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Fireside corrosion on T24 steel pipes and HVOF NiCr coatings exposed to different salt mixtures

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Abstract

Fireside corrosion of T24 steel and HVOF NiCr-coated counterparts is investigated. The samples were exposed to different deposits of NaCl, KCl, Na₂SO₄ and K₂SO₄ at 650 °C for 360 h in dry air. The deposit with the highest chloride content (NaCl-KCl) was the most aggressive followed by the ones combining chlorides and sulfates. In contrast, the sulfate-based salts did not produce severe damage. The NiCr coating maintained the integrity of the substrate but the chlorides induced a great attack on the coating. The formation of K₂CrO₄ and the penetration of chlorides are identified as the main factors of this attack.

Keywords: A. Metal coatings; A. Steel; B. SEM; B. XRD; C. High temperature corrosion; C. Hot corrosion

1. INTRODUCTION

Global warming is leading the energy industry to reduce greenhouse gas emissions. In fact, 41% of worldwide CO₂ emissions are derived from electricity and heat production [1]. For this reason, the replacement of conventional fossil fuels by renewable sources

including biomass is continuously growing. Biomass is considered carbon-neutral and it is expected that its use will take the lead over pulverized coal-fired power plants [2]. Co-firing low amounts of biomass has proved to be a successful way to introduce carbon-neutral fuels. Further reductions in CO₂ emissions can be achieved increasing the efficiency of co-firing power plants by working at higher temperatures and pressures. Conventional power generation plants operate at an efficiency of 36%, however, an increase of 1% in the efficiency can produce a reduction of 3% in CO₂ emissions [3]. Therefore, it is expected that working temperatures will be in excess of 650 °C and the presence of biomass in co-firing power plants will be increased [4]. One of the most limiting factors in increasing the efficiency of power plants is the availability of materials to withstand these aggressive conditions [5]. This would require the substitution of conventional ferritic steels used so far by more expensive materials, such as Ni-base alloys, whose price can be up to 10 times higher [6].

In the particular case of biomass in co-firing power plants, the surface of the materials can be exposed to different salts deposits of various compositions. The continuous change in the deposit chemistry can modify the corrosion mechanisms [7,8]. Therefore, the boiler environments become more aggressive than using only coal as fuel. For heat exchanger pipes, fireside corrosion can be a critical life-limiting factor. Metal-loss due to chemical reactions can lead to pipe failure through metal-loss itself or cracks formation. The extent of the attack by fireside corrosion mainly depends on the exposure temperatures and the composition of the deposits.

An alternative to reduce material costs is the use of Ni-based alloys as protective coatings on conventional ferritic steel substrates [9]. In this context, Ni-based coatings could be just as effective as bulk Ni-based alloys as long as the coating is dense, compact and completely adhered to the substrate. The use of advanced deposition techniques such as

high velocity oxy-fuel (HVOF) becomes essential to obtain these coating properties. This technique also provides low porosity and a high degree of compaction of the metallic powders due to the high spraying velocities [10]. Moreover, the low exposure time of the metallic powders to flame produces coatings with a low oxide content. This prevents the presence of cracks and defects and facilitates the anchoring of the particles to the substrate [11,12].

Despite the growing number of works on fireside corrosion in biomass-like environments as those of Uusitalo et al. [13–15], who pioneered the studies on active chlorine corrosion in HVOF coatings in chlorine containing environments, the role of the salts on the degradation mechanisms is not fully understood. Li et al. [16] investigated the hot corrosion behavior of different Fe-Cr rich alloys with NaCl-KCl deposits and found a great reactivity of Cr and Cr_2O_3 with the chlorides. They also found that the corrosion trend was very similar to the behavior caused by individual KCl or NaCl. However, their tests were performed for just 48 h, which often corresponds to the onset of corrosion. Sarvghad et al. [17] demonstrated that the most vulnerable steels are those with the lowest Cr content when exposed to molten NaCl- Na_2SO_4 at 700 °C. Mlonka-Medralla et al. [18] conducted a thorough study where the effect of the composition of the salts deposited on a low-alloyed steel was analyzed. They found that pure KCl was the most aggressive salt at 550 °C but the eutectic KCl- K_2SO_4 mixture was the most aggressive at 600 °C. The authors associated this behavior to the melting point of the ash (774 and 694 °C for pure KCl and eutectic KCl- K_2SO_4 mixture, respectively). However, our work intends to shed light on the degradation mechanisms of both a low alloyed T24 steel and a HVOF Ni20Cr coating as a function of salt composition at 650°C to accelerate degradation. The salt mixtures based on NaCl, KCl, Na_2SO_4 and K_2SO_4 have been selected according to their eutectic point and because were used as standard deposits employed in the studies

