Chapter 3

Injection of SiC particles in Al

3.1 Introduction

In 1825 Hans Christian Oersted was the first man who isolated aluminium in Denmark. Nowadays, Al alloys are commonly used metals because they possess a relatively low density (2.7 g/cm$^3$ as compared to ± 7.9 g/cm$^3$ of steel), high thermal and electrical conductivity and a resistance to corrosion in common environments. However, the number of applications is strongly reduced by the poor surface properties, especially wear resistance and hardness. Protecting Al with wear resistant coatings may improve the surface properties without affecting the excellent bulk properties. Reinforcing the surface of Al by adding SiC particles is such a possible way. To achieve this, the possibilities of the Laser Melt Injection process are studied because it is a potential technique to produce a Metal-Matrix Composite (MMC) layer in the top layer of a metal workpiece [1,2,3,4].

Research has been devoted to different techniques to produce SiC$_p$/Al MMC's. For example powder metallurgy techniques [5], casting methods [6] and spray forming [7] are extensively studied. At present, SiC$_p$/Al MMC's are commercially available. All these methods are suitable to produce bulk MMC's, but are unsuitable for producing MMC coatings on bulk Al. Because in many applications it is sufficient or even desirable to have the reinforcement only at the top of a workpiece, it is worthwhile to investigate techniques that can coat Al workpieces by an MMC layer. In this field of research, less work is done on the production of SiC$_p$/Al MMC's [2,8,9,10] and it is still a challenge to create a
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proper reproducible MMC layer in the top layer of Al. This chapter will explore the use of high power lasers to produce SiCp/Al MMC layers.

Laser treatment of Al alloys faces certain problems [11]. Solid Al has a very low laser light absorptivity. For the wavelength of radiation produced by a Nd:YAG laser \((\lambda=1.06 \mu m)\) the reflectivity of solid Al is about 90\% [12]. Therefore a high energy density of the laser beam is needed to create a melt. A second problem is the oxide skin that is formed on Al. This oxide layer on molten Al has a substantial influence on the wetting behavior of ceramic particles with liquid Al [13]. Usually the oxide skin acts as an energy barrier for the particles to penetrate. However, the strength of this barrier depends on the temperature of the melt pool. For instance, at low temperatures (660-850 °C) the contact angle between SiC particle and Al melt, which is determined by the interface tensions, is about 130° (no wetting behavior), while at higher temperatures (>1100 °C) the contact angle is decreased to about 50° (wetting behavior). The importance of this difference for the laser melt injection process will become clear in this chapter.

In this chapter the laser processing of a SiCp/Al MMC layer on top of Al, regarding the processing parameters, is studied in detail. Further, the injection process is discussed by using a theoretical analysis of a solid particle penetrating in a liquid, with special attention to the role of the oxide skin on Al. In the last part the microstructure of the produced coatings is analyzed with Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Electron Back-Scatter Diffraction (EBSD).

3.2 Laser melt injection process

SiC particles with a mean size of 80 µm were injected in aluminium plates with the dimensions of 100 mm × 40 mm × 10 mm with a Nd-YAG laser. An SEM micrograph of the SiC powder (before injection) is shown in Fig. 3.1. The SiC particles are single crystals (6H polytype) and are angular. Rather pure Al (99.6 wt-% purity) is chosen to use as substrate material instead of the commercial Al alloys. We want to provide a study of a model system from which the step to process the Al alloys is small. To validate this, also laser melt injection experiments were carried out on some commercially Al alloys, but no significant differences were found