The chapter deals with the characterisation of the coatings deposited on T91 boiler steel, in as-deposited and post-treated condition in view of the behaviour relevant to high temperature corrosive environment applications. The characterisation has been done with the help of optical microscopy (OM), XRD and FE-SEM/EDS analysis, porosity evaluation and microhardness testing.

4.1 SUBSTRATE STEEL

The actual chemical composition for the substrate steel was determined by spectroscopy. Actual (as measured) and nominal composition is given in Table 4.1.

<table>
<thead>
<tr>
<th>Type of steel</th>
<th>ASME code</th>
<th>Composition</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Nb</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-91</td>
<td>SA213-T-91</td>
<td>Nominal</td>
<td>0.07–0.14</td>
<td>0.30–0.60</td>
<td>0.20–0.50</td>
<td>≤0.02</td>
<td>0.06–0.10</td>
<td>≤0.02</td>
<td>8.0–9.5</td>
<td>0.85–1.05</td>
<td>0.18–0.25</td>
<td>≤0.4</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Actual</td>
<td>0.12</td>
<td>0.41</td>
<td>0.28</td>
<td>0.01</td>
<td>0.08</td>
<td>0.02</td>
<td>8.2</td>
<td>0.87</td>
<td>0.20</td>
<td>0.13</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

4.2 FEEDSTOCK MATERIALS

4.2.1 SEM Analysis

SEM micrographs presented in Fig. 4.1 for NiCr, Cr$_3$C$_2$-NiCr, Al$_2$O$_3$ and Cr$_2$O$_3$ powders, verify the grain size and shape of the powders. Micrographs show that NiCr and Cr$_3$C$_2$-NiCr particles are irregular in shape, whereas Al$_2$O$_3$ and Cr$_2$O$_3$ particles show the angular shape. The details of these feedstock powders are given in Table 4.2.

4.2.2 XRD Analysis

The diffraction patterns for the NiCr, Cr$_3$C$_2$-NiCr, Al$_2$O$_3$ and Cr$_2$O$_3$ powders used as feedstock materials in the present investigation are shown in Fig 4.2 to Fig. 4.5 on the reduced scale. XRD peaks of the NiCr powder reveal the presence of Ni as the main phase and peaks for the Cr$_3$C$_2$-NiCr powder reveals the presence of Cr$_3$C$_2$ and Ni as the
phases. For Al\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) powders, Al\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) are observed as the main phases respectively.

4.3 SEALING MATERIAL

The HVOF-sprayed NiCr and Cr\(_3\)C\(_2\)-NiCr coatings on T91 steel were sealed with commercially available sealant (503-VGF-C, Aremco Products, USA) composed of aluminum oxide and aluminum phosphate. XRD pattern and SEM micrograph of the sealant are shown in Fig. 4.6 (a) and Fig. 4.6 (b) respectively. XRD peaks of the sealant reveal the presence of Al(PO\(_3\))\(_3\), Al\(_2\)O\(_3\) and P as the phases.

4.4 AS-DEPOSITED AND POST-TREATED COATINGS

4.4.1 Visual Examinations

(a) As-deposited coatings

The composition of the NiCr and Cr\(_3\)C\(_2\)-NiCr coatings sprayed on T91 boiler steel is given in Table 4.2. The macrographs for the as-deposited NiCr and Cr\(_3\)C\(_2\)-NiCr coatings shown in Fig. 4.7, reveals the uniform and smooth surface free from cracks. Macrograph of the NiCr coating reveals dull grey colour, whereas macrograph of the Cr\(_3\)C\(_2\)-NiCr coating reveals grey colour.

(b) Duplex coatings

Four types of duplex coating systems were developed by spraying thin layer of Al\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) on NiCr and Cr\(_3\)C\(_2\)-NiCr coated T91 steel. Duplex coating systems developed are as follows: (i) a duplex coating system consisting of a Cr\(_2\)O\(_3\) top layer and a NiCr interlayer; (ii) a duplex coating system consisting of an Al\(_2\)O\(_3\) top layer and NiCr interlayer; (iii) a duplex coating system consisting of a Cr\(_2\)O\(_3\) top layer and a Cr\(_3\)C\(_2\)-NiCr interlayer and (iv) a duplex coating system consisting of an Al\(_2\)O\(_3\) top layer and Cr\(_3\)C\(_2\)-NiCr interlayer. The macrographs for the coating systems shown in Fig. 4.8, reveals blackish grey colour for duplex coatings with Cr\(_2\)O\(_3\) top layer, and off-white colour for duplex coating with Al\(_2\)O\(_3\) top layer. Critical visual examination found these coating systems to be free from surface cracks.
### Table 4.2: Composition of the feedstock powders.

<table>
<thead>
<tr>
<th>Feedstock powder</th>
<th>Chemical composition, wt.%</th>
<th>Particle size</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_3$C$_2$-NiCr (FST K-856.23)</td>
<td>75 Cr$_3$C$_2$-25(Ni-20Cr)</td>
<td>$-45 , \mu m +15 , \mu m$</td>
<td>Irregular</td>
</tr>
<tr>
<td>NiCr (H.C stark GmbH)</td>
<td>80Ni-20Cr</td>
<td>$-53\mu m+15 , \mu m$</td>
<td>Irregular</td>
</tr>
<tr>
<td>Cr$_2$O$_3$ (H.C stark GmbH)</td>
<td>Cr$_2$O$_3$</td>
<td>$-22\mu m+5 , \mu m$</td>
<td>Angular</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (H.C stark GmbH)</td>
<td>Al$_2$O$_3$</td>
<td>$-45\mu m+5.6 , \mu m$</td>
<td>Angular</td>
</tr>
</tbody>
</table>

![SEM micrographs](image)

**Fig.4.1** SEM micrographs of alloy powders (a) NiCr; (b) Cr$_3$C$_2$-NiCr and (c) Al$_2$O$_3$; (d) Cr$_2$O$_3$. 
Fig. 4.2  XRD pattern of NiCr powder.

Fig. 4.3  XRD pattern of Cr$_3$C$_2$-NiCr powder.
Fig. 4.4  XRD pattern of Al₂O₃ powder.

Fig. 4.5  XRD pattern of Cr₂O₃ powder.
Fig. 4.6  (a) XRD pattern and (b) SEM micrograph of 503-VGF-C sealant.
(c) **Sealed coatings**

HVOF sprayed NiCr and Cr$_3$C$_2$-NiCr coatings on T91 steel were sealed with 503-VGF-C sealant, discussed in section 4.3. Macrographs of the sealed NiCr and Cr$_3$C$_2$-NiCr coatings shown in Fig. 4.9, reveals smooth surface free of cracks.

