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# High temperature cyclic oxidation behavior of magnetron sputtered Ni–Al thin films on Ni- and Fe-based superalloys

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ABSTRACT

Ni–Al thin films were deposited on Ni- and Fe-based superalloys by RF magnetron sputtering in this work. The microstructures of the as-deposited films were characterized by XRD, AFM, and FE-SEM/EDS. The grain size of the Ni–Al thin films, using XRD results, was found to be 8.1 nm, 9.22 nm and 16.04 nm for Superni 76 (SN 76), Superni 750 (SN 750) and Superfer 800 (SF 800), respectively. The surface roughness of NiAl coated superalloys was calculated by using its AFM images and it showed a regular smooth surface. The Ni–Al thin films deposited superalloys were subjected to oxidation studies at 900 °C for 100 cycles. The kinetics of oxidation was determined from the weight change of the samples monitored under cyclic conditions. The oxide scales formed on the bare and Ni–Al deposited superalloys were characterized to elucidate the mechanisms of high temperature oxidation. The SF 800 superalloy has provided a better oxidation resistance in the given environment compared to SN 76 and SN 750 alloy. The weight gain was high in case of Ni–Al coated SN 750 but it was less on the coated SF 800 alloy, indicating a better protection among the coated superalloys.



## 1. Introduction

Ni–Al alloys exhibit a wide range of favorable physical and mechanical characteristics, such as low density, high melting temperature, high thermal conductivity, high stiffness, good oxidation resistance, and metal-like electrical conductivity. These superior properties of Ni–Al are exploited for various applications including high pressure turbine blades, interconnections in electronic components, high temperature corrosion protective coatings, surface catalysts and high temperature environmental coatings [1–5]. The importance of NiAl intermetallic material stems from: (i) excellent resistance to oxidation; (ii) maintaining strength at high temperature; and (iii) low density [6]. Aluminide coatings deposited either by pack cementation or by chemical vapor deposition techniques (CVD), have been applied to gas turbine vane and blade airfoils since 1970 [7]. Lee et al. [8] fabricated very thin (thickness = 100 nm) NiAl underlayer films using magnetron sputtering using a NiAl target with the same composition as desired in the film. Nickel aluminides thin films are generally produced by solid-state reactions between Ni and Al during heating of the Ni–Al multilayer thin films. The other routes to deposit NiAl thin films are based on dual magnetron co-sputter deposition using either NiAl alloy targets or separate targets of Ni and Al. For high temperature applications in aerospace industries, two types of diffusion techniques are generally employed in order to form the NiAl-type protective coatings [9]. It is very essential to investigate the high temperature oxidation behavior of sputter deposited NiAl thin films for its potential applications in aero and land-based turbine engines. The literature is scarce on the high temperature oxidation behavior of sputtered Ni–Al thin films on Ni- and Fe-based superalloys. Therefore, this work has been focused to investigate the high temperature cyclic oxidation behavior of Ni–Al thin films on Ni- and Fe-based superalloys in air at 900 °C. The oxidised specimens were characterised using the combined techniques of XRD, AFM, and FESEM/EDS to elucidate the mechanisms of high temperature oxidation in this work.

## 2. Experimental details

### 2.1. Substrate material

Three superalloy substrates, viz. SN 76, SN 750, and SF 800, were used in this study. The superalloys were procured from Mishra Dhatu Nigam Limited, Hyderabad (India) in the rolled sheet form. The chemical composition of the substrate materials is reported in Table 1. The specimens, each measuring approximately 20 mm × 15 mm × 5 mm, were cut from the alloy sheets. The specimens were mirror polished with different grade of SiC papers.

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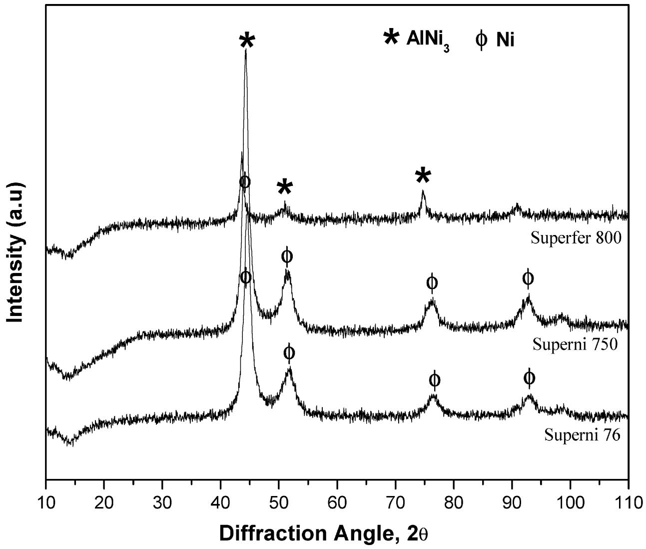


**Fig. 1.** XRD patterns indicating the Ni–5Al film deposited on different superalloy substrates by RF magnetron sputtering.

