CHAPTER 5

LIQUIDNITRIDING OF STAINLESS STEEL CLADDING
AND OPTIMISATION OF LIQUIDNITRIDING PROCESS

5.1 INTRODUCTION

Stainless steels are preferred in industrial applications for their corrosion resistance but their poor tribological behaviour has been a barrier for their wider usage. Corrosion environments are frequently found in food processing and marine equipments as well as chemical and nuclear components. The poor corrosion wear resistance of the stainless steels was investigated by Jean-Paul lebrun during 1971 (Bell 2002). Despite the wide significance of corrosion wear comparatively lesser research has been undertaken in this area as compared with the widespread studies on pure forms of mechanical wear and corrosion. Hence it has been identified that there is a dearth of research on which corrosion wear conditions can be mitigated through appropriate surface engineering. Thus it has become necessary to develop new technologies that can effectively improve the corrosion wear resistance of stainless steel.

In this chapter, the claddings produced at different heat inputs and at optimum heat input conditions are liquid nitried (LN) with optimum LN process parameters. The direct and interaction effects of the LN process parameters on the compound layer are discussed.
5.2 CONVENTIONAL LIQUID NITRIDING OF STAINLESS STEELS

The conventional liquid nitriding of stainless steels with temperatures between 580 to 600 °C are generally characterised by the precipitation of chromium nitride, which depletes the chromium in the austenitic solid solution and the material loses its corrosion resistant properties (Souza et al 2009). Also, they were based on cyanide-carbonate baths which are highly toxic and requiring elaborate precautions for human safety and effluent disposal thereby damaging the environment (Nascimento and Chinelatto 2009). The growing environmental awareness, coupled with the ever increasing cost of detoxification of effluents has created the necessity to develop a non-toxic equivalent for this process.

A typical conventional liquid nitriding bath is composed of a mixture of molten sodium and potassium salts, including cyanides, cyanates and carbonates. At nitriding temperatures, the cyanate, for example, is decomposed and nascent nitrogen is released according to the equation,

\[ 4\text{NaCNO} \rightarrow \text{Na}_2\text{CO}_3 + 2\text{NaCN} + 2\text{N} \]

The released nascent nitrogen is very active and it diffuses into a component forming a diffusion layer and iron nitride compounds on the surface (Liang et al 2000). Since liquid nitriding involves the use of such toxic salts as cyanides, it causes serious environmental and working condition problems and is regarded as environmentally harmful process.
5.3 MODIFICATIONS MADE IN THE PRESENT INVESTIGATION

The conventional liquid nitriding processes are based on cyanide-carbonate baths which are highly toxic and requiring elaborate precautions for human safety and effluent disposal (Ceschini and Minak 2008). In the present investigation, the nitriding bath consists of a base salt containing only cyanate and carbonate salts of lithium, sodium and potassium, thereby making the process neither pollutive nor toxic. Cyanate provides a rich source of nitrogen and the presence of lithium increases the nitriding potential. The sources of nitrogen are mainly due to nitrogen generated because of the dissociation of cyanates present in the base salt and oxidation of cyanates.

The sodium and potassium salts form a eutectic mixture with lithium salts to maintain high fluidity. Sulphur is also added in small amounts to form potassium sulphide. The addition of sulphur increases the nitriding potential of the bath and most importantly, in the oxidised form it neutralizes any traces of cyanides formed. Hence, this process can be regarded as a non pollutive, very safe and an ideal replacement for the conventional liquid nitriding processes was implemented for SS cladding. Being highly activated, the nitriding bath gave a very compact compound layer to a depth ranging from 30-32 microns. Diffusion layer is obtained until a depth of 0.6-1 mm, which stabilises the epsilon nitride and increases the surface fatigue resistance considerably.

- The sodium salts, which comprise 60 to 70% (by weight) of the total mixture, consist of 96.5% NaCN, 2.5% Na₂CO₃, and 0.5% NaCNO.

- The potassium salts 30 to 40% of the mixture consist of 96% KCN, 0.6% K₂CO₃, 0.75% KCNO, and 0.5% KCl. The operating temperature of this salt bath is 565°C.
Thus suitable modifications have been incorporated to overcome these detrimental environmental effects by filling the liquid nitriding bath with base salts of cyanate and carbonate of lithium, sodium and potassium which enabled the formation of a precipitation free hard and ductile nitride layer on the surface thereby making the process neither pollutive nor toxic. This enhances the product service life and lowers the maintenance procedures thereby saving money and material. Hence, this method can be regarded as an eco-friendly, non-pollutive, economical, safe and an ideal replacement for the conventional cyanide liquid nitriding process which promoted an alternative way thereby saving the environment from the ill effects of cyanide pollution.