(d) **Heat treated coatings**

HVOF sprayed NiCr and Cr$_3$C$_2$-NiCr coatings on T91 steel were heat treated as explained in section 3.3.2. Macrograph of the heat treated coating shown in Fig. 4.10, reveals the dark grey colour for NiCr coating and blackish grey colour for Cr$_3$C$_2$-NiCr coating. Further both the coatings are found to be free from any visible surface cracks.

### 4.4.2 Measurements of Coating Thicknesses

FE-SEM micrographs were taken along the cross-sections of the as-deposited NiCr and Cr$_3$C$_2$-NiCr coatings, as well as for duplex coatings with Cr$_2$O$_3$ and Al$_2$O$_3$ as top layers. The coating thickness was measured from the Back Scattered Electron (BSE) images obtained along the cross-section of the coated specimens and the average thickness of each coating is reported in Table 4.3. BSE images of these samples are shown in Fig. 4.11 to 4.13.

### 4.4.3 Surface Roughness (Ra) and Porosity Analysis

The corrosion resistance is also associated to the surface roughness, in a way in which the higher surface roughness, the higher the corrosion attack due to higher surface area. The centre line average (CLA) method was used to obtain the Ra values. The measured values of surface roughness are reported in Table 4.4. Porosity is also an important coating feature that strongly influences coating properties, as due to this physical property corrosion resistance of different thermal spray coatings may differ. It is well established that the dense coatings usually provide better corrosion resistance than porous coatings. The porosity measurements were made for the as-sprayed and post-treated coatings, and are reported in Table 4.4.
### Table 4.3  Average coating thickness

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Coating thickness (µm)</th>
<th>Inner layer</th>
<th>Top coat</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCr</td>
<td></td>
<td></td>
<td></td>
<td>315</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr</td>
<td></td>
<td></td>
<td></td>
<td>322</td>
</tr>
<tr>
<td>NiCr with Cr$_2$O$_3$ top coat</td>
<td>315</td>
<td></td>
<td>50</td>
<td>365</td>
</tr>
<tr>
<td>NiCr with Al$_2$O$_3$ top coat</td>
<td>315</td>
<td></td>
<td>45</td>
<td>360</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr with Cr$_2$O$_3$ top coat</td>
<td>322</td>
<td></td>
<td>50</td>
<td>372</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr with Al$_2$O$_3$ top coat</td>
<td>322</td>
<td></td>
<td>60</td>
<td>382</td>
</tr>
</tbody>
</table>

### Table 4.4  Porosity and surface roughness of the coatings

<table>
<thead>
<tr>
<th>Type of Coating</th>
<th>Porosity (%)</th>
<th>Surface roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCr</td>
<td>&lt; 1.75</td>
<td>8.21</td>
</tr>
<tr>
<td>NiCr heat treated</td>
<td>&lt; 1.4</td>
<td>7.66</td>
</tr>
<tr>
<td>NiCr sealed</td>
<td>&lt; 1</td>
<td>3.14</td>
</tr>
<tr>
<td>NiCr with Cr$_2$O$_3$ top coat</td>
<td>&lt; 3</td>
<td>4.84</td>
</tr>
<tr>
<td>NiCr with Al$_2$O$_3$ top coat</td>
<td>&lt; 2.5</td>
<td>7.66</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr</td>
<td>&lt; 2</td>
<td>5.27</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr heat treated</td>
<td>&lt; 1.6</td>
<td>5.33</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr sealed</td>
<td>&lt; 1</td>
<td>2.29</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr with Cr$_2$O$_3$ top coat</td>
<td>&lt; 3</td>
<td>3.20</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-NiCr with Al$_2$O$_3$ top coat</td>
<td>&lt; 2.5</td>
<td>6.58</td>
</tr>
</tbody>
</table>
Fig. 4.7 Macrographs of HVOF sprayed coatings on T91 steel: (a) NiCr coating and (b) Cr$_3$C$_2$-NiCr coating.

Fig. 4.8 Macrographs of HVOF sprayed coatings on T91 steel: (a) NiCr coating with Al$_2$O$_3$ top coat; (b) Cr$_3$C$_2$-NiCr coating with Al$_2$O$_3$ top coat; (c) NiCr coating with Cr$_2$O$_3$ top coat and (d) Cr$_3$C$_2$-NiCr coating with Cr$_2$O$_3$ top coat.
Fig. 4.9  Macrographs of HVOF sprayed coatings on T91 steel: (a) sealed NiCr coating and (b) sealed Cr$_3$C$_2$-NiCr coating.

Fig. 4.10  Macrographs of HVOF sprayed coatings on T91 steel: (a) heat treated NiCr coating and (b) heat treated Cr$_3$C$_2$-NiCr coating.
**Fig. 4.11** SEM micrograph along the cross-section of HVOF spray coatings on T91 boiler steel in as-sprayed condition: (a) NiCr coating and (b) Cr$_3$C$_2$-NiCr coating.
Fig. 4.12 SEM micrograph along the cross-section of HVOF spray coatings on T91 boiler steel in as-sprayed condition: (a) NiCr coating with Cr$_2$O$_3$ top coat and (b) NiCr coating with Al$_2$O$_3$ top coat.
Fig. 4.13 SEM micrograph along the cross-section of HVOF spray coatings on T91 boiler steel in as-sprayed condition: (a) Cr$_3$C$_2$-NiCr coating with Cr$_2$O$_3$ top coat and (b) Cr$_3$C$_2$-NiCr coating with Al$_2$O$_3$ top coat.
4.4.4 Microhardness Measurements

The microhardness values of the coatings on the given boiler steel have been measured across the coating-substrate interface and plotted in Fig. 4.14. At each distance from coating-substrate interface, three readings are taken and each point in the Fig. 4.14 shows the average of three readings. The average microhardness value for the substrate steel has been found to be 244Hv. The microhardness values for the NiCr coating lies in the range of 265–310 Hv, while the Cr$_3$C$_2$-NiCr coating has microhardness in the range of 800-900 Hv. Furthermore, a slight increase in the microhardness of the substrate has been observed near the coating-substrate interface in both the cases (reference points at a distance of -40 µm).

4.4.5 Metallographic studies of the Coatings

(a) Surface Microstructures

(i) NiCr Coating

Optical micrographs for NiCr coating on T91 steel before and after post-treatment (i.e. heat treatment and sealing) are shown in Fig. 4.15. Optical micrograph of the original sprayed coating indicates the microstructure consisting of fully molten splats, which are irregularly shaped with distinct boundaries, as can be perceived from Fig. 4.15 (a). Most of the splats are well formed without any sign of disintegration. Porosity and inclusions are identified as black spots with some depth and dark grey spots of in-plane orientation, respectively. Presence of some oxide stringers along the splat boundaries are also noticed in the coating microstructure. A clear cut splat-like morphology can be perceptible from the micrograph of the NiCr coating.