*2.2. Deposition of Ni–Al films*

Ni–Al thin films were deposited on Ni- and Fe-based superalloys by RF magnetron sputtering. The substrate was cleaned by acetone prior to the deposition of the film. The sputtering target was prepared by thermal spraying of Ni–5Al wire coating on 50.8-mm diameter and 5-mm thick stainless steel disc. The process parameters used for the deposition of NiAl thin films are shown in Table 2. XRD (Bruker AXS) measurements were made using Cu Kα radiation to characterize the Ni–Al thin films. The scan rate used was $1^\circ\,min^{-1}$ and the scan range was from 10° to 110°. The grain size of the thin films was estimated from the Scherrer formula [10], as given in Eq. (1)

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where λ, θ and B are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and line width at half-maximum, respectively. The instrumental broadening of 0.1° has been incorporated for the grain size calculations. The surface topography and microstructures of the NiAl thin films were characterized by using scanning probe microscope (NT-MDT: NTEGRA Model) and field emission scanning electron microscopy (FESEM), respectively.

*2.3. Cyclic oxidation studies*

Oxidation studies were conducted at 900 °C in a laboratory silicon carbide tube furnace (Digitech, India make). The furnace was calibrated to an accuracy of ±5 °C using platinum/platinum-13% rhodium thermocouple fitted with a temperature indicator of Electromek (Model-1551 P), India. The uncoated specimens were polished down to 1 μm alumina wheel cloth polishing before being subjected to oxidation run. The specimens were washed properly with acetone and dried in hot air to remove the moisture. During experimentation, the prepared specimen was kept in an alumina boat and the weight of boat and specimen was measured. The

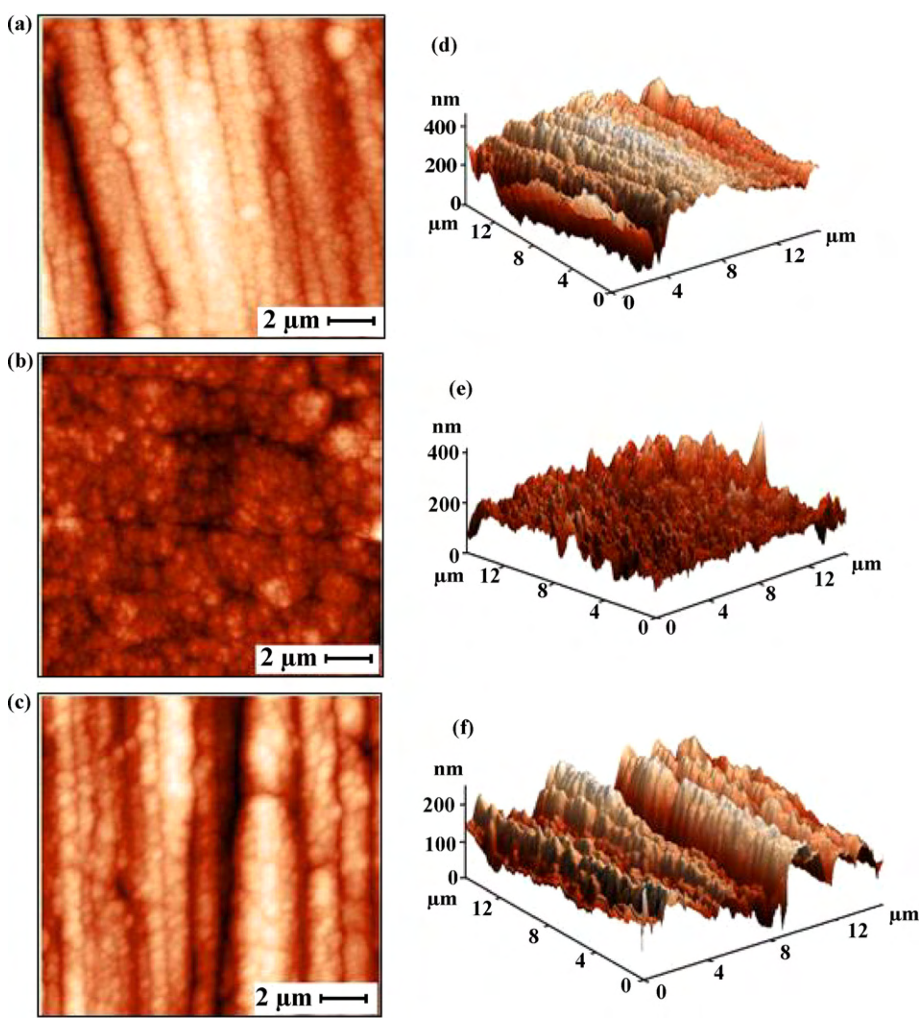


**Fig. 2.** 2D and 3D AFM images of Ni–Al film on Superni 76 (a, d), Superni 750 (b, e) and Superfer 800 (c, f) by RF magnetron sputtering.