Even though it is presumed to have a cyanide free liquid nitriding bath, a small amount of cyanide, usually up to 1.0%, is produced as part of the reaction in the active bath (Fernandez et al 2008). Since this is a relatively lower concentration and these compositions have gained widespread acceptance within the heat treating industry because they do contribute substantially to the alleviation of a potential source of pollution.

The nitriding bath consists of a base salts containing only cyanate and carbonate salts of lithium, sodium and potassium which enabled the formation of a precipitation free, hard and ductile nitride layer on the surface thereby making the process neither pollutive nor toxic. If this process is carried out below 580°C, the carbide precipitation will be suppressed with an enhancement in surface hardness. Thus an improvement in the wear resistance without reduction in the corrosion resistance of the cladding can be achieved.

The first phase of this investigation was carried out with an aim to predict and optimise the liquid nitriding process parameters. The experiments based on the design matrix were carried out with AISI 316 L austenitic stainless steel cladded over carbon steel plate of AISI 1040 / IS: 2062 by the optimised PTAW process. In the second phase of this investigation, the
liquidnitriding process was carried out with its optimised nitriding parameters on the claddings.

5.4 PLAN OF INVESTIGATION

The present investigation has been carried out in the following sequence:

**Phase I:**

1. Identify the important liquidnitriding process parameters and predict them by developing mathematical models using RSM technique

2. Optimise the liquidnitriding process parameters by using Microsoft Excel.

**Phase II:**

1. To carry out the optimised liquid nitriding process for the specimen cladded with the optimum PTAW process parameters.

Also, it has been planned to conduct the corrosion and wear tests as per ASTM procedures for the specimens in the as cladded condition and as nitrided condition to compare their corrosion and wear resistance in the subsequent chapters.

5.4.1 Prediction of important liquidnitriding process parameters

From the literature the independently controllable vital liquid nitriding process parameters have been identified. They were the nitriding temperature and the soaking time. The limits of the process parameters and their factor levels are shown in Table 5.1.
Table 5.1 Liquid nitriding process parameters and their levels

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Notation</th>
<th>Units</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitriding temperature</td>
<td>$T_N$</td>
<td>°C</td>
<td>-1.414   -1  0  1  1.414</td>
</tr>
<tr>
<td>Soaking time</td>
<td>$T_S$</td>
<td>min</td>
<td>92  96 106 116 120</td>
</tr>
</tbody>
</table>

The upper limit of the factor was coded as 1.414 and its lower limit as -1.414. The coded values of the intermediate levels being calculated from the relationship.

$$Xi = 2 \left[ 2X - (X_{max} + X_{min}) \right] / \left( X_{max} - X_{min} \right)$$ where,

$Xi$ is the required coded value of a variable $X$, $X$ is any value of the variable from $X_{min}$ to $X_{max}$. Also, $X_{min}$ is the lower level of the variable and $X_{max}$ is the highest level of the variable.

5.4.2 Developing the experimental design matrix and to conduct experiments as per design matrix.

The experiments were formulated with the central composite rotatable design of second order which is found to be an efficient tool in Response Surface Methodology (RSM). The 13 set of coded conditions used to form the design matrix were shown in Table 5.2. The carbon steel (AISI 1040/IS: 2062) specimen of size 25x15x20 mm³, cladded with AISI 316L austenitic stainless steel powder with optimised PTA cladding process parameters (Amos and Murugan 2010) were used for conducting the liquid nitriding experiments.
Table 5.2 Design matrix with measured value of nitrided layer thickness

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Process variables</th>
<th>T, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1, -1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>1, -1</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>-1, 1</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>1, 1</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>-1.414, 0</td>
<td>27.5</td>
</tr>
<tr>
<td>6</td>
<td>1.414, 0</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>0, -1.414</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>0, 1.414</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>0, 0</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>0, 0</td>
<td>27</td>
</tr>
<tr>
<td>11</td>
<td>0, 0</td>
<td>29</td>
</tr>
<tr>
<td>12</td>
<td>0, 0</td>
<td>26</td>
</tr>
<tr>
<td>13</td>
<td>0, 0</td>
<td>29</td>
</tr>
</tbody>
</table>

(T_N = Nitriding temperature, T_S = Soaking time, T = Nitrided layer thickness)