Optical micrograph of the heat treated NiCr coating is shown in Fig. 4.15 (b), which also reveals the splat like structure as observed for the originally sprayed coating. However, the amount of oxide stringers along the splat boundaries became more prominent and thick after heat treatment of the coating. Optical micrograph of the NiCr coating after sealing treatment is shown in Fig. 4.15 (c), which reveals the same structure as that of originally sprayed coating, with the presence of sealant into the surface voids of the coating.
Fig. 4.14  Micro-hardness profiles of the HVOF-sprayed coatings on T91 boiler steel.
(ii) **Cr$_3$C$_2$-NiCr Coating**

Optical micrographs for Cr$_3$C$_2$-NiCr coating on T91 steel before and after post-treatment (i.e. heat treatment and sealing) are shown in Fig. 4.16. Optical micrograph showing surface morphologies of the originally Cr$_3$C$_2$-NiCr coating on T91 steel is shown in Fig. 4.16 (a). The flat splats of irregular shape are almost uniformly distributed in the coating. Some limited voids, inclusions and un-melted particles are also visible in the structure of the coatings. Fig. 4.16 (b) shows the optical micrographs for Cr$_3$C$_2$-NiCr coating on T91 steel after heat treatment. Micrograph shows the formation of oxides (black patches) in the coating microstructure present at the places of voids and in-between the splat boundaries after the heat treatment. Optical micrograph of the Cr$_3$C$_2$-NiCr coating after sealing treatment is shown in Fig. 4.16 (c), which reveals the same structure as that of originally sprayed coating, with the presence of sealant into the surface voids of the coating.

(b) **Cross-Section Microstructures**

(i) **As-deposited coatings**

The coatings have been deposited on stationary substrate by moving the HVOF gun and the required thickness of the coatings has been obtained by varying the number of passes. This led to the development of lamellar structure of both the coatings, as is evident from the micrographs shown in Figs. 4.17. The optical micrographs not only depict the typical lamellae structure of thermal spray coatings but also the distinct boundaries. Microstructure of NiCr coating [Fig. 4.17 (a)] is highly lamellar with distinct splat boundaries and splats oriented parallel to the substrate surface as compared to Cr$_3$C$_2$-NiCr coating, Fig. 4.17 (b). Inclusions and porosity have been observed in the structure of both the coatings. It is evident that the coatings are dense with low porosity. Tiny sized inclusions are indicated in the coatings or at the coating–substrate interface in the form of dark spots. A slight amount of oxides formed in the coatings may be because of oxidation of in-flight particles between successive runs and appeared in the intersplat lamellae or globules, oriented parallel to the substrate surface. Comparatively presences of few pores in NiCr coating confirm the higher density of the NiCr coating than Cr$_3$C$_2$-NiCr coating.
(ii) Post-treated coatings

Optical micrographs showing cross-sectional morphologies of the heat treated NiCr and Cr$_3$C$_2$-NiCr coating on T91 boiler steel are shown in Fig. 4.18. Microstructures reveal the splat like structure, with splats oriented parallel to the substrate surface for both the coatings, as observed for the originally sprayed coatings. However, after heat treatment oxide stringers are more prominent in the microstructure. After heat treatment the interdiffusion between the splats has resulted in diminishing splat boundaries, which led to a dense structure. Optical micrographs showing cross-sectional morphologies of the sealed NiCr and Cr$_3$C$_2$-NiCr coating on T91 boiler steel are shown in Fig. 4.19. Microstructure reveals the similar feature as observed for the originally sprayed coating, except the presence of sealant on the top surface of the coatings.

The top coat of Cr$_2$O$_3$ and Al$_2$O$_3$ could be seen clearly on the surface of NiCr coated T91 steel in the Fig. 4.20. Fig. 4.21 shows the presence of Cr$_2$O$_3$ and Al$_2$O$_3$ top coats on Cr$_3$C$_2$-NiCr coated T91 steel. The structure of the NiCr and Cr$_3$C$_2$-NiCr interlayer remained same as the originally sprayed NiCr and Cr$_3$C$_2$-NiCr coating after the deposition of Cr$_2$O$_3$ and Al$_2$O$_3$ top coats.

4.4.6 XRD Analysis

(a) NiCr Coating

The XRD analysis for the surfaces of the as-sprayed coatings, as well as post treated coatings was performed and the diffraction patterns are shown in Fig. 4.22 to Fig 4.26. In all the cases XRD analysis identified the phases similar to the composition of top coat. NiCr as-coated steel has indicated the Ni as the main phase on the surface; whereas, after heat treatment NiO, NiCr$_2$O$_4$ and Cr$_2$O$_3$ additional phases were indicated along with the phase observed for as-sprayed coating. For sealed NiCr coating (Fig. 4.24), XRD reveals Al$_2$O$_3$ as the main phase and; Al(PO$_4$) and AlNi as the minor phase. For duplex coating system with Cr$_2$O$_3$ top layer and NiCr as interlayer, XRD patterns (Fig. 4.25) revealed the presence of Cr$_2$O$_3$ as the main phase. XRD patterns (Fig. 4.26) revealed the presence of Al$_2$O$_3$, as the main phase for duplex coating system with Al$_2$O$_3$ top layer.
Fig. 4.15 Optical micrograph showing surface morphologies (polished) of HVOF sprayed coatings on T91 boiler steels in as-sprayed and post-treated condition: (a) NiCr as-deposited; (b) NiCr heat treated and (c) NiCr sealed.
Fig. 4.16  Optical micrograph showing surface morphologies (polished) of HVOF sprayed coatings on T91 boiler steels in as-sprayed and post-treated condition: (a) Cr$_3$C$_2$-NiCr as-deposited; (b) Cr$_3$C$_2$-NiCr heat treated and (c) Cr$_3$C$_2$-NiCr sealed.
Fig. 4.17 Optical micrograph showing cross-section morphologies of HVOF sprayed coatings on T91 boiler steels in as-sprayed condition: (a) NiCr and (b) Cr$_3$C$_2$-NiCr.
Fig. 4.18  Optical micrograph showing cross-section morphologies of HVOF sprayed coatings on T91 boiler steels after heat treatment: (a) NiCr and (b) Cr₃C₂-NiCr.
Optical micrograph showing cross-section morphologies of HVOF sprayed coatings on T91 boiler steels after sealing treatment: (a) NiCr and (b) Cr$_3$C$_2$-NiCr.
![Optical micrograph showing cross-section morphologies of HVOF sprayed NiCr coatings on T91 boiler steels: (a) NiCr with Al₂O₃ top coat and (b) NiCr coating with Cr₂O₃ top coat.](image)

**Fig. 4.20** Optical micrograph showing cross-section morphologies of HVOF sprayed NiCr coatings on T91 boiler steels: (a) NiCr with Al₂O₃ top coat and (b) NiCr coating with Cr₂O₃ top coat.
Fig. 4.21 Optical micrograph showing cross-section morphologies of HVOF sprayed Cr₃C₂-NiCr coatings on T91 boiler steels: (a) Cr₃C₂-NiCr with Al₂O₃ top coat and (b) Cr₃C₂-NiCr coating with Cr₂O₃ top coat.
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Fig. 4.22 X-ray diffraction profiles of the HVOF-sprayed NiCr coating on T91 boiler steel.

