

Hot Corrosion Behavior of Detonation Gun Sprayed $75\text{Cr}_3\text{C}_2$ - $25(80\text{Ni}-20\text{Cr})$ Coating in Molten Salt Environment

*Subhash Kamal^a, Chennupati Vijya Kumar^B, Achhaibar Singh^a,

^aSchool of Engineering & Technology (SET), Sharda University, Uttar Pradesh,
Greater Noida - 201 303 U.P, INDIA

^bSSIT, B. Gagaram (V), Sathupally-Khammam. Andhra Pradesh, INDIA

Abstract

Hot corrosion is one of the serious problems in the turbine engines used for aircraft and thermal power plant applications. Nickel based superalloys form the key structural components of the turbine engines due to its superior strength and high temperature creep properties. However, they do not show an adequate stability against hot corrosion in the high temperature corrosive environments. Therefore, it requires protective coatings, which could impart hot corrosion resistance in the deleterious high temperature environments. Detonation gun sprayed coatings exhibit desirable microstructural morphologies with higher adhesive strength, low porosity and less compressive residual stresses as compared to other thermal spray processes as evident from the literature. The present work has been focused to develop Cr_3C_2 -NiCr coating on the superalloy substrate by Detonation gun spray technique and measure its hot corrosion behavior in the molten salt environment ($75\text{wt.}\% \text{Na}_2\text{SO}_4 + 25\text{wt.}\% \text{K}_2\text{SO}_4$) at 900°C under cyclic conditions for 100 hrs. Thermogravimetry technique was used to measure the kinetics of corrosion of coated and bare superalloy substrates. XRD, SEM and FE-SEM/EDAX were used to characterize the corrosion products. It was found that Cr_3C_2 -NiCr coating served as an effective solid-state diffusion barrier between oxygen (or other gaseous) and the base superalloy substrates. The hot corrosion resistance of the Cr_3C_2 -NiCr coating was due to the formation of protective scales such as oxides and spinels of Ni and Cr.

Key words: - Detonation gun coating, Hot corrosion, superalloys, Cr_3C_2 -NiCr coating

1.0 Introduction

Thermal sprayed coatings play a vital role in protecting turbine engines against high temperature oxidation and hot corrosion at elevated temperatures [1]. Cr_3C_2 -NiCr coating is extensively used to minimize wear and corrosion due to its superior wear resistance, high thermal stability, and oxidation resistance. In this coating, the corrosion resistance is provided by NiCr matrix while the wear resistance is mainly due to the carbide ceramic phase [2]. The Cr_3C_2 -25%NiCr coatings are considered to be a preferable alternative to hard chrome platings due to the strict environmental regulations and cost concerns with regard to the electroplating process [3]. Detonation-gun (D-gun) spray coating process is a thermal spray process, which gives an extremely good adhesive strength, low porosity, and coating surfaces with compressive residual stress (4). Detonation process (D-Gun) offers highest velocity ($800\text{--}1200\text{ms}^{-1}$) for the sprayed

powders that are unattainable by the plasma and HVOF conditions. D-gun spraying processes minimize decomposition of the carbide phase due to lower heat enthalpy and shorter duration involved in the coating processes. The higher particle velocity during deposition of coating results in desirable characteristics such as lower porosity and higher hardness of the coatings [5].

Cr_3C_2 -NiCr coatings, deposited on selected superalloys superni 75 superni 718 and superfer 800H using the detonation gun process, showed a higher hot corrosion resistance in the molten salt environment ($\text{Na}_2\text{SO}_4+25 \text{ wt.}\% \text{K}_2\text{SO}_4$) at 900°C for 100 cycles as compared to the uncoated super alloys[6]. Therefore, the present work has been focused to study the influence of D-gun sprayed Cr_3C_2 -NiCr coating on hot corrosion behaviour of Ni based superalloy. Thermogravimetry technique was used to study the kinetics of corrosion of D-gun sprayed Cr_3C_2 -NiCr coating and bare

superalloy substrates. XRD, SEM and FE-SEM/EDAX were used to characterize the corrosion products of the coated and bare samples in order to render an insight in to the corrosion mechanisms

