



# Oxidation and Hot Corrosion Resistance of HVOF WC-NiCrFeSiB Coating on Ni- and Fe-based Superalloys at 800 °C

T.S. Sidhu, A. Malik, S. Prakash, and R.D. Agrawal

(Submitted February 28, 2007; in revised form April 26, 2007)

The present work evaluates the oxidation and hot corrosion resistance of high velocity oxy-fuel (HVOF) sprayed WC-NiCrFeSiB coating deposited on Ni-based superalloy (Superni 75) and Fe-based superalloy (Superfer 800H). The coated as well as uncoated specimens were exposed to air and molten salt ( $\text{Na}_2\text{SO}_4$ -25% NaCl) environment at 800 °C under cyclic conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. The corrosion products were characterized using the combined techniques of x-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe micro analyser (EPMA). The WC-NiCrFeSiB coating provides necessary resistance against oxidation and hot corrosion to both the nickel and iron-based superalloys in the given environmental conditions at 800 °C. The oxides of active elements of the coatings, formed in the surface scale as well as at the boundaries of nickel and tungsten rich splats, have contributed for the oxidation and hot corrosion resistance of WC-NiCrFeSiB coatings, as these oxides act as barriers for the diffusion/penetration of the corrosive species through the coatings.

**Keywords** hot corrosion, HVOF, oxidation, superalloys, WC-NiCrFeSiB coating

## 1. Introduction

Oxidation is the most important high-temperature corrosion reaction, which occurs when metals or alloys are heated in oxidizing environments, such as a combustion atmosphere with excess air or oxygen. Metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This mode of attack is called hot corrosion (Ref 1), which consumes the material at an unpredictably rapid rate. Consequently, the load-carrying ability of the components

reduces quickly, leading eventually to their catastrophic failure (Ref 2).

Hot corrosion degradation of metals and alloys has been identified as a serious problem for many high temperature aggressive environment applications, such as boilers, internal combustion engines, gas turbines, fluidized bed combustion, and industrial waste incinerators. 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 sulfur as impurities. These impurities react together to form low melting point compounds, known as ash, which deposit on the surface of materials and induce accelerated oxidation (hot corrosion). Corrosion occurs when these molten compounds dissolve the protective oxide layers that naturally form on materials during boiler/gas turbine operation. The inability to either totally prevent the 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/infrastructures (Ref 3).

This article is an invited paper selected from presentations at the 2007 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Global Coating Solutions, Proceedings of the 2007 International Thermal Spray Conference*, Beijing, China, May 14-16, 2007, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2007.

**T.S. Sidhu**, Mechanical Engineering Department, Shaheed Bhagat Singh College of Engineering and Technology, Ferozepur 152004, Punjab, India; and **T.S. Sidhu, A. Malik, S. Prakash**, and **R.D. Agrawal**, Metallurgical and Materials Engineering Department, Indian Institute of Technology Roorkee, Roorkee, Uttranchal, India. Contact e-mail: tssidhu@rediffmail.com.

Gurrappa (Ref 4), during hot corrosion studies on CM 247 LC superalloy in  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4 + \text{NaCl}$  mixtures at 900 °C, observed that bare CM 247 LC got severely corroded in just 4 h, while it was completely consumed in 70 h when tested in 90%  $\text{Na}_2\text{SO}_4 + 10\%$  NaCl at 900 °C. The results revealed that a chloride containing melt is more corrosive than pure sodium sulfate. The presence of sulfur in the form of sulfates can cause internal sulfidation of the alloy beneath the external oxide layer. Chlorides cause the formation of volatile species, which form voids and pits at grain boundaries, thus forming an easy path for flow of corrodents (Ref 5).

The specific difficulties in the protection of metallic components at high temperatures derive from the

extreme reactivity of the environment and the high mobility of the metallic species, leading to rapid diffusion and thus to the instability of the protective layer. The role of the coating is to provide a metal surface composition which will react with the environment to produce the most protective scale possible combining corrosion resistance with long-term stability and resistance to cracking or spallation. In hot corrosion conditions, the protective oxide scale should not react with the corrosive environment and at the same time, should not allow the corrosive species to diffuse into the coating (Ref 4). Therefore, identification/development of suitable coatings is of great interest for higher temperature applications in boilers and gas turbines (Ref 6).

