CHAPTER 3: EXPERIMENTAL METHOD

3.1 Aluminization of substrates of superalloys 690 and 800

3.1.1 Pack aluminization of substrates of superalloys at 1173-1273 K in argon atmosphere

Commercially available superalloys 690 and 800 were used as substrate materials in the present investigation. The alloys were available in mill-annealed condition. The typical chemical compositions of the alloys are shown in Table 3.1.

Table 3.1: Typical chemical compositions of superalloys 690 and 800 (wt.%)  

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Ti</th>
<th>Al</th>
<th>S</th>
<th>P</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>Bal</td>
<td>28.0</td>
<td>9.6</td>
<td>0.03</td>
<td>0.17</td>
<td>0.04</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>30.0</td>
<td>19.5</td>
<td>Bal</td>
<td>0.03</td>
<td>0.7</td>
<td>0.4</td>
<td>-</td>
<td>0.5</td>
<td>0.3</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Pack aluminizing process was used to form aluminide coating on superalloys 690 and 800 specimens having initial dimensions 15 mm x 10 mm x 5 mm and 15 mm x 10 mm x 1.5 mm respectively. All the sides of the specimens were ground up to 600 grit emery paper, cleaned, dried, and weighed. In pack aluminizing process, the pack mixture was composed of 10 wt.% Al powder (particle size finer than 200 micron), 5 wt.% NH₄Cl and 85 wt.% Al₂O₃ powder. In alumina crucibles, the substrate specimens were embedded in the pack mixture one by one after proper ramming of the space in-between. After putting each alumina lid, the entire crucible was covered with high temperature cement and kept for drying for two days. The pack cementation was carried out at 1173-1273 K in a resistance heating horizontal type furnace having a constant temperature zone of about 200 mm. Prior to carrying out pack cementation experiments, the temperature range was optimized. Low-temperatures (lower than 1173 K) pack aluminization leads to the formation of Ni₂Al₃ due to lower diffusivities of the elements. In the case of pack aluminization above 1273 K, kinetics of NiAl formation are very fast. Keeping this in view, pack cementation in the present study was done between 1173 K and 1273 K with
different pack compositions and soaking periods. As service temperature for metallic melter pot is in the vicinity of 1273 K, aluminizing parameters for superalloy 690 have been optimized around 1273 K. For the sake of comparison, the aluminizing parameters of superalloy 800 have also been optimized at similar range of temperature. That is why, aluminizing experiments on Alloys 690 and 800 involving temperatures other than 1273 K were not included. The process was standardized at 1273 K with a soaking period of 10 hours for superalloy 690 and 8 hours for superalloy 800. Each process was carried out in argon atmosphere with a heating and cooling rate of 4 K/min. After each treatment, the crucible was allowed to cool to room temperature under controlled atmosphere (argon). After cooling, the specimens were removed from the pack, cleaned, dimensions were measured and weighed. In order to find out the type of Ni-aluminide that formed using a low aluminium-containing pack and to examine its properties as well as the performance of diffusion barrier coating, pack aluminization was also standardized on superalloy 690 substrates (of initial dimensions about 10 mm x 10 mm x 4 mm) with a pack mixture consisting of 2 wt.% Al powder, 2 wt.% NH₄Cl and 96 wt.% Al₂O₃ at 1273 K in argon atmosphere with a soaking period of 4 hours. The other experimental conditions of pack aluminization were similar to those as mentioned earlier.

3.2 Microstructural characterization of aluminides

Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out on metallographically polished aluminized (with pack mixture containing 10 wt.% Al) specimens of the superalloys 690 and 800 along the cross-section. SEM using secondary electron (SE) image mode was used to examine the surface morphologies of the aluminized samples, whereas back-scattered electron (BSE) image mode was chosen to examine the cross-section of aluminized substrates. For EPMA, X-ray profiles for different elements were acquired.
across the cross-section to determine the difference in composition and wavelength dispersive spectroscopy (WDS) mode was used. Chemical compositions of various layers were determined by using quantitative chemical analysis on point-to-point basis and pure elemental standards were used for calibration of the spectrometer. For compositions of phases, values were obtained in wt.% (±1%), which were converted to at.%.