2. Experimental procedure

2.1 Development of coatings

2.1.1 Substrate material, Coating powders

Superni 75 substrate materials selected for the study, which were provided by Mishra Dhatu Nigam Limited, Hyderabad (India) in the rolled sheet form. The nominal chemical composition of the substrate superni 75 is Fe3.0%, Cr 77.1%, Ni19.5%, Ti0.3% and C 0.1%, Specimens with dimensions of

approximately 20 mm x 15 mm x 5 mm were cut from the alloy sheets, polished using emery papers of 220, 400, 600 grit sizes and subsequently on 1/0, 2/0, 3/0 and 4/0 grades. Prior to deposition of the coatings by the Detonation Gun process, the substrate material is grit blasted with alumina powders (Grit 45). A commercially available 75%Cr₃C₂-25%(80Ni-20Cr) powder (AMPERIT 584.072) with its particle size 10-38µm was used. The powder particles show an irregular shape with a wide particle size ranging from 9.3-36.10 µm, which was measured using its BSEI images shown in Fig.1. The measured size was consistent with the nominal size range provided by the manufacturer

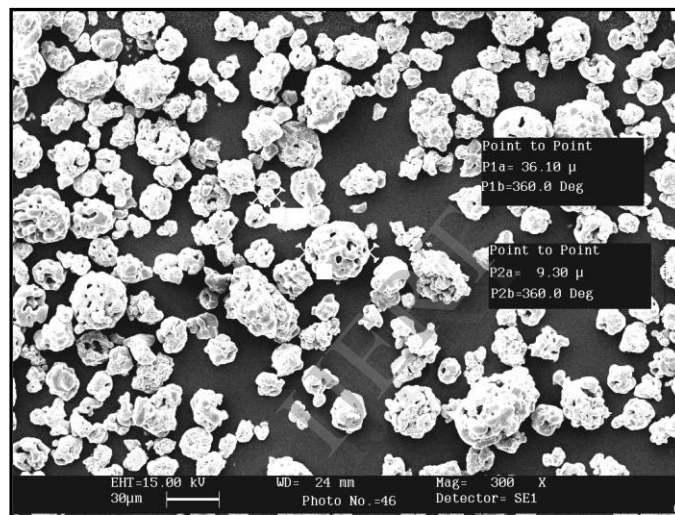


Figure 1 (a) SEM of Cr₃C₂-NiCr powder showing the particle size

2.1.2 Detonation–gun technique

D-gun was used to apply Cr₃C₂-NiCr coatings on the superalloy substrates at SVX Powder M Surface Engineering Pvt Ltd, New Delhi (India). Standard spray parameters were designed for depositing the Cr₃C₂-NiCr coatings. All the process parameters, including the spray distance, were kept constant throughout coating process. The spraying parameters are acetylene flow rate(C₂H₂) 2240 SLPH, oxygen flow rate (O₂) 2720 SLPH, carrier gas flow rate (N₂) 960 SLPH, frequency 3shots/s, diameter of spot size 22mm, spraying distance from nozzle165mm, powder flow rate 1.0 to 2.0 grams/shot.

2.1.3 Characterisation of the coating

The coated samples were wheel cloth polished and then subjected to FE-SEM (FEI, Quanta 200F) with EDAX Genesis software attachment to characterize its surface morphology. XRD analysis was carried out using a Bruker AXS D-8 Advance diffractometer (Germany) with Cu Ka radiation for identifying the phases in the coating

2.2. Hot corrosion test

Hot corrosion studies were performed in a molten salt (75%Na₂SO₄ + 25%K₂SO₄) for 100 cycles under cyclic conditions. Each cycle consisted of 1 hour heating at 900 °C in a silicon carbide tube furnace followed by 20 minutes cooling at room temperature. The studies were performed for uncoated as well as

