Chapter IV

Laser Surface Modification of Al-Si Alloy with Al-Si-SiC
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4.1 Introduction

While forming Al-SiC MMC layers on Al and its alloys, occurrence of pronounced shrinkage cavities in the layer-substrate interface is a frequently reported phenomenon [25, 76&27]. Initiation of vehement convective flow and lower fluidity of the melt liquid could be reasoned for the introduction of shrinkage cavities. When a high degree of dissimilarity exists between the thermal characters of the coating and the substrate materials, a remarkable temperature gradient is said to arise between the layer and the melt pool region, which originates intense thermo-capillary convectional current.

The molten liquid would be driven to both corners of the layer by the thermo-capillary driving force and could not flow back as it is rapidly cooled, thereby resulting in cavities [25, 76&27] and leading to layer debonding during sample preparation. Hence elimination of shrinkage cavities has become inevitable so as to improve the quality of the MMC. S.L.Chen et al. [91] has followed the vibration assisted laser cladding technique, to deposit ceramic-metal composite on Al alloys (i.e.) the substrate was vibrated during laser irradiation. The experimental results showed significant modification in the shrinkage cavity quality.

In this work, Al-Si-SiC coating was selected for deposition on the Al-Si base for LSM trial. The reason for this is that, the dissimilarity in the thermal characteristics between the base and the coating would be lower when compared
to the SiC coating alone on the Al alloy bases [25, 76&27]. Thus, when the major constituent elements (Al and Si) of the Al-Si substrate are incorporated in the coating, substrate-coating thermal compatibility may be approached, which may in turn reduce the degree of convective flow. This could lead to the reduction / elimination of shrinkage cavities.

Remarkable hardness enhancement was reported during LSM of Al and its alloys with Al incorporated precoats [55, 92-94]. 1200HV hardness was reported while laser alloying Al-Si substrate with Ni-Cr-Al coating [92]. Ni-Cr-Al laser clad coating on an Al-Si alloy was found to possess Ni-based amorphous structures of 600-800HV hardness, which have reduced the granular phase peeling from the matrix during the wear analysis and the wear amount was quite small [55]. An Al-Fe-bronze layer produced on an Al-Si alloy by laser processing showed higher bond strength and hardness [93]. Improvement in surface hardness as well wear resistance was reported while laser treating A319 Al alloy with Al-Si coating and the improvement in hardness exhibited a linear correlation with the amount of Si in the coating [94].

Laser treatment of Al with prelaid pure Si was also found to enhance hardness. Laser alloying of Al substrates with Si as well as laser cladding of Si on Al has resulted in hardness enhancement (450HV). Increasing Si content was found to be effective in improving hardness [95].

Tribological character enhancement through LSM of Al alloys with ceramic precoat is a well established fact [67,79, 96-102]. TiC layer deposited on 2024 and 6061 Al alloys through LSM, showed enhanced knoop hardness (400kg/mm²) [79]. Laser deposited WC-Co composite layer on an Al-Si alloy
exhibited a five fold increment in hardness (520HV) [96]. MMC developed on AA6061 alloy by laser track overlapping showed a five fold increase in hardness - 420HV [97]. Laser assisted SiC/Si$_3$N$_4$ MMC layers on the same alloy had 410HV hardness [67]. Ni-SiC composite layer of 450HV hardness was produced on Al-Si alloy by LSM process [98].

Role of SiC in the SiCp/Al-Si composite is remarkable in enhancing the tribological characters [99]. Massive wear resistance enhancement was reported during the laser melt injection of SiC into the melt pool of the Al-Si alloy [100]. Remarkable corrosion potential increment and corrosion current decrement were reported in the Al-2009/SiCw composite developed through LSM technique [101]. Appreciable tribological character enhancement was observed while laser treating a Ni based alloy with Al-10wt% SiC and Al-50wt% SiC precursors [102].