WC-based coatings are generally used as erosion and wear resistant coatings, but there are many applications where erosion-corrosion problems are predominant. In the present investigation, WC-NiCrFeSiB powder is used as a feedstock alloy. The constituents of this powder provide a number of special properties to the system, e.g., tungsten carbide brings the wear resistance, nickel brings excellent wettability which promotes good cohesion, chromium improves the tribo-mechanical properties, boron reduces the melting point, silicon increases self-fluxing properties, iron modifies the diffusion rates (Ref 7).

This paper presents experimental data on the cyclic oxidation and hot corrosion behaviour of (HVOF) sprayed WC-NiCrFeSiB coating exposed to 800 °C in the laboratory tube furnace for 50 cycles.

## 2. Experimental Procedure

### 2.1 Substrate Materials and Coating Formulations

The Superni 75 (19.5Cr-03Fe-0.3Ti-0.1C-bal Ni, wt.%) and Superfer 800H (32Ni-21Cr-1.5Mn-01Si-0.3Ti-0.3Al-01C-bal Fe, wt.%) were used as a substrate material in the present study. The specimens with dimensions of approximately  $20 \times 15 \times 5 \text{ mm}^3$  were ground with SiC papers down to 180 grit and subsequently grit blasted with alumina powders (Grit 45) before development of the coatings by HVOF process.

A commercially available WC-NiCrFeSiB powder with chemical composition 28.3W-46.5Ni-9.9Cr-4.2Co-2.9Si-2.7Fe-02B-2.7C, wt.% and particle size  $-45 + 15 \mu\text{m}$  was used for depositing the coatings on the substrate superalloys. The coating was sprayed at M/S Metallizing Equipment Co. Pvt. Ltd., Jodhpur (India) with Hipojet-2100 HVOF system, using liquefied petroleum gas (LPG) as a fuel. The thickness of the coating was kept in the range of 250-300  $\mu\text{m}$  in the present study, to ensure integrity of the coatings (Ref 3). Thick coatings have better corrosion resistances, but self-disintegration of thicker coatings restricts the thickness of the coatings. The details for specimen preparations, spray parameters, and equipment/instruments used for characterization of the coating/corrosion products have been reported in the earlier publications of the authors (Ref 8-10).

## 2.2 Oxidation and Hot Corrosion Tests

Oxidation and hot corrosion studies were performed in air and  $\text{Na}_2\text{SO}_4$ -25% NaCl salt environments, respectively, for 50 cycles under cyclic conditions. Each cycle consisted of 1 h heating at 800 °C in a silicon carbide tube furnace followed by 20 min cooling at room temperature. For hot corrosion studies, a salt of  $\text{Na}_2\text{SO}_4$ -25% NaCl (wt.%) was properly mixed in distilled water. After washing with acetone, the specimens were then heated in an oven to about 250 °C. The heating of the specimens were found necessary for proper adhesion of the salt layer. Thereafter, a layer of mixture  $\text{Na}_2\text{SO}_4$ -25% NaCl was applied uniformly on the warm polished specimens with the help of a camel hairbrush. Amount of the salt coating was kept in the range of 3.0-5.0  $\text{mg}/\text{cm}^2$ . The salt-coated specimens as well as the alumina boats were then kept in the oven for 3-4 h at 100 °C. Then, they were again weighed before exposing to hot corrosion tests in the tube furnace. During oxidation and hot corrosion runs, the weight of boats and specimens were measured together at the end of each cycle with the help of Electronic Balance Machine Model 06120 (Contech, Mumbai, India) with a sensitivity of 1 mg. The spalled scale was also included at the time of measurements of weight change to determine total rate of corrosion. Efforts were made to formulate the kinetics of corrosion. XRD, SEM/EDX, and EPMA techniques were used to analyze the corrosion products.

