



A study on hot corrosion behaviour of Ni–5Al coatings on Ni- and Fe-based superalloys in an aggressive environment at 900 °C

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Abstract

Ni–5Al coating was deposited on Ni- and Fe-based superalloys by high velocity oxy fuel (HVOF) process to enhance their high-temperature corrosion resistance. Hot corrosion studies were conducted on bare as well as HVOF-coated superalloy specimens after exposure to a molten salt environment at 900 °C under cyclic conditions. Each cycles consisted of 1 h heating in the silicon carbide tube furnace followed by 20 min cooling in air. Thermogravimetric technique was used to approximate the kinetics of corrosion. Techniques like X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDAX) were used to characterize the corrosion products. The coatings and the oxide scale formed on the exposed surface were found to be intact with the superalloys. Superfer 800 with Ni–5Al coating has provided a good protection to the superalloys in the given molten salt environment.

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1. Introduction

Advances in the development of high-temperature materials and cooling schemes are expected to increase the life time of gas turbines, boilers, and industrial waste incinerators with their improved strength, creep and fatigue properties. The combination of high temperature with contaminants of environment and low-grade fuels, such as sodium, sulphur, vanadium, and chlorine, manifested in the gas turbine environments require special attention as they lead to the phenomenon of hot corrosion. This form of corrosion consumes the material at an unpredictably rapid rate [1]. The corrosive nature of the gaseous environment may cause rapid material degradation and result in premature failure of components [2,3]. The usage of residual fuel oil refinery furnaces, boilers and gas turbines is limited by the severe degradation of materials [4]. Unlike the conventional concept of frequent renewal of the superheaters made of low cost materials, the new concept exploits the high performance corrosion-resistant materials to realise the reduction of overall plant costs [5]. A case study of boiler tube failure in coal fired

boilers has been conducted by Prakash et al. [6] covering 1 year and it was observed that more than 50% of the failures were attributed to the hot corrosion and erosion due to ash. Although corrosion problems cannot be completely remedied, it is estimated that corrosion related costs could be reduced by more than 30% with the development and use of better corrosion control technologies such as corrosion inhibitors, cathodic protection and coatings [7]. Coatings can add value to products up to 10 times the cost of the coating [8]. Nickel aluminide coatings are of relatively recent origin [9] and they are reported to possess high-temperature mechanical strength as well as oxidation resistance [10,11]. It has been reported in the literature that nickel aluminide coatings on steel have improved the oxidation and corrosion resistance as well as the elevated temperature tribological properties of the substrate [10,12].

Superalloys are extensively used for high-temperature applications. The degradation by high-temperature oxidation is one of the main failure modes of hot-section components, made up of superalloys, in gas turbines. These superalloys are not able to meet both high-temperature strength and the high-temperature corrosion resistance simultaneously; and therefore, protective coatings are used to counter the latter [13]. One of the most common methods used to combat hot corrosion problems in gas turbines involves the utilization of surface coatings. Coatings for

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superalloys are usually designed in such a way that on exposure to reactive environments, the selective oxidation of an element occurs to form a protective oxide film such as Cr_2O_3 , Al_2O_3 or SiO_2 [14].

The high velocity oxy fuel (HVOF) process is reported to be a versatile technology and has been adopted by many industries due to its flexibility, cost effectiveness and the superior quality of coating produced. The hypersonic velocity of the flame shortens the time of interaction between the powder and flame, whereas low temperature of flame limits the grain growth and decomposition of coating. Due to the high impact velocity of particles, the coatings show a high adhesive strength and cohesive strength of individual splats, uniform microstructure, high density and low porosity [15–18].

There is no available literature on the behaviour of Ni–5Al coatings on superalloys subjected to molten salt environment under cyclic conditions. Therefore, an attempt has been made in the present investigation to develop Ni–5Al coating by HVOF process on the superalloys and investigate its high-temperature corrosion behaviour under cyclic conditions at 900 °C in an aggressive environment of Na_2SO_4 –60% V_2O_5 . The cyclic conditions constitute a more realistic approach towards solving metal corrosion problems. Thermogravimetric technique was used to approximate the kinetics of corrosion of coated and bare superalloy substrates. XRD, and SEM/EDAX analysis techniques have been used to characterise the corrosion products formed during hot corrosion studies under cyclic conditions.

2. Experimental design

2.1. Substrate materials and coating formulation

Three types of superalloys namely, Superni 76, Superni 750 and Superfer 800 were used in the present investigation. The superalloys were procured from M/s Mishra Dhatu Nigam Limited, Hyderabad, India in the rolled sheet form. The chemical compositions of the superalloys used are shown in Table 1. Each specimen measuring approximately 20 mm × 15 mm × 5 mm were cut from the rolled sheet and polished by using 180, 220, 400, and 600 grade SiC emery papers. The specimens were blasted using alumina powder (grit 20) prior to coating. Commercially available Ni–5Al powder was used to coat on all the superalloys by HVOF thermal spray process. The particle size of the powder used was in the range 70–81 μm. The coatings were formulated in M/s Metallizing Equipments Pvt Limited, Jodhpur, India by using commercial Hipojet-2100 gun. The spray parameters employed for Hipojet-2100 system were: oxygen flow rate 250 LPM, fuel (LPG) flow rate 60 LPM, air flow rate 600 LPM, spray distance 200 mm, fuel pressure 6 kg/cm², oxygen pressure 8 kg/cm², and air pressure 6 kg/cm². The specimens were cooled with compressed air jets during and after spraying.

2.2. Hot corrosion studies

Hot corrosion studies under cyclic conditions were performed in molten salt (Na_2SO_4 –60% V_2O_5) environment up to 100 cycles for the as sprayed Ni–5Al-coated samples. A coating of uniform thickness with 3–5 mg/cm² of Na_2SO_4 –60% V_2O_5 was applied with camel hairbrush on the preheated samples at 250 °C for 1 h. The heating of the samples were found necessary for the adhesion of the salt layer. The samples were kept in the alumina boats and then inserted inside the SiC tube furnace. Each cycle consisted of 1 h heating at 900 °C followed by 20 min cooling at room temperature. The samples were then subjected to weight change measurements after visual observation at the end of each cycle with help of an electronic balance Model CB-120 (Contech, Mumbai, India) with a sensitivity of 1 mg. As spalled scale if any was also included in weight change determination. The kinetics of corrosion was determined from the weight change measurements. After the hot corrosion studies, the corroded samples were analysed by using XRD and SEM/EDAX techniques. The corroded samples were cut using Isomet 1000 precision cutter across the cross-section and mounted in transoptic powder for the cross-sectional analysis using SEM/EDAX and elemental X-ray mapping.

3. Results

3.1. Visual observation

In case of bare Superni 76 alloy, Fig. 1(a), spalling was observed after the completion of 2nd cycle. A brownish grey scale appeared on the surface and the scale turned dark in color with the course of the study. A small amount of sputtering was observed after 21 cycles and a crack was seen on the oxide scale. The spalled scale was included in the boat during the mass change measurements, whereas in case of bare Superni 750 alloy, Fig. 1(b), brown color was observed after 2nd cycle, which turned into dark brown after subsequent cycles. After the completion of seven cycles, spalling of the scale was observed in. In case of bare Superfer 800 alloy, Fig. 1(c), brown color was observed after the 2nd cycle, which turned dark during the study. The spallation of the scale has started after 10th cycle and it was included during the mass change measurements. The spalling after few cycles might have resulted from the differential co-efficient of thermal expansion (or mismatch) of coating, and the scale formed during hot corrosion.

