

Hot corrosion and performance of nickel-based coatings

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Understanding the behaviour of metals and alloys at elevated temperatures, especially their corrosion behaviour and providing protective surface layers has become an object of scientific investigation since long. No alloy is immune to hot corrosion attack indefinitely, although there are some alloy compositions that require a long initiation time at which the hot corrosion process moves from the initiation stage to the propagation stage. Nickel-based coatings have been reported to be widely used as they combine several advantages such as abrasion, erosion and resistance to high-temperature corrosive atmospheres. In this article, a brief review of the performance of nickel-based coatings has been made to understand their hot corrosion mechanism.

Keywords: Alloys, hot corrosion, nickel-based coatings, protective coatings.

CORROSION is the deterioration of a material by its reaction with the surroundings. It adversely affects those properties that are to be preserved. At higher temperature, this mode of degradation is known as oxidation or dry corrosion. Metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing atmosphere at elevated temperatures. This mode of attack is called 'hot corrosion', where a porous, non-protective oxide scale is formed at the surface and sulphides in the substrate.

Advances in materials development and cooling schemes will lead to increased operation temperatures of gas turbines, boilers and industrial waste incinerators. The combination of such high temperatures with contaminants of environment and low-grade fuels, such as sodium, sulphur, vanadium and chlorine, require special attention to the phenomenon of hot corrosion¹. This form of corrosion, unlike oxidation, consumes the material at an unpredictably rapid rate. Consequently, the load-carrying ability of the components is reduced, leading eventually to its catastrophic failure. The inability to either totally prevent hot corrosion or at least detect it at an early stage has resulted in several accidents, leading to loss of life and/or destruction of engines.

Hot corrosion has been observed in boilers, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerators since the 1940s. How-

ever, it became a topic of importance and popular interest in the late 1960s when gas turbine engines of military aircraft suffered severe corrosion attacks during the Vietnam conflict while operating over and near sea water².

During operation, blades and vanes of gas turbines are subjected to high thermal stresses and mechanical loads. In addition, they are also attacked chemically by oxidation and/or high-temperature corrosion. Only composite materials are able to meet such a demanding spectrum of requirements; the base material provides the necessary mechanical properties and coatings provide protection against oxidation and corrosion³.

The coating can be defined as a layer of material formed naturally or synthetically or deposited artificially on the surface of an object made of another material, with the aim of obtaining required technical or decorative properties⁴. Coating provides a way of extending the limits of use of materials at the upper end of their performance capabilities, by allowing the mechanical properties of the substrate materials to be maintained, while protecting them against wear or corrosion⁵. Among the different coatings, nickel-based coatings show good high temperature erosion-corrosion and wear resistance properties, and are widely used at higher temperatures in corrosive environments^{6,7}.

Hot corrosion

Hot corrosion may be defined as an accelerated corrosion, resulting from the presence of salt contaminants such as Na_2SO_4 , NaCl , and V_2O_5 that combine to form molten deposits, which damage the protective surface oxides⁸.

Hot corrosion occurs when metals are heated in the temperature range 700–900°C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase surrounding the metals^{8,9}. At higher temperatures, deposits of Na_2SO_4 are molten (m.p. 884°C) and can cause accelerated attack on Ni- and Co-based superalloys. This type of attack is commonly called 'hot corrosion'. Accelerated corrosion can also be caused by other salts, viz. vanadates or sulphates–vanadate mixtures and in the presence of solid or gaseous salts such as chlorides¹⁰.