## 3. Results and Discussions

### 3.1 Corrosion Kinetics and Scale Thickness

The weight gain/unit area results for the WC-NiCrFeSiB coated Superni 75 and Superfer 800H superalloys during cyclic exposure to air and  $\text{Na}_2\text{SO}_4$ -25% NaCl molten salt environments at 800 °C for 50 cycles are shown in Fig. 1. The cumulative weight gain/unit area for the bare and coated superalloys after 50 cycles of exposure to both the environments is shown in Fig. 2. The coated superalloys show much lower weight gains than that gained by uncoated specimens in both the environments. Further, the coated alloys follow nearly parabolic rate law

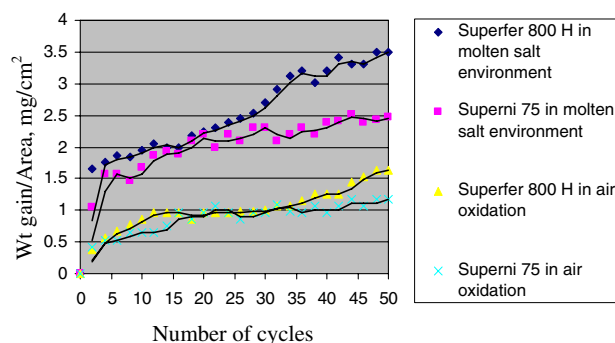
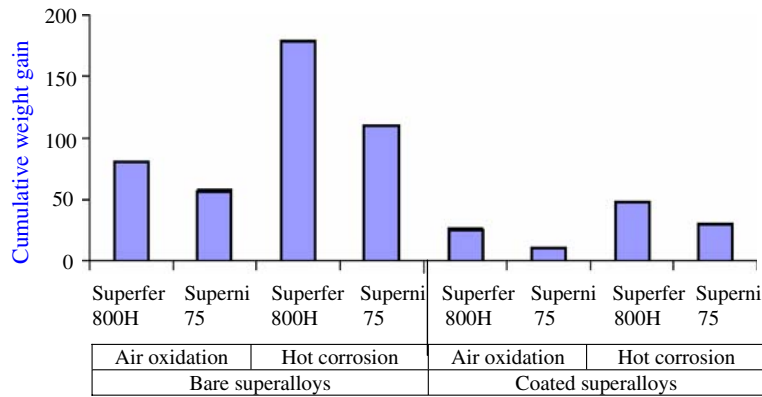
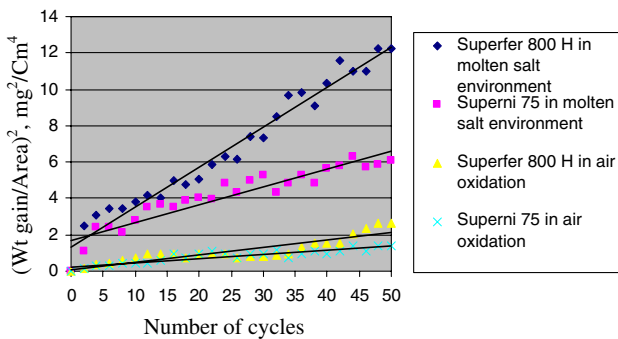


Fig. 1 Weight gain vs. number of cycles plot for coated superalloys



**Fig. 2** Cumulative weight gain of the bare and WC-NiCrFeSiB coated specimens after 50 cycles of exposure

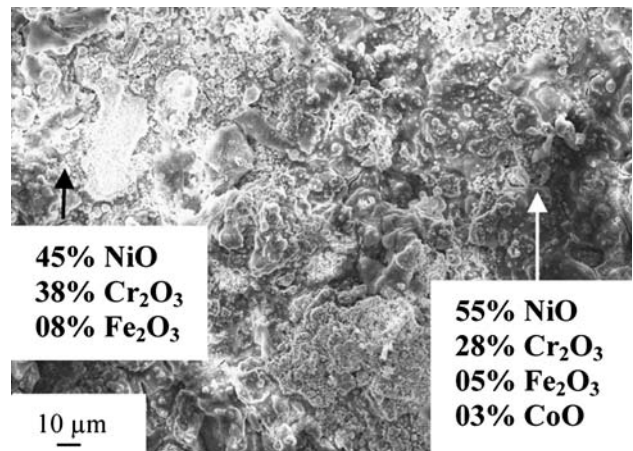


**Fig. 3** (Weight gain/area)<sup>2</sup> vs. number of cycles plot for coated superalloys

of oxidation as can be observed from the graph shown in Fig. 3. Therefore, it can be inferred that the HVOF sprayed WC-NiCrFeSiB coating have a tendency to act like diffusion barriers to the corroding species.

