Chapter VIII

Laser Surface Modification of Al-Si Alloy with Fe-Cr-Si
8.1 Introduction

An ever spelt problem during LSM of substrates entrenched with Cr and Cr included precoats, is the occurrence of unmelt/partially melt Cr rich regions of high hardness which act as the springing source for fracture nucleation. In Chapter-VII, complete melting of Cr was observed while laser melting the Fe-Cr-SiC precursor. Mechanism behind the arrival of layer-melt pool continuance was explained in Chapter-V.

In this sequence, another trial for complete melting of Cr was tried with Fe-Cr-Si coating on an Al-Si substrate. As the thermal diffusivity value of Cr (0.27 cm²/s) lies between those of Fe (0.226 cm²/s) and Si (0.9 cm²/s), complete melting of Cr would be expected. High thermal retaining capability of Fe would also share the duty of melting Cr, thereby the laser treated regions may be expected to be free from highly brittle chunks. The mechanism is similar to that of the cases of LSM of Al-Si substrates with Fe-Cr-SiC and Ti-Cr-SiC precursors. As Si is selected instead of SiC, the problem of Al₄C₃ formation and its elimination does not arise.

LSM of Al alloys with Fe included precoats has resulted in modification of the tribological parameters as explained in Chapter-VII (163-166). Among these, laser processed Al-Fe coating on A5052 Al alloy was found to be enriched with fine needle like FeAl₃ and Fe₂Al₅ compound structures. The laser alloyed
region exhibited microstructural transformation and the hardness distribution was in accordance with the structural and resolidification conditions [165]. Role of Cr in hardness enhancement is unambiguous, as explained in Chapter-V [105-107, 110-117].

After LSA, Al alloys exhibit few co-existing problems viz. defects of alloying and physical properties variation midst the alloyed zone and the substrate. It is more cost effective, if Si is utilized to enhance the tribological characters of Al alloy through LSA. It is because of the fact that, Si increases the fluidity of the melt pool liquid which results in good surface state, negligible defects and identical physical properties between the melt zone and substrate. While laser alloying Al alloys with Si and Si included precursors, surface hardness and wear resistance were found to be improved and the degree of Si in the coating has decided the degree of hardness improvement [94&95]. Apart from tribological characters enhancement, Si addition would encourage the melt fluidity, so that the laser treated region may exhibit structural uniformity and it could facilitate in complete elimination of shrinkage cavity as explained in Chapter-IV [28].

In this work, the Al-Si substrate was laser alloyed with Fe-Cr-Si and the high hardness bearing laser alloyed region was expected to be free from cracks initiating Cr rich deposits. Owing to higher cooling rates of laser alloying process, formation of derogatory $\delta$-Al$_4$FeSi$_2$ and $\beta$-Al$_3$FeSi ternary intermetallics would be precluded as mentioned in Chapter-VII.
8.2 Experimental Procedure

Different mixtures of fine Fe, Cr and Si powders were coated on Al-Si substrates. After laser treatment, sample-A (20Fe-60Cr-20Si), sample-B (40Fe-50Cr-10Si) and sample-C (60Fe-30Cr-10Si) (all in wt. %) were obtained. Various laser processing parameters involved in this trial are given in Table-8.1.

<table>
<thead>
<tr>
<th>Sample-A (20Fe-60Cr-20Si Wt.%)</th>
<th>Sample-B (40Fe-50Cr-10Si Wt.%)</th>
<th>Sample-C (60Fe-30Cr-10Si Wt.%)</th>
<th>Laser Power kW</th>
<th>Scan Speed m/min.</th>
<th>Fluence (Jmm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>B1</td>
<td>C1</td>
<td>1.5</td>
<td>0.5</td>
<td>180</td>
</tr>
<tr>
<td>A2</td>
<td>B2</td>
<td>C2</td>
<td>2.5</td>
<td>0.5</td>
<td>300</td>
</tr>
<tr>
<td>A3</td>
<td>B3</td>
<td>C3</td>
<td>2.5</td>
<td>1.5</td>
<td>100</td>
</tr>
</tbody>
</table>

8.3 Results and Discussion

The laser treated regions exhibit morphological variations in accordance with the coating materials composition as well as with the laser processing parameters. Influence of these factors could be understood from the following.

8.3.1 Optimization of the Coating Materials Composition

Figure 8.1 shows the microstructure of the laser treated sample-A2 (20Fe-60Cr-20Si wt.%) consisting of a fine, dense mixture of intermetallic compounds. The microstructure of high integrity exhibits no porosity or crack. Similar microstructure was observed while laser treating an Al-12Si alloy with premixed
Fig. 8.1: Optical micrograph - Sample A2
Fe-Al powder. Variations in microstructure were correlated to the changes in the orientation of the dendrites and their chemical content [166].