Due to depletion of high-grade fuels and for economic reasons, use of residual fuel oil in energy generation systems is well known. Residual fuel oil contains sodium, vanadium and sulphur as impurities. Sodium and sulphur

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react to form Na_2SO_4 in the combustion system. During combustion of the fuel, vanadium reacts with oxygen to form an oxide V_2O_5 (m.p. 670°C). Thus V_2O_5 is a liquid at gas turbine operating temperature. These compounds, known as ash, deposit on the surface of materials and induce accelerated oxidation (hot corrosion) in energy generation systems. Corrosion occurs when these molten compounds dissolve the protective oxide layers, which naturally form on materials during gas turbine/boiler operation. Further, vanadate compounds are good oxidation catalysts and allow oxygen and other gases in the combustion atmosphere to diffuse rapidly to the metal surface and cause further oxidation. As soon as the metal is oxidized, the cycle starts over again and high corrosion rates occur. Further, in coal-gasification processes, hot corrosion is expected to be a problem because the gas environment generally has large sulphur and low oxygen activities and also contains substantial amount of salts¹¹.

Characteristics and mechanism of hot corrosion

Hot corrosion can occur at high temperatures, where the deposit is in the liquid state right from the beginning, or the solid deposit turns into liquid during exposure as a result of reaction with the environment. These two types of hot corrosion processes are termed as High Temperature Hot Corrosion (HTHC) or Type I and Low Temperature Hot Corrosion (LTHC) or Type II respectively^{8,12}.

Type I hot corrosion

This form of hot corrosion is observed^{9,13} mainly within the temperature range $850\text{--}950^\circ\text{C}$. HTHC starts with the condensation of fused alkali metal salts on the surface of the components. A cycle of subsequent chemical reactions takes place, initially attacking the protective oxide film and progressing to deplete the chromium element from the substrate materials. With chromium depletion, oxidation of the base material accelerates and porous scale begins to form.

The macroscopic appearance of HTHC is characterized in many cases by severe peeling of metal and by significant colour changes. For instance, a greenish tone appears on the surface of metals and alloys due to the formation of NiO in the area of accelerated attack. Microscopically, the morphology of Type I is characterized by a sulphidation and depletion region beneath the porous, non-protective scale. The reaction products frequently exhibit oxide precipitates dispersed in the salt film².

Type II hot corrosion

LTHC is observed^{9,14,15} mainly within the temperature range $650\text{--}800^\circ\text{C}$. In this form of hot corrosion, low melting

point eutectic mixtures of Na_2SO_4 and CoSO_4 (the melting temperature of the $\text{Na}_2\text{SO}_4\text{--CoSO}_4$ eutectic is 540°C) cause typical pitting in the localized areas. The localized nature of attack is related to localized failure of the scale as a result of thermal cycling, erosion or chemical reactions. As opposed to Type I hot corrosion, in Type II corrosion neither microscopic sulphidation nor chromium depletion is generally observed^{9,16}.

Mechanism of hot corrosion

The initiation of HTHC is due to failure of the protective oxide layer, which allows the molten salt to access directly the substrate metal. This failure may result from erosion, thermal stresses, erosion-corrosion, chemical reactions, etc. The mechanisms proposed for the HTHC propagation stage are the sulphidation-oxidation mechanism and the salt fluxing mechanisms¹⁴. The salt fluxing mechanism was originally proposed by Goebel and Pettit^{17,18}. According to this model, protection efficiency of the surface oxide layer might be lost as a result of fluxing of this layer in the molten salt. Fluxing can be caused either by combination of oxides with O^{2-} to form anions (i.e. 'basic fluxing'), or by decomposition of oxides into the corresponding cations and O^{2-} (i.e. 'acidic fluxing'). Acidic fluxing takes place when the O^{2-} activity in the molten salt is markedly lowered; it leads to much more severe oxidation compared to basic fluxing. As opposed to basic fluxing, acidic fluxing can be self-sustaining, since displacement of the salt from stoichiometry does not become progressively more difficult as the reaction proceeds¹⁴.

Ni-based protective coatings

No alloy is immune to hot corrosion attack indefinitely. Superalloys have been developed for high temperature applications. However, these alloys may not be able to meet both the high temperature strength requirements and high temperature corrosion resistance simultaneously for longer life. So protective coatings are used to counter the latter.