coated specimens for comparison. The specimens were mirror polished down to 1 μm alumina on a wheel cloth-polishing machine. A salt of 75% Na_2SO_4 + 25% K_2SO_4 is thoroughly mixed with distilled water. After washing with acetone, the specimens were washed with acetone and then heated in an oven to about 250 $^\circ\text{C}$. The heating of the specimens was found essential for proper adhesion of the salt layer. A salt of 75% Na_2SO_4 + 25% K_2SO_4 is thoroughly mixed with distilled water and a layer of this salt mixture was applied uniformly on the warm polished specimens with the help of a camel hair brush. The amount of salt coating was kept in the range of 3.0–5.0 mg/cm^2 . The salt coated specimens as well as the alumina boats were then kept in the oven for 3–4 hours at 100 $^\circ\text{C}$, subsequently, they were again weighed before exposing to hot corrosion tests in the silicon tube furnace. During hot corrosion runs, the weight of boats and specimens was measured together at the end of each cycle with the help of a thermogravimetric balance model 06120 (Contech, 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. The corrosion rate was calculated using the weight change measurements of the bare and coated samples. The samples after corrosion tests were analysed using FE-SEM/EDAX and XRD for surface and cross-sectional analysis of the scale.

3.0 Results

3.1 Surface morphology

SEM micrograph of Cr_3C_2 -NiCr coated surface indicates nodules of different sizes similar to the morphology of the coating powder (Fig.2). The as sprayed surface is fairly rough, dense, with pores, but show the presence of partially melted particles. An incorporation of oxygen in the coating may be due to in flight oxidation of the powder particles. The carbide particles are uniformly clad with the metallic binder, as it shows lower carbide dissolution giving a better carbide distribution, which leads to a better binder protection

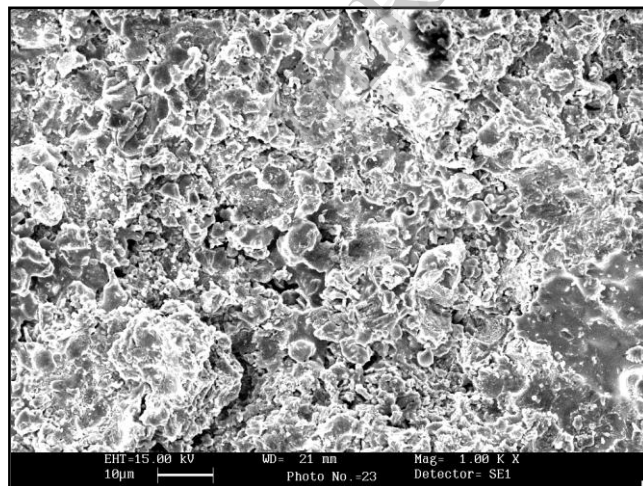


Figure.2 SEM micrographs showing surface morphology of detonation gun as-sprayed Cr_3C_2 -NiCr coating on superalloy Superni 75

3.2 Cyclic Hot corrosion in Molten Salt

Fig.3 shows the weight gain/unit area for the bare and coated superalloy subjected to 75% Na_2SO_4 + 25% K_2SO_4 salt mixture at 900 $^\circ\text{C}$ for 100 cycles. The bare superalloy Superni 75 shows a higher weight gain as compared to coated sample. The weight gain data reveals that the Cr_3C_2 -NiCr coating is found to be more hot corrosion resistance than

the bare superalloys. It is evident that Cr_3C_2 -NiCr coated superalloys obey parabolic rate law and exhibit the tendency to act like diffusion barriers to the corroding species. The weight gain square (mg^2/cm^4) versus time (number of cycles) plots are shown in Fig.4 to establish the rate law for the hot corrosion. It is observed from the graph that the coating follows a nearly parabolic rate law. The parabolic rate (Fig.4) constant K_p was

calculated by a linear least-square algorithm to a function in the form of $(W/A)^2 = Kp t$, where W/A is the weight gain per unit surface area

(mg/cm^2) and 't' indicates the number of cycles, represents the time of exposure.