Fig. 4.23 X-ray diffraction profiles of the HVOF-spray NiCr coating on T91 boiler steel after heat treatment.
(b) Cr₃C₂-NiCr Coating

The X-ray diffractograms of the HVOF sprayed Cr₃C₂-NiCr coating in as-deposited and post-treated condition are depicted in Fig. 4.27 to 4.31. The analysis indicates the formation of Cr₃C₂ and CrNi as the phases for the as-deposited Cr₃C₂-NiCr coating. Heat treatment produced several changes in the coating composition, as after heat treatment XRD has revealed the presence of CrNi, C, Cr₂O₃, Cr₃C₂ and NiCr₂O₄ phases in the coating composition. For sealed Cr₃C₂-NiCr coating, XRD reveals Al₂O₃, Al(PO₄) and Cr₃C₂ as the phases. For duplex coating system with Cr₂O₃ top layer and Cr₃C₂-NiCr as interlayer, XRD patterns (Fig. 4.30) revealed the presence of Cr₂O₃ as the main phase. In case of duplex coating system with Al₂O₃ top layer, XRD patterns (Fig. 4.31) revealed the presence of Al₂O₃, as the main phase.

4.4.7 FE-SEM/EDS ANALYSIS

(a) Surface Morphology

(i) NiCr coating

The SEM micrograph of as-sprayed NiCr coating is shown in Fig. 4.32 (a). The microstructure consists of interlocked particles with irregular morphology. It can be observed from the microstructures that coatings in general possess some porosity, inclusions and partially melted particles. The structure by and large, seems to be dense. The surface appears to be uneven; however, in majority of the microstructure, a proper coalescence of the particles has taken place. There is a presence of some tiny particles in the coatings. The regions marked ‘M’ in these micrographs might have formed from the impact of fully molten feedstock droplets. The EDS analysis at selected points indicates the dominance of Ni along with Cr in the composition of the coating, which is nearly approaching the composition of the sprayed powder. The presence of traces of Mo, Mn and Nb in the surface indicates the diffusion of these elements from the substrate to the coating. The marginal presence of O in the composition of the coatings indicates the chances of the formation of oxides in the coating.

The SEM micrograph of the heat treated NiCr coating shown in Fig. 4.32 (b) reveals uniform microstructure. EDS analysis for heat treated coating reveals the presence of Cr and Ni along with O. Presence of O along with Cr and Ni in the composition indicates the possible formation of oxides of Cr and Ni. SEM micrograph of the sealed NiCr coating in
Fig. 4.32 (c) reveals the smooth structure. EDS analysis reveals the presence of Al, Cr, P and O on the surface. Presence of Al, P and O on the surface indicates the existence of sealant on the surface.

In the case of duplex coating system with Al$_2$O$_3$ top coat, flat splats of irregular shape are almost uniformly distributed in the coating, Fig. 4.33 (a). The uniform microstructure of the coating indicates that a high proportion of the feedstock powder has been fully melted prior to impacting the substrate. EDS analysis reveals the presence of Al along with O, which is nearly approaching the composition of the sprayed Al$_2$O$_3$ topcoat.

The SEM micrograph of the NiCr coating with Cr$_2$O$_3$ top layer shown in Fig. 4.33 (b) reveals uniform microstructure with globules on the surface. The EDS analysis at selected points indicates the dominance of Cr along with O in the composition of the coating, which is nearly approaching the composition of the sprayed Cr$_2$O$_3$ topcoat. Traces of Nb and Mo are also detected on the surface.

(ii) Cr$_3$C$_2$-NiCr coating

The FE-SEM micrograph of as-sprayed Cr$_3$C$_2$-NiCr coating is shown in Fig. 4.34 (a). The micro-structure consists of interlocked particles with irregular morphology. It can be observed from the microstructures that coatings in general possess some porosity, inclusions and partially melted particles. Porosity may be depicted in the form of black contrast regions. As revealed from EDS analysis of the microstructure, it consists of NiCr metallic binder phase corresponding to the white region in the micrograph and the dark grey region are the carbides. The NiCr metallic binder material is present in amorphous/nanocrystalline form, likely to melt first and dissolve some chromium carbide to form a liquid phase which may be rich in Cr and C, and gets supersaturated. The presence of minor amount of Mo, Mn and Nb on the surface indicates the diffusion of these elements from the substrate to the coating as observed in the EDS analysis. The marginal presence of O in the composition of the coating indicates the chances of the formation of oxides in the coating.

The SEM micrograph of the heat treated Cr$_3$C$_2$-NiCr coating shown in Fig. 4.34 (b) reveals uniform microstructure without any white and dark grey contrast regions, as in case of as-sprayed coating. EDS analysis for heat treated coating reveals the presence of Cr, Ni, C and O. High Presence of O along with Cr and Ni in the composition indicates
Fig. 4.24  X-ray diffraction profiles of the HVOF-spray NiCr coating on T91 boiler steel after sealing.

Fig. 4.25  X-ray diffraction profiles of the HVOF-spray NiCr coating on T91 boiler steel with Cr$_2$O$_3$ top coat.
Fig. 4.26  X-ray diffraction profiles of the HVOF-spray NiCr coating on T91 boiler steel with Al₂O₃ top coat.

Fig. 4.27  X-ray diffraction profiles of the HVOF-sprayed Cr₃C₂-NiCr coating on T91 boiler steel.
**Fig. 4.28**  X-ray diffraction profiles of the HVOF-spray Cr$_3$C$_2$-NiCr coating on T91 boiler steel after heat treatment.

**Fig. 4.29**  X-ray diffraction profiles of the HVOF-spray Cr$_3$C$_2$-NiCr coating on T91 boiler steel after sealing.
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Fig. 4.30  X-ray diffraction profiles of the HVOF-spray Cr$_3$C$_2$-NiCr coating on T91 boiler steel with Cr$_2$O$_3$ top coat.