LSM of commercially pure Al as well 6061 and 8090 Al alloys with pre-deposited SiC has resulted in Al–SiC MMC layers with enhanced hardness. When the MMC thickness was increased beyond 50μm, shrinkage cavities were observed in the layer-melt zone interfaces. The thicker the SiC predeposit coatings, the larger the cavity formed [25]. Composite layers with 4-5 fold hardness increment were developed by laser treating AA2014, AA2219 and Russian 1441 Al alloys with SiC precursor. Among these, the composite layer formed on the AA2219 alloy contained cracks and pores and the composite layer deposited on the Russian 1441 alloy was found to be separated from the substrate [27].
Similarly shrinkage cavities were observed during laser cladding of SiC and Al-12\%Si alloy (matrix) onto various Al alloys viz. A6061, A2124, A1050 and A5052 (all with a negligible Si content). In this trial, Al-Si alloy powder was used instead of Al, as Si would prevent the formation of Al$_4$C$_3$. On cladding WC+Al onto A6061 under same laser processing parameters, the clad layer showed better quality i.e. less shrinkage cavity area. During WC+Al cladding onto A6061, the temperature of the melt (~1440°C) was thermally matched to the thermal characteristics of WC, and hence this gave rise to negligible shrinkage [76]. Presence of Al in the precoat on an Al alloy (with minimum Si content) could have also assisted in reaching layer-substrate thermal characteristics compatibility, thereby moderately reducing the degree of convection current. Thus a move towards ensuring of base-coating compatibility would reduce the cavity formation probability.

Si addition in the coating apart from hardness enhancement [94&95], yields additional benefits too. Lee et al. [103] suggested that Si addition in the coating/substrate would reduce the formation of Al$_4$C$_3$ (i.e) Si addition to the Al matrix would reduce the Al activity with the carbon atoms (obtained from SiC dissociation), thereby suppressing the formation of Al$_4$C$_3$. As a result, the layers would be devoid of Al$_4$C$_3$. L.R. Katipelli et al. [28] added 10\% Si to the TiC precoat on A6061 and the TiC layer produced by LSM was bereft of Al$_4$C$_3$. Addition of Si was intended to increase the wettability and fluidity of Al in the coating as well in the substrate and the enhanced melt liquid flow might have assisted in the elimination of cavities. Therefore Si addition would assist in the birth of cavity free interfaces along with hardness enhancement.
In this work, it was proposed to coat Al-Si (the major constituents of the Al-Si substrate)-SiC on the Al-Si substrate and laser melt. As a result, formation of a composite layer of higher hardness, free of Al₄C₃ was expected. Shrinkage cavity free layer-substrate interface was also expected.

4.2 Experimental Procedure

Two different series [Series-I (60Al-10Si-30SiC wt.%) and Series-II (30Al-20Si-50SiC wt.%)] of fine Al-Si-SiC powders were individually mixed with polyvinyl alcohol glue and the slurry was deposited manually onto the surface of the Al-Si substrate. Laser processing was carried out at different levels of laser power and traverse speed as in Table-4.1.

<table>
<thead>
<tr>
<th>Laser Processing Parameters</th>
<th>Beam dia = 1 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series-I (60Al-10Si-30SiC wt. %)</td>
<td>Series-II (30Al-20Si-50SiC wt. %)</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>A1</td>
<td>B1</td>
</tr>
<tr>
<td>A2</td>
<td>B2</td>
</tr>
</tbody>
</table>

4.3 Results and Discussion

4.3.1 Analysis of Layer Morphology

Optical micrographs of the laser treated samples of series-I & II (Figs.4.1 & 4.2) exhibit three different regions viz. layer, laser melt zone and substrate. In series-I, sample-A (Fig.4.1-a) shows the formation of a well incorporated layer of almost uniform thickness – about 120μm, without any discontinuity, whereas layers of samples-A1 (Fig. 4.1-b) and A2 (4.1-c) contain discontinuities in addition to thickness variation. On the other hand, well incorporated layers are
Fig. 4.1a - c: Optical micrographs - Samples A, A1 and A2

Fig. 4.2a & b: Optical micrographs - Samples B and B2
observed in series-II under all the laser parameters. However, there is some minor non-uniformity in the layer of samples-B2 (Fig.4.2-b) and B3.

The microstructure of sample-A (Fig.4.1-a) shows that the parameters used (P=2.5kW and v=0.5m/min with F=300Jmm^-2) are sufficient to develop higher surface temperature (around 2300K) which is capable of melting the coated materials completely so as to form a sound layer. On the other hand, lower laser fluences owing to lower laser power (Sample-A1:1.5 kW) or faster scan rate (Sample-A2:1.0 m/min.) could develop lower surface temperatures only. Such temperatures can partially melt the coated materials as well as the top of the substrate. On resolidification, the layer gets contracted and results in irregularities of layer morphology. The difference between the degrees of layer discontinuity of the samples-A1 and A2 could be correlated to the difference in the surface temperatures generated. Similar observations were reported during the laser treatment of AA2014, AA2219 and Russian 1441 Al alloys with SiC predeposited coating [27].