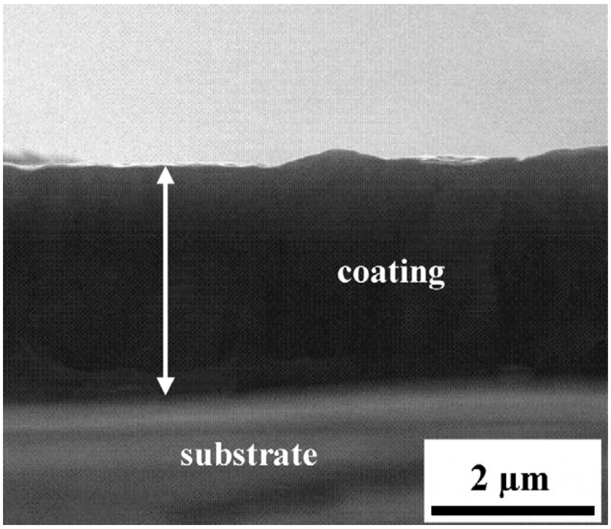


**Fig. 3.** Thickness of Ni–5Al film deposited on superalloy by RF magnetron sputtering.

alumina boats used for the studies were pre-heated at a constant temperature of 1200 °C for 12 h. Then, the boat containing the specimen was inserted into hot zone of the furnace maintained at a temperature of 900 °C. The weight of the boat loaded with the specimen was measured after each cycle, the spalled scale if any was also considered during the weight change measurements. Holding time in the furnace was 1 h in still air followed by cooling at the ambient temperature for 20 min. The weight of the boat along with specimen was measured and this constituted one cycle of the oxidation study. Electronic Balance Model CB-120 (Contech, Mumbai, India) having a sensitivity of $10^{-3}$ g was used to conduct the weight change analysis. The specimens were subjected to visual observations after the end of each cycle with respect to colour or any other physical aspect of the oxide scales being formed.

## 3. Results

### 3.1. *Characterisation of the Ni–Al films*

#### 3.1.1. *XRD analysis of the as-deposited Ni–Al films*

The XRD patterns of Ni–Al films deposited on different superalloy substrates for a period of 2 h and 30 min is shown in Fig. 1. The main phase obtained thin films in case of superalloy substrates