Fig. 4.31  X-ray diffraction profiles of the HVOF-spray Cr$_3$C$_2$-NiCr coating on T91 boiler steel with Al$_2$O$_3$ top coat.
Fig. 4.32  FE-SEM with EDS analysis for HVOF spray coating on T91 boiler steel showing elemental composition (wt.%) at selected points: (a) as-deposited NiCr coating; (b) heat treated NiCr coating and (c) sealed NiCr coating.
Fig. 4.33 FE-SEM with EDS analysis for HVOF spray coating on T91 boiler steel showing elemental composition (wt.%) at selected points: (a) NiCr coating with Al₂O₃ top coat and (b) NiCr coating with Cr₂O₃ top coat.
the possible formation of oxides of Cr and Ni. The SEM micrograph of the sealed Cr$_3$C$_2$-NiCr coating shown in Fig. 4.34 (c) reveals two contrast regions, light grey and dark grey. Light grey region indicates the composition of coating, rich in Cr, C and Ni; whereas, dark grey region indicates the composition of sealant, with presence of Al, O, P and C. Sealant can also be seen into the voids of the coating.

The SEM micrograph of the Cr$_3$C$_2$-NiCr coating with Cr$_2$O$_3$ top layer shown in Fig. 4.35 (a), reveals the microstructure with irregular morphology, having partially and fully melted particles. The regions marked ‘M’ in these micrographs might have formed from the impact of fully molten feedstock droplets. Some fragmented particles and pores can also be revealed in the microstructure. Pores may be depicted in the form of circular black contrast regions. The EDS analysis at selected points indicates the dominance of Cr along with O in the composition of the coating, which is nearly approaching the composition of the sprayed Cr$_2$O$_3$ topcoat. The SEM micrograph of the Cr$_3$C$_2$-NiCr coating with Al$_2$O$_3$ top layer shown in Fig. 4.35 (b) reveals uniform and dense microstructure. Limited voids and un-melted particles are also visible in the structure of the coatings. EDS analysis reveals the presence of Al along with O, which is nearly approaching the composition of the sprayed Al$_2$O$_3$ topcoat.

(b) Cross-sectional Morphology

(i) NiCr coating

The cross-sectional Back Scattered Electron (BSE) Image of the HVOF sprayed NiCr coating on the T91 boiler steel has been shown in Fig. 4.36. The coating has been deposited on stationary substrate by moving the HVOF torch and the required thickness of the coating has been obtained by varying number of passes. This leads to the formation of uniform and dense microstructures and exhibits characteristic splatlike, layered morphologies due to the deposition and resolidification of molten or semimolten droplets. The long axis of the impacted splats are oriented parallel to the substrate surface. The interface is intact and free from defects. Some voids and inclusions are present in the microstructure that is typical characteristics of the HVOF sprayed coatings. Fig. 4.36 (inset) show that the microstructure of NiCr coating consists of the following areas (indicated by arrows): the light grey contrast matrix (arrow 1), medium grey contrast areas (arrow 2), dark grey contrast areas (arrow 3) and a very low content of porosity,
which appears black (arrow 4). This range of grey level is generally associated with oxide phases in the microstructure, which are believed to be formed as a result of the oxidation of in-flight particles between successive runs. These appeared in the microstructure in the form of intersplat lamellae or globules that are oriented parallel to the substrate surface. Medium and dark grey contrast areas found to be consisted of oxide phases.

EDS analysis (Fig. 4.37) at the cross-section of NiCr coated T91 boiler steel specimen shows the composition almost similar to that of the substrate, with rich percentage of iron and minor percentage of chromium and other elements at point 1 and 2. Point 3, 4, 5, 6 and 7 are rich in nickel and chromium; representing nominal composition of HVOF sprayed NiCr coating. Further point 3, 4, 5, 6 and 7 also show the presence of traces of Mo, Nb, Fe, Mn, V and P, which indicates the diffusion of these elements from the substrate to the coating.

The cross-sectional BSE image of the heat treated NiCr coating on T91 boiler steel has been shown in Fig. 4.38 (a), which also indicated a dense and lamellar appearance similar to one exhibited by the originally sprayed NiCr coating. A high magnification of the BSE image in Fig. 4.38 (b) reveals the formation of oxide stringers (dark grey in colour) along the splat boundaries and at the places of porosity after heat treatment of the coating. As revealed by EDS analysis, these oxide stringers are formed along the nickel rich splats. These oxide stringers are rich in Cr and depleted of Ni in comparison to the coating nominal composition, which suggests that Cr has higher affinity for oxygen in comparison to nickel.

EDS analysis was carried out at different point of interest along the cross-section of the heat treated NiCr coating on T91 boiler steel and the results are given in Fig. 4.39 (a). EDS analysis at the cross-section of the heat treated NiCr shows the composition almost similar to that of the originally sprayed coating. However, the top surface reveals the presence of Ni and Cr along with traces of oxygen, which suggests the formation of oxides and spinals of Ni and Cr on the top surface during heat treatment of the coating. EDS analysis along the cross-section of the sealed NiCr coating on T91 boiler tube steel [Fig. 4.39 (b)], also indicated the similar compositional feature, as observed for the originally sprayed coating, except the presence of Al, O and P on the top surface (point 5). Presence of these elements on the top surface indicates the existence of sealant.
Fig. 4.34  FE-SEM with EDS analysis for HVOF spray coating on T91 boiler steel showing elemental composition (wt.%) at selected points: (a) as-deposited Cr$_3$C$_2$NiCr coating; (b) heat treated Cr$_3$C$_2$NiCr coating and (c) sealed Cr$_3$C$_2$NiCr coating.
Fig. 4.35  FE-SEM with EDS analysis for HVOF spray coating on T91 boiler steel showing elemental composition (wt.%) at selected points: (a) Cr$_3$C$_2$NiCr coating with Cr$_2$O$_3$ top coat and (b) Cr$_3$C$_2$NiCr coating with Al$_2$O$_3$ top coat.
The cross-sectional BSE image of the NiCr duplex coating with Al$_2$O$_3$ top layer and Cr$_2$O$_3$ top layer are shown in Fig. 4.40 (a) and Fig. 4.40 (b) respectively. The microstructure of the NiCr coating for both the duplex coating systems is almost similar to that for the originally sprayed coating. The interface between the coating and the top coats is free from any defects and therefore the adhesion strength of the top coat is expected to be excellent. For duplex coating system with Al$_2$O$_3$ top layer, EDS analysis [Fig. 4.40 (a)] reveals the presence of Al on the top surface, thereby indicating the presence of Al$_2$O$_3$ top layer. A corresponding analysis of the duplex coating system with Cr$_2$O$_3$ top layer [Fig. 4.40 (b)] reveals Cr rich top surface, indicating the presence of Cr$_2$O$_3$ top layer.