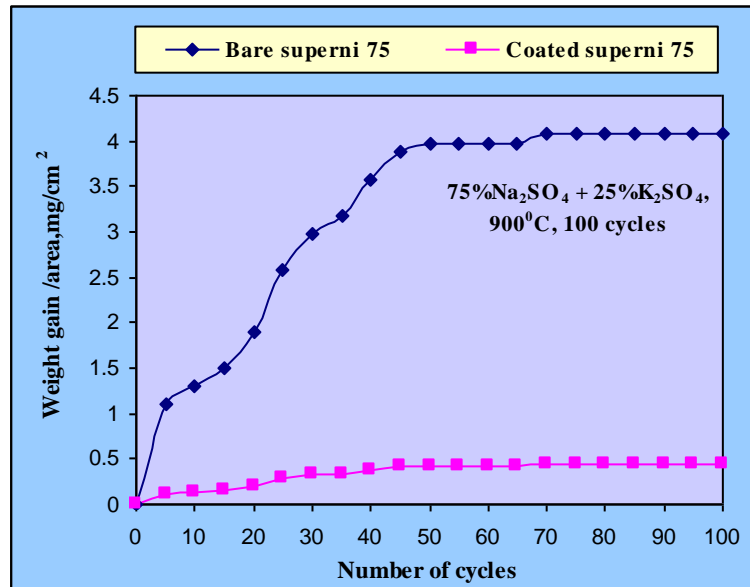


Figure 3 weight gain/area versus number of cycles plot for coated and bare superalloy subjected to cyclic oxidation for 100 cycles in $75\% \text{Na}_2\text{SO}_4 + 25\% \text{K}_2\text{SO}_4$ at 900°C

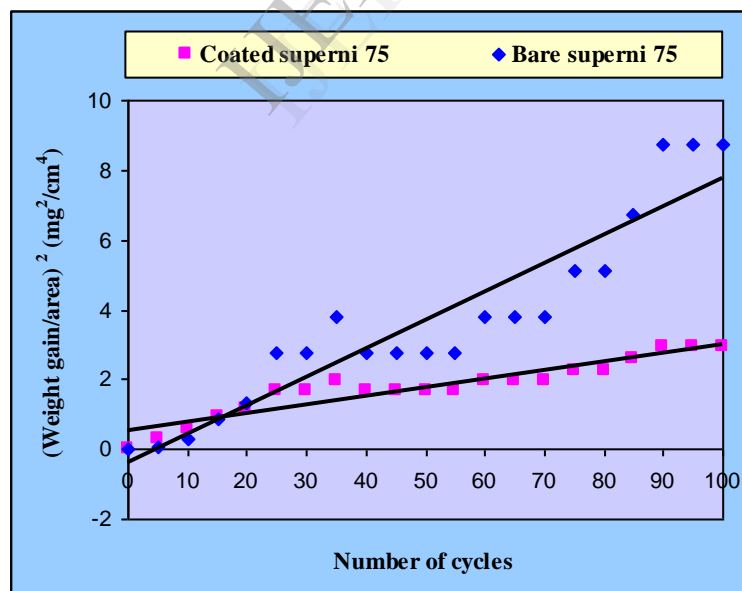


Figure 4 $(\text{weight gain}/\text{area})^2$ versus number of cycles plot for coated and bare superalloy subjected to cyclic oxidation for 100 cycles in $75\% \text{Na}_2\text{SO}_4 + 25\% \text{K}_2\text{SO}_4$ at 900°C

3.3 X-ray diffraction analysis (XRD) of scale

The XRD patterns for the corroded surfaces of bare and coated superalloys exposed to 75%

$\text{Na}_2\text{SO}_4 + 25\% \text{K}_2\text{SO}_4$ environment at 900°C after 100 cycles are shown in the Fig.5. The main phases identified are NiCr_2O_4 , $\text{Cr}_2\text{Ti}_2\text{O}_7$, Cr_7C_3 , Cr_{23}C_6 , NiTi_2 , Cr_3C_2 , Ti_3S_4 , NiTiO_3 , NiS , Cr_2O_3 and Ni