described above [16–18]. Metal damage of each substrate-coating-deposit system is quantified by gravimetric measurements and dimensional metrology and the corrosion mechanisms are elucidated with the advent of SEM/EDX and XRD techniques.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Ferritic-martensitic ASTM-SA213-T24 steel pipes (manufactured by Vallourec Co) of 7 mm thickness and 44 mm external diameter were employed as substrate material. The external surface of steel pipes was sandblasted with 1 mm diameter alumina particles to increase surface roughness before the deposition of the Ni20Cr alloy coating by HVOF technique. The optimization of HVOF thermal spray process was performed in a previous study [19].

2.2. Exposure conditions

The uncoated and the coated steel pipes were cut into segments of approximately 5 mm long, and with a 30 mm and 20 mm exterior and interior chord, respectively. These samples were subjected to high temperature corrosion test at 650 °C in a Nabertherm LT 5/12/P330 furnace in air atmosphere for 360 h following the standard ISO/FDIS 17224:2014 for high temperature corrosion tests [20]. Four salt mixtures were deposited to simulate different fireside corrosion environments in the heat exchanger tubes employed in co-fired power plants. The composition of each salt mixture is shown in Table 1. The condition S0 (Salt 0) refers to the isothermal test without any deposit and these S0 samples were used as reference. The composition of the S1, S2 and S3 salts was selected according to their relatively low eutectic point. Further, the S4 salt mixture was selected for being a standard deposit widely employed for screening tests in fireside

corrosion to represent the composition of alkali-iron tri-sulfate [21]. No SO₂/SO₃ was added to the system to underline the effect of the salts solely.

The samples were covered with the different salt mixtures and they were placed in alumina crucibles before thermal testing. The deposit-recoat test method was used and samples were recoated (~15 mg/cm²) every 90 h until 360 h. This method has been used extensively by other authors [22,23].

Table 1 Salt mixtures nomenclature, composition of deposits used in fireside corrosion tests (mol %) and theoretical melting temperatures (°C).

Salt mixture nomenclature	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Fe ₂ O ₃	T _m (°C)
S0	-	-	-	-	-	-
S1	50.6	49.4	-	-	-	657
S2	53.3	-	46.7	-	-	626
S3	-	74	-	26	-	690
S4	-	-	37.5	37.5	25	>650

2.3. Damage analysis

The damage produced by the deposits on T24 steel samples was analyzed by gravimetric tests (evolution of the mass change every 90 h) and dimensional metrology (measuring metal loss). The first method allows us to compare the effect of each deposit with time and it gives a very good indication of oxide delamination. However, this method is not useful for the coated samples because only the external surface was coated. For this reason, dimensional metrology was also employed to quantify metal damage in terms of metal loss distribution. This method has been extensively employed by other authors because it provides a good quantification of the corrosion rate [22]. To perform this analysis, one hundred measurements of samples thickness were done at equidistant distances before and after thermal test. In this manner, the entire cross-section of the sample was assessed. The difference between the initial and final thickness was

considered as metal loss. These measurements were done on cross-section micrographs of the samples using LAS.V4 Leica image analysis software.

2.4. Samples characterization

The microstructural analysis of the cross-sectioned samples was performed before and after high temperature test. These samples were cold-mounted and polished using water-free lubricants and suspensions to avoid the removal of water-soluble salts and corrosion products. The analyses were performed employing a Leica/DMR optical microscope (OM) and a Hitachi S3400N SEM. Semi-quantitative compositional analysis were also carried out using the X-ray dispersive energy (EDX) technique with a Bruker XFlash 5010 detector.

X-ray diffraction (XRD) was also employed to characterize the reaction products presented in samples surface after the corrosion tests. A Panalytical X'Pert PRO diffractometer was employed using monochromatic $K_{\alpha}Cu$ (1.54056 Å) as the radiation source with 45 kV and 40 mA. The diffraction patterns were recorded in an angular interval of 20–90°, with the step of $\Delta(2\theta) = 0.04^\circ$ and time per step of 1 s.