The coated superalloys have shown higher weight gain during exposure to molten salt environment as compared to that gained during air oxidation. From the weight gain plots, it is found that the WC-NiCrFeSiB coating provides better oxidation and hot corrosion resistance to Superni 75 as compared to that of Superfer 800H and has been found successful in reducing the overall weight gain by 80% of that gained by a bare Superni 75.

Figure 1 shows that weight gains are relatively higher during the early cycles of the molten salt corrosion study, and thereafter the rate of weight gain is slow. The initial high oxidation rate of the coated specimens have been attributed to the rapid formation of oxides at the surface (Fig. 4) and splat boundaries of the coating, and within open pores due to the penetration of the oxidizing species along the splat boundaries as shown in the cross section EDX analysis. Once the oxides are formed in places of porosity and splat boundaries, and all the accessible internal surfaces have been oxidized, the coating becomes dense and the diffusion of oxidizing species to the internal portions of the coatings gets slowed down and the growth of the oxides becomes limited mainly to the surface of the



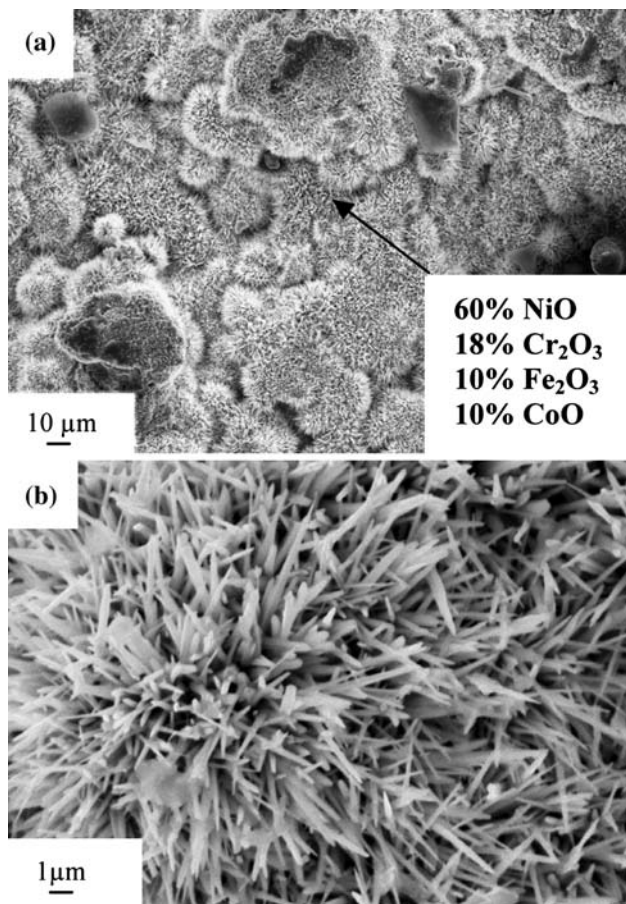
**Fig. 4** SEM/EDAX analysis of coated Superni 75 superalloy after 50 cycles of exposure to air at 800 °C

specimens. This, in turn, will make the weight gain and hence the oxidation rate steady with the progress of exposure time. The slow rate of weight gain during the subsequent cycles might have also been attributed to the mass loss through oxidation of carbon.

Scale thickness was measured from the SEM back-scattered images taken across the cross section of the corroded specimens. These micrographs were taken at the locations where the scale thickness was the least. The average scale thickness values in the molten salt environment and air oxidation are found to be 98 and 45 μm, respectively.

### 3.2 Scanning Electron Microscopy/Energy-Dispersive Analysis

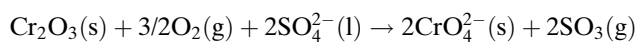
SEM photographs showing surface morphology of the coated specimens after cyclic oxidation in air and molten salt environments have been shown in Figs. 4 and 5. A uniform, adherent, and continuous scale formed on coated Superni 75 after 50 cycles of exposure in air oxidation shows the presence of Cr<sub>2</sub>O<sub>3</sub>, NiO, and Fe<sub>2</sub>O<sub>3</sub> as main phases (Fig. 4). A globular surface scale is formed on the



**Fig. 5** SEM/EDAX analysis of coated Superni 75 superalloy after 50 cycles of exposure to molten salt environment ( $\text{Na}_2\text{SO}_4$ -25% NaCl) at 800 °C