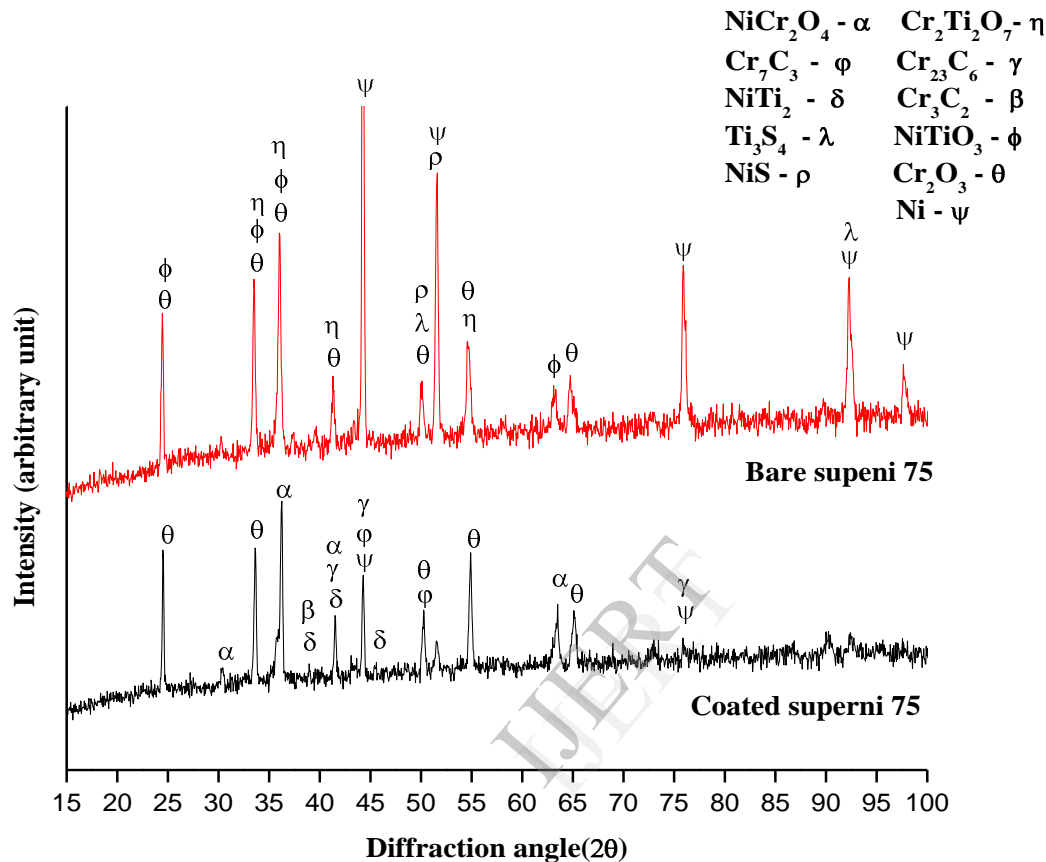


Figure 5 X-ray diffraction patterns for bare and Cr_2C_3 -NiCr coated superalloy exposed to cyclic oxidation in $75\% \text{Na}_2\text{SO}_4 + 25\% \text{K}_2\text{SO}_4$ environment for 100 cycles at 900°C

3.4. FE-SEM/EDAX analysis of the scale

3.4.1 Surface morphology of the scale

FE-SEM micrographs with EDS spectrum reveals the surface morphology of the Cr_3C_2 -NiCr coated and bare superalloy superni 75 substrate specimens after cyclic oxidation in $75\% \text{Na}_2\text{SO}_4 + 25\% \text{K}_2\text{SO}_4$ environment for 100

cycles at 900°C as shown in Figs.6 and 7, respectively. It clearly indicates the formation of Cr_2O_3 and NiO as predominant oxides on coated and bare superalloy Superni 75. It also shows the presence of weak EDS peaks of TiO_2 and Fe_2O_3 . SEM micrograph (Fig.6) shows the carbide flakes uniformly distributed along the NiCr binder in the coating