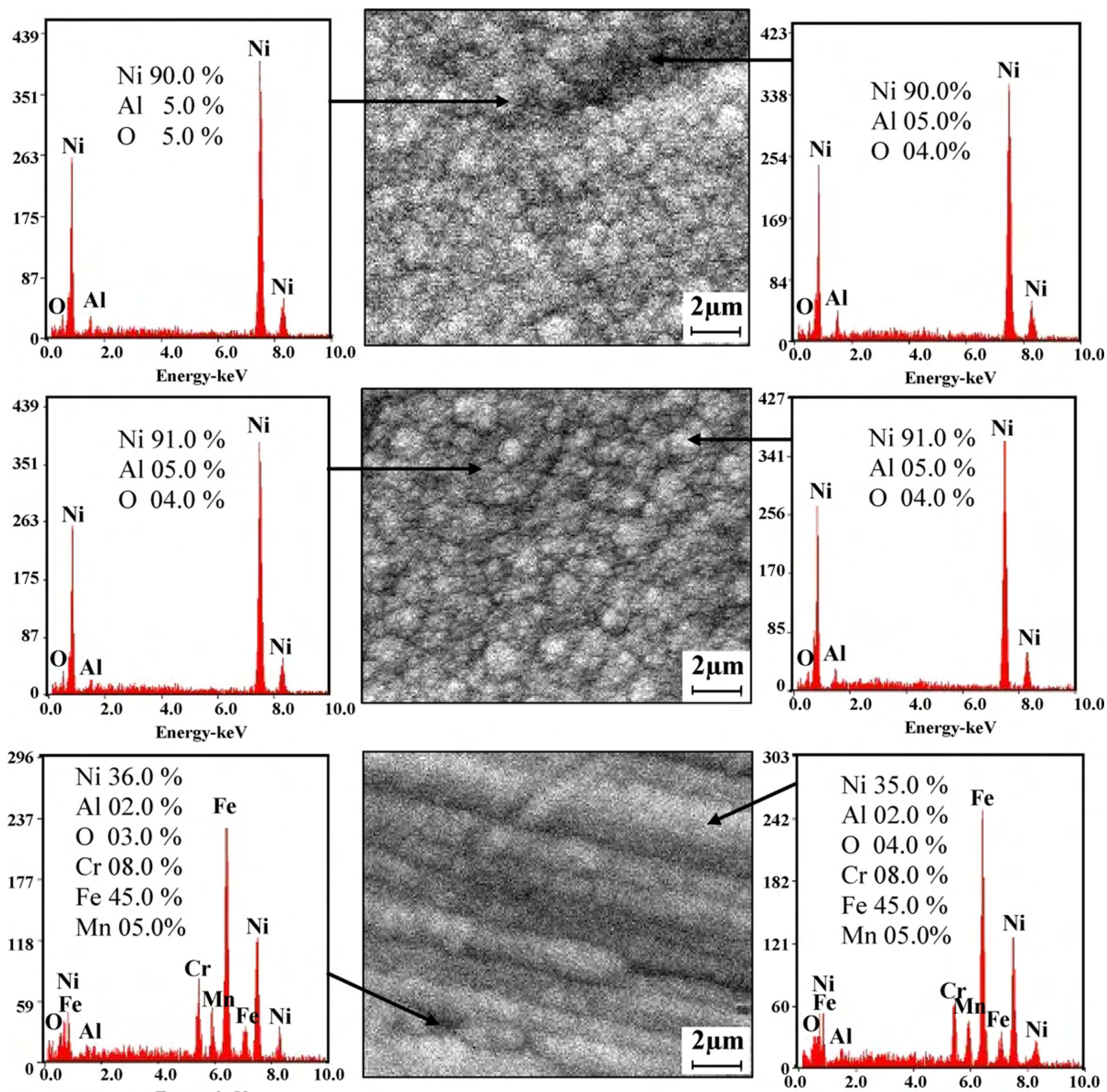


**Fig. 4.** Surface morphology and EDS analysis of Ni–Al film deposited on (a) Superni 76, (b) Superni 750, and (c) Superfer 800 alloy.

**Table 1**
Chemical composition of the superalloys.

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

SN 76 and SN 750 was Ni, and in case of SF 800 substrate, the $Ni_3Al$ phase was observed. The XRD results have shown that the deposited NiAl film has a crystallite size of 8.1 nm, 9.22 nm and 16.04 nm for SN 76, SN 750, and SF 800 respectively.

#### *3.1.2. AFM analysis of the as-deposited Ni–Al films*

The surface morphology of the films was studied using atomic force microscope (NT-MDT: NTEGRA Model) in semi-contact mode. Fig. 2 shows the AFM images of the films deposited on different superalloy substrates. The surface roughness of NiAl film deposited on the substrate such as SN 76, SN 750, SF 800 was 57.2 nm, 31.6 nm, and 60.1 nm, respectively.

#### *3.1.3. FESEM/EDS analysis of the Ni–Al films*

The Ni–Al deposited specimen was cut across the cross-section to measure the film thickness as shown in Fig. 3. The coating thickness was measured at different locations along the cross-sections for all the three superalloys and it was found to be around 2–3 μm. FESEM micrographs of Ni–Al film deposited by RF magnetron sputtering on all three superalloys are shown in Fig. 4 and it is observed that the deposited film is uniform over the surface. It is noticed from the FESEM/EDS analysis that in case of SN 76 and SN 750 superalloys, the deposited film is rich in nickel with small amount of aluminum. EDS analysis was carried out at different points of interest along the cross-section of Ni–Al deposited film on SN 750 as shown in Fig. 5 using FE-SEM with EDS Genesis software attachment. It is observed that the film is rich in nickel with aluminum in small amounts.

### *3.2. Cyclic oxidation studies at 900 °C in air*

The weight gain per unit area versus number of cycles plots for the bare and coated superalloys is depicted in Fig. 6. The weight gain is high in case of bare (uncoated) superalloys compared to Ni–Al deposited superalloys under the same conditions. In case of coated SN 76 and SF 800 superalloys, the weight loss was observed after 3rd cycle and 10th cycle of the experiment. Furthermore, adherent oxide scale was formed on the surface of the coated specimens during subsequent cycles and due to that spallation has ceased. The square of weight gain per unit area versus number of cycles indicates that the Ni–Al coated SN 76 and SF 800 followed the parabolic rate law; whereas, coated SN 750 alloy slightly deviated from the parabolic rate law as observed