(ii) **Cr$_3$C$_2$-NiCr coating**

The cross-sectional Back Scattered Electron image of the Cr$_3$C$_2$-NiCr coating on T91 boiler steel has been shown in Fig. 4.41. The coating has a dense appearance, in general. The coating-substrate interface is intact and continuous, which is a characteristic feature of good adhesion between the coating and the substrate. The long axis of the impacted splats are oriented parallel to the substrate surface. A slight amount of oxides appear in the microstructure in the form of inter-splat lamellae or globules that are oriented parallel to the substrate surface. Some voids (circular black areas) and inclusions (black areas) are present in the microstructure that is a typical characteristics of the HVOF sprayed coatings. Tiny sized inclusions are indicated in the coating or at the coating–substrate interface in the form of dark spots. A high magnification of the BSE image of the coatings cross-section in Fig. 4.41 (inset) reveals the presence of three different zones in the microstructure. The first zone is dark which indicates the presence of primarily Cr and C, revealing a Cr$_3$C$_2$ phase. The second zone is of grey colour, besides Cr and C this area also contains Ni. A third zone is white and consists of a NiCr phase, mainly.

EDS analysis (Fig. 4.42) at the cross-section of Cr$_3$C$_2$-NiCr coated T91 boiler steel specimen shows the composition almost similar to that of the substrate at point 1 and 2. Point 3, 4, 5, 6 and 7 show the presence of chromium, nickel and carbon, which
indicates the nominal composition of Cr$_3$C$_2$-NiCr coating. Point 3, 4, 5, 6 and 7 also reveal the presence of traces of Mo, Mn, Fe, V and P. Black areas at the coating/substrate interface of the coatings might be the inclusions of aluminum oxide.

The cross-sectional BSE image of the heat treated Cr$_3$C$_2$-NiCr coating on T91 boiler steel has been shown in Fig. 4.43 (a), which also indicated a dense and lamellar appearance similar to one exhibited by the originally sprayed Cr$_3$C$_2$-NiCr coating. A high magnification BSE image [Fig. 4.43 (b)] of the heat treated coating reveals the formation of oxide along the splat boundaries and at the places of porosity. EDS analysis [Fig. 4.43 (b)] at selected points indicates the presence of Ni and Cr along with oxygen, indicating the formation of oxides. EDS analysis along the cross-section of the heat treated coating Fig. 4.44 (a) reveal the composition almost similar to that of the originally sprayed coating. However, the top surface reveals the presence of Ni and Cr along with traces of oxygen, which suggests the formation of oxides and spinals of Ni and Cr on the top surface during heat treatment of the coating.

EDS analysis along the cross-section of the sealed Cr$_3$C$_2$-NiCr coating on T91 boiler steel [Fig. 4.44 (b)], also indicated the similar microstructural and compositional features, as observed for the originally sprayed coating, except the presence of Al, O and P, along with Ni and Cr on the top surface (point 5). Presence of Al, O and P on the top surface indicates the existence of the sealant.

The cross-sectional BSE image of the Cr$_3$C$_2$-NiCr coating with Al$_2$O$_3$ top layer and Cr$_3$C$_2$-NiCr coating with Cr$_2$O$_3$ top layer are shown in Fig. 4.45. The microstructural and compositional features of the Cr$_3$C$_2$-NiCr coating, for both the duplex coating systems are similar to the originally sprayed Cr$_3$C$_2$-NiCr coating. Uniform and adherent top layer of Cr$_2$O$_3$ and Al$_2$O$_3$ on Cr$_3$C$_2$-NiCr coating can be revealed from Fig. 4.45 (a) and Fig. 4.45 (b) respectively. For duplex coating system with Al$_2$O$_3$ top layer, EDS analysis reveals the presence Al on the top surface, thereby indicating the presence of Al$_2$O$_3$ top layer. A corresponding analysis of the duplex coating system with Cr$_2$O$_3$ top layer reveals the Cr rich top surface, indicating the presence of Cr$_2$O$_3$ as top layer.
4.4.8 Elemental X-ray mapping

(a) NiCr coating

The X-ray mappings for the as-coated and post treated NiCr coatings are shown in Fig. 4.46 to Fig. 4.50. Composition image and elemental mappings of the as-sprayed NiCr coating (Fig. 4.46) shows a typical lamellar structure consisting of mainly Ni-rich splats along with chromium. Molybdenum, vanadium and manganese have shown marginal diffusion from the substrate to coating. Similar analysis of the heat treated NiCr coating (Fig. 4.47) shows that in addition to the presence of basic elements of the coatings, oxygen diffused along the splat boundaries. Oxygen is revealed along with Cr in the form of thin stringers. Top surface shows the presence of continuous layer of Ni and Cr along with oxygen. Elemental map of Fe shows diffusion from the substrate to coating in trace amounts. A typical lamellar structure has been revealed for heat treated NiCr coating as is clear from Fig. 4.47.

Composition image (SEI) and elemental mappings for the sealed NiCr coating is shown in Fig. 4.48. The coating zone is mainly composed of Ni and Cr. Thin layer of aluminium can be seen on the top surface, where Ni and Cr are absent. Phosphorous and oxygen has also shown its presence along with Al on the top surface. Presence of Al and P along with O on the top surface indicates the presence of sealant. Diffusion of alloying elements from the substrate towards the coating has been observed, as observed for the originally sprayed NiCr coating. Iron has been found to be restricted to the substrate steel.

A similar analysis of the duplex coating with NiCr as inner layer and Al$_2$O$_3$ as top layer (Fig.4.49) shows that the element distribution for the inner coating zone is very similar to the originally sprayed NiCr coating (Fig.4.45) and the coating is mainly composed of Ni and Cr. Top surface shows the presence of thin continuous layer of Al, where Ni and Cr are absent. The NiCr duplex coating with Cr$_2$O$_3$ top layer (Fig. 4.50) has shown a compositional distribution similar to the originally sprayed coating for inner coating (NiCr) zone. Thin and continuous layer of Cr can be
revealed on the top surface, where Ni is absent, which is very well anticipated for the top coat.

**(b) \( \text{Cr}_3\text{C}_2\)-NiCr coating**

The elemental mappings for the \( \text{Cr}_3\text{C}_2\)-NiCr coating (Fig. 4.51) show that the nickel-rich splats are uniformly distributed in the chromium-rich matrix. Very small amounts of Mo, Mn, S, V and Nb have diffused from the substrate to the coating mainly through the splat boundaries and formed thin stringers in the form of intersplat lamellae as observed in Fig.4.51. Inclusions exclusively of aluminum appeared at the coatings-substrate interface.