The Ni–5Al-coated Superni 76 showed a brown color after the second cycle, which turned dark after sixth cycle. After completion of 16 cycles light green patches were observed on the surface of the sample. The oxide scale was intact with the coating and marginal spalling was observed from the surface as shown in Fig. 1(d). In case of coated Superni 750, green color was seen on the surface after third cycle, which turned dark brown after fifth cycle. A little amount of spalling and sputtering of the

Table 1
Chemical composition of the superalloys used in the study

Midhani grade	Chemical composition (wt.%)												
	Fe	Ni	Cr	Ti	Al	Mo	Mn	Si	Co	W	P	C	S
Superni 76	19.69	Balance	21.49	–	–	9.05	0.29	0.39	1.61	0.6	0.005	0.086	0.002
Superni 750	7.32	Balance	15.28	2.37	0.59	–	0.06	0.07	0.05	–	0.85	0.07	0.004
Superfer 800	Balance	30.8	19.5	0.44	0.34	–	1.0	0.6	–	–	–	0.10	0.006

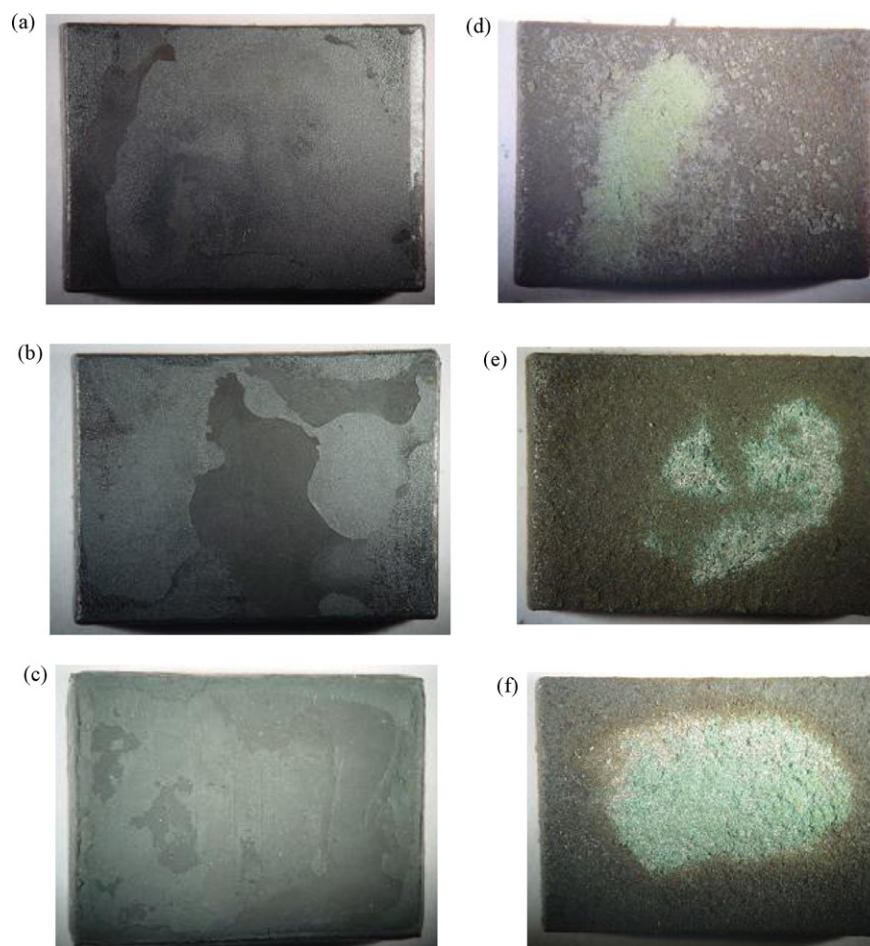


Fig. 1. Surface macrographs of bare Superni 76 (a), Superni 750 (b), Superfer 800 (c) and Ni–5Al-coated Superni 76 (d), Superni 750 (e) and Superni 800 (f) after 100 h exposure to molten salt (Na_2SO_4 –60% V_2O_5) environment at 900 °C.

scale were observed during the course of the study as observed from Fig. 1(e). Few patches of light green color appeared on the surface of the substrate and lasted up to the end of the study, while in case of Superfer 800, the scale formed on the surface were brown in color. The scale started spalling from the surface after 11 cycles and it was marginal. The scale formed on the surface was intact with the coating and a light greenish patch was observed on it (Fig. 1(f)).

Porosity of the as sprayed Ni–5Al coating was measured by Zeiss Axiovert 200MAT inverted optical microscope with stereographic image analysis software based on ASTM B276 and was found less than 2.0%.

3.2. Corrosion kinetics in molten salt environment

The mass gain per area versus number of cycles plots for the bare as well as coated superalloys in the presence of molten salt (Na_2SO_4 –60% V_2O_5) environment under cyclic conditions indicate that the mass gain of the coated superalloys is lower compared to that of bare superalloys in the molten salt environment. Superfer 800-coated with Ni–5Al has shown a minimum mass gain. Superni 750-coated with Ni–5Al has shown a slightly higher mass gain. The weight gain data indicates that the bare superalloys are prone to hot corrosion attack whereas the HVOF

Table 2

Parabolic rate constant, K_p values of bare and Ni–5Al coated by HVOF process after hot corrosion studies at 900 °C

Substrate	K_p values ($\times 10^{-10} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$)
Bare Superni 76	37.08
Bare Superni 750	39.71
Bare Superfer 800	22.36
Coated Superni 76	5.08
Coated Superni 750	5.01
Coated Superni 800	1.63

sprayed Ni–5Al coating provided a better protection to the superalloys from hot corrosion to a considerable extent.

The parabolic rate constant K_p is calculated from the slope of the linear regression fitted line from $(\text{mass gain}/\text{area})^2$ versus number of cycles and is shown in Table 2. The nature of fit, a parabolic rate law, for hot corrosion experiments is also shown in Fig. 2. There is a visible deviation from the parabolic rate law in case of bare superalloy substrates whereas the Ni–5Al-coated specimens follow the parabolic behaviour up to 100 cycles. Fig. 3 shows the cumulative weight gain/unit area in all three cases of bare/coated superalloys.

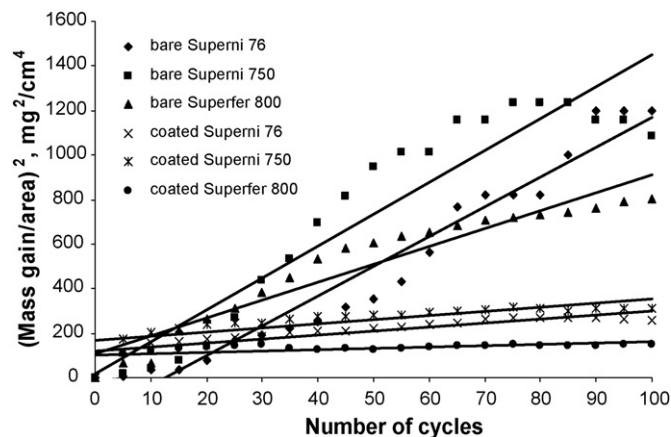


Fig. 2. (Mass gain/area)² vs. number of cycles for bare and Ni-5Al-coated superalloys subjected to Na₂SO₄-60%V₂O₅ environment at 900 °C for 100 cycles.