3. RESULTS

3.1. Characterization of the starting materials

Fig. 1 shows a cross-section of the HVOF Ni20Cr coating on a T24 ferritic-martensitic steel. Their full characterization was previously reported in [19]. In essence, the steel has a ferritic-martensitic microstructure with an average grain size of 14 μm while the coating is homogeneous, well adhered to the substrate (29 ± 7 MPa) and fully dense with very low porosity (<1 vol%) and high micro-hardness (460 ± 30 HV_{0.1}). In addition, it shows a low oxide content (4 ± 1 vol%) and presents an average minimum thickness of 260 ± 20 μm [19].

Fig 1 Cross-section micrograph of HVOF Ni20Cr coating on T24 steel [19].

3.2. Measurement of metal damage

3.2.1. Thermogravimetric analysis

Fig. 2(a) shows the mass gain of T24 steel substrate after 360 h of exposure to different salt mixtures. The mass gain increases markedly during the first 90 h and then tends to slow down. One can also observe significant differences as a function of the composition of the salt. Based on the trend of Fig. 2(a), the aggressiveness of the different salt mixtures in T24 steel would follow the sequence $S0 \approx S4 < S2 \approx S3 < S1$. This clearly suggests that the presence of chlorides in the S1, S2 and S3 mixtures significantly increases the corrosion kinetics. In particular, the S1 deposit, which has the highest concentration of chlorides, is the most aggressive (59.6 mg/cm^2) followed by the deposits S3 and S2 (42.7 and 34.1 mg/cm^2 , respectively). Different authors have demonstrated that the presence of chlorides causes severe damage and also accelerates corrosion through a mechanism usually called chlorine-induced “active oxidation” [24–26]. Although during the first steps of isothermal test the Na-containing S2 salt is more aggressive, the trend changes

after 90 h. The K-rich S3 deposit is in contrast more aggressive after 360 h of test. This could be associated with the presence of KCl, which weakens the protective Cr-rich oxide layer through the formation of either potassium chromate K_2CrO_4 or dichromate $K_2Cr_2O_7$. Finally, the deposit S4 produced low corrosion rate, similar to that of reference sample S0. This could be due to two main reasons: (i) the absence of chlorides in S4 deposit and (ii) because it has a melting temperature well above 650 °C. In contrast, the S1, S2 and S3 deposits have chlorides and theoretical melting temperatures of 657, 626 and 690 °C, respectively [16–18]. This means that these deposits partially or totally melted during isothermal tests producing a severe attack. In relation with the S1 and S3 deposits, which have a melting point above 650 °C, Skrifvars et al. [27] showed that corrosion may take place below the melting temperature of the synthetic alkali salt when chlorine was present in their studied salt mixtures.

The effect of the different salt mixtures on the integrity of oxide scale layers and their possible spallation during time is reported in Fig 2(b). After 90 h of exposure, the trend of the curves is very similar to that of Fig. 2(a) because no delamination of the oxide scale occurred irrespective of the salt. However, the oxides start to delaminate beyond 90 h under all tested conditions, but spallation is more drastic on the Cl-containing S1, S2 and S3 deposits. Such enhanced spallation has been previously reported by Habib et al. [28]. They studied the high temperature corrosion behavior of NiCrAlY coatings on AISI 304 stainless steel at 650 and 700 °C using synthetic air + 1% Cl_2 and they suggested that chlorine alters the defect structure of the scale because chloride ions may replace oxygen ions increasing the concentration of cation vacancies. These vacancies precipitate as voids resulting in pitting and spalling of the scale.

Fig 2 Evolution of mass variations of T24 steel substrate with time and salt mixture at 650 °C: (a) mass gain and (b) mass change without the spalled oxides.