**Table 2**
Deposition conditions used in RF magnetron sputtering.

| Parameter | Condition |
|---|---|
| Substrate | Ni- and Fe-based superalloys |
| Base pressure | $3 \times 10^{-6}$ Torr |
| Deposition pressure | 10 mTorr |
| RF power | 190 W |
| Substrate temperature | 250 °C |
| Deposition time | 2 h 30 min |
| Target to substrate distance | 50 mm |
| Deposition atmosphere | Ar |

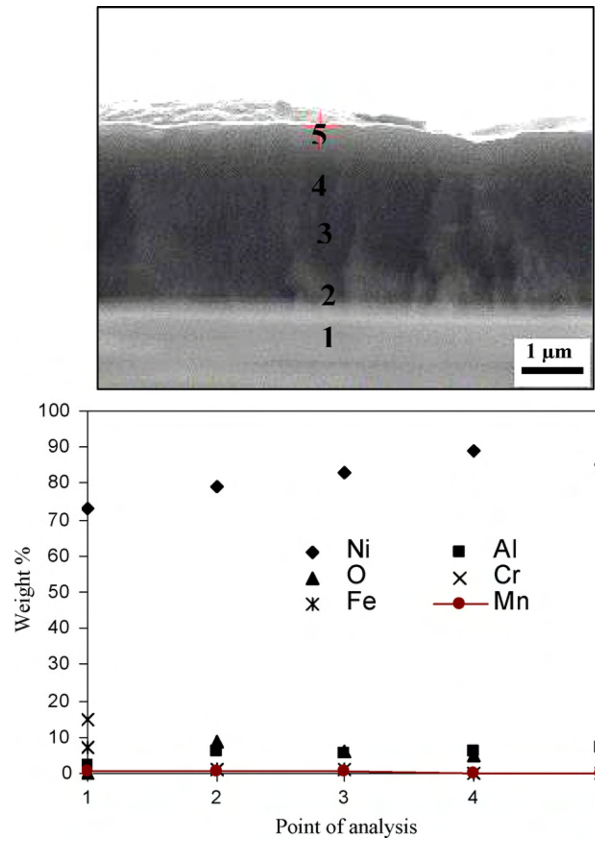


**Fig. 5.** Cross-sectional EDS analysis of RF magnetron sputtered Ni–Al film on Superni 750.

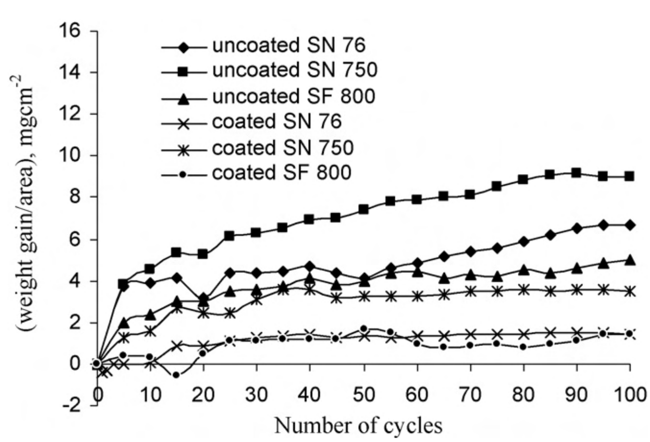


**Fig. 6.** Mass gain/area versus number of cycles plot for Ni–Al coated specimens oxidized in air at 900 °C for 100 cycles.

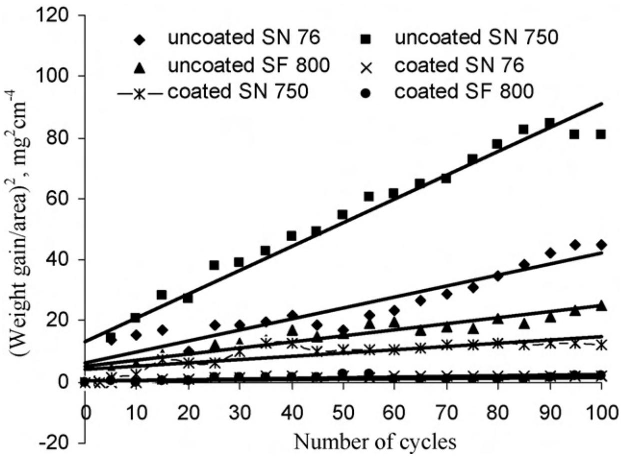


**Fig. 7.** (Mass gain/area)$^2$ versus number of cycles plot for Ni–Al coated superalloy specimens oxidized in air at 900 °C for 100 cycles.

from Fig. 7. The bare alloys slightly deviate from the parabolic rate law. The maximum weight gain (mg cm$^{-2}$) was observed in case of bare SN 750 whereas bare SF 800 shows a minimum weight gain in the given environment. In case of coated superalloys, SF 800 alloy indicated the least weight gain and coated SN 750 has shown the higher weight gain. The parabolic rate constant $k_p$ values for the uncoated and Ni–Al coated superalloys are shown in Table 3.