3.3. X-ray diffraction analysis

The XRD analysis was carried out with Bruker AXS D-8 Advance Diffractometer (Germany) with Cu K α radiation. The XRD patterns of the hot corroded samples after 100 cycles are shown in Fig. 4. XRD patterns of the Ni-5Al coatings revealed that the presence of NiO, NiAl₂O₄, NiCr₂O₄ and Cr₂O₃ as the main phases. Furthermore, very weak phases indexed as belonging to Al₂O₃, FeVO₄ and MnO are identified.

3.4. SEM/EDAX analysis of the scale

3.4.1. Surface analysis

SEM micrographs with EDAX analysis (Joel Scanning Microscope (JSM-840A) with EDAX attachment, Link ISIS) at some selected points of interest of hot corroded bare samples are shown in Fig. 5. The scale formed on the bare Superni 76 shows (Fig. 5a) spalling in nature and EDAX analysis shows the presence of Cr₂O₃, Fe₂O₃ and NiO phases in the scale. In case of bare Superni 750 alloy (Fig. 5b), large numbers of small pores are seen on the surface of the specimen. The major oxide formed

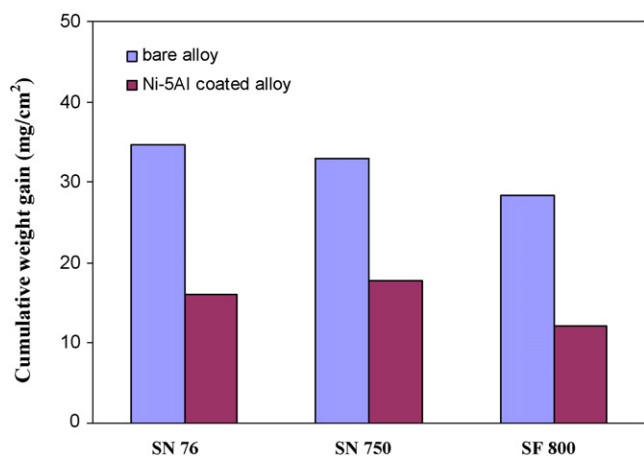


Fig. 3. Bar chart showing cumulative weight gain per unit area for bare and Ni-5Al-coated superalloys subjected to cyclic oxidation for 100 cycles at 900 °C.

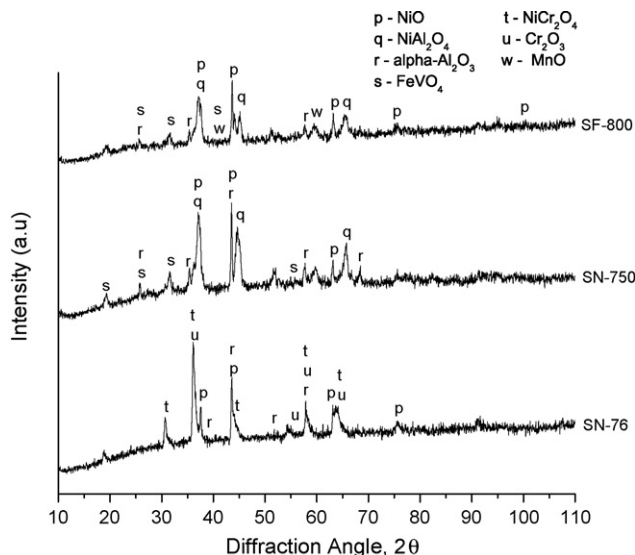


Fig. 4. X-Ray Diffraction pattern of Ni-5Al-coated superalloys after 100h exposure to molten salt (Na₂SO₄-60%V₂O₅) environment at 900 °C.

on the surface of Superni 750 is nickel oxide along with small percentage of Cr₂O₃, Fe₂O₃ and V₂O₅. The SEM micrograph of bare Superfer 800 (Fig. 5c), indicates few cracks on the surface and the surface scale consists of Cr₂O₃, Fe₂O₃, NiO and MnO as revealed by EDAX analysis.

The SEM images showing the surface morphology of Ni-5Al-coated superalloys after cyclic hot corrosion studies at 900 °C are given in Fig. 6. For Superni 76, Fig. 6(a), the point analysis shows the higher percentages of NiO, Cr₂O₃ and Al₂O₃ along with presence of Fe₂O₃ and Na₂O. The EDAX of Superni 750 scale indicated the dominance of Al₂O₃ in the shining area (point 2) along with NiO and Cr₂O₃. NiO occurs as the main phases along with Fe₂O₃ in the black area (point 1) as shown in Fig. 6(b). The scale of Superfer 800 specimen (Fig. 6(c)), indicated Al₂O₃ as the main phase with NiO and Na₂O as the other phases.

3.4.2. Cross-sectional analysis

EDAX analysis was carried out at different points of interest along the cross section of HVOF sprayed Ni-5Al-coated corroded samples viz. Superni 76, Superni 750 and Superfer 800 as shown in Fig. 7(a)–(c), respectively, using Field Emission Scanning Electron Microscope (FESEM, FEI, Quanta 200F) company, with EDAX Genesis software attachment. EDAX analysis of the oxide scale across the cross section of Ni-5Al-coated Superni 76 alloy after 100 cycles at 900 °C in molten salt environment indicates a light grey layer in the top part of the scale (point 1) shown in Fig. 7(a), which is rich with oxides of nickel. The presence of about 28 wt.% oxygen at point 1 shows that oxygen has penetrated through the scale formed on the Ni-5Al-coated Superni 76. Point 2 in Fig. 7(a), indicates the presence of oxides Ni, Al and Cr. Al and Cr are present at the Ni splat boundaries. Points 3, 4 and 5 show the presence of higher amount of Ni and oxygen in lower amount, which indicate that Ni has partially oxidized. EDAX analysis for Fe, Cr and Mn elements revealed outward diffusion from the substrate.