3.2.2. Dimensional metrology analysis

Fig. 3(a) shows the metal loss or the equivalent thickness reduction data versus the cumulative probability for each tested sample of T24 steel exposed to different salt mixtures at 650 °C for 360 h. The results indicate more corrosion damage on T24 steel in the presence of chlorides. At the median point (50% cumulative probability), the metal loss is higher in the samples with the deposits S1, S2 and S3 (604, 463 and 483 μm metal loss, respectively) than in S0 and S4 (155 and 189 μm metal loss, respectively). In addition, different trends can be observed in Fig. 3(a). The plots of samples exposed to S0 and S4 deposits are straight and the metal loss values are almost constant. This means that no localized attack was produced. However, the plots of samples exposed to S2 and S3 deposits show that approximately 75 % of the sample underwent severe damage while 25 % of the sample suffered less corrosion attack. Table 2 shows the average metal loss data of T24 steel exposed to the different salt mixtures from which the corrosion damage increases in the sequence $S0 \approx S4 < S2 \approx S3 < S1$. This ranking is the same as the one established from the gravimetric tests, with S1 again as the most aggressive deposit with an average metal loss of 638 μm after 360 h exposure at 650 °C.

Fig 3(b) displays the metal loss (in μm) versus the cumulative probability (in %) of NiCr coatings exposed to the same salt mixtures for 360 h. A huge reduction of the damage in the parent material was achieved compared to the uncoated one (Fig. 3(a)). However, the coatings themselves underwent severe damage in some conditions, as will be shown later by SEM. The highest attack occurs again in the presence of chlorides (Table 2) but no marked difference between the Cl-containing S1, S2 and S3 deposits can be made.

Fig 3 Measurement of metal loss (μm) vs cumulative probability (%) showing the behavior of (a) T24 steel substrate and (b) NiCr coating exposed to different salt mixtures at 650 °C for 360 h.

Table 2 Comparison of the average metal loss (μm) of T24 steel and NiCr coatings after their exposure to different salt mixtures.

Sample / Salt	S0	S1	S2	S3	S4
T24	169	638	424	431	185
NiCr coating	23	92	107	80	27

3.3. XRD analysis after the corrosion tests

Fig. 4(a) shows the main characteristic peaks of the steel substrate after exposure to the different deposits at 650°C for 360 h. The S0 sample without any deposit shows the characteristic peaks of ferritic steel ($\alpha\text{-Fe}$) and two iron oxides, mainly hematite (Fe_2O_3) and magnetite (Fe_3O_4). The peaks of $\alpha\text{-Fe}$ disappeared when the steel was exposed to the

different salts. The X-ray pattern of the samples exposed to the S1 deposit displays the peaks of salt mixtures (NaCl and KCl), of iron oxides (Fe_2O_3 and Fe_3O_4) and of sodium ferrite ($NaFeO_2$). The latter has been described by Soleimani et al. [29] as a typical corrosion product in molten salts. In our case, $NaFeO_2$ could form from reaction between NaCl and Fe_2O_3 under oxidizing conditions according to Equation (1). Sodium ferrite is also accompanied by the formation of $Cl_{2(g)}$ [17,30]. Therefore, the dominant corrosion mechanism involves (i) the initial production of chlorides, (ii) their subsequent diffusion through metal oxide layer and their reaction with the metal according to Equation (2) and (iii) the formation of volatile metal chlorides such as $FeCl_2$ at the substrate/oxide layer interface, Equation (3).

Otherwise, the X-ray patterns of the samples exposed to S2 and S4 deposits did not provide any additional information other than the presence of the salt mixtures. This suggests that the deposits did not fully react with the substrate at 650°C. In addition, the XRD patterns of the samples exposed to S3 deposit revealed the exclusive formation of Fe_2O_3 .

The XRD patterns of NiCr coating after exposure to the different salts at 650°C for 360 h are shown in Fig 4(b). The samples without any deposit S0 exhibit three major peaks of the austenitic γ -Ni and some small peaks associated with Cr_2O_3 and $NiCr_2O_4$ spinel. After reaction with the S1 deposit, the patterns now include peaks of the salt mixture (NaCl and KCl) and of a new phase identified as potassium chromate (K_2CrO_4), in addition to the Cr_2O_3 and $NiCr_2O_4$. Otherwise, the peaks of Na_2SO_4 , NaCl and $NiCr_2O_4$ spinel are

revealed in the sample with S2 deposit. In contrast, no reflections from the S3 salt appear but just the peaks of Cr_2O_3 , NiCr_2O_4 and K_2CrO_4 . The latter, shown also in the samples exposed to S1 deposit, is a bright yellow precipitate [31] formed by the reaction of chromium oxides with KCl, as different authors pointed out in connection to chlorine-induced high temperature corrosion [32]. As for the sample with the S4 deposit, the peaks of Cr_2O_3 and of the deposit mixture (Na_2SO_4 , K_2SO_4 and Fe_2O_3) can be unambiguously identified.