The liquid nitriding furnace designed and fabricated by M/s. Ashwathi Furnaces, Bangalore, India, was employed to conduct the liquid nitriding experiments at the Best Heat Treatment Services, Coimbatore, as per the design matrix. The stainless steel specimens weld cladded with optimised PTAW parameters for conducting the liquid nitriding experiments in order to optimise its process parameters are shown in Figure 5.1.
5.4.3 Experimental procedure, Recording the responses and Regression modelling

The liquid nitriding process was carried out by treating the components in this bath at the predefined time and temperature as per the design matrix. The samples were taken out of the furnace and were air cooled until it reaches a temperature of 200 °C to avoid the traces of cyanides formed and then quenched in water. The nitrided specimens were quenched with water. The surface hardness was measured with Mitutoyo microhardness tester. The specimens were sliced at their midsection and the nitrided layer thickness was observed carefully after preparing the cross sectional surface with standard metallographic procedures.

The response function representing any of the nitriding process parameters can be expressed as \( Y = f(T_N, T_S) \), where \( Y \) is the response or yield, \( T_N \) is the nitriding temperature and \( T_S \) is the soaking time. The values of the coefficients of the polynomial equation were determined by using Systat statistical software.
5.4.4 Accessing the adequacy of the models and to test their coefficients for significance

The adequacies of the models were tested using the analysis of variance technique (ANOVA). In this, if the calculated value of the ‘F’ ratio of the model does not exceed the standard tabulated value for a desired level of confidence (95%) and the calculated value of the ‘R’ ratio of the model exceeds the standard tabulated value for a desired level of confidence (95%), then the model may be considered adequate within the confidence limit. The data presented in Table 5.3 reveal that all the models were adequate.

**Table 5.3 Analysis of variance for testing the adequacy of models**

<table>
<thead>
<tr>
<th>Model</th>
<th>F – ratio</th>
<th>R - ratio</th>
<th>Whether Model is adequate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrided layer thickness, T</td>
<td>2.9</td>
<td>14.5</td>
<td>Yes, Adequate</td>
</tr>
</tbody>
</table>

F-ratio (10, 6, 0.05) = 4.09, R-ratio (14, 6, 0.05) = 3.96

The final models were developed only with the significant coefficients. The square multiple R values of the full models and the reduced models are presented in Table 5.4 which shows that the reduced models are better than the full models.

**Table 5.4 Comparison of square multiple R values and standard error of estimate of full and reduced model**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Adjusted Square Multiple R</th>
<th>Standard error of estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full model</td>
<td>Reduced model</td>
</tr>
<tr>
<td>Nitrided layer thickness, T</td>
<td>0.8503</td>
<td>0.9390</td>
</tr>
</tbody>
</table>
5.4.5 **Determination of final model**

The final mathematical models determined by the above analysis are as follows:

Nitrided layer thickness, \( T = 25.962 - (0.422T_N) + (2.488T_S) + (1T_NT_S), \mu m \)

5.5 **RESULTS AND DISCUSSION**

5.5.1 **Direct effects of nitriding process parameters**

5.5.1.1 **Effect of nitriding temperature on nitrided layer thickness**

The effect of nitriding temperature with the nitrided layer thickness is presented in Figure 5.2. The nitrided layer is called as the epsilon or compound layer. It is evident from the figure that the nitriding temperature is highly significant in varying the nitrided layer thickness of the cladding. The thickness of the compound layer is found to be around 28 to 30 \( \mu m \) between 555–575°C.

![Figure 5.2 Effect of nitriding temperature on nitrided layer thickness](image)
The nitrided layer thickness increases as the nitriding temperature increases due to the continuous deposition of the nitrides on the surface of claddings.

5.5.1.2 Effect of processing time on nitrided layer thickness

It is evident from Figure 5.3 that the processing time during liquid nitriding also plays a significant role in deciding the nitrided layer thickness of the cladding. The nitrided layer thickness first increases and then decreases with increase in processing time.

![Figure 5.3 Effect of processing time on nitrided layer thickness](image)

5.5.2 Interaction effect of nitriding process parameters

5.5.2.1 Interaction effects of nitriding temperature and processing time on nitrided layer thickness

The interaction effects of nitriding temperature and processing time on nitrided layer thickness is presented in Figure 5.4. It is found that the nitrided layer thickness decreases with increase in nitriding temperature at
lower processing time periods. But the nitrided layer thickness increases with an increase in nitriding temperature during higher processing time periods. This is because of the deeper penetration of nitrogen during the prolonged duration. The higher time duration and treatment temperatures lead to the formation of chromium nitrides, which despite producing high hardness reduces the corrosion resistance of the material. This is due to formation of different phases (CrN, Fe₄N and Fe₃N) distributed in the surface region of the sample by the nitriding process at higher temperature. However, the nitrided layer thickness is not so much affected with increase in nitriding temperature when the processing time period is 106 min.