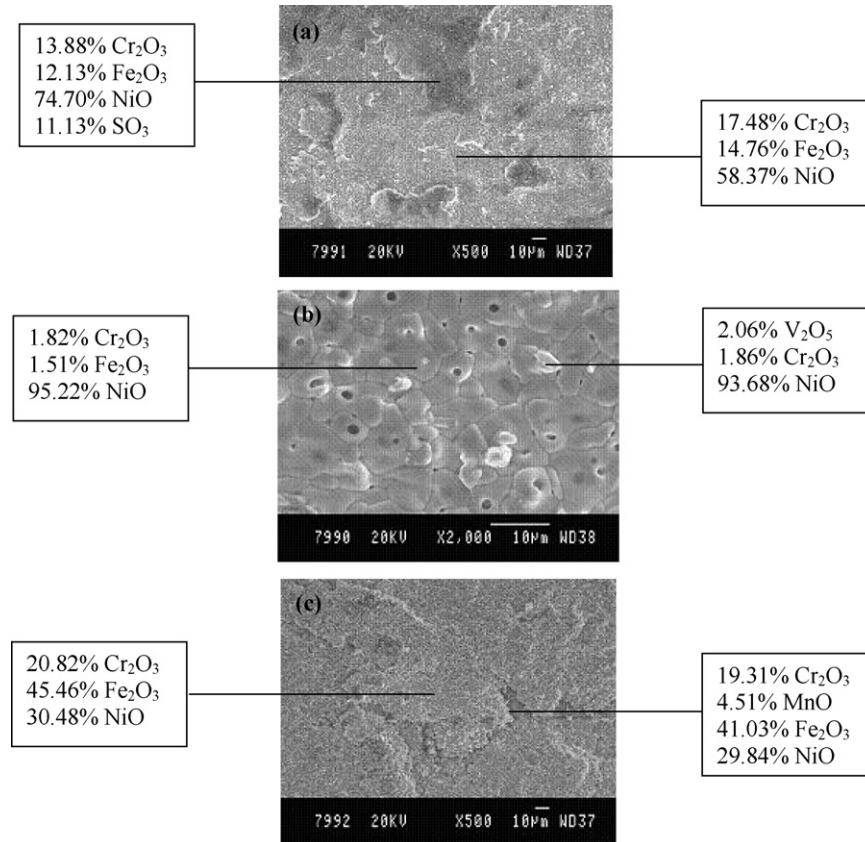


Fig. 5. SEM/EDAX analysis of the bare superalloys, Superni 76 (a), Superni 750 (b), and Superfer 800 (c) exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900 °C after 100 cycles.

For Superni 750 alloy with Ni-5Al coating indicates that the oxide scale is intact and the upper layer is rich in NiO and Al_2O_3 . Presence of oxygen indicates the penetration through the oxide scale formed on the coating. EDAX analysis indicated that the inner layer (points 3 and 4) in Fig. 7(b) composed of aluminum, nickel, chromium, oxygen and iron. Little amount of oxygen is present near the coating substrate interface, which might have penetrated during the initial period of exposure.

In case of Ni-5Al-coated Superfer 800 alloy, the formation of oxides of Ni, Cr, and Al are observed. The light grey color at the upper layer indicates the presence of nickel oxide (points 1 and 2) in Fig. 7(c). The black contrast area indicates the presence of chromium (point 3). Some cracks are observed on the upper part of the coating. EDAX analysis at point 4 shows a lower amount of oxygen indicating the partial oxidation of nickel. Point 5 indicates the presence of nickel, chromium, aluminum and oxygen. Very little amount of oxygen is to be present near the coating substrate interface, suggesting that some oxygen might have penetrated during initial cycles of hot corrosion runs. The splat boundaries and pores present in the coating are clogged due to formation of oxides, which might have blocked the penetration of reacting species towards the base alloy.

3.5. X-ray mapping of different elements

The corroded samples were cut using Buehler ISOMET 1000 precision saw and then it is mounted in transoptic powder for

mirror polishing prior to studying its cross-sectional features. The polished samples were then carbon coated to facilitate the X-ray mapping of different elements present across the corroded samples by using FESEM (FEI, Quanta 200F). X-ray mapping for the Ni-5Al-coated on Superni 76 at 900 °C after 100 cycles in molten salt (Na_2SO_4 -60% V_2O_5) environment is shown in Fig. 8 (a). The elemental maps for Ni, Cr, Fe and O indicates that the scale is mainly rich in oxides of nickel, chromium and iron. Aluminum oxide is present in the subscale regions. Small amount of sodium has diffused from the environment into the scale through the splat boundaries as seen in the Fig. 8(a). Traceable amount of Mo has diffused into the coating from the substrates. The scale of Ni-5Al-coated Superni 750 indicates the top scale mainly consists of aluminum oxide and nickel oxide as shown in Fig. 8(b). The elemental maps reveal that the Ni-rich splats, which are present beneath the top scale, is mostly unoxidised. Chromium and Iron shows a relatively higher percentage near the coating-substrate interface indicating their diffusion from the substrate to coating. Sodium and silicon are also found in the scale in very small amount, which may have diffused along the splat boundaries. The X-ray mapping for Ni-5Al-coated on Superfer 800 alloy is shown in Fig. 8(c). A dense and thick scale consisting mainly of aluminum and nickel oxide is observed. Fe and Cr are present near the coating-substrate interface indicating the diffusion behaviour of the substrate into the coating. Higher percentage of iron has diffused into the substrate compared to the chromium. Titanium has migrated from the substrate