**Table 3**
Parabolic rate constants values for the uncoated and Ni–Al coated superalloys.

| Superalloy substrate | $k_p$ ($\times 10^{-10}$ g$^2$ cm$^{-4}$ s$^{-1}$) |
|---|---|
| Uncoated Superni 76 | 1.0 |
| Uncoated Superni 750 | 2.15 |
| Uncoated Superfer 800 | 0.55 |
| Coated Superni 76 | 0.06 |
| Coated Superni 750 | 0.29 |
| Coated Superfer 800 | 0.03 |

### 3.3. Surface scale analysis

#### 3.3.1. X-ray diffraction analysis

X-ray diffractograms of the Ni–Al coated films on superalloy substrates after cyclic oxidation in air for 100 cycles at 900 °C are shown in Fig. 8. The oxides formed on the scale of the Ni–Al coated SN 76 superalloy consists of NiO, $Fe_2O_3$, Ni and AlNi. In case of coated SN 750, the scale consists of only NiO. The oxide formed on the scale of the coated SF 800 indicates the formation of $Al_2O_3$, $MnFe_2O_4$ and $AlNi_3$.

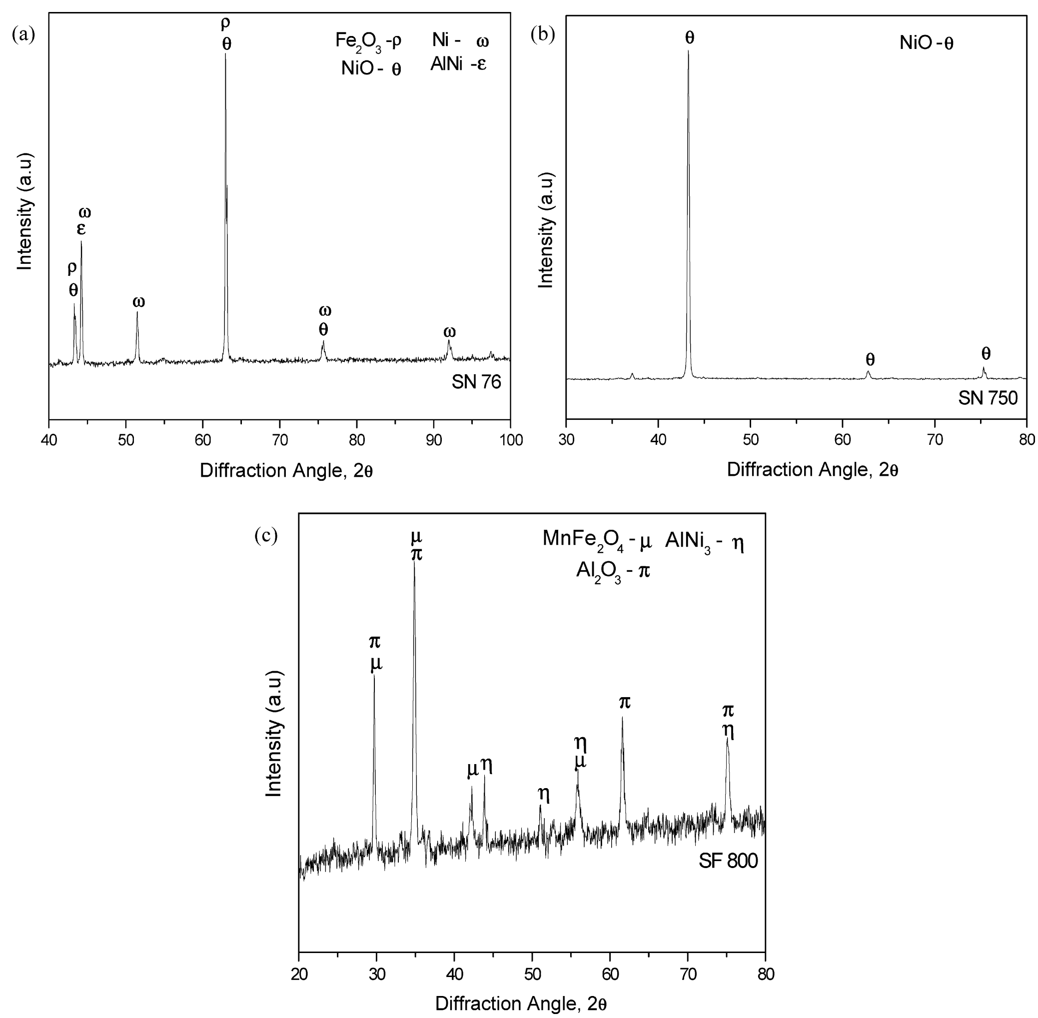


**Fig. 8.** X-ray diffractograms of Ni–Al coated thin films on (a) SN 76, (b) SN 750, and (c) SF 800 after oxidation at 900 °C for 100 cycles.