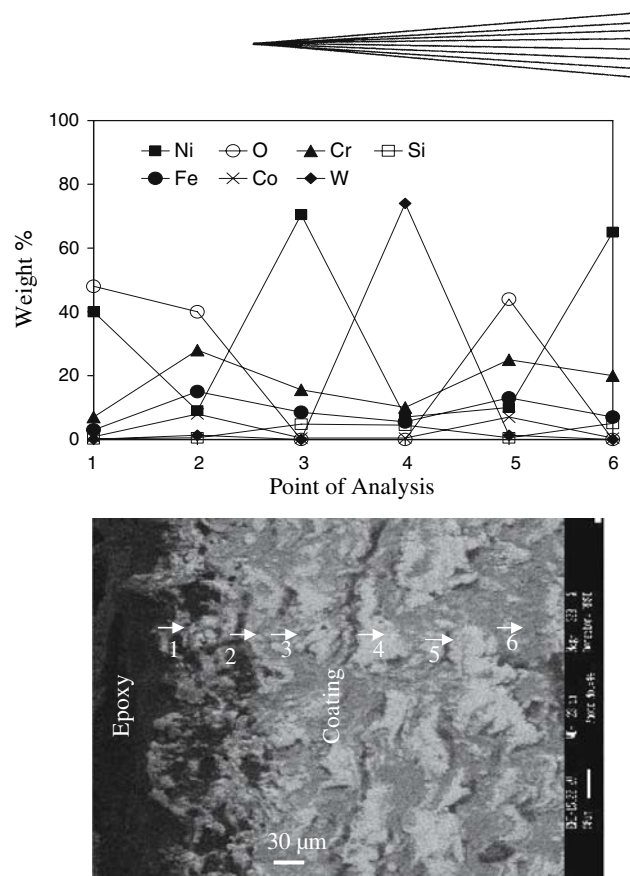
coated Superni 75 specimen after 50 cycles of hot corrosion in  $\text{Na}_2\text{SO}_4$ -25% NaCl molten salt environment (Fig. 5a). At higher magnification, the scale appears to be like a loosely held hairy structure (Fig. 5b). Chlorine generated by the dissociation of NaCl reacts with alloying elements such as chromium, nickel, and iron forms highly volatile metal chlorides, which diffuse out of the scale and react with oxygen present near the scale by releasing chlorine, thus forming a discontinuous and loose oxide scale.

The molten  $\text{Na}_2\text{SO}_4 + \text{NaCl}$  can cause hot corrosion and flux the normally protective oxides such as  $\text{Cr}_2\text{O}_3$  by the following reaction (Ref 11):



Therefore, the non-protective oxide ( $\text{Fe}_2\text{O}_3$ ) or less protective oxides (NiO) are formed in the surface scale, which allows the penetration of corrosive species through the scale to the coating. EDX analysis of the scale shows NiO to be the predominant phase. This NiO formed in the surface scale is porous due to reprecipitation by fluxing action.

BSE image and EDX analysis at some selected point of interest along the cross section of coated Superni 75 corroded in molten salt for 50 cycles at 800 °C are shown



**Fig. 6** Oxide scale morphology and variations of elemental composition along the cross section of HVOF coated Superni 75 after 50 cycles of exposure to molten salt environment