Observation of well incorporated layers in series-II (3CAl-20Si-50SiC wt. %) under all processing conditions when compared to that of series-I (60Al-10Si-30SiC wt. %) could be attributed to the presence of higher amount of Si and SiC – they having higher absorption coefficients at 10.6μm laser wavelength viz. 75 wt.% and 20 wt.% respectively, as well to the lesser content of Al of lower absorption coefficient - 10% in the coating. The combined effect of these two factors produces high temperatures in all these samples resulting in the formation of well incorporated layers.
Figures- 4.1&2 show neither shrinkage cavities nor pores at the layer-substrate interface, owing to the fact that, considerable amount of Al (Series-I:60 wt.% and Series-II:30 wt.%) and Si (Series-I:10 wt.% and Series-II:20 wt.%), the major constituents of the (Al-Si) substrate are found in the coatings. Thus the incorporation of Al and Si in the coating along with SiC might have introduced compatibility midst the thermal characters of the layer and the substrate constituents, thereby developing shrinkage cavity free interfaces. Role of Si in the precoat is also remarkable in enhancing the fluidity of the melt liquid thereby assisting in the elimination process of shrinkage cavities [28]. Such thermal compatibility as well enhanced melt liquid fluidity might have been absent, while laser treating SiC on other Al alloy substrates viz.A6061, A2124, A1050 and A5052 (all with a negligible Si content), where shrinkage cavity formation was predominant [25&27].

4.3.2 Microstructure and EDS Analysis

The SEM micrograph of the layer of sample-A (Fig.4.3) reveals the presence of two distinct regions viz. white (a) and grey (b) whereas SEM micrograph of sample- B (Fig.4.4) exhibits three regions i.e. white (a), grey (b) and grey regions with clusters of tiny dots (c). The white regions in sample-A appear as fine streaks dispersed in most of the layer region whereas in sample-B they are in the form of coarse islets. EDS was used to analyze the distribution of the coated materials. The results of the EDS analysis (Table-4.2) exhibit that the white regions in samples-A&B are rich in Si and C. The grey regions of both samples are found to be Al rich. The grey regions with clusters of tiny dots of sample-B contain almost same amount of Al and Si.
Fig. 4.3: SEM micrograph of the layer - Sample A

Fig. 4.4: SEM micrograph of the layer - Sample B
Table – 4.2
Relative Percentages of the Elements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>Al (wt. %)</th>
<th>Si (wt. %)</th>
<th>C (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>a</td>
<td>3.81</td>
<td>60.13</td>
<td>36.06</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>91.98</td>
<td>7.71</td>
<td>0.31</td>
</tr>
<tr>
<td>B</td>
<td>a</td>
<td>1.96</td>
<td>62.09</td>
<td>35.95</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>86.91</td>
<td>11.82</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>51.32</td>
<td>42.43</td>
<td>6.25</td>
</tr>
</tbody>
</table>

4.3.3 XRD and EDS Analyses

XRD spectra of the samples-A&B (Figs.4.5&4.6) exhibit the prominent presence of Al, Si and SiC along with Al₂O₃ and Al₄SiC₄ minor phases (Table-4.3). The EDS results corresponding to the white regions (a) of samples-A&B confirm higher relative percentages of Si and C. By correlating this with the SiC major peaks of the XRD spectra, the white regions could be identified as SiC deposits. By linking the Al richness of the grey regions (b) of both samples with the Al peaks of the XRD spectra, the grey regions are identified as aluminium.

EDS analysis in region (c) of sample-B shows the presence of almost same amount of Al and Si. The XRD spectrum (Fig.4.6) shows no aluminium-silicon (Al-Si) intermetallic phase but the presence of Al and Si peaks. These results suggest that (c) is the region where aluminium and silicon coexist.
Fig. 4.5: XRD Spectrum of Sample-A

Fig. 4.6: XRD Spectrum of Sample-B
Table- 4.3
Phases Identified - Samples - A and B