It should be noted that the microstructure of the alloyed zone comprises of three distinct regions across the depth viz. Region-I (up to 110μm), Region-II (110-310μm) and Region-III (310-420 μm). The needle structures in the laser melt pool show gradual refinement - from branched coarse columnar to fine columnar. Similar stratified layer formation was reported while laser cladding Al-Cu-Fe on pure Al substrate [167].

Increased Fe content in the coating, results in the occurrence of pores and cracks. Microstructure of sample-B2 (40Fe-50Cr-10Si wt.%), with less regional demarcation (Fig.8.2) compared with that of sample-A2 exhibits the presence of a pore (shown by the arrow) and a white region (possessing no specific microstructure) from which cracking propagates. Reduction in Si content could have reduced the fluidity of the melt liquid thereby pores as well as sedimentation of such deposits would have occurred. Figure-8.3 the microstructure of sample-C2 (60Fe-30Cr-10Si wt.%) demonstrates the effect of high Fe content in developing higher degree of cracking.

Similar phenomenon was reported by Krishanu Biswas et al. [167]. Alloy homogeneity becomes too poor leading to an anisotropic mechanical behaviour of the track, while Fe proportion in the coating exceeds 30 wt.%. In short, increased Fe proportion reduces the homogeneity of the laser treated region, as a result of which the region concerned is prone to structural degeneration. It has been reported that the stress due to thermal expansion mismatch and the effects of plastic deformation are responsible for the failure mechanism. Volume
Fig. 8.2: Optical micrograph - Sample B2

Fig. 8.3: Optical micrograph - Sample C2

Fig. 8.4: Optical micrograph - Sample A3
shrinkage and residual tensile stresses in the superficial coat initiate crack networks [168]. Higher degree of thermal mismatch might have led to the extensive occurrence of profound cracks throughout the depth of the melt pool (Fig. 8.3). The existence of interconnected porosity and segmented cracks not only affect the mechanical properties but also deteriorate the oxidation and corrosion resistances of the region concerned.

In brief, among the three compositions, Series-A (20Fe-60Cr-20Si all in wt.%) is found to be fit for developing laser alloyed regions completely free from chunky deposits (of no specific microstructure) as well pores and cracks.

### 8.3.2 Optimization of the Processing Parameters

The role of laser fluency in tribological parameters enhancement is remarkable. In sample-A2, F=300Jmm\(^{-2}\) (P=2.5kW and v=0.5m/min.), the heat generated is sufficient enough to develop reasonable temperature gradient as well as the required degree of convection current. As a consequence, the coated materials could be completely melted and circulated within the melt pool several times resulting in proper mixing prior to resolidification (Fig. 8.1). The concerned resolidification rate gives rise to superior fine-grained microstructure with proper alloy composition and extended solubility of alloying elements, resulting in higher degree of alloying.

On the other hand, reduction in fluence either by decreasing the laser power [Sample A1 with F=180Jmm\(^{-2}\) (P=1.5kW and v=0.5m/min.)] or by increasing the scan speed [Sample A3 with F=100Jmm\(^{-2}\) (P=2.5kW and v=1.5m/min.)-Fig. 8.4], could generate comparatively lower surface temperatures. As a consequence of this, occurrence of comparatively lower
temperature gradients as well convection currents might only lead to partial alloying. In such experimental environments, accumulations of unmelt/semi-melt coated materials in the laser melt pool are quiet common. Prominent distribution of white islets is exhibited by sample-A3 (Fig.8.4), which may affect the homogeneity of the alloyed region.

Thus it is deduced that, the alloyed region is found to be free from unmelt/semi-melt Cr rich deposits under 300Jmm$^{-2}$ laser fluence. (i.e.) at 2.5kW laser power and 0.5m/min. traverse speed.

8.3.3 SEM and EDS Analyses

Figure-8.5 represents the SEM micrograph of sample-A2, depicting the uniform microstructural variation. Needle structure refinement is also clearly portrayed. EDS analysis in different regions of the alloyed zone reveals the relative chemical compositions of each region concerned (Table-8.2). Figure 8.6 - the SEM micrograph of Region-I (Fig.8.1), reveals the presence of two sub-regions with structural demarcation. EDS analysis in the top most location (A-grey) of Region-I, spells Si richness along with Al and moderate Cr content (Fig.8.7-A). On the other hand, the bottom location (B-black & white) of Region-I exposes Si and Cr richness along with Al (Fig.8.7-B). Location-B of region-I shows white islets distributed amidst the matrix (black). The white islet in location-B is found to be rich in Si (81.13 wt.%) and Cr (11.89 wt.%) with minimum Al and negligible Fe where as the black matrix exhibits Al richness (89.34 wt.%) with minimum Si and Cr content. Surface Si richness in this trial is quite expected, as Si possesses the lowest density compared to that of the remaining coating constituents as well the Al melt as in Chapter-IV (89).
Fig. 8.5: SEM micrograph - Sample A2