Due to continuously rising cost of the materials as well as increased material requirements, the coating techniques have been given more importance in recent times. Coatings can add value to products up to ten times the cost of the coating¹⁹. The necessity to preserve good mechanical properties of alloys at elevated temperature under the highly oxidizing and corrosive conditions led to the development of coating materials^{20,21}. The composition and structure of the coatings are determined by the role that they play in various material systems and performance environments and may vary from one system to another according to the requirements. In the service environment, the coatings are expected to form protective oxides such as Al_2O_3 , Cr_2O_3 and SiO_2 . So the coatings are designed to serve as a reservoir for the elements forming or contributing to form these surface oxides.

Nickel-based alloy coatings show good high-temperature wear and corrosion resistance. They have good wear resistance after adding W and Mo elements to the alloy⁷. Ni-based coatings are used in applications when wear resistance combined with oxidation or hot corrosion resistance is required. Nickel-based self-fluxing alloys are mainly used in the chemical industry, petrol industry, glass mould industry, hot working punches, fan blades and mud purging elements in cement factories. Their advantages are especially related to coating large-sized components such as piston rods, earth-working machines, etc.²².

Nickel–chromium alloys have been used as coatings to deal with oxidation environments at higher temperatures. When nickel is alloyed with chromium, this element oxidizes to Cr_2O_3 at rates which could make it suitable for use up to about 1200°C , although in practice²³ use is limited to temperatures below about 800°C . A better understanding of the service behaviour of such coatings is needed in order to determine the mechanical and metallurgical changes and interactions, and the degradation mechanisms of these materials with post-combustion gases when used in high-temperature regions of boilers^{24,25}.

Hot corrosion of LPPS 80Ni–20Cr coating on type 304 stainless steel, by a thin film of Na_2SO_4 and 0.7 mol fraction Na_2SO_4 –0.3 mol fraction of NaVO_3 at 900°C in a 1% SO_2 – O_2 gas atmosphere, shows that the coating was successful in resisting hot corrosion. The formation of Cr-rich oxide layer of approximately $30\text{ }\mu\text{m}$ after 16 h exposure is mainly responsible for protecting the coated alloy from hot corrosion attack. Formation of chromatic solute anions prevented sulphidation of the alloy²⁶. Ni–20Cr, Ni–50Cr and Cr-coated boiler tubes performed well for seven years in the actual incineration plant without any problems. Investigation of high-temperature corrosion resistance of Ni–50Cr-coated boiler tubes in a laboratory test at 873 K , revealed that the coating exhibited good corrosion resistance²⁷.

Singh²⁸ developed Ni–20Cr coatings on boiler steels, namely GrA1, T11, T22 by plasma spray process and evaluated their oxidation and hot corrosion performance in laboratory tests at 900°C . The coatings were also tested in the actual boiler environment. He observed an increase in the resistance towards air oxidation as well as hot corrosion with the application of coatings. Weight change (mg/cm^2) variation as a function of time expressed in number of cycles for Ni–20Cr-coated steels after hot corrosion in Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles is shown in Figure 1. After plasma coating all the steels showed much lesser overall weight gain as compared to uncoated specimens in the given molten salt environment. The formation of phases like Cr_2O_3 and NiCr_2O_4 in the protective scale of the coatings was suggested to induce requisite resistance in the boiler steels. The probable mechanism of corrosion attack for this Ni–20Cr-coated T11 steel exposed to Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles is shown in Figure 2.