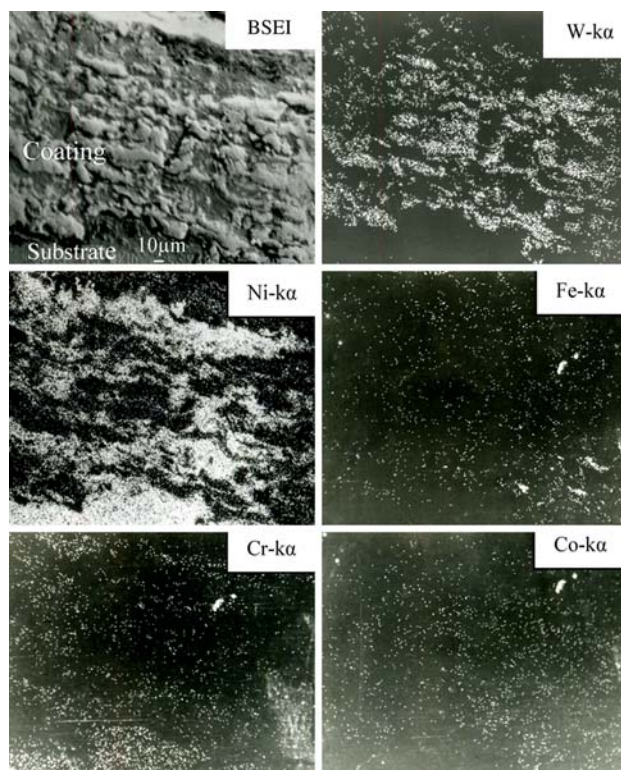
in Fig. 6. The micrographs show that the scales have mostly maintained their lamellar structure during the course of study and there is no crack visible in the scale. EDX analysis shows that the upper part of the scale mainly consists of NiO (Point 1). The light grey phase (Points 3 and 6) and white phase (Point 4) in the scale consist of mainly Ni- and W-rich flat splats, which remain in the un-reacted state as O is found to be absent at these places. Chromium, iron, and cobalt co-exist with O at the boundaries of these splats (Points 2 and 5), indicating the formation of their oxides at the splat boundaries.

### 3.3 X-Ray Diffraction Analysis (XRD) of the Scales

The XRD analysis for the coated Superni 75 and Superfer 800H superalloys after 50 cycles of exposure to air at 800 °C revealed the formation of NiO,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiCr}_2\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$  as main phases, whereas mainly NiO,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiCr}_2\text{O}_4$ ,  $\text{FeCr}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , CoO, and  $\text{CoCr}_2\text{O}_4$  phases are formed after 50 cycles of exposure to  $\text{Na}_2\text{SO}_4$ -25% NaCl molten salt environment. The formation of large number of oxide phases after 50 cycles of exposure to the molten salt environment indicates the presence of accelerated oxidation.

### 3.4 EPMA Analysis of the Scales

The hot corroded samples were cut across the cross section and mounted in transparent mounting resin, mirror



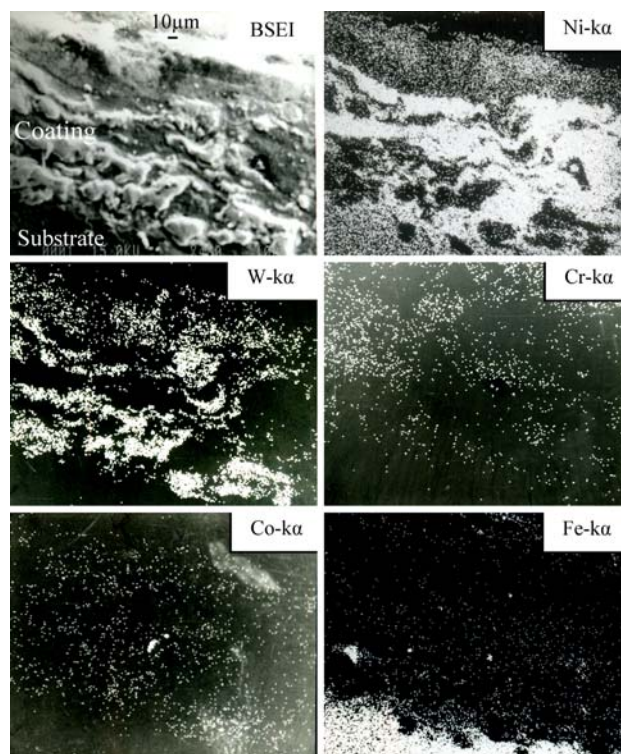
**Fig. 7** EPMA analysis of WC-NiCrFeSiB coated Superni 75 superalloy after 50 cycles of exposure to molten salt environment

polished, and carbon coated to facilitate the x-ray mapping of the different elements present across the scale. X-ray mappings for WC-NiCrFeSiB coated Superni 75 after 50 cycles of hot corrosion at 800 °C indicate the formation of a porous nickel oxide layer in the uppermost part of the scale (Fig. 7). The remaining part of the scale consists of nickel and tungsten rich splats, which are present at alternative positions with chromium, cobalt, and iron mainly exist at the splat boundaries. The back scattered image shows that the coating is adherent and protects the substrate from the attack of degrading species.