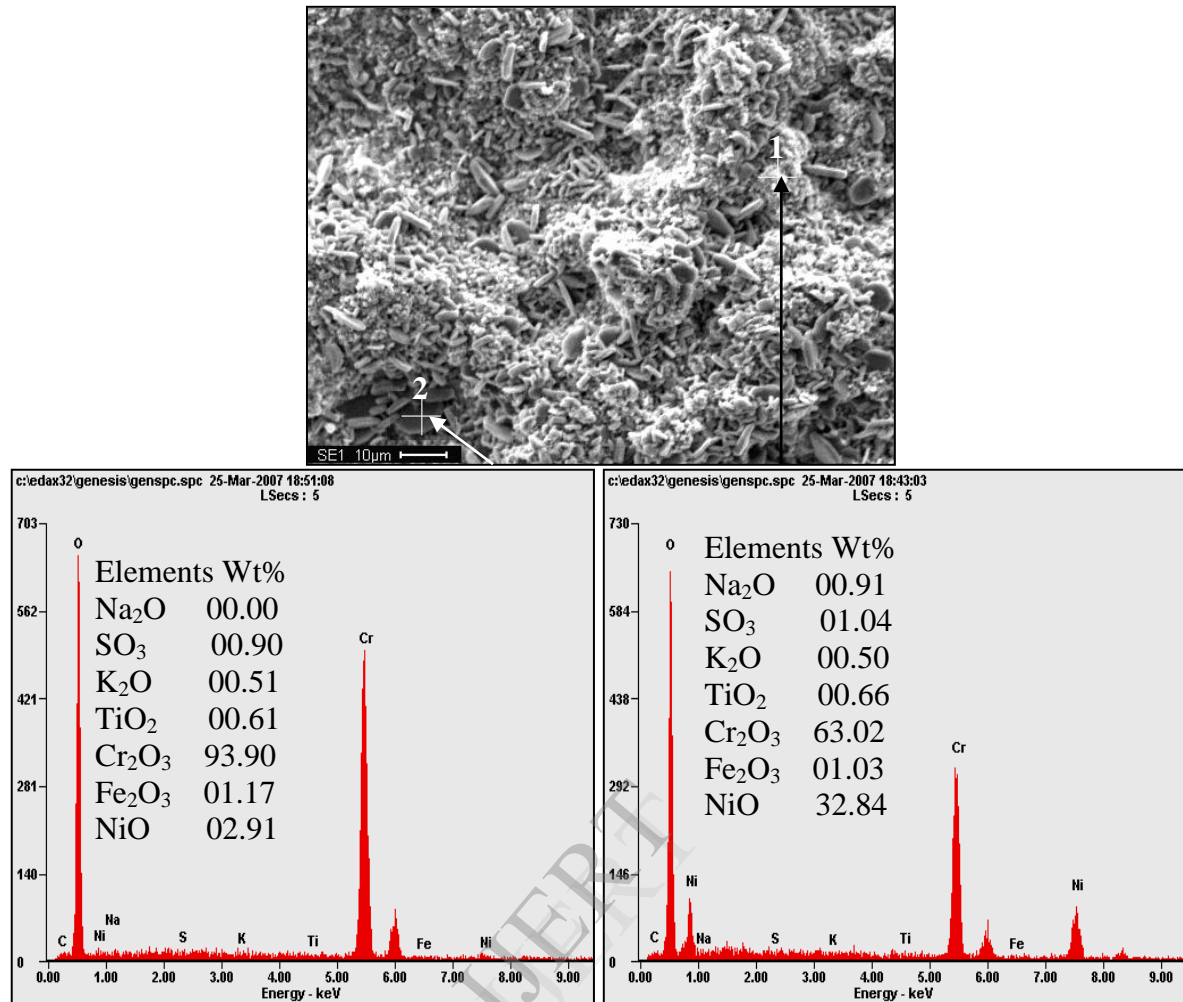


Figure 6 FE-SEM/EDAX micrographs with EDS spectrum of the coated superalloy superni 75 specimens showing surface morphology after cyclic hot corrosion in 75%Na₂SO₄ + 25%K₂SO₄ environment for 100 cycles at 900^oC

3.5 Discussion

The weight gain curves for detonation gun Cr₃C₂-NiCr coated Superalloy followed nearly a parabolic behaviour (Fig.3), but bare superalloy show a small deviation from the parabolic rate law, which is due to cyclic scale growth. The higher weight gain of the specimens during the first few cycles may due to the rapid formation of oxides at the splat boundaries and within the open pores due to the penetration of the oxidizing species.

Afterwards, the subsequent increase in weight is gradual. During the course of hot corrosion studies on bare and detonation gun Cr₃C₂-NiCr coated superalloys, the parabolic rate constant for the bare superalloy is found to be greater than the coated superalloy. The parabolic rate constants for bare and coated superalloy superni 75 calculated on the basis of 100 cycles data are $22.64 \times 10^{-12} \text{ gm}^2\text{cm}^{-4}\text{s}^{-1}$ and $6.88 \times 10^{-12} \text{ gm}^2\text{cm}^{-4}\text{s}^{-1}$ respectively. The Cr₃C₂-NiCr coated superni