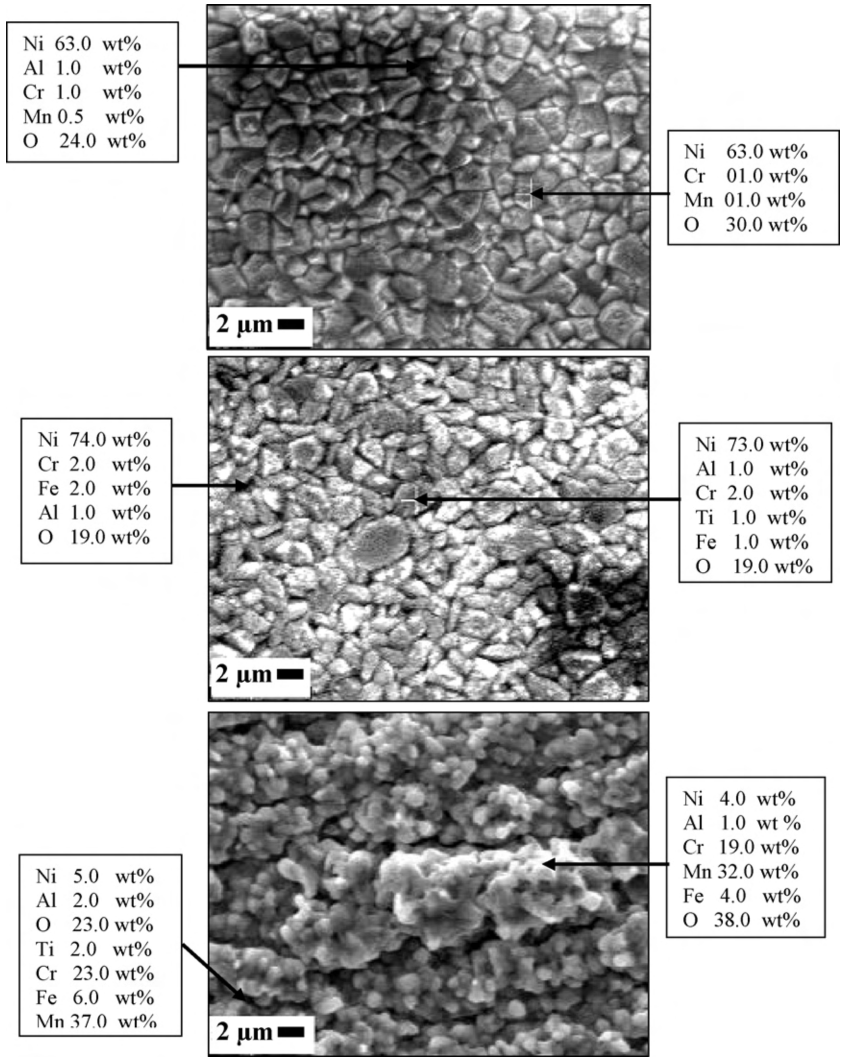


**Fig. 9.** Surface scale morphology and EDS composition of Ni–Al coated thin film after oxidation studies on (a) SN 76, (b) SN 750, and (c) SF 800.

*3.3.2. SEM/EDS analysis of the surface scale*

The surface scale morphology of the coated superalloys oxidised at 900 °C for 100 cycles is shown in Fig. 9. It is observed that the scale formed on the surface of the Ni–Al coated SN 76 and SN 750 superalloys exhibits the irregular shaped granules. NiO is the prominent phase formed on the surface in both the cases, which is also confirmed by XRD results. Furthermore, the surface scale is composed of alumina, chromium oxide, iron and manganese. In case of SF 800 alloy, the surface scale consists of small spherical particles in agglomerated form and mainly consists of iron oxide. The as coated Ni–Al film also indicated the presence of iron in higher amount. Other oxides formed on the surface of the oxidised SF 800 alloy are NiO, $Al_2O_3$, $Cr_2O_3$, and MnO.