Fig 4 XRD patterns after high temperature corrosion tests in presence of different salt mixture at 650 °C for 360 h of: (a) T24 steel substrate and (b) NiCr coated steel substrate.

3.4. Microstructural characterization

3.4.1. Samples without salts

The high temperature corrosion resistance of the NiCr-coated and the uncoated T24 steel exposed to air at 650 °C for 360 h was analyzed in detail in a previous study [19]. The uncoated steel grew a non-protective oxide layer composed of an inner layer of Fe_3O_4 and an outer scale of Fe_2O_3 of around 120 μm . In some areas, this solid layer suffered spallation from metal surface. In contrast, the NiCr coating protected the steel substrate through the formation of a thin layer of protective Cr_2O_3 oxide and NiCr_2O_4 spinel. The

microstructural analysis did not reveal any damage neither in the coating nor in the substrate after 360 h exposure in air without salt at 650°C.

3.4.2. Samples exposed to the NaCl-KCl salt mixture

Fig. 5 shows SEM micrograph of the surface of T24 steel exposed to NaCl-KCl salt mixture (S1 deposit). Fig. 5 reveals two different areas, the external area marked with (1) corresponds to an oxide layer completely cracked formed by iron oxides while the inner area marked with (2) is the surface after spallation of the oxide. The spot EDX analyses (not shown in Fig 5) indicate the presence of salt elements (Na, Cl and K) as well as of Fe and O.

Fig 5 SEM micrograph of the surface of T24 steel exposed to the NaCl-KCl salt mixture at 650 °C for 360 h.

The cross-section (Fig. 6a) shows the oxide layers and the underlying metal partially attacked. The internal layer is rich in Cl, O, Na and K according to the X-ray maps. The external oxide layer is mainly formed by Fe_3O_4 and Fe_2O_3 , as revealed at higher magnification (Fig. 6b). This non-protective oxide layer seems cracked and spalled all throughout the sample surface. In addition, the dark corrosion products can be clearly seen in Fig. 6(c). The EDX analyses and the XRD reveal Cl-K-Na rich products and

NaFeO₂, which is a typical corrosion product of iron based alloys in molten salts [29,33]. It thus appears that the Cl_{2(g)} released upon the reaction of the alkali chlorides with iron oxide (Equation (1)) diffuse through the non-protective porous and cracked Fe-rich oxides to the oxides-metal interface leading to the formation of iron chloride (FeCl_{2(s)}). The high volatility of the iron chloride brings about its diffusion backwards (FeCl_{2(g)}) through the non-protective Fe-rich oxide layer [34].

Once a sufficient oxygen partial pressure (P_{O₂}) is reached, the chlorides destabilize and form Fe₂O₃, while Cl_{2(g)} regenerates following Equation (4). These reaction steps are endlessly repeated causing severe damage [30], let alone that corrosion is fostered through the alloy grain boundaries (Fig. 6d) as also demonstrated upon chromizing an austenitic AISI 304 stainless steel due to the volatilization of FeCl₂ [35].

Fig 6 SEM micrographs of T24 steel exposed to the NaCl-KCl salt mixture at 650°C for 360 h: (a) EDX maps analysis of the cross-section and (b-d) three micrographs at higher magnification of different zones marked in figure (a).

Fig. 7(a) shows the cross-sectional analysis of the NiCr coating after exposure to the NaCl-KCl salt mixture at 650°C for 360 h. It seems that the coating maintains its structural integrity despite the great penetration of the salts. In addition to coating composition, the microstructural features of the coating processed by HVOF, i.e. inclusions of oxides, porosity content or splat boundaries are also important when assessing their effectiveness at high temperatures [36]. This is demonstrated in Fig 7(b) where the aggressive salts progressed easily between the splat boundaries. In addition, the clustered particles are corroded along the interface between the grains. This phenomenon is only observed at the outer part of the coating, because these external semi-molten particles are less compact. The EDX maps reveal that Cr diffuses through each particle generating a layer of Cr_2O_3 between them. However, the salts seem to induce corrosion through two major steps: (i) the K reacts with the protective Cr-rich oxides forming K_2CrO_4 that weakens the Cr-rich oxide layer and (ii) the weakened chromia layer leaves an easy-accessible pathway for chlorides to advance through the coating.