Performance of HVOF-sprayed Ni–49Cr–2Si coatings on ferritic and austenitic boiler steels in oxidizing atmosphere of 500 vppm HCl, 3% O_2 , 14% CO_2 , 20% H_2O and argon as balance was good as no corrosion products were detected at the coating surface. There was also no internal attack or attack on the substrate through the coatings. The high temperature behaviour of the same coatings in the presence of a salt environment of 40% Na_2SO_4 –40% K_2SO_4 –10% NaCl –10% KCl in two environments, viz. oxidizing environment of N_2 –20% H_2O –14% CO_2 –3% O_2 –500 vppm HCl, and reducing environment of N_2 –20% H_2O –5% CO –0.06% H_2S –500 vppm HCl revealed that the corrosion was more severe in oxidizing environments compared to the reducing environment. Active oxidation was responsible for the accelerated corrosion in oxidizing environments. The coatings were prone to chlorine attack in both atmospheres through interconnected oxide network at splat boundaries. In reducing conditions, materials with high chromium content were able to form a protective layer containing chromium, sulphur and sodium. The corrosion resistance of this layer increased with increasing chromium content. The corrosion resistance of nickel-based high chromium coating materials was satisfactory under test conditions^{29,30}. Further, the corrosion behaviour of arc-sprayed coatings of commercially available Ni70–Cr30 and laboratory-developed high chromium nickel-based powder, exposed to mixed gas environments containing 10% H_2S at 400, 500, 600°C indicates that the coatings made from high chro-

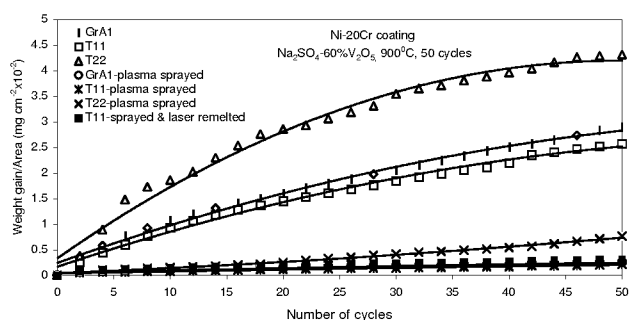


Figure 1. Weight gain plot for uncoated and Ni–20Cr-coated steels with bond coat exposed to Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles²⁸.

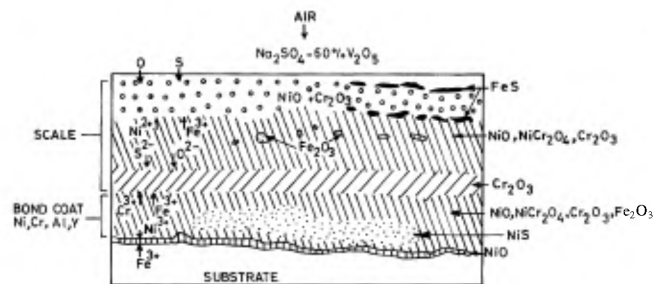


Figure 2. Schematic diagram showing probable hot corrosion mechanism for Ni–20Cr-coated T11 steel exposed to Na_2SO_4 –60% V_2O_5 at 900°C for 50 cycles²⁸.

mium alloy show excellent resistance to sulphidation and are suitable for use as protective layers of boiler tubes³¹.

Study of the electrochemical behaviour of HVOF-sprayed coatings in hydrochloric acid medium showed that alloys with high level of Ni–Cr can be said to be highly corrosion-resistant to hydrochloric acid³². HVOF-sprayed Ni-based coatings with carbide could have hardness of 1150 Hv and adhesion strength of 200 MPa. Using the smaller primary size coating powder³³, adhesion strength can be further improved to 250 MPa with a Ni–Cr content rate of 20 mass%.

A study of the corrosion of intermetallic compound Ni₃Al containing small additions of Ti, Zr and B in a combustion gas at 600–800°C has shown that the corrosion rate of this alloy was significantly accelerated by the presence of Na₂SO₄–NaCl salt mixture. The scales grown on salt-free Ni₃Al contained mainly alumina at 600°C, but a complex mixture of oxides NiO–Al₂O₃ and sulphides of both alloy components at 700 and 800°C. During hot corrosion, appearance of a molten-salt layer at the scale surface, which also contained NiSO₄ at 600 and 700°C, accelerated corrosion rate by increasing the relative amount of nickel compounds in the scales and by favouring the formation of metal sulphides in the inner region of the scale³⁴.