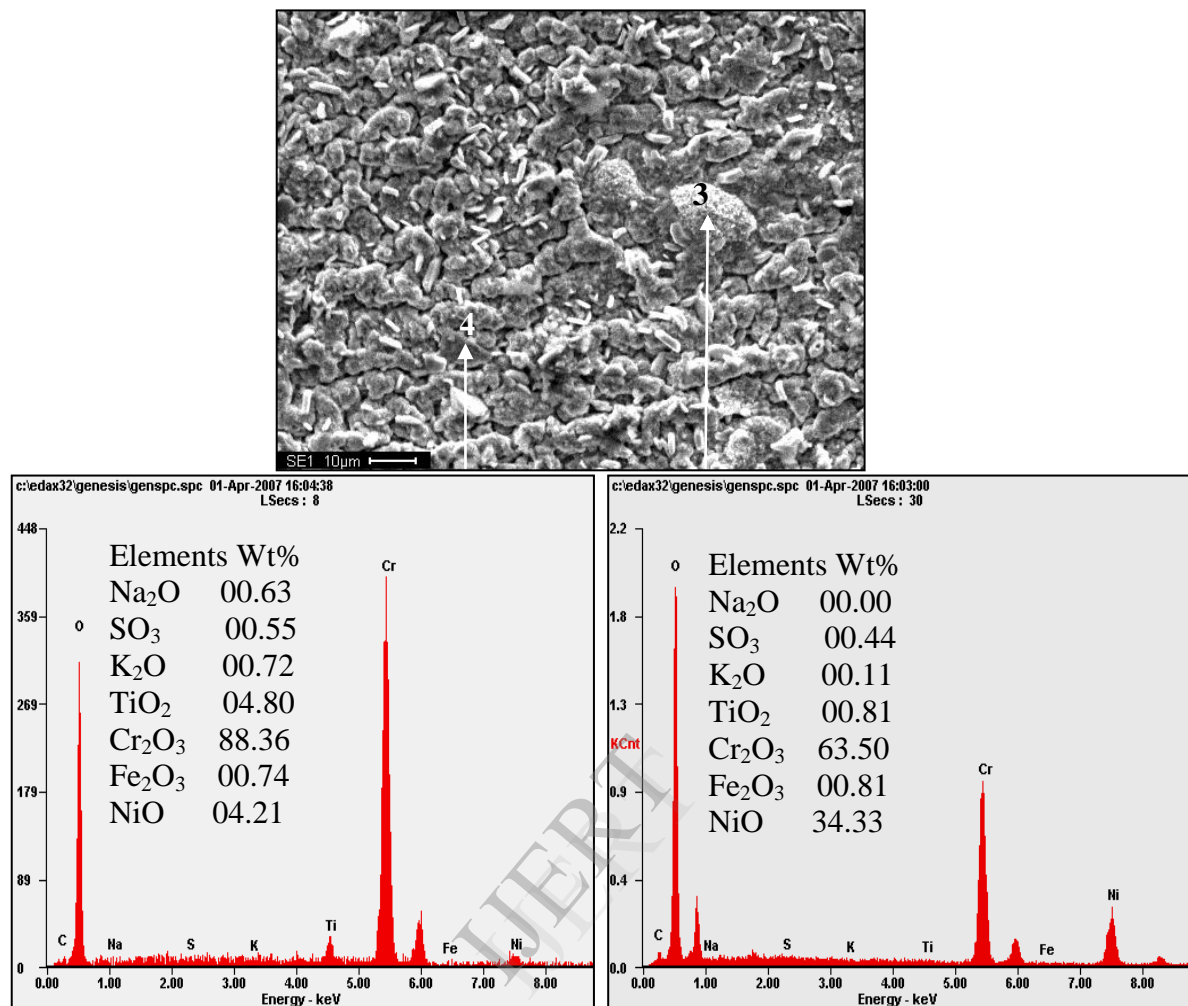


Figure 7 FE-SEM/EDAX micrographs with EDS spectrum of the bare superalloy superni 75 specimen showing surface morphology after cyclic hot corrosion in 75%Na₂SO₄ + 25%K₂SO₄ environment for 100 cycles at 900°C