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Sample-A</th>
<th>Sample-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al, SiC</td>
<td>Al, Si, Al$_2$O$_3$</td>
</tr>
<tr>
<td>2</td>
<td>Al, Si</td>
<td>Si, SiC</td>
</tr>
<tr>
<td>3</td>
<td>SiC, Al$_4$SiC$_4$</td>
<td>SiC, Al$_4$SiC$_4$</td>
</tr>
<tr>
<td>4</td>
<td>Si, Al$_4$SiC$_4$</td>
<td>Al, Al$_2$O$_3$</td>
</tr>
<tr>
<td>5</td>
<td>Al, Al$_2$O$_3$</td>
<td>SiC, Al$_4$SiC$_4$</td>
</tr>
<tr>
<td>6</td>
<td>SiC</td>
<td>Al, Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

While producing Al-SiC MMC layers by laser treating the SiC coating on Al alloys, Al$_4$C$_3$ as well as Al$_4$SiC$_4$ are found to occur as minor phases in accordance with either of the following chemical reactions [25]:

\[
4\text{Al} + 3\text{SiC} \rightarrow \text{Al}_4\text{C}_3 + 3\text{Si}
\]

\[
4\text{Al} + 4\text{SiC} \rightarrow \text{Al}_4\text{SiC}_4 + 3\text{Si}
\]

However, when the SiC content in the melt liquid exceeds 20%, Al$_4$SiC$_4$ should be preferably formed from the molten liquid rather than Al$_4$C$_3$ [25]. Similarly, the presence of high Si content in the coating/substrate would suppress the formation of Al$_4$C$_3$ [106]. XRD spectra of samples-A&B show the presence of the Al$_4$SiC$_4$ minor phase, whereas Al$_4$C$_3$ is completely absent. This may be attributed to the presence of SiC in an appreciable amount: sample-A:30 wt.%, sample-B:50 wt.% [25] as well as Si: sample-A:10 wt.%, sample-B:20 wt.% in the coatings [106].
Furthermore, SiC could be dissociated into Si and C during laser processing. This is supported by the presence of Al₄SiC₄ peaks in the XRD spectra. Al₄C₃ as well as SiC are found to be formed when the carbon atoms (from SiC dissociation) combine with Al as well Si atoms (recombination) respectively. L.R. Katipelli et al. [28] showed the change in Gibbs free energy of formation ($\Delta G$) and the corresponding temperature ($T$) ranges for Al₄C₃ formation through the following reaction

$$\frac{4}{3} \text{Al} + C \rightarrow \frac{1}{3} \text{Al}_4\text{C}_3,$$

are

$$\Delta G = -71.315 + 0.013T \text{ kJ/mole (}0 < T < 900 \text{ K)}$$
$$\Delta G = -91.055 + 0.033T \text{ kJ/mole (}900 < T < 3200 \text{ K)}$$

Similarly $\Delta G$ and $T$ values for SiC formation during

$$\text{Si} + C \rightarrow \text{SiC}$$

reaction are given as

$$\Delta G = -71.258 + 0.0078T \text{ kJ/mole (}0 < T < 1700 \text{ K)}$$
$$\Delta G = -120.3 + 0.0368T \text{ kJ/mole (}1700 < T < 3200 \text{ K)}$$

From the more negative $\Delta G$ value of SiC in the temperature range of interest, there is a higher tendency for the formation of SiC (through recombination) than Al₄C₃ [28]. Presence of Si in the coatings might have further facilitated complete extinction of Al₄C₃ by trapping the free carbon atoms to form SiC rather allowing them to react with Al to form Al₄C₃.
4.3.4 BSE and EDS Studies

Figure-4.7, the optical micrograph of sample-B shows the presence of a thin black strip like region in the lower part of the layer. EDS analysis across the depth of sample-B (Fig.4.8) shows that the upper portion of the layer is rich in Al (Al: 80 wt.% and Si: 20 wt.%) whereas the lower part is Si rich (Si: 91.3 wt.% and Al: 8.7 wt.%). It is also observed that, the Al concentration in the layer pre-dominates up to a depth of 90 \(\mu\)m and beyond that there is an abrupt increase in the relative proportion of Si over 90-130\(\mu\)m range.

The Back Scattered Electron image of sample-B (Fig.4.9) clearly depicts the strip-like region. The results of the Electron Probe Microanalysis (EPMA) – Fig.4.9a&b, along the depth show strong silicon (a) and carbon (b) peaks in that region. Correlating these results with the SiC peak of the XRD spectrum, the strip could be identified as the region of SiC deposition. Higher SiC proportion in the coating (50 wt.%) as well the highest density of SiC (3.217g/cm\(^3\)) compared to that of Al (2.7g/cm\(^3\)) and Si (2.33g/cm\(^3\)) in the Al-Si-SiC system [89], might be the reason for such an accumulation. The high surface concentration of Si- 20 wt.%, observed (Fig.4.8), could be related to the lowest density of Si among the remaining constituents.