EPMA of WC-NiCrFeSiB coated Superfer 800H superalloys after air oxidation for 50 cycles shows the formation of thick band of nickel oxide in the topmost scale (Fig. 8). Similar to hot corroded specimen shown in Fig. 6, the remaining part of the scale also consists of nickel and tungsten rich splats with chromium, cobalt, and iron mainly exist at the splat boundaries.

#### 4. Conclusions

The WC-NiCrFeSiB coating is found to be resistant to the oxidation and hot corrosion modes of degradations, and protects the nickel- and iron-based superalloys in the given environmental conditions at 800 °C. The coating shows better resistance to oxidation as compared to hot

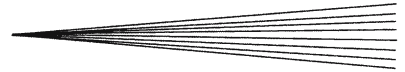


**Fig. 8** EPMA analysis of WC-NiCrFeSiB coated Superfer 800H superalloy after 50 cycles of exposure to air oxidation at 800 °C

corrosion mode of degradation. The protective oxide of mainly chromium, and relatively less protective oxides of nickel and cobalt, and their spinels formed in the surface scale and at the boundaries of nickel and tungsten rich splats have contributed to the oxidation and hot corrosion resistance of the WC-NiCrFeSiB coating in the given environments. These oxides plug/seal all possible diffusion paths in the coatings, thereby block or slow down the penetration of aggressive species.

#### References

1. R.A. Rapp and Y.S. Zhang, Hot Corrosion of Materials: Fundamental Studies, *JOM*, 1994, **46**(12), p 47-55
2. N. Eliaz, G. Shemesh, and R.M. Latanision, Hot Corrosion in Gas Turbine Components, *Eng. Failure Anal.*, 2002, **9**, p 31-43
3. T.S. Sidhu, "Studies on the Hot Corrosion Behaviour of HVOF sprayed Coatings on Some Ni- and Fe- Based Superalloys," Ph.D. Thesis, Indian Institute of Technology, Roorkee, India, May, 2006
4. I. Gurrappa, Hot Corrosion Behavior of CM 247 LC Alloy in Na<sub>2</sub>SO<sub>4</sub> and NaCl Environments, *Oxid. Metal*, 1999, **51**(5), p 353-382
5. D. Deb, S.R. Iyer, and V.M. Radhakrishnan, A Comparative Study of Oxidation and Hot Corrosion of a Cast Nickel Base Superalloy in Different Corrosive Environments, *Mater. Lett.*, 1996, **29**, p 19
6. I. Gurrappa, Identification of Hot Corrosion Resistant MCrAlY Based Bond Coatings for Gas Turbine Engine Applications, *Surf. Coat. Technol.*, 2001, **139**(2-3), p 272-283
7. V. Stoica, R. Ahmed, T. Itsukaichi, and S. Tobe, Sliding Wear Evaluation of Hot Isostatically Pressed (HIPed) Thermal Spray Cermet Coatings, *Wear*, 2004, **257**, p 1103-1124



8. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Hot Corrosion Behaviour of HVOF Sprayed NiCrBSi Coatings on Ni- and Fe-Base Superalloys in  $\text{Na}_2\text{SO}_4$ -60%  $\text{V}_2\text{O}_5$  Environment at 900°C, *Acta Mater.*, 2006, **54**(3), p 773-784
9. T.S. Sidhu, S. Prakash, and R. D. Agrawal, Hot Corrosion Resistance of HVOF Sprayed Coatings on a Ni-Based Superalloy in Molten Salt Environment, *J. Therm. Spray Technol.*, 2006, **15**(3), p 387-399
10. T.S. Sidhu, S. Prakash, and R.D. Agrawal, Performance of High Velocity Oxy-Fuel Sprayed Coatings on a Fe-Based Superalloy in  $\text{Na}_2\text{SO}_4$ -60%  $\text{V}_2\text{O}_5$  Environment at 900°C. Part II: Hot Corrosion Behaviour of the Coatings, *J. Mater. Engg. Perform.*, 2006, **15**(1), p 130-138
11. I. Gurrappa, Identification of Hot Corrosion Resistant MCrAlY Based Bond Coatings for Gas Turbine Engine Applications, *Surf. Coat. Technol.*, 2001, **139**, p 272-283