In case of heat treated \( \text{Cr}_3\text{C}_2\)-NiCr coating on T91 boiler tube steel, the elemental mappings (Fig.4.52) shows that in addition to the presence of basic elements of the coatings, Mo, Mn, S and V diffused from the substrate towards the coating. Elemental map of oxygen shows the presence of oxygen along the splat boundaries. The elemental mappings for sealed \( \text{Cr}_3\text{C}_2\)-NiCr coating (Fig. 4.53) show that the nickel-rich splats are present in the chromium-rich matrix. Top surface shows the presence of Al and P along with O, indicating the existence of sealant on the top surface. Traces of Mo, Mn and Nb have diffused from the substrate to the coating.

A similar analysis of the duplex coating with \( \text{Cr}_3\text{C}_2\)-NiCr as inner layer and \( \text{Al}_2\text{O}_3\) as top layer (Fig.4.54) shows that the element distribution for the inner coating zone is very similar to the originally sprayed \( \text{Cr}_3\text{C}_2\)-NiCr coating (Fig.4.51) and the coating is mainly composed of Ni and Cr. Top surface shows the presence of thin continuous layer of Al. Clusters of Al are also observed at the coating-substrate interface. The X-ray mapping analysis of the duplex coating with \( \text{Cr}_3\text{C}_2\)-NiCr as inner layer and \( \text{Cr}_2\text{O}_3\) as top layer is shown in Fig.4.55. Inner layer of \( \text{Cr}_3\text{C}_2\)-NiCr shows the elemental distribution similar to that of originally sprayed coating; whereas, top surface reveals the presence of thin continuous layer of Cr, where Ni is absent.
Fig. 4.36  SEM micrograph along the cross-section of HVOF sprayed NiCr coating on T91 boiler steel in as-sprayed condition.

Fig. 4.37  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed NiCr coating on T91 boiler steel in as-sprayed condition.
**Fig. 4.38** SEM micrograph along the cross-section of HVOF sprayed NiCr coating on T91 boiler steel after heat treatment.
Fig. 4.39  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed coating on T91 boiler steel: (a) heat treated NiCr coating and (b) sealed NiCr coating.
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Fig. 4.40  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed coating on T91 boiler steel: (a) NiCr coating with Al₂O₃ top coat and (b) NiCr coating with Cr₂O₃ top coat.

Fig. 4.41  SEM micrograph along the cross-section of HVOF sprayed Cr₃C₂-NiCr coating on T91 boiler steel in as-sprayed condition.
Fig. 4.42  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed Cr$_3$C$_2$-NiCr coating on T91 boiler steel in as-sprayed condition.
Fig. 4.43 SEM micrograph along the cross-section of HVOF sprayed Cr$_3$C$_2$-NiCr coatings on T91 boiler steel after heat treatment.
Fig. 4.44  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed coating on T91 boiler steel: (a) heat treated Cr$_3$C$_2$-NiCr coating and (b) sealed Cr$_3$C$_2$-NiCr coating.
Fig. 4.45  Cross-sectional morphology and variation of elemental composition across the cross-section of the HVOF sprayed coating on T91 boiler steel: (a) Cr$_3$C$_2$-NiCr coating with Al$_2$O$_3$ top coat and (b) Cr$_3$C$_2$-NiCr coating with Cr$_2$O$_3$ top coat.
Fig. 4.46  Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed NiCr coating on T91 boiler steel in as-sprayed condition.
Fig. 4.47 Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed NiCr coating on T91 boiler steel in heat treated condition.
Fig. 4.48  Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed NiCr coating on T91 boiler steel after sealing.
Fig. 4.49 Composition image (SEI) and X-ray mappings across the cross-section of NiCr duplex coating system with Al₂O₃ top coat.
Fig. 4.50  Composition image (SEI) and X-ray mappings across the cross-section of NiCr duplex coating system with Cr$_2$O$_3$ top coat.
Fig. 4.51  Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed Cr$_3$C$_2$-NiCr coating on T91 boiler steel in as-sprayed condition.
Fig. 4.52  Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed Cr$_3$C$_2$-NiCr coating on T91 boiler steel in heat treated condition.
Fig. 4.53 Composition image (SEI) and X-ray mappings across the cross-section of the HVOF sprayed Cr$_3$C$_2$-NiCr coating on T91 boiler steel after sealing.
Fig. 4.54  Composition image (SEI) and X-ray mappings across the cross-section of Cr$_3$C$_2$-NiCr duplex coating system with Al$_2$O$_3$ top coat.
Fig. 4.55  Composition image (SEI) and X-ray mappings across the cross-section of Cr₃C₂-NiCr duplex coating system with Cr₂O₃ top coat.
4.5 DISCUSSION

HVOF process with LPG fuel is successfully used to deposit NiCr and Cr$_3$C$_2$-NiCr coatings on T91 boiler steel in the present work. LPG fuel is chosen as it is very cost effective in comparison to hydrogen fuel. Due to the higher velocity, relatively lower temperatures and higher impact of the powder particles on the substrate material, the coatings with dense microstructure and less porosity are formed in HVOF process. The HVOF sprayed coatings have shown a typical splat surface morphology with distinct splat boundaries (Fig.4.36 and Fig. 4.41), due to the deposition and re-solidification of molten or semimolten droplets. Microstructure of NiCr coating (Fig.4.36) is highly lamellar with distinct splat boundaries and long axis of the splats oriented parallel to the substrate surface as compared to microstructure of Cr$_3$C$_2$-NiCr coating (Fig.4.41). The splats parallel to the substrate provides a necessary protection against corrosive species penetrating into the coating (Kamal et al, 2009B). Further NiCr coating observed to be denser than Cr$_3$C$_2$-NiCr coating. A limited number of unmelted particles can be observed in the microstructures of both the coatings. The coatings possess some voids and oxide inclusions that are typical characteristics of the HVOF sprayed coatings. The oxides may form due to the in-flight oxidation during spraying process and/or pre-existing in the feed material. Sidhu et al (2006L) also observed the similar features of HVOF sprayed coatings.