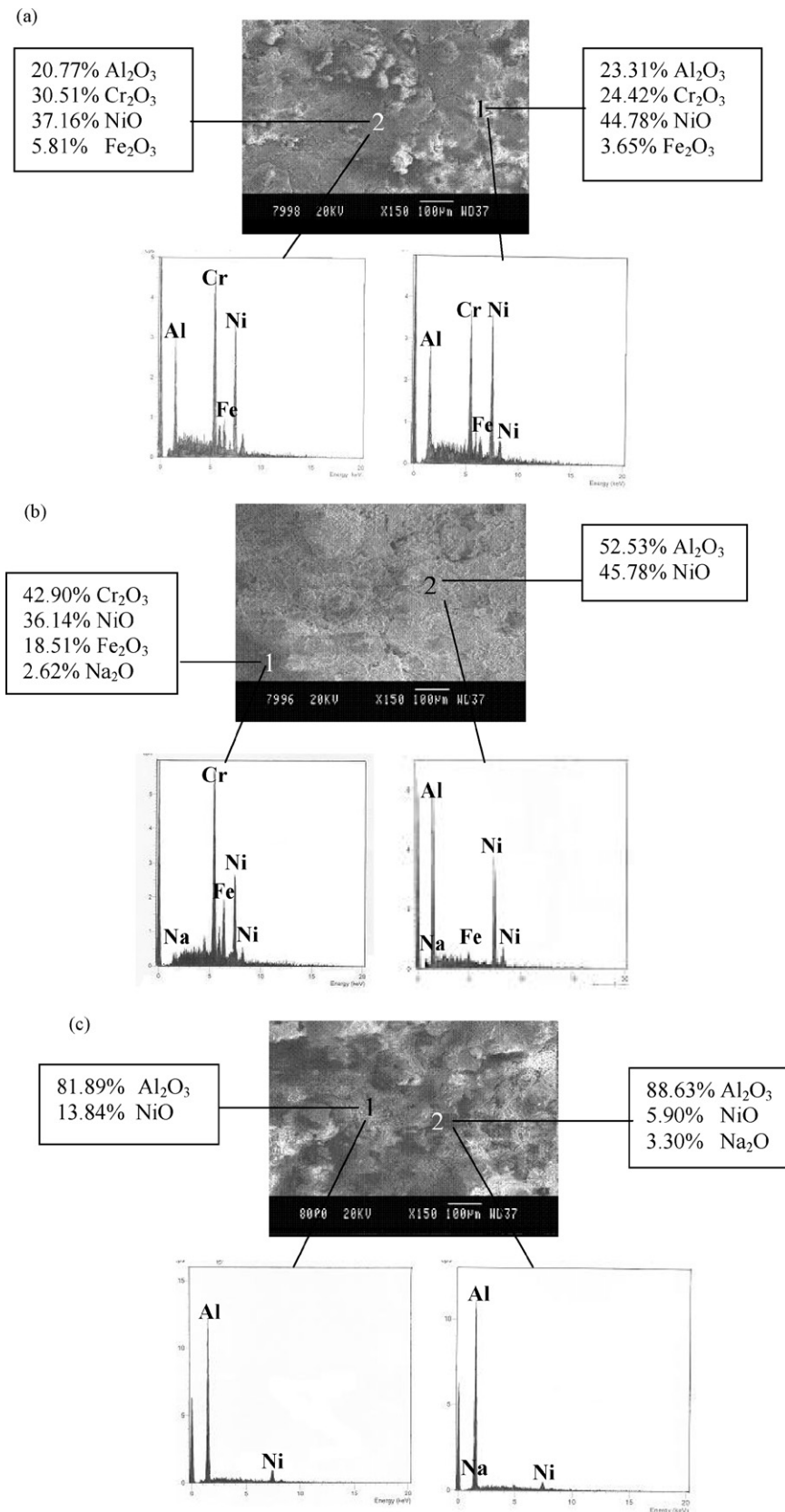


Fig. 6. (a) Surface-scale morphology and EDAX patterns from different spots on Ni-5Al-coated Superni 76 in molten salt ($\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$) environment at 900 °C after 100 cycles. (b) Surface-scale morphology and EDAX patterns from different spots on Ni-5Al-coated Superni 750 in molten salt ($\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$) environment at 900 °C after 100 cycles. (c) Surface-scale morphology and EDAX patterns from different spots on Ni-5Al-coated Superfer 800 in molten salt ($\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$) environment at 900 °C after 100 cycles.

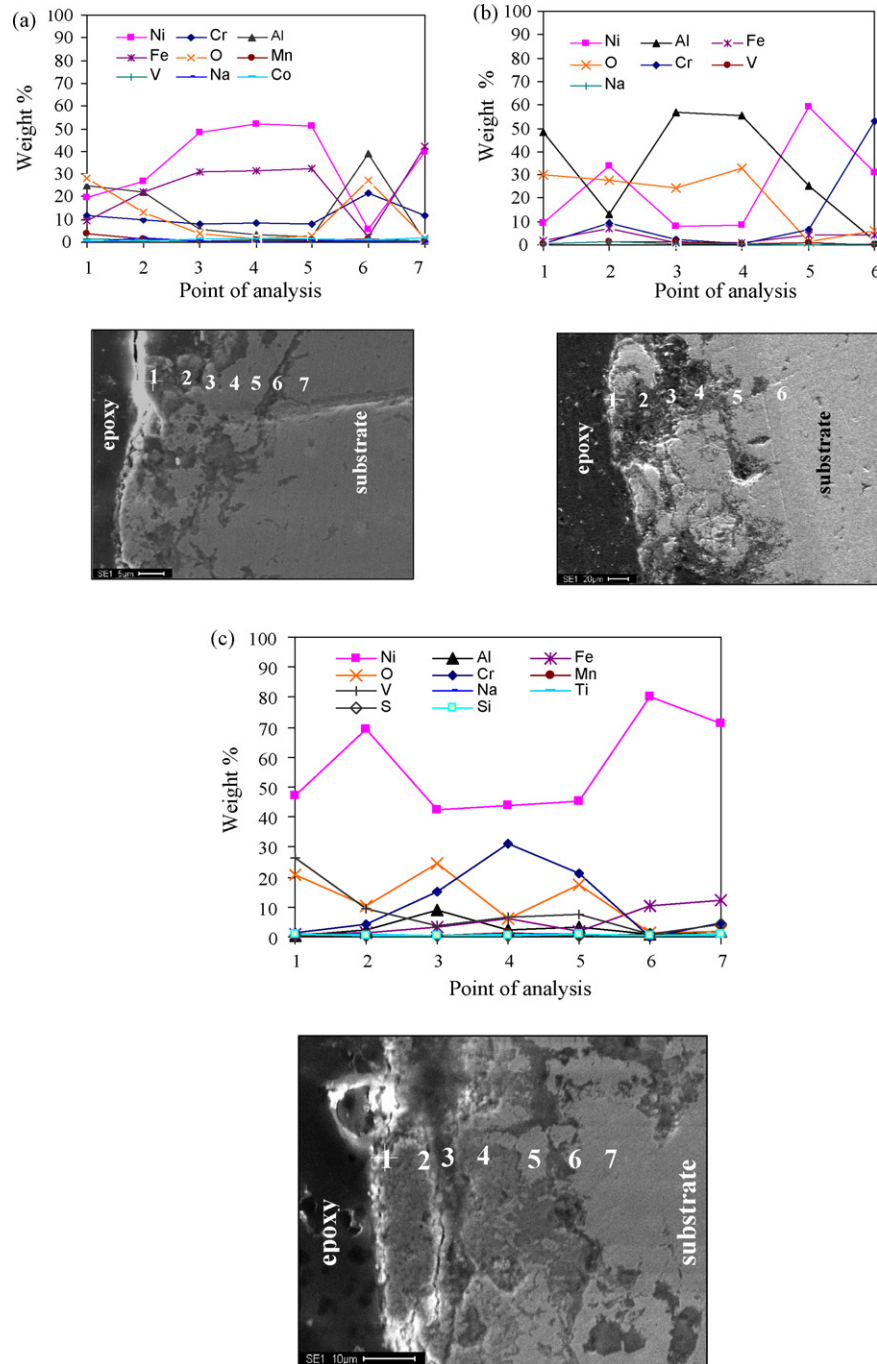


Fig. 7. Oxide scale morphology and variation of elemental composition across the cross-sections of the Ni-5Al-coated Superni 76 (a), Superni 750 (b) and Superfer 800 (c) subjected to the cyclic oxidation at 900 °C in molten salt environment after 100 cycles.

to the coating and is present along splat boundaries. Streaks of manganese oxide are present in the oxidized coating near the substrate coating interface.

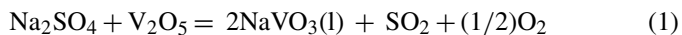
4. Discussions

The surface macrographs of bare and Ni-5Al-coated superalloys after hot corrosion studies are shown in Fig. 1. It is observed from the macrographs that the oxide scale was intact with the coating and marginal spalling was observed from the surface.

Few light green patches were seen on the surface of the corroded samples. The greenish color of the scale in the case of coated superalloys may be attributed to the presence of NiO in the scale, which is identical to the findings of Bornstein et al. [19] and Sidhu [20].