Fig 7 SEM micrographs of NiCr coating exposed to the NaCl-KCl salt mixture at 650°C for 360 h. Cross-sectional analysis at (a) x300 and (b) x2000 magnification with EDX map analyses.

3.4.3. Samples exposed to the NaCl-Na₂SO₄ salt mixture

Fig. 8(a) shows a typical SEM micrograph of T24 steel surface exposed to NaCl-Na₂SO₄ salt mixture deposit. Contrary to what occurred with the previous S1 mixed chlorides deposit, T24 steel does not have a spalled oxide layer full of cracks in the surface. In contrast, a dense oxide layer was observed. Moreover, the cross-sectional analysis did not reveal either severe damage or detachment of the oxide scale layer (Fig. 8b). A multilayer oxide scale composed by different phases is readily observed in the chemical distribution maps of Fig. 8(b). From the gas interface towards the substrate, the multilayer is formed by: (1) a layer rich in salts, (2) Fe₂O₃, (3) a second layer rich in salts, (4) Fe-Cr spinels and (5) an inner layer rich in S. Since the Na distribution appears in the same locations as S, it seems that this multilayer microstructure arises from the deposit-recoating method employed in this study. However, no chlorides were observed at the interface between

the oxide layer and the steel substrate. This suggests that the very thick Fe-rich oxide layer formed at 650°C for 360 h is able to limit the penetration of chlorides until the substrate-oxide layer interface.

Fig 8 SEM micrographs of T24 steel exposed to NaCl-Na₂SO₄ salt mixture at 650°C for 360 h: (a) sample surface and (b) EDX spot and mapping analysis of the cross-section.

Fig. 9 illustrates the SEM cross-section of the NiCr coating exposed to NaCl-Na₂SO₄ salt mixture. Compared to the previous S1 chlorides deposit, there was less penetration of the salts, although the attack was still very aggressive. The dark Cl-rich corrosion products inside the coating can be readily observed, as in the case of the S1 chloride deposit. Salt mixture attack was particularly rapid near splat boundaries where the oxides were present.

Fig 9 SEM micrograph of NiCr coating exposed to NaCl-Na₂SO₄ mixture deposit at 650°C for 360 h.

3.4.4. Samples exposed to the KCl-K₂SO₄ salt mixture

Fig. 10(a) shows SEM plain view micrographs of T24 steel surface exposed to the KCl-K₂SO₄ salt mixture. Similar to the sample with the S2 chloride/sulfate deposit, the Fe-rich oxide layer maintained the integrity and underwent less spallation than the sample solely exposed to chlorides (S1). Rough and smooth areas with different chemistry can be observed. Indeed, the smoother surface contains only Fe and O, while the constituents of the salt and Fe and O are detected in the EDX spectra of the rough areas. At higher magnification, insert in Fig. 9(a), the rough surface shows octahedral crystals, which can be associated with iron oxides. The high melting point of this salt (690 °C) and its heterogeneous distribution along substrate surface suggests that the salt partially melted, so that the attack proceeded with the salt in semi-solid condition. In agreement with the opinion of Skrifvars et al. [37], it is though assumed that the molten phase gives a better contact between the salt particles and the steel surface that results in greater corrosive attack than when the salts are still solid. Fig. 9(b) shows the presence of salts below the Fe-rich oxide layer, as in the samples exposed to the S1 chlorides deposit. In addition, some chlorides can be observed at the interface between the oxide layer and the steel

substrate. At higher magnification, the penetration of the chlorides into the steel substrate (marked with arrows) can be readily observed in Fig. 10(b). A low amount of chlorides seems to trigger the active oxidation mechanism and K seems to accelerate it.

Fig 10 SEM micrographs of T24 steel exposed to the KCl-K₂SO₄ salt mixture at 650°C for 360 h: (a) sample surface and (b) cross-section micrograph and EDX map analyses.