75 (Fig.3) superalloy has shown a minimum weight gain, whereas bare superni 75 revealed a higher weight gain, which is 89.3% more than that of the former.. The bare superalloy indicates the formation of Cr₂O₃, Ni, NiS and NiTiO₃ as major phases, oxide scale of corroded Cr₃C₂-NiCr coating indicates the formation of Cr₂O₃, Cr₇C₃, Cr₂₃C₆ and NiCr₂O₄ spinel as major phases as observed from the Fig. 5. The presence of minor phase such as NiTiO₃ on the surface of hot corroded Cr₃C₂-NiCr indicates the diffusion of Ti from the substrate during hot corrosion of the specimens at temperature about 900°C. The growth of oxide scale typically displays a parabolic dependence with time and its longevity is dependent upon the concentration

of the scale-forming element in the coating material, temperature, oxidising conditions and alloy microstructure [7..6]. The surface morphology and EDAX analysis of hot corroded Cr₃C₂-NiCr coated scale and bare alloy shows the formation of Cr₂O₃ and NiO as major phases on all the superalloys as shown in Fig. 6 and 7. Coated superni 75 (Fig 6) shows 63.02% Cr₂O₃ with 32.84% NiO at point1 and 93.96% Cr₂O₃ with 2.91% of NiO in grey region (point 2). The presence of weak EDS peaks of TiO₂ and Fe₂O₃ indicates the diffusion of these elements from the substrate in to the coating during hot corrosion run. The surface micrographs of corroded bare superalloys superni 75 indicate the spalling behaviour of the scale as shown in Figs.7. The

EDAX analysis of the scale indicates the presence of 63.50% Cr₂O₃ with 34.33% NiO at point 3 and 88.36% Cr₂O₃ with 4.21% NiO

at point 4 as the main phase along with very small percentage of K₂O, SO₃, Na₂O, TiO₂ and Fe₂O₃ as indicated by EDS spectrum

3.6 Conclusions

- Cr₃C₂-NiCr coating was successfully deposited on Ni based superalloy substrates by Detonation gun spraying process, the coating show nearly uniform, adherent and dense microstructure
- Weight gain data for Cr₃C₂-NiCr coated superalloy indicated less weight gain as compared to bare super alloy
- Cr₃C₂-NiCr coating shows a better hot corrosion resistance as compared to the bare superalloy Superni 75.
- A saving in overall cumulative weight gain for Cr₃C₂- NiCr coated Superni 75 with respective to the bare alloy is 89.3%

References

- [1] Yamada, K.; Tomono, Y.; Morimoto, J.; Sasaki, Y.; Ohmori, A., (2002). Hot corrosion behavior of boiler tube materials in refuse incineration environment. *Vacuum*, 65, pp533–540
- [2] Guilemany, J.M. ; Espallargas, N.; Suegama, P.H.; Benedetti, A.V., (2006). Comparative study of Cr₃C₂-NiCr coatings obtained by HVOF and hard chromium coatings. *Corrosion Science*, 48, pp2998–3013
- [3] Murthy, J.K.N.; Venkataraman, B., (2006). Abrasive wear behaviour of WC-CoCr and Cr₃C₂-20(NiCr) deposited by HVOF and detonation spray processes. *Surface & Coatings Technology*, 200, pp2642– 2652
- [4] Subhash Kamal, R Jayaganthan, S Prakash, (2010) Hot corrosion Studies of detonation-gun-sprayed NiCrAlY+0.4wt%CeO₂ coatings on superalloys in molten salt environment, *Journal of Materials Engineering and Performance*, Volume 20, Issue 6, pp1068-1077.
- [5] Hao Du, Weigang Hua, Jiangang Liu, Jun Gong, Chao Sun, Lishi Wen, (2005). Influence of process variables on the qualities of detonation gun sprayed WC-Co coatings. *Materials Science and Engineering A*, 408, pp202–210
- [6] Subhash Kamal, R. Jayaganthan , Satya Prakash, (2009).Evaluation of cyclic hot corrosion behaviour of detonation gun sprayed Cr₃C₂-25%NiCr coatings on nickel- and iron-based super alloys, *Surface & Coatings Technology*, 203, pp1004–1013
- [7] Subhash Kamal, R. Jayaganthan, S. Prakash, (2009). High temperature oxidation studies of detonation-gun-sprayed Cr₃C₂-NiCr coating on Fe- and Ni-based superalloys in air under cyclic condition at 900 °C, *Journal of Alloys and Compounds* 472, pp378–389