The mass gain of the bare alloys is gradual whereas the mass gain of the Ni-5Al-coated superalloys was high during the initial stages and then it becomes nearly constant as observed in Fig. 3. The rapid increase in the mass gain during the initial period of exposure to molten salt environment at 900 °C may

by due to the rapid diffusion of oxygen through the molten salt layer. Kotla et al. [21] proposed that in the temperature range of 900 °C, the Na₂SO₄ and V₂O₅ will combine to form NaVO₃, as represented by Eq. (1) having a melting point of 610 °C [22]:



This NaVO₃ acts as a catalyst and also serves as an oxygen carrier to the base alloy through the open pores present on the surface, which will lead to the rapid oxidation of the base elements of the substrates to form a protective oxide scale. So, an increase in the mass gain of the bare superalloys occurs in the early stages of hot corrosion. There may also be simultaneous dissolution of Cr₂O₃ in the molten salt due to the reaction [23,24]:

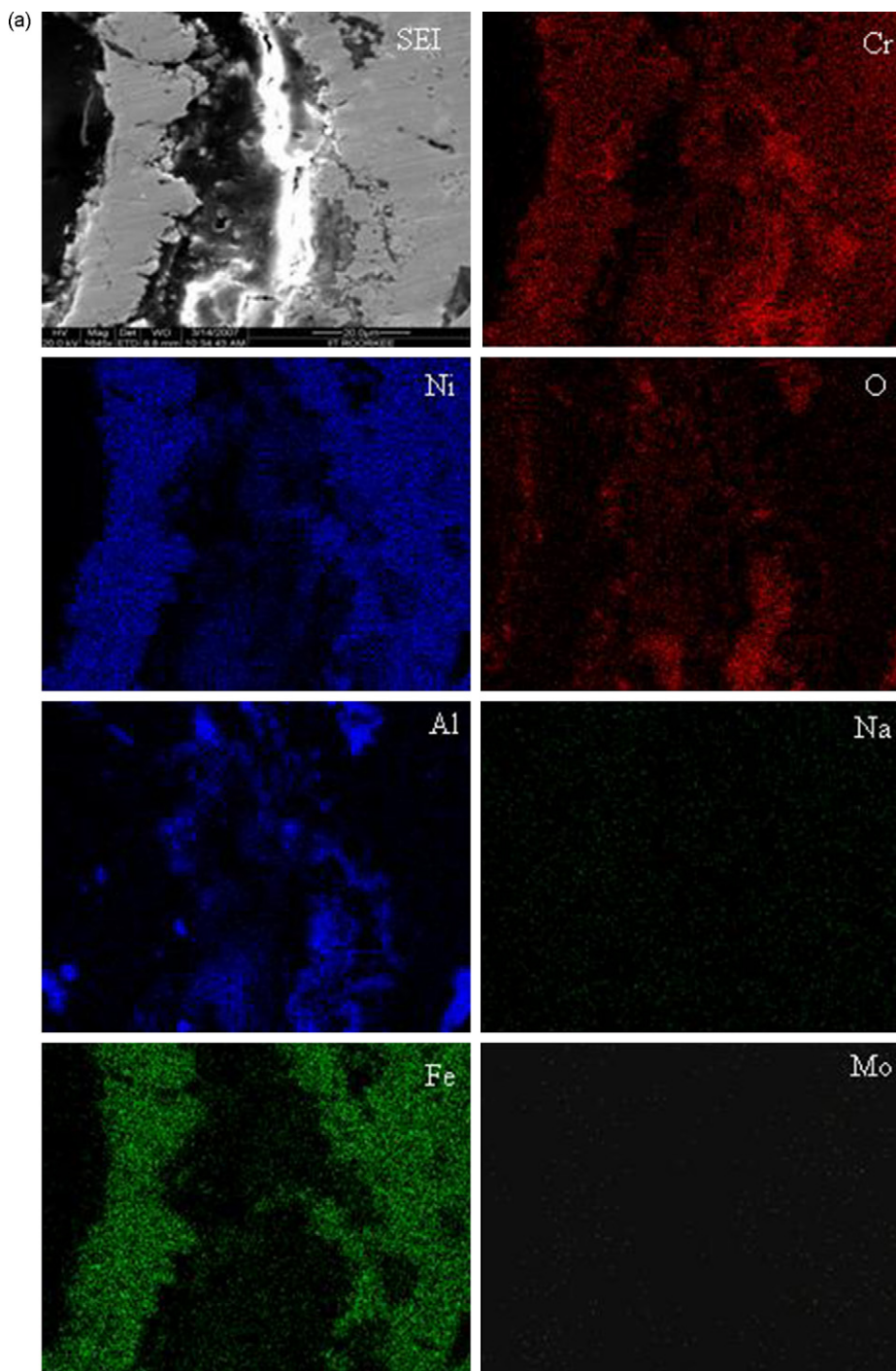


Fig. 8. (a) Composition image (SEI) and X-ray mapping of the cross-section of SN-76 coated with Ni-5Al subjected to cyclic oxidation in Na₂SO₄-60%V₂O₅ environment at 900 °C. (b) Composition image (SEI) and X-ray mapping of the cross-section of SN-750 coated with Ni-5Al subjected to cyclic oxidation in Na₂SO₄-60%V₂O₅ environment at 900 °C. (c) Composition image (SEI) and X-ray mapping of the cross-section of SF-800 coated with Ni-5Al subjected to cyclic oxidation in Na₂SO₄-60%V₂O₅ environment at 900 °C.

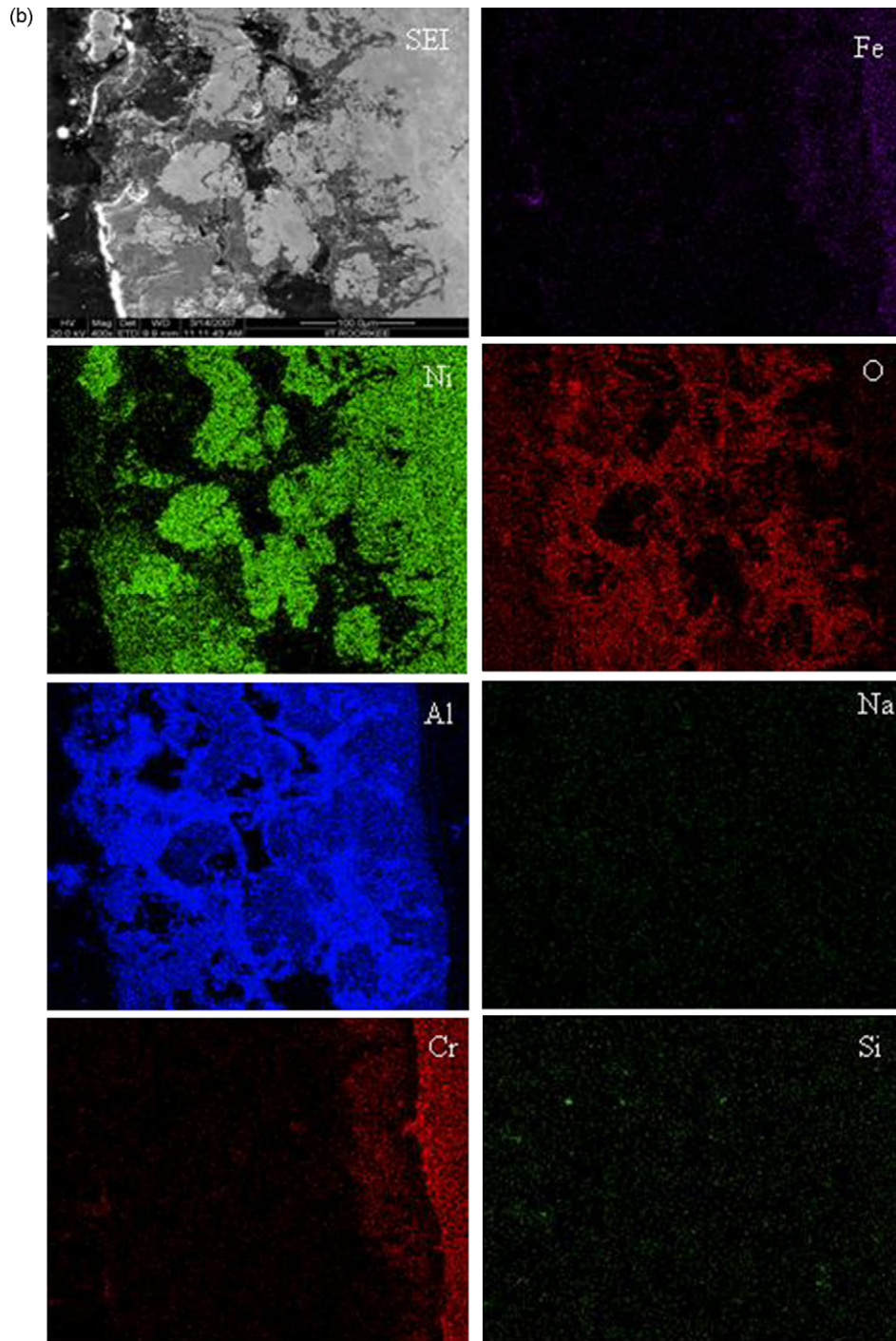
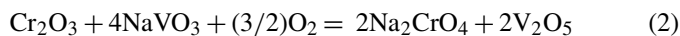