For aluminized superalloy 800 substrates, X-ray diffraction (XRD) studies were performed along the top surface after controlled grinding layer by layer using emery paper of grit number 80 up to 400. Digital micrometer screw gauge was used to measure the reduction of specimen thickness. Readings were taken on a number of locations of specimen surface and an average value was considered. The first XRD scan was taken on the metallographically ground surface after removing a layer of 140 μm. The second XRD scan was done after removal of 100 μm layer, whereas the third one was taken after removal of 300 μm layer. XRD studies at room temperature were performed by using CuKα radiation of wavelength 1.5406 Å with a scan rate of 0.02°/s in 2θ range of 20° to 100°. All the XRD peak intensities were converted to normalized values and the peaks were ascertained by using 1998 JCPDS-International Centre for Diffraction Data.

For specimens of superalloy 690 those were aluminized with pack mixture containing 2 wt.% Al, XRD at ambient temperature was carried out on the surface of an aluminized sample. SEM was performed along with energy dispersive X-ray spectroscopy (EDXS) analysis along the cross-section of metallographically polished specimen. Point analysis was done at various locations along the cross-section. To resolve the aluminide at a finer scale, transmission electron microscopy (TEM) was conducted. For preparing sample of cross-sectional transmission electron microscopy, very thin sections containing the aluminides and the substrates were cut precisely.
The portions of the thin sections containing the aluminides were held together face to face tightly using a 3 mm diameter Ti grid and by applying a non-reactive glue. The 3 mm diameter disc (Ti grid containing glued specimen) was then subjected to dimple grinding. After the dimple grinding of the specimen from both the sides of the disc, further thinning was done using argon ion gun operated initially at 4 kV and finally at 6 kV for a very short duration. TEM examination was performed on the specimen using bright-field and dark-field image conditions. Selected area diffraction (SAD) patterns were obtained from certain locations. EDXS analysis was performed on a few points. Besides this, high-solution TEM was performed.

3.3 Microhardness of aluminides

Microindentation method, suitable for thin sheet, was used to measure microhardness values of metallographically polished aluminized (with pack mixture containing 10 wt.% Al) specimens of superalloys 690 and 800 along the cross-section. Knoop hardness values were measured for the specimens at specific distances along the cross-section. A load of 50 gm was applied each time for 10s to determine the microhardness value. A magnification of 400X was chosen during the measurements. Adequate gap (about 50 µm) was maintained between two successive indentations and sufficient margins were left on either side while measuring microhardness values to avoid error due to edge effects. For specimens of superalloy 690 those were aluminized with pack mixture containing 2 wt.% Al, Vickers hardness values were measured along the cross-section of the sample by applying a load of 100 gm at each time for 5s to determine the microhardness.

3.4 Wear, friction and adherence tests of aluminides

Wear and friction tests were carried out in a dry medium using reciprocating sliding wear and friction machine on the aluminized (with pack mixture containing 10 wt.% Al) specimen of
superalloy 690 using 6 mm diameter grade 10 tungsten carbide (WC) ball at the load level of 15 N and varying the frequency values at 10, 15 and 20 Hz resulting sliding speed of 20, 30, and 40 mm/s respectively. Sliding amplitude was 1 mm. The duration of test at each frequency was 1800s. The coefficients of friction both static and dynamic were measured during the tests. The wear was measured for the WC ball as well as for the aluminized specimen at the three selected frequencies. After each test, the wear scar on specimen was scanned with a Taylor Hobson Form Telesurf Series-2 profilometer and the wear volume was calculated from the 3D-profile of the wear track. The ball scars were also examined using an optical microscope.