Fig. 11(a) collects the SEM micrographs and the X-ray maps of the NiCr coating exposed to the KCl-K₂SO₄ salt mixture. The coating seems to maintain the integrity and a good adherence to the substrate. However, severe damage occurs at the outermost area of the coating as shown at higher magnification in Fig. 11(b). It has some cracks normal to the gas/coating interface, which are often associated with tensile stresses due to the mismatch in the thermal expansion coefficients of the constituent of the layers [38]. Such chemical differences through the layers are clearly shown in the EDX analyses. The outermost layer is rich in K₂SO₄. The second layer is rich in Cr, O and K, suggesting the formation of the K₂CrO₄ previously detected by XRD analysis. The third layer is rich in Ni, Cr and O in line with the NiCr₂O₄ spinel and Cr₂O₃ identified by XRD. The Cr-poor layer below the Ni-Cr-rich layers likely occurs by chlorination because the enthalpy of formation of CrCl_{3(g)} is favored with respect NiCl_{2(g)} [39]. The reaction between Ni and Cl₂ is less thermodynamically favored than the reaction between Cr with Cl₂, because the free energy of Ni-chlorides formation is less than that of Cr-chlorides (−371.6 kJ/mol for

CrCl₃ and –174 kJ/mol for NiCl₂ at 600 °C). In our view, the chlorination occurs deep in the coating because the P_{O2} is too low to form any chromium oxide while that of P_{Cl2} increases. As a result, the coating becomes severely damaged. These results agree with the studies of Varis et al. [40], who also observed a heavily Cr-depleted layer of their thermally sprayed NiCr coating exposed to a KCl–K₂SO₄ salt mixture at 600 °C and with the studies of Sadeghimeresht et al. [39]. The latter also observed Cr depletion in their NiCrAlY and NiCrMo coatings at 600 °C. They observed voids distributed mainly beneath the top formed oxide scale produced by the vaporization of metallic chlorides (CrCl₃ and CrCl₂). In our case, these voids were observed largely beneath the top formed oxide scale because our testing temperature (650 °C) is higher than theirs (600°C) [33]. In contrast, the inner part of the coating seems to be unaffected after 360 h of exposure. This reveals that the access of chlorine to deeper zones is hampered by the tortuosity created by the splats of the coating.

According to these results, the corrosion mechanism may in essence occur following the sequence: (i) formation of protective NiCr₂O₄ and Cr₂O₃ oxides at 650°C; (ii) formation of K₂CrO₄ according to Equation (5); (iii) the presence of K₂SO₄ enhances the break-up of the protecting oxide layer and, finally, (iv) Cr–Cl rich (CrCl₃) inter-lamellar inclusions were formed in the area which leads to a heavy depletion of Cr.

Pettersson et al. [32] studied the effect of KCl and K₂SO₄ on the corrosion of 304 stainless steel at 600°C and also showed the formation of K₂CrO₄ under KCl rich deposits. They proposed that K₂SO₄ does not accelerate the corrosion significantly and that KCl is the main cause of the attack. Despite the clear differences between the 304 steel and our NiCr coatings, both possess austenitic matrices and the Cr contents are about the same (~18 vs.

20 wt%, respectively). Therefore, our findings compare rather well even if our temperatures (650°C) are higher (600°C) than theirs.

Fig 11 SEM micrographs of NiCr coating exposed to the KCl-K₂SO₄ salt mixture at 650°C for 360 h at different magnifications: (a) x100 and (b) x200 with an EDX maps.

3.4.5. Samples under Na₂SO₄-K₂SO₄-Fe₂O₃ salt mixture

Fig. 12(a) shows SEM micrographs of T24 steel exposed to Na₂SO₄-K₂SO₄-Fe₂O₃ salt mixture. The steel matrix has barely suffered any damage probably because of the absence of chlorides. The attack initiates through the grain boundaries shown by the arrow marks in Fig. 12(a). However, the attack does not seem severe after 360 h of exposure at 650 °C compared with the other deposits. Furthermore, the NiCr coating exposed to the S4 sulfates/oxides mixture does not exhibit any attack (Fig 12(b)).

Fig 12 SEM micrographs of (a) T24 steel and (b) NiCr coating, exposed to the $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ salt mixture at 650°C for 360 h.