Fig. 8. (Continued)



During the subsequent cycles, the formations of oxides have blocked the diffusion of corrosive species by covering the pores and the splat boundaries. The formation of oxides at the splat boundaries is confirmed by the X-ray mapping analysis (Fig. 9). The rapid increase in the mass gain during the initial period was also reported by Sidhu et al. [25], Singh et al. [26], Tiwari and Prakash [27] and Ul-Hamid [28] during their studies on the hot corrosion of superalloy materials.

In case of coated alloys aluminum from the coating and chromium, iron and titanium diffused from the alloy and gets oxidized and nickel splats has remained unoxidised. Once these oxides of aluminum, chromium has formed at the intersplat regions, they must be blocking the diffusion of corrosive species across the coating. That's why in the initial stages there is a fast rate of oxidation and furthers the curve levels off indicating the protection provided by the partially oxidized coating. This coating was compact and adherent up to 100 cycles.

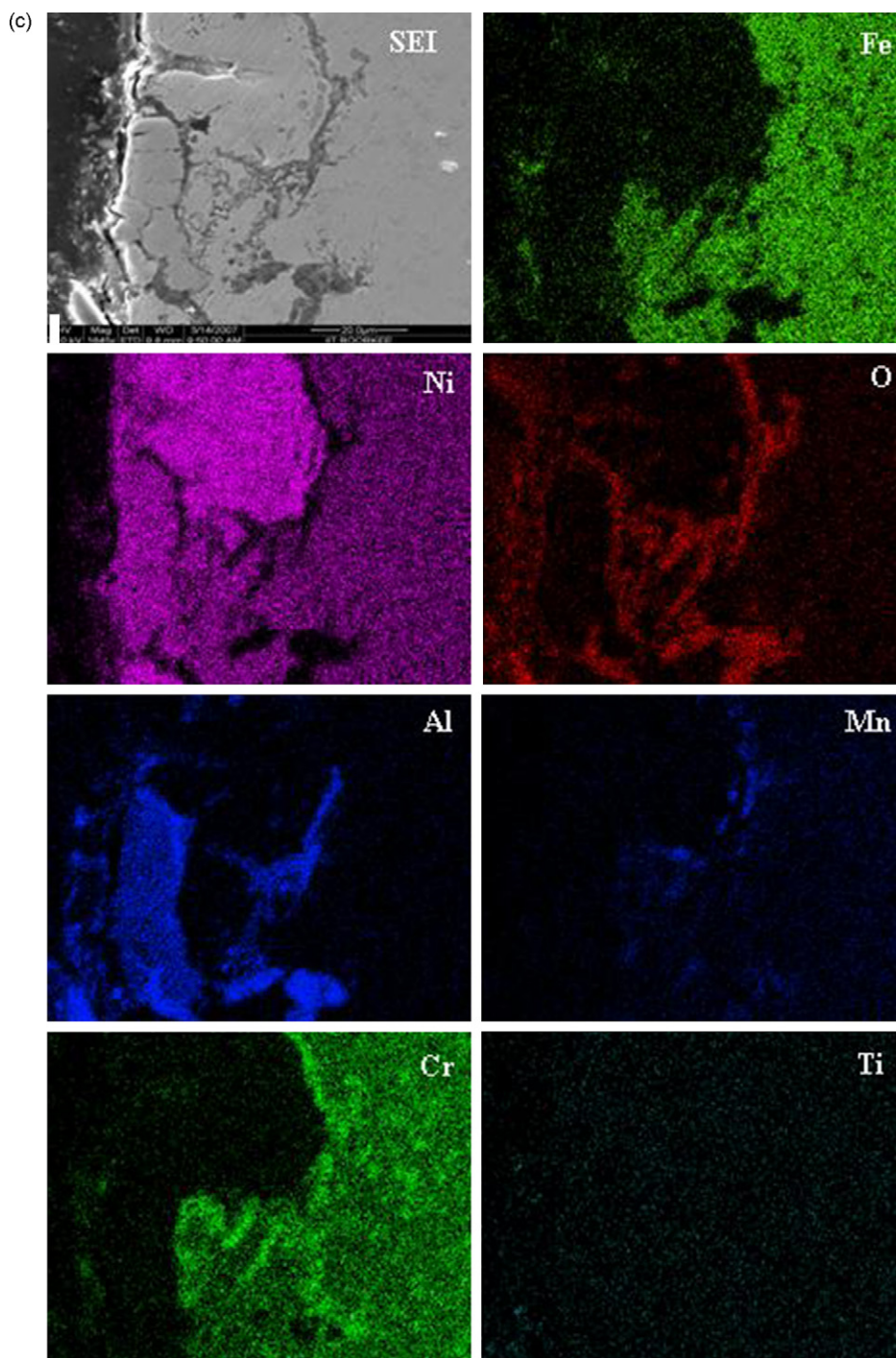


Fig. 8. (Continued)

The parabolic rate constant for the bare superalloy is found to be greater than that of Ni–5Al-coated superalloys. It can be inferred that the HVOF sprayed Ni–5Al coating has provided the necessary protection to the superalloys. Particularly, Ni–5Al-coated on Superfer 800 has shown a high resistance to hot corrosion and provided the best protection.