Molten salt-induced oxidation on nickel aluminide intermetallic compound (Ni₃Al) in the 1%SO₂/air gas mixtures showed the formation of only NiO at 605°C, and NiO and NiAl₂O₄ at 800 and 1000°C as XRD phases. EDAX analysis revealed the presence of AlS_x and/or NiS_x beneath the oxide scale at all the temperatures. NiO oxide formation consumed oxygen in the molten salt, which locally reduced the oxygen and increased sulphur partial pressure in the molten salt. As the increased partial pressure of sulphur reaches equilibrium, partial pressure region of NiS_x and/or AlS_x, NiS_x and/or AlS_x will form at the salt/alloy interface through sulphidation reaction. The consumption of sulphur will balance out the sulphur and oxygen partial pressure increases in the molten salt. This forces NiO to form. NiO, NiS_x and/or AlS_x are produced simultaneously. As the sulphides are thermodynamically unstable when the oxygen partial pressure increases, it is possible for sulphide to convert into oxides NiO, Al₂O₃ and NiAl₂O₄ through necessary reactions. There are two possibilities of formation of spinel phase, either through the reaction of Al and Ni with oxygen in the molten salt or through the evolution of sulphides³⁵.

Plasma-sprayed Ni₃Al coatings on boiler steels in oxidation and molten salt environments at 900°C are found effective in decreasing corrosion rate in air as well as in the molten salt, due to the formation of protective oxide scales³⁶ of NiO and Al₂O₃. Singh *et al.*³⁷ studied the hot corrosion behaviour of some plasma-sprayed nickel-based coatings in Na₂SO₄ + 60%V₂O₅ environment at 900°C under cyclic conditions. Weight gain vs number of cycles plot for coated and uncoated superalloy 800H subjected to cyclic oxidation for 50 cycles in Na₂SO₄–

60%V₂O₅ at 900°C is shown in Figure 3. NiCrAlY coating is found to be the most protective followed by Ni–20Cr and Ni₃Al coatings respectively. XRD, EDAX and EPMA analysis shows that the formation of oxides and spinels of nickel, aluminium and chromium contributed to the development of hot corrosion resistance of these coatings. X-ray mappings for NiCrAlY-coated superalloy superfer 800H (Figure 4) indicate a scale consisting of a top layer containing oxides of nickel, chromium and aluminium. In the lower portion of the scale, Ni-rich splats are encircled by oxides of aluminium. Cr is also seen forming stringers along the splat boundaries and pores/voids, and seems to have been oxidized. Diffusion of iron from the substrate to the lower layers of the scale is also evident. Vanadium diffuses into the entire scale, and its concentration is high in the top layers. Sulphur penetrates into the base superalloy to get segregated with chromium at the places, where Ni and Fe are absent.

The addition of CeO₂ and Cr to HVOF-sprayed NiAl intermetallic-based coatings improves the wetting and bond strength of the coatings to the substrate, which decreases the tendency of brittle peeling during thermal spraying. These coating layers have higher hardness, improved elastic modulus with less cracks and pores. The NiAl coatings exhibit excellent carburization resistance at high temperature³⁸.

The largely employed Ni-based powder belongs to the Ni–B–Si system, with the addition of other alloying elements. Addition of chromium promotes the oxidation and corrosion resistance at elevated temperatures and increases the hardness of the coating by formation of hard phases. Boron depresses the melting temperature and contributes to the formation of hard phases. Silicon is added to increase the self-fluxing properties. Carbon produces hard carbides with elevated hardness that promotes wear resistance of the coatings^{39,40}.