3.5. Role of the salts

The composition of the salts clearly affects the corrosion behavior of the uncoated and the NiCr-coated T24 steel. As such, the corrosivity of the salts can be ranked from the least to the most aggressive ($\text{S0} \approx \text{S4} < \text{S2} \approx \text{S3} < \text{S1}$). The samples exposed to S4 deposit maintained their integrity because in under the current experimental conditions (650°C , air atmosphere and 360 h exposure), both K and Na sulfates did not react with the samples avoiding the formation of metallic sulfates, such as NiSO_4 that form eutectic compositions with the alkali sulfates. According to Xue-mei et al. [41], the melting points of $\text{K}_2\text{SO}_4\text{-NiSO}_4$ and $\text{Na}_2\text{SO}_4\text{-NiSO}_4$ eutectics range from 550 to 700°C . Furthermore, the eutectic of $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-NiSO}_4$ is much lower. As in our case, they did not identify the formation of metallic sulfates when air atmosphere was employed. They reported the formation of NiSO_4 only when $\text{SO}_{3(\text{g})}$ -rich atmosphere was employed. For low alloyed steels, other authors [42,43] reported that at this temperature (650°C), $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ mixture reacts with surface oxides in the presence of SO_3 to form complex liquid sulfates ($\text{Na}_3\text{Fe}(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{SO}_4)_3$) that result in rapid corrosion. However, in this work, there is no aggressive atmosphere containing SO_3 and the P_{SO_3} is too low to make both $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ salts alive. Therefore, oxidation was the main mechanism occurring on

the samples exposed to S4 deposit and the presence of Na and K sulfates did not accelerate the attack in the studied conditions.

According to the results obtained for S4 deposit, it can be derived that the damage suffered by the samples exposed to the S2 and S3 deposits was mainly induced by the presence of NaCl and KCl, respectively. The samples exposed to the S3 deposit were slightly more attacked than the samples exposed to S2 deposit probably because of two main factors: (i) the higher presence of chlorides in S3 than in S2 deposit and (ii) the greatest aggressiveness of K than of Na. Indeed, K_2CrO_4 has been identified and it is assumed that it enhanced the break-up of the protective Cr_2O_3 layer. However, the difference is quite small because if their melting temperatures are taken into account the S2 deposit was completely melted ($T_m = 626\text{ }^{\circ}C$) under our testing conditions while the S3 deposit would be probably partially melted ($T_m = 690\text{ }^{\circ}C$). It thus seems that the T24 steel and the NiCr coating underwent both electrochemical and chlorine-induced active oxidation mechanisms during the exposure to S2 and S3 deposits.

In light of the obtained results, S1 was the most aggressive deposit because it presented the highest chlorides concentration and its melting temperature was near to that employed in this study. The high concentration of chlorides increased the $P_{Cl_{2(g)}}$ against the $P_{O_{2(g)}}$ and favored the formation of metallic chlorides ($FeCl_{2(s)}$ for the T24 steel and $CrCl_{3(s)}$ for the NiCr coating) at the substrate or coating /oxide layer interface. The high concentration of chlorides was evidenced by the formation of different species as $NaFeO_2$ in the uncoated samples or K_2CrO_4 in the NiCr coating. The volatility of the metallic chloride brings about its diffusion backwards oxide scale and once a sufficient P_{O_2} is reached, the chlorides destabilize and form again $Cl_{2(g)}$. Therefore, in the presence of S1 deposit, the main corrosion mechanism is chlorine-induced active oxidation.

4. CONCLUSIONS

- The aggressiveness of the different salt mixtures would follow the sequence $S0 \approx S4 < S2 \approx S3 < S1$.
- The NaCl-KCl (S1) deposit was the most aggressive because it has the highest concentration of chlorides. The presence of NaFeO₂ in substrate samples and of K₂CrO₄ in NiCr-coated samples evidenced that Cl_{2(g)} favored the formation of metallic chlorides.
- The samples exposed to NaCl-Na₂SO₄ (S2) and KCl-K₂SO₄ (S3) deposits suffered less damage compared to the previous S1 deposit, although the attack was still very aggressive. The chlorides seem to trigger the active oxidation mechanism and the presence of K seems to accelerate it.
- The NiCr coating exposed to Na₂SO₄-K₂SO₄-Fe₂O₃ (S4) salt mixture barely suffered any damage due to the absence of chlorides and low P_{SO₃}.
- The microstructural features of the NiCr coating processed by HVOF (i.e. oxides or splat boundaries) were important when assessing their effectiveness at high temperatures. The chloride-rich salts progressed readily between the splat boundaries.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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