In order to evaluate the adherence of aluminide coatings, scratch tests were performed on metallographically polished aluminized samples of superalloys 690 and 800 by CSM Scratch tester using a Rockwell indenter of 200 micron tip radius. For superalloy 690 aluminized with 10 wt.% Al, a length of 3 mm was chosen on the surface, whereas for aluminized superalloy 800, a length of 1 mm along the cross-section was taken into consideration. The load levels chosen for the alloys were 0.9 to 20 N and 0.9 to 10 N respectively with a loading rate of 30 N/minute to evaluate the adherence of aluminides. The load sensor had a resolution of 0.003 N, while depth sensor was having a resolution of 7.5 nm. For superalloy 690 aluminized with 2 wt.% Al, a scratch length of 0.4 mm was considered along the cross-section keeping a constant load level of 2 N. Friction curves and depth penetration curves were recorded for the specimens of the superalloys.Appearances of scratched surfaces at different regions with different loads were recorded using a light microscope that was attached to the instrument. Selections of type of test and test parameters were done based on the dimensions of the specimens of the alloys, type of previous test and applications of the superalloys.
3.5 Modeling of Ni (111)/NiAl(110) interface structure for aluminized superalloy 690 substrate

First-principle calculations on Ni(111)/NiAl(110) interface were performed to estimate ideal work of adhesion (W_{ad}(ideal)) between Ni and NiAl and to understand nature of bonding across the interface and its structure. The purpose of selection of Ni(111) and NiAl(110) surfaces to form the respective interface was to get lowest bound values on the interfacial adhesion as these are the most closed packed planes in their respective systems. The methodology consisted of understanding cohesion in the bulk structures, viz., Ni (fcc, Fm-3m) and NiAl (B2, Pm-3m) and then studying Ni(111)/NiAl(110) interface between the substrate (Ni(111)) and the coating (NiAl(110)) surfaces. All the calculations were performed using the plane wave based Vienna Ab-initio Simulation Package (VASP) [48,49]. VASP is based on the density functional theory (DFT) and generalized gradient approximation was used for the exchange and correlation potentials as parameterized by Perdew, Burke and Ernzerhof [50]. The projector augmented wave potentials [51] were used for the ion-electron interactions. The Brillouin-zone integration was done using the Monkhorst-Pack [52] k-point mesh. The Methfessel-Paxton technique [53] was used for free energy calculations with a modest smearing of 0.1 eV, which resulted in a very small entropy term (<0.1 meV/atom) in all the cases. Full optimization was carried out with respect to E_{cut} and k-point meshes to ensure convergence of total energy to within a precision of 1 meV/atom. The total energy was optimized with respect to volume (or lattice parameter), c/a ratio and atomic positions as permitted by the space group symmetry of the crystal structure ensuring that residual force on each atom was less than 1 meV/Å. Slab model was used for the interface simulations. Seven mono-layers of Ni(111) substrate were taken to ensure no interaction between the top and bottom surfaces in the isolated surface slab. The substrate slab consists of 56 Ni atoms with
surface area of 42.85 Angstrom\(^2\). Three monolayers of NiAl(110) containing 12 atoms (6 atoms each of Ni and Al, respectively) were used as coating on Ni(111) substrate. In the present simulations, all the atoms of the NiAl(110) coating and atoms in only three topmost monolayers of Ni(111) in the interface slab were allowed to relax. Similar calculations have also been performed by replacing 2 Ni atoms by 2 Cr atoms at the interface plane and by replacing 1 Ni atom by 1 Cr atom below the interface plane and determining ideal work of adhesion for the interface.