Fig. 8.6: SEM micrograph - Region (I) of Fig. 8.1

Fig. 8.8: SEM micrograph of the - Region (II) of Fig. 8.1
Fig. 8.7-A: EDS analysis on Region I-A – Sample A2

Fig. 8.7-B: EDS analysis on Region I-B – Sample A2
Figure-8.8 shows the SEM micrograph of the needle structures in the Region-II, comprising of white and black regions. EDS analysis in the needle structures exhibits higher Si proportion with Fe and Cr richness. Fine grains in the Region-III near the interface exhibit higher relative percentage of Cr.

Table 8.2
Relative Percentages of the Elements

<table>
<thead>
<tr>
<th>Region</th>
<th>Al (wt.%)</th>
<th>Fe (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Si (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-A</td>
<td>45.37</td>
<td>---</td>
<td>6.37</td>
<td>48.26</td>
</tr>
<tr>
<td>I-B</td>
<td>57.32</td>
<td>5.07</td>
<td>12.23</td>
<td>25.38</td>
</tr>
<tr>
<td>II-Needles</td>
<td>45.83</td>
<td>19.12</td>
<td>14.45</td>
<td>20.60</td>
</tr>
<tr>
<td>III</td>
<td>62.37</td>
<td>1.18</td>
<td>30.01</td>
<td>6.44</td>
</tr>
</tbody>
</table>

8.3.4 XRD and EDS Analyses

XRD spectrum of sample-A2 (Fig.8.9) picturizes the occurrence of CrSi, FeAl₃ and Al₃Fe₂ peaks along with the Al, Cr and Si peaks. Surface richness of Si could be correlated with the Si peaks of the XRD spectrum. EDS analysis in the needles of Region-II shows that Fe and Al content gradually vary from top to bottom. Fe richness along with Al of the needle structures could be correlated with the FeAl₃ and Al₃Fe₂ formation. Presence of Cr peak speaks of the presence of melted Cr particles in the melt pool, owing to the convection current which controls the coated materials distribution in the melt pool.
Fig. 8.9: XRD Spectrum of Sample-A2

Fig. 8.10: Microhardness Profile of Sample-A2
8.3.5 Microhardness Analysis

Microhardness profile of sample-A2 (Fig.8.10) shows 505HV - peak hardness. A fairly large dispersion of hardness values recorded might be related to the variations in the microstructure of the laser treated zone. The three different regions in the laser melt pool (Fig.8.1) exhibit hardness in the range of 505-425, 320-240 and 155-130HV respectively. Variations in hardness might be due to the relative chemical concentration proportion/gradient of the coated materials submerged in the laser melt pool as well the intermetallics formed in the concerned regions.

Sample-B2 with slightly lesser regional demarcation also exhibits almost similar hardness variation characteristics. However it exhibits higher hardness (about 1100 HV) in the white region, wherefrom the crack originates. Samples-A1&A3 exhibit 450-483HV peak hardness. Arbitrary peaks in their hardness

Table 8.3
Phase Identification – XRD Analysis

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Phases Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₃FeAl₃</td>
</tr>
<tr>
<td>2</td>
<td>Al₃Fe₂, Al</td>
</tr>
<tr>
<td>3</td>
<td>FeAl₃, Si</td>
</tr>
<tr>
<td>4</td>
<td>Cr, Si</td>
</tr>
<tr>
<td>5</td>
<td>FeAl₃</td>
</tr>
<tr>
<td>6</td>
<td>Cr, CrSi</td>
</tr>
<tr>
<td>7</td>
<td>CrSi, Cr</td>
</tr>
</tbody>
</table>
profile (around 970HV) could be correlated to the presence of randomly distributed white islets in the melt pool.

8.4 Conclusion

- Higher degree of laser alloying is found to occur in Al-Si substrate with 20Fe-60Cr-20Si: all in wt.% precoat under 300Jmm\(^{-2}\) - laser fluence (2.5kW: laser power and 0.5m/min. traverse speed).
- A six fold hardness increment (505HV) is observed.
- In addition, gradual hardness variation throughout the melt region is also exhibited.
- The alloyed region is found to be free from unmelt/semi-melt coated materials.
- No pores or cracks are observed.