The corrosion resistance of HVOF-sprayed NiCrBSi coatings has been evaluated by Zhao *et al.*⁴¹ using electrochemical tests. They reported that these coatings have

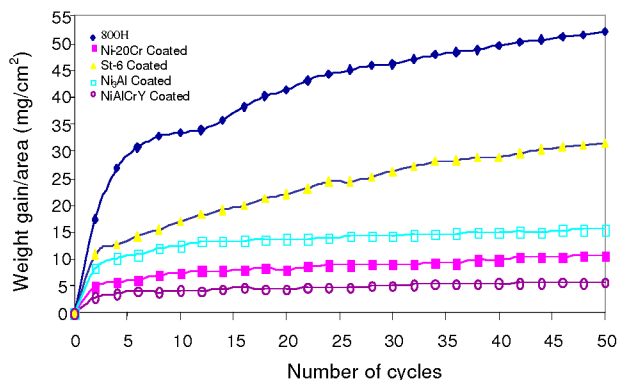


Figure 3. Weight gain vs number of cycles plot for coated and uncoated superalloy 800H subjected to cyclic oxidation for 50 cycles in Na₂SO₄–60%V₂O₅ at 900°C (after Singh *et al.*³⁷).

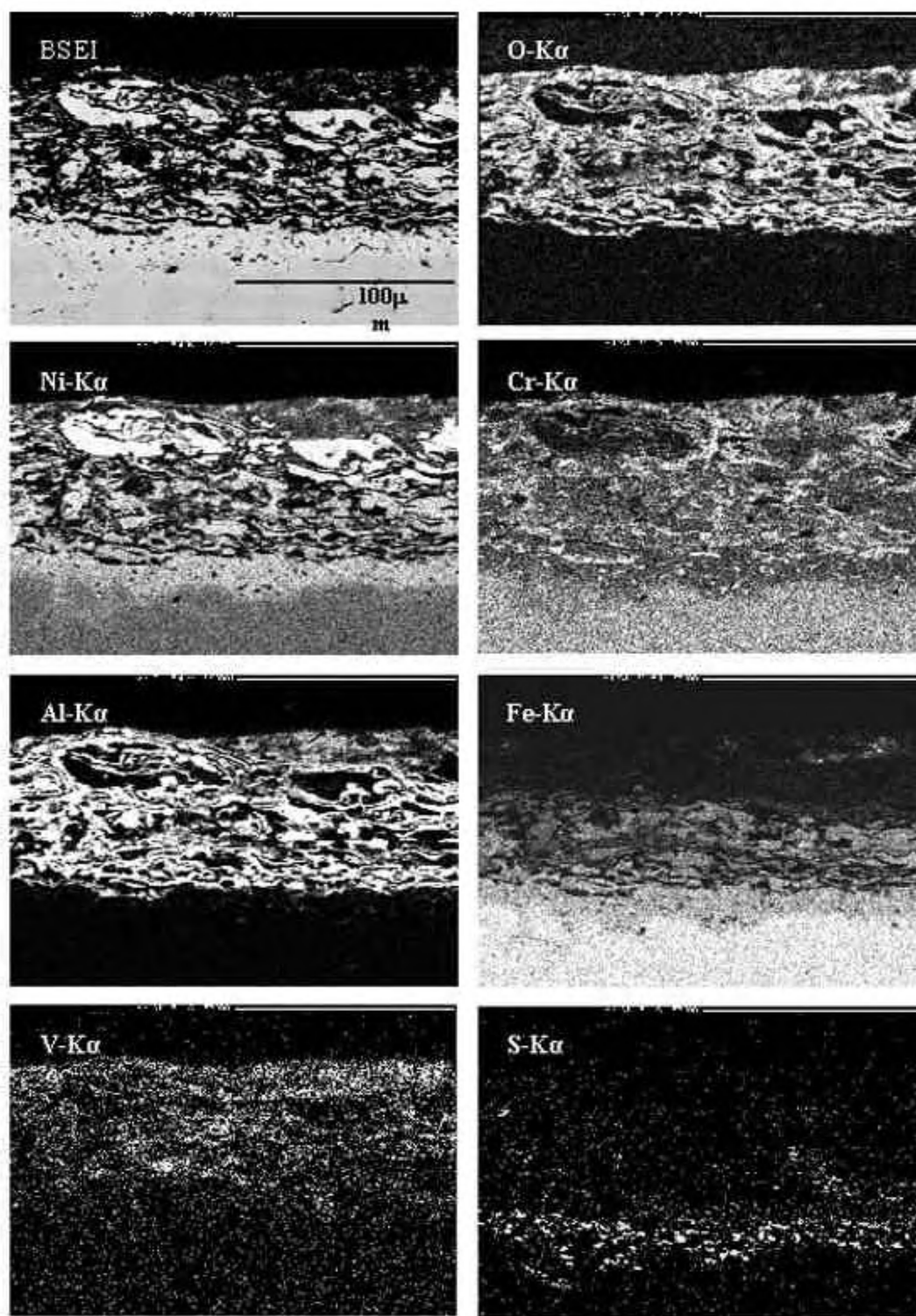


Figure 4. BSEI and X-ray mappings of the cross-section of NiCrAlY-coated superalloy superfer 800H subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 at 900°C after 50 cycles³⁷.

excellent corrosion resistance in alkali solutions, as the surface can form a protective film and keep in a self-passivation condition. The corrosion current of the coatings in sour solution is bigger than that in 3.5% NaCl ⁴¹. Corrosion of the NiCrBSi coating first occurred around parti-

cles that had not melted during spraying and then defects such as pores, inclusions and microcracks, followed by development along the paths formed by pores, microcracks and lamellar structure, resulting in exfoliation or laminar peeling-off. Adjusting the thermal spraying para-

meters to reduce electrochemical unevenness or sealing the pores can improve corrosion resistance of the coatings⁴². The effects of porosities on early corrosion of the coatings are not serious unless there are penetrating porosities. However, porosities can do harm to the persistent corrosion resistance of the coatings and the presence of porosities may weaken the cohesive strength within the coatings⁴¹.

