in NiCo-25Cr coating, showing the typical “pitting corrosion behavior”. However, Ni-22Cr and NiCo-25Cr coatings presented similar pitting behavior with more prominent corrosion pits on the Ni-22Cr coating’s surface. This might have contributed to the depletion of nickel oxide layer on the surface of both coatings (Ni-22Cr and NiCo-25Cr).
- The slightly improved performance of Co-25Cr and NiCo-25Cr coatings compared to Ni-22Cr coating can be attributed to the ability of Co to prevent corrosive attack.
- Ni-25Cr was the only coating that remained unaffected on the surface of E-250 steel, while the other three suffered similar types of corrosion attacks. A slow-growing and well-adherent protective oxide scale can be seen on the surface of the Ni-25Cr coating, which slows down further chlorine attack, making the coating more corrosion resistant under given conditions.

The best performing coating (Ni-25Cr) had higher Ni and Cr content as compared to other coatings. Whereas the other three coatings have varying amounts of additional alloying elements, they were less effective under given conditions. From EDX maps, it has been revealed that the other three coatings formed relatively fast-growing thick oxide layers, which likely led to spalling of these oxide layers, presenting the repeated exposure of renewed coating surface to corrosive environment.

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