### 3.6 Oxidation test

Pack aluminized (with pack mixture containing 10 wt.% Al) samples of superalloys 690 and 800 were ground up to 320 grit emery paper to remove particles, which got adhered to the surface during aluminization treatment and to have a surface that was neither very rough nor very smooth. The specimens were cleaned and weighed. Thermal oxidation of aluminized specimens was conducted at 1273 K for 2 hours in each time with a total period of 4 hours in a resistance heating horizontal furnace without using any controlled atmosphere followed by air cooling. After each oxidation treatment, the specimens were cleaned and weighed. For samples of superalloy 690 those were aluminized with pack mixture containing 2 wt.% Al, thermal oxidation was performed at 1273 K for a total period of 8 hours (4 x 2-hour) in a resistance heating horizontal furnace without using any controlled atmosphere. After every 2 hours of holding at 1273 K, the samples were taken out and allowed to cool in air. Weight gains were recorded for the first 3 x 2-hour cycles during thermal oxidation while that was negligible during last 2-hour cycle. As the service temperature of the component (superalloy 690 as metallic melter pot) has been close to 1273 K, similar temperature for thermal oxidation was chosen and an attempt has also been made to evaluate the behaviour of oxidation. Similar oxidation tests were
also conducted on bare superalloy substrates for a total period of 12 hours (6 x 2-hour) to compare the oxidation behaviour of aluminized substrates of superalloys with those of bare substrates.

3.7 Characterization of oxide layer for aluminized superalloy 690

Aluminized (10 wt.% Al) and oxidized (1273 K for 4 hours) superalloy 690 substrate containing thermally grown oxide layer was examined along the cross-section using SEM under BSE as well as SE image modes. EDXS analysis was also carried out for elements on a quantitative basis at different locations along the cross-section of the specimen on point-to-point basis. XRD studies at room temperature were carried out on pack aluminized (with pack mixture containing 2 wt.% Al) sample thermally oxidized in air at 1273 K for 8 hours. It is to be mentioned that for aluminized superalloy 800 substrates, investigation was kept restricted up to evaluation of oxidation resistance.

3.8 Evaluation of stability of thermally oxidized aluminides in borosilicate melt

To evaluate the stability of the coating, aluminized superalloy 690 substrates (pack aluminized with either 10 wt.% or 2 wt.% Al in the pack mixture) with thermally grown oxide layer were exposed in sodium borosilicate melt at 1248 K for a total period of 192 hours. This exposure was restricted to superalloy 690 samples but not conducted with superalloy 800 specimens keeping in view the applications of the alloys. The composition of borosilicate glass used in the present investigation is shown in Table 3.2.

<table>
<thead>
<tr>
<th>Compositions of oxides, wt.%</th>
<th>Compositions of elements, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>48.0</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Table 3.2: Composition of borosilicate glass
The glass composition is of interest. The glass formulation for immobilization of high level radioactive liquid waste is judiciously chosen to ascertain optimal waste loading, modest processing requirements and desirable product characteristics. About 6 g of sodium borosilicate glass beads were taken in one set of sillimanite crucibles of internal diameter of about 17 mm and height of 18 mm and the crucibles were placed inside a pre-heated (1248 K) chamber type furnace in air atmosphere. The samples were dipped in the glass when it reached molten state and the temperature of the molten glass was maintained at 1248 K for a total period 192 hours. In each crucible, the volume of molten glass was around 6 times to that of the specimen. Superalloy 690 bare substrates were also kept in another set of crucibles under identical experimental condition for comparison of results.

After the exposure of the specimens in borosilicate melt, the cross-section of the specimens (aluminized + thermally oxidized and bare alloy samples) with adhered glass were metallographically polished and microstructural characterization was carried out using SEM under BSE as well as SE image modes. EDXS analysis using a polymer-based thin window for detector entrance allowing detection of X-rays down to 100 eV was performed for elements on a quantitative basis at various locations along the cross-section on point-to-point basis for the specimens. The analyses of substrates for the samples and aluminides were found to be reproducible and accurate. EDXS analysis of glass phase excluding B was carried out only in close vicinity of specimen/glass interface. The glass phase in each case that was far away from interface was not considered to avoid possibility of any contamination from crucible surface. Besides this, some overestimation of elements only in glass phase because of omission of B was kept in mind.
XRD studies at ambient temperature were performed on the surface of aluminized (10 wt.% Al) and thermally oxidized superalloy 690 substrate after exposure in borosilicate melt.