The measured value of porosity for the as-deposited and post treated coatings is reported in Table 4.4. The porosity of HVOF-sprayed NiCr and Cr$_3$C$_2$–NiCr coatings was found to be less than 2%, which is in close agreement with the finding of Sahraoui et al (2006); Lih (2000) and Sidhu (2006F). The low value of porosity might be due to high kinetic energy of the powder particles. The high degree of flattening and very less splat fragmentation during HVOF spraying contribute for the less porosity value in the as-deposited coatings. In the HVOF process, the powder particles are propelled out of the gun nozzle at high velocities toward the substrate. Due to the high velocity impact of the sprayed powder particles, there may be an excellent joining of flat disc particles with the substrate and with an interlayer. Thus the coatings produced by HVOF spraying process are very dense (Sidhu et al, 2006F). The porosity of coatings is a prime parameter in the hot corrosion studies. The dense coatings are supposed to provide very good corrosion
resistance as compared to porous coatings, as porosities are the preferential corrosion paths through which the corrosive species can penetrate the coatings to reach the substrate and may cause rapid corrosion attack (Sidhu and Prakash, 2006A; Zhao et al, 2004; Zhao et al, 2005 and Sidhu et al, 2006L).

Post treatment of the HVOF sprayed NiCr and Cr$_3$C$_2$–NiCr coatings by heat treatment and sealing (by 503-VGF-C) resulted in decreasing the porosity. Decrease in porosity of the heat treated coatings may be attributed to the formation of oxide pockets at the places of porosity as revealed by cross-sectional analysis (Fig. 4.38 and Fig. 4.43). Sealant resulted in decreasing the surface porosity of the coatings by penetrating into the surface pores of the coatings.

Hardness is the most frequently quoted mechanical property of the coatings (Tucker, 1994). Higher values of hardness as observed for the coatings in comparison to the substrate may be due to the high density and cohesive strength of the individual splats as a result of the high impact velocity of the coating particles as suggested by Verdon et al (1998). It is evident from the Fig. 4.14 that the microhardness of the coating varies with the distance from coating–substrate interface. The non-uniformity of the hardness values of the coatings, along the distance for both coatings, probably attributed to the microstructural changes along the cross-section of the coatings (Staia et al 2001). These microstructural changes might be due to the presence of porosity; oxidised, melted, unmelted and semi-melted particles in the coating structure as observed in SEM and optical micrographs. The variation in the hardness values along the cross-section of the as-sprayed coatings is identical to the results obtained by Sidhu et al (2007F). An increase in hardness value of coating with depth is attributed to the presence of oxide and the lower hardness value in some location of the coating may be due to the slight amount of porosity. Further, a slight increase in the microhardness of the substrate has been observed near the coating-substrate interface (reference points at a distance of -40 μm in Fig. 4.14), which might be due to the work-hardening effect of sandblasting the substrate prior to the coating process as suggested by Sundrarajan et al (2004B). The substrate hardening may also be partly attributed to the high-speed impact of the coating particles during HVOF spraying. Similar phenomenon has also been observed by Sidhu and Prakash (2003) and Hidalgo et al (2000).
The measured values of surface roughness for the as-deposited and post treated coatings are reported in Table 4.4. Surface roughness is one of the important parameters of the coatings need to be measured for its better performance in the high temperature applications. For example, in thermal power plants, the coatings employed on the boiler-tube components are subjected to solid particle erosion and therefore it is essential to ensure the erosion resistance of the coatings with respect to its surface features such as surface roughness and morphology of the grain. It may be mentioned that higher surface roughness of the coated component would result in the higher erosion rate (S. Kamal, 2010).

As revealed from XRD of alloy powders and HVOF coatings, little change in the coating composition is observed for the HVOF sprayed Cr$_3$C$_2$-NiCr coating, whereas no change is observed for the NiCr coating. Ni has been observed as the main phase for the as-sprayed NiCr coating. For Cr$_3$C$_2$-NiCr coating, Cr$_3$C$_2$ and CrNi are observed as the main phases, which have further been confirmed by the EDS analysis. Heat treatment of NiCr and Cr$_3$C$_2$-NiCr produced several changes in the coating composition, as after heat treatment XRD has revealed the presence of CrNi, Cr$_2$O$_3$, Cr$_3$C$_2$ and NiCr$_2$O$_4$ phases for the Cr$_3$C$_2$-NiCr (Fig. 4.28) and presence of Ni, NiO, Cr$_2$O$_3$ and NiCr$_2$O$_4$ phases for the NiCr coating (Fig. 4.23).

EDS analysis from surface [Fig. 4.32 (a)] and cross-section (Fig. 4.37) of NiCr coating shows the coating rich in Ni and Cr, close to powder composition (80Ni-20Cr), along with the traces of other elements such as Mo, Mn, Nb and V. Further EDS (Fig. 4.37) and X-ray mapping (Fig. 4.46) analysis shows the uniformity in the chemical composition of NiCr coating, with Ni and Cr co-existing with each other. EDS analysis from surface [Fig. 4.34 (a)] and cross-section (Fig. 4.42) of the as-sprayed Cr$_3$C$_2$–NiCr coating indicates the formation of the required composition for HVOF coating, with NiCr metallic binder phase corresponds to the white region in the micrograph and the dark grey region as the carbides. Marginal presence of O in the composition of both the NiCr and Cr$_3$C$_2$–NiCr coatings indicates the chances of formation of oxides. Similar formations of oxides in the HVOF coatings have also been reported by Dent et al (2001) and Kong et al (2003). Further the presence of traces of substrate elements in the coatings as revealed by EDS and X-ray mapping analysis indicates the diffusion from substrate towards coating.
Diffusion of traces of elements from the substrate to the coating in HVOF spray process is also reported by Sidhu et al (2006).

Heat treatment of the NiCr and Cr$_3$C$_2$–NiCr coatings resulted in the formation of oxide stringer along the splat boundaries and at the places of porosity as revealed by EDS and X-ray mapping analysis. Further these oxides may block the interconnected porosity, which in turn suppose to improve the corrosion resistance of the coatings. EDS [Fig. 4.39 (b)] and X-mapping (Fig. 4.48) analysis of the sealed NiCr and Cr$_3$C$_2$–NiCr coatings, reveal the presence of sealant on the top surface. Sealant may improve the corrosion resistance of the coating by blocking the surface pores, as these are the preferential path for the corrosive spices. The cross-sectional BSE images of the duplex coating systems with Al$_2$O$_3$/Cr$_2$O$_3$ top layer on NiCr/Cr$_3$C$_2$–NiCr coating show that the interface between the coatings and the top coats is free from any defects and therefore, the adhesion strength of the top coat is expected to be good.

Black areas at the coating-substrate interface are observed invariably in both the coatings, which might be the inclusions of aluminum oxide. The X-mapping analysis also indicates that the islands of alumina present at the coating-substrate interface, which do not match with the elements of substrate or coating powders. It is believed that some alumina particles might have retained in the asperities during grit blasting of the substrate prior to deposition of the coatings. Similar islands of aluminium oxides due to retained alumina powder were also reported by Sundararajan et al (2003).