The XRD analysis (Fig. 4) of the Ni–5Al-coated superalloys after hot corrosion study at 900 °C in molten salt environment indicates that the Ni–5Al coating has provided the better protection to the superalloys which may be due to the formation of

α -Al₂O₃, NiO, Cr₂O₃, as confirmed by EDAX analysis. These oxides are very protective as reported by Ul-Hamid [28] and Sundararajan et.al [29]. The presence of NiAl₂O₄ and NiO also reported by Lee and Lin [30] during their hot corrosion studies on Ni₃Al intermetallic compound at 800 and 1000 °C. They opined that the NiAl₂O₄ spinel might have better hot corrosion resistance than NiO since the solubility of NiAl₂O₄ spinel is thermodynamically smaller than that of NiO in the molten salt. The role of coating is sacrificial. They act as reservoir for the formation of oxides or spinels. In case of coated Superfer 800

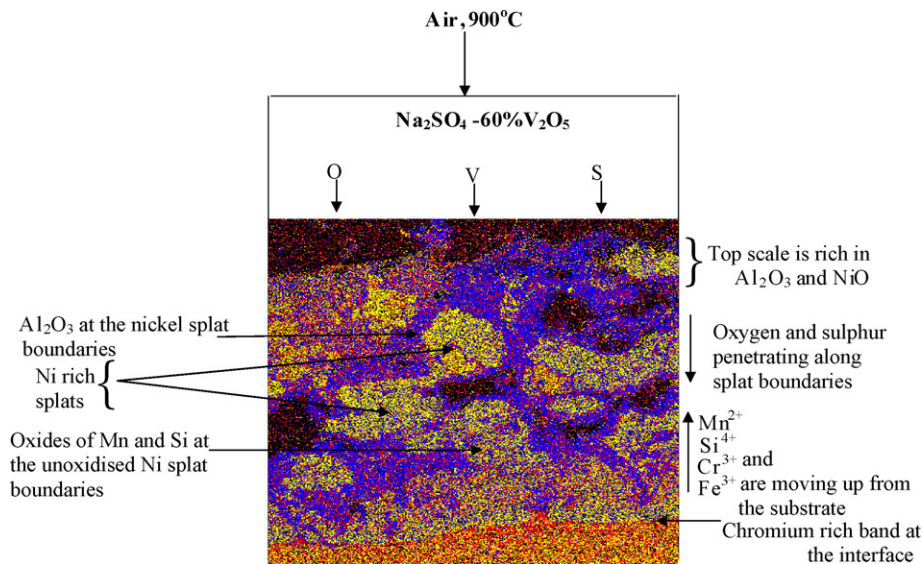


Fig. 9. Schematic diagram showing the possible hot corrosion mode for the Ni-5Al-coated Superni 750 exposed to the Na₂SO₄-60%V₂O₅ environment at 900 °C for 100 cycles.

alloy, protective oxides such as Al₂O₃, NiO and NiAl₂O₄ spinel have provided the best protection to the substrate alloy. Other oxides formed after the exposure to molten salt environment are, NiCr₂O₄, FeVO₄ and MnO.

EDAX analysis (Fig. 5) revealed that in the case of bare Superni 750 after exposing to molten salt environment small pores are seen there by indicating possible escape of vapourised phases. These pores can help corroding species to easily penetrate into the substrate and cause the damage. Whereas, in the case of Superni 76 and Superfer 800 the mass gain was comparatively lower. The EDAX analysis of the scale for the Ni-5Al-coated (Fig. 6) specimens has shown Al₂O₃, Cr₂O₃, Fe₂O₃ and NiO phases. The presence of these oxides at the surface decrease oxygen availability in the underlying alloy and favor the most thermodynamically stable oxide i.e. Cr₂O₃ [28]. The results of EDAX are further supplemented by XRD analysis, which confirmed the presence of Al₂O₃, NiO, and Cr₂O₃. The Ni-5Al coating on all the superalloys was effective in reducing the hot corrosion in the given molten salt environment, thus indicating the protective nature of the coating used.

Cross-sectional EDAX analysis for coated Superni 76 alloy (Fig. 7(a)) indicates that the top scale is rich in NiO. The presence of oxides of Al and Cr in the subscale region might have acted as diffusion barrier to the inward diffusion of corrosive species. Formation of small amount of Fe₂O₃ as indicated by EDAX and supported by X-ray mapping may be due to their diffusion of Fe from substrate to coating at high temperature. For Ni-5Al-coated SN 750 alloy it is indicated that the oxide scale is intact and the upper layer is rich in nickel oxide and aluminum oxide. Nickel-rich splats are present in the subscale regions which are unoxidised as observed from Fig. 7(b). In case of Ni-5Al-coated SF 800 alloy (Fig. 7(c)), protective oxides of nickel, chromium and aluminum have formed on the surface. Thereafter, the splat boundaries and pores present in the coating are clogged due to formation of oxides, which might have blocked the penetration of reacting species towards the

base alloy. Small amount of chromium, iron and titanium have diffused from the substrate into the coating at high temperature.

The elemental mapping shows that in case of Ni-5Al-coated Superni 76 alloy (Fig. 8(a)), nickel, chromium, aluminum, iron and oxygen coexists with each other suggesting the formation of oxides of nickel, chromium, aluminum and iron which is well supported by surface XRD and EDAX analysis. Iron and chromium have diffused into the coating from the substrate. The scale of Ni-5Al-coated Superni 750 indicates the top scale is rich in aluminum oxide and splats of unoxidised nickel, beneath the top surface are found as shown in Fig. 8(b). Aluminum is found at the periphery of nickel-rich splats. At some places nickel and oxygen coexists indicating the formation of nickel oxide on the top surface. The elemental maps reveal that the Ni-rich splats mostly unoxidised beneath the top scale. This is confirmed by cross-sectional XRD and EDAX analysis. A band of chromium is present near the coating substrate interface. The X-ray mapping for Ni-5Al-coated on Superfer 800 alloy is shown in Fig. 8(c) which indicates that nickel is partially oxidized and aluminum is found at the nickel-rich splat boundaries. A dense and thick scale consisting of aluminum, nickel and oxygen coexist suggesting the formation of oxides of aluminum and nickel. A thick band of chromium is present near the coating substrate interface. The results are justified with surface EDAX and XRD analysis. On the basis of the results of X-ray mapping, SEM, EDAX (surface/cross-section) and XRD analyses, schematic representation of the possible hot corrosion mode for the Ni-5Al-coated Superni 750 subjected to the molten salt environment for 100 cycles at 900 °C is shown in Fig. 9.

5. Conclusions

In the present work, hot corrosion behaviour of HVOF sprayed Ni-5Al coatings on Superni 76, Superni 750 and Super-

fer 800 alloys in aggressive environment of Na_2SO_4 –60% V_2O_5 at 900 °C has been investigated and the following conclusions are made.

1. The HVOF spray process could be used successfully to deposit Ni–5Al coating on different superalloys. Compared to bare superalloys, the HVOF sprayed Ni–5Al coating improved the hot corrosion behaviour in aggressive environment of Na_2SO_4 –60% V_2O_5 at 900 °C.
2. The bare superalloys have shown spalling and peeling of the scale and the mass gain was relatively more than the Ni–5Al-coated superalloys.
3. The parabolic rate constants of Ni–5Al-coated superalloys were much lower than the bare superalloys subjected to cyclic oxidation in molten salt environment indicating the protective behaviour of the HVOF sprayed Ni–5Al coating.
4. Ni–5Al coating has led to the reduction in weights of about 53, 46 and 57% for Superni 76, Superni 750 and Superfer 800 alloys, respectively. The necessary protection of the Ni–5Al coating to the substrates in molten salt environment which followed the sequence: Superfer 800 > Superni 76 > Superni 750.
5. The hot corrosion resistance of Ni–5Al-coated Superfer 800 was better compared to other two Ni–5Al-coated superalloys in the given molten salt environment. This may be due to the presence of thick band of chromium near the coating substrate interface. The better hot corrosion resistance may also be attributed to the formation of NiAl_2O_4 spinels revealed by XRD analysis. The surface scale was compact and adherent to the coating.
6. There is perceptible diffusion of some elements from the substrate to the coating as observed in the elemental mapping analysis.

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