![Graph showing interaction effects of nitriding temperature and processing time (PT) on nitrided layer thickness](image)

**Figure 5.4** Interaction effects of nitriding temperature and processing time (PT) on nitrided layer thickness

### 5.6 Optimisation of Nitriding Process Parameters Using Excel Solver

The optimisation of the process parameters were carried out with Microsoft Excel to increase the nitrided layer thickness of the cladded samples to promote better wear properties without sacrificing the corrosion
properties. The prediction results confirm that the case depth during liquid nitriding of austenitic stainless steels claddings was found to depend on the processing temperature. At the same time, the processing time plays a vital role in deciding the corrosion properties of the claddings. The optimized process parameters are shown in Table 5.5.

**Table 5.5 Optimised liquid nitriding process parameters**

<table>
<thead>
<tr>
<th>No</th>
<th>Process parameters</th>
<th>Predicted Response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitriding Temperature, ((T_N))^\circ C</td>
<td>Soaking Time, ((T_S)) min</td>
</tr>
<tr>
<td></td>
<td>Coded value</td>
<td>Natural value</td>
</tr>
<tr>
<td>1</td>
<td>-1.37</td>
<td>553 (^\circ) C</td>
</tr>
</tbody>
</table>

It is evident from Figures 5.5 - 5.6 that the high concentration of nitrogen combines with stainless steel and other nitride forming elements to produce an outer layer of epsilon nitride through catalytic reaction, which is thin, hard and ductile with exceptional engineering and wear properties.

![Microscopic cross section of cladding nitrided at optimum condition (X400)](image)
This layer is also known as the epsilon or compound layer, which has increased the surface hardness to enhance anti-galling characteristics and also lowers the coefficient of friction.

![SEM showing the cross section of the cladding nitrided at optimum condition](image)

Figure 5.6 SEM showing the cross section of the cladding nitrided at optimum condition

A surface harness of 1365 HV$_{100}$ and a nitried layer thickness of 32 µm were observed at the optimum processing temperature and a processing time of 553 °C and 93 minutes respectively. Beyond this optimised limits the depletion of chromium on the layer due to the formation of chromium nitrides (CrN) could be possible to detoriate the corrosion resistance on the surface of the claddings.

Nitrogen of lower concentration continues to diffuse below the compound layer and forms a solid solution with the layer below. Subjacent to the compound zone is another distinctive region, the diffusion zone and is noted for its improvement in fatigue strength. This compound layer has excellent wear properties and has enhanced resistance to wear, corrosion and
galling. The corrosion and wear resistance properties of the liquid-nitrided layer are dealt in the subsequent chapters.

5.7 HARDNESS–DEPTH PROFILE OF THE NITRIDED SPECIMENS CLADDED AT DIFFERENT HEAT INPUTS

The hardness–depth profile of the nitrided claddings at different heat inputs are depicted in Figure 5.7. In the near surface region, the nitrided specimen weld cladded with low heat input possessed surface hardness between 1100 - 1200 HV\textsubscript{100}. It was surprising to note that the hardness retained up to a case depth of 20 μm followed by a steeper transition to the lower case depth in to the weld cladded region. Whereas, the nitrided specimen weld cladded with optimum heat input possessed surface hardness between 1200 - 1340 HV\textsubscript{100} followed by a smoother and gradual transition to the lower case depth in to the weld cladded zone.

The surface hardness of the nitrided specimen cladded with high heat input was less than 800 HV\textsubscript{100}, though nitrided under similar conditions. Even though an increase in thickness of the compound layer was observed in this specimen, a lower hardness of the nitrided case was noticed with a gradual drop in hardness from 800 to 400 HV\textsubscript{100} over a much narrow region of within 10 μm.
Figure 5.7 Hardness depth profiles of nitrided claddings

5.8 SUMMARY

The liquid nitriding process parameters were found to have a significant influence on deciding the nitrided layer thickness of the stainless steel cladding. Liquid nitriding of stainless steels produced a compound or epsilon layer and a diffusion layer which has resulted in hardness improvement on the surface of stainless steels. This has ultimately created new avenues in liquid nitriding of stainless steel with lower temperatures and processing duration.