## 4. Discussion

The Ni–Al films were deposited uniformly on all the superalloy substrates by RF magnetron sputtering process. The deposited films consist of spherical shaped particles in case of SN 76 and SN 750 alloy, whereas in case of Superfer 800 alloy, the particle shape was not clearly visible in SEM micrograph. The grain size of the deposited film was measured by using Scherrer formula and a crystallite size of 8.1 nm, 9.22 nm and 16.04 nm for SN 76, SN 750 and SF 800 respectively were observed from the XRD analysis. The surface roughness of the as-deposited films was analysed by using atomic force microscope (AFM). A surface roughness of 55 nm, 26 nm and 86 nm was found in case of SN 76, SN 750 and SF 800 respectively. The FESEM/EDS analysis of the as-deposited film indicated the presence of higher amount of nickel in SN 76 and SN 750, whereas in case of SF 800, higher amount of Ni and Fe was observed.

The weight loss has been observed in SN 76 and SF 800 alloy and this may be attributed to the spalling of the scale formed on the surface of the coated specimens during initial stages of the oxidation study. The high temperature oxidation behaviour of the Ni–Al coated film on superalloys mostly followed the parabolic rate law. There is slight deviation in parabolic rate law in case of coated SN 750. This may be due to the formation of rapid inhomogeneous scale on the surface of the superalloy as identified by our earlier work on thermal sprayed coating [11]. The formation of oxide layer would minimize the weight gain and the steady state oxidation behaviour can be obtained for longer duration of exposure. The $k_p$ values are lower for all Ni–Al coated superalloys thereby indicating better resistance to oxidation in the given environment at 900 °C.

The XRD analysis of SN 76 indicates that the formation of NiO, $Fe_2O_3$, face centered cubic Ni and AlNi on the top surface of oxidised sample. In case of SN 750 superalloy, NiO in the only phase detected by XRD after oxidation. Whereas, in case of SF 800, $Al_2O_3$, $AlNi_3$ and spinel of manganese and iron are formed on the top scale which is supplemented by EDS analysis of the top surface. The nanosized grains found in the Ni–Al thin films, using XRD, improves the reactivity of Ni and Al by facilitating its faster diffusion and thereby helps in selective oxidation of these elements to form a uniform protective layer on the surface of the specimen. The layer formed on the specimen surface prevents the permeation of the oxidising species into the substrate, resulting in a better protection. FESEM analysis of the coated SN 76 and coated SN 750 shows the formation of NiO as the main phase with small amount of $Al_2O_3$. In case of coated SF 800, the top scale contains higher amount of $Fe_2O_3$, along with NiO and $Cr_2O_3$, which is protective at elevated temperature.

## 5. Conclusions

1. The Ni–Al film was deposited on the three different superalloys using RF magnetron sputtering process with a thickness of around 3 $\mu$m. The AFM analysis indicates the film was uniformly deposited on the surface of all the superalloys and the surface roughness of films was in the range 31–60 nm.
2. The XRD analysis of the as coated film revealed the presence of face centered cubic Ni rich phase in case of Superni 76 and Superni 750 alloys, whereas $Al_2O_3$, $AlNi_3$ and spinel of Mn and Fe were detected in case of Superfer 800 alloy.
3. The surface and cross-sectional EDS analysis of the as-deposited film indicate the presence of Ni in higher amounts which is further supported by XRD analysis.
4. The weight gain of the Ni–Al coated superalloys was lower as compared to that of bare superalloys. The oxidation behaviour of the Ni–Al coated SN 76 and SF 800 superalloys was nearly parabolic and in case of coated SN 750, a slight deviation was observed.
5. Among the three coated superalloys, SF 800 showed a better resistance to oxidation at 900 °C under cyclic conditions.

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## References

[1] J.T. Chang, A. Davison, J.L. He, A. Matthews, Surf. Coat. Technol. 200 (2006) 5877.
[2] D. Zhong, J.J. Moore, T.R. Ohno, J. Disam, S. Thiel, I. Dahan, Surf. Coat. Technol. 130 (2000) 33.
[3] G.W. Goward, JOM 22 (1970) 31.
[4] A.J. Hickl, R.W. Hecket, Metall. Trans. 6A (1975) 431.
[5] J.L. Smialck, C.E. Lowell, J. Electrochem. Soc. 121 (1974) 800.
[6] R.S. Rastogi, K. Pourrezaei, J. Mater. Process. Technol. 43 (1994) 89.
[7] G.W. Goward, Surf. Coat. Technol. 108–109 (1998) 73.
[8] Li-lien Lee, D.E. Laughlin, D.N. Lambeth, IEEE Trans. Magn. 31 (6) (1995) 2728.
[9] R. Pichoir, in: D.R. Holmes, A. Rahmel (Eds.), Materials and Coatings to Resistant High Temperature Corrosion, Applied Science Publishers, London, 1978, p. 271.
[10] B.D. Cullity, Elements of X-ray Diffraction, 2nd ed., Addison-Wesley Pub. Co., MA, 1978.
[11] R.A. Mahesh, R. Jayaganthan, S. Prakash, Mater. Sci. Eng. A 475 (2008) 327.