Arc ion plating-deposited NiCoCrAlY and NiCoCrAlYSiB coatings improved the hot corrosion resistance of DZ125 and DSM11 superalloys due to the formation of a continuous or relatively continuous α -Al₂O₃ scale on the surface of the coatings. The hot corrosion resistance of the coatings with addition of Si and B can be improved by promoting the growth of a dense and continuous α -Al₂O₃ scale in the initial stage and improving the adherence of oxide scale to the coatings in the subsequent hot corrosion process⁴³.

The corrosion resistance of HVOF-sprayed Ni–Cr–W–Mo–B coating can be improved by heat treatment due to increased microstructural and chemical homogeneity, such as reduction of porosity, densification and reduction of the eutectic phase⁴⁴. Uusitalo *et al.*⁴⁵ conducted studies on laser remelting of HVOF-sprayed Ni–50Cr, Ni–57Cr, Fe₃Al, Ni–21Cr–9Mo coatings and reported that laser-melted HVOF coating did not suffer from any corrosion damage, whereas as-sprayed coating was penetrated by corrosive species. Laser remelting efficiently removed the interconnected network of voids and oxides at splat boundaries of the HVOF coating.

Concluding remarks

Hot corrosion is a serious problem in power generation equipment, gas turbines for ships and aircraft, and in other energy conversion and chemical process systems. Under Indian conditions, hot corrosion further poses a severe problem as the use of low-grade fuels is well known and justified due to depletion of high-grade fuels as well as high cost involved in removing the impurities. Nickel-based coatings such as Ni–Cr, Ni₃Al, NiCrBSi and NiCrAlY have been found to exhibit excellent hot corrosion resistance. The formation of oxides and spinels of nickel, aluminium and chromium contributed to the development of hot corrosion resistance of these coatings. However, better understanding of the hot corrosion performance of such coatings is needed in order to establish the mechanism of hot corrosion in different aggressive environments.

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