BSE image of sample-B (Fig.4.9) also reveals the presence of needle structures in the upper portion of the layer. EDS results in the upper portion of the layer reveal Al richness (Fig.4.8). X-ray dot mapping too confirms the aluminium and oxygen richness in the needle structures. By correlating these with the Al\(_2\)O\(_3\) peaks of the XRD spectrum, the needle structures in the BSE image of sample-B could be identified as Al\(_2\)O\(_3\). Occurrence of oxidation could
Fig. 4.7: Optical micrograph of the layer - Sample B

Fig. 4.9a & b: BSE image - Sample B and corresponding EPMA results - Silicon (a) and Carbon (b)
Fig. 4.8: EDS Analysis in the Strip like region-Sample B
be attributed to the contaminants in the aluminium powder (small amount of AI₂O₃) in the precoat as well the argon gas used.

Presence of aluminium oxide in the molten aluminium has a substantial influence on the interface tension thereby on the wetting behaviour of the ceramic particles with the liquid aluminium. There exists always a difference between the interface tension values of the SiC in the Al melt containing Al₂O₃ and the SiC in the Al melt free from Al₂O₃. This difference owing to the presence of Al₂O₃ promotes the degree of SiC wettability in the liquid Al. At low temperatures (930-1100K), the contact angle (which is determined by the interface tension) between SiC particle and the Al melt is high (about 130°), thereby exhibiting poor wetting behaviour. In contrast at higher temperatures (greater than 1400K) the contact angle is decreased to about 50° thereby the wetting behaviour of SiC gets improved [104]. Owing to this, enhancement in the mechanical quality of the layer could be expected. In this study also such improvement could be expected owing to the presence of Al₂O₃.

4.3.5 Hardness Analysis

Hardness measurements were made across the depth of the laser treated zones. Figure-4.10 represents the microhardness profiles of the samples-A&B with hardness distribution from the peak 520 HV and 570 HV down to base 85HV respectively which are almost 6 times that of the substrate. High hardness values within the layer can be attributed to the SiC reinforcement. No sudden variation in hardness is observed in sample-A, which could be due to the uniform distribution of the coated materials, especially the fine streaks of SiC.
Fig. 4.10: Microhardness Profiles of Samples A & B
In contrast, sample-B exhibits a sudden increment in hardness in the bottom most region (90-130μm) of the layer (i.e.) in the vicinity of the layer-melt pool interface. Higher hardness (830HV) in the islet structures in the strip like region might be correlated to its SiC richness as identified through EPMA (Fig.4.9a&b). Comparatively higher hardness recorded in the layer of sample-B may be due to the distribution of coarse SiC in contrast to the fine SiC streaky distribution in sample-A.

The composite layers of samples-A2, B1 and B2 exhibit comparatively lower microhardness (i.e.) 350-410HV. Sample-A1 exhibits 485HV peak hardness in the agglomerated region.

As all the melt pools other than those of samples-A1&A2 underwent only remelting and consequential microstructure refinement, they exhibit very marginal increase in the hardness (120-140HV). On the other hand, significant increase in hardness was observed in the melt pools of samples-A1&A2 (~230HV) indicating coated materials dispersion in the melt region.

4.4 Conclusion

- While laser treating Al-Si substrates with
  - 60Al-10Si-30SiC wt.% and
  - 30Al-20Si-50SiC wt.% precursors under 2.5kW laser power and 0.5m/min. scan rate, Al-Si- SiC composite layers are found to be formed.
- The composite layers exhibit a six fold hardness increment (520-570HV).
- No cracks and pores are observed.
The layer-melt pool interface is found to be free from shrinkage cavities owing to the thermal compatibility between the substrate and coating.

Complete extinction of Al$_4$C$_3$ might be due to

- the preferential formation of Al$_4$SiC$_4$ rather than Al$_4$C$_3$, as the coatings contain 30 wt.% and 50 wt.% SiC.
- the presence of Si in the coating which facilitates complete trapping of carbon atoms to form SiC rather than allowing Al to form Al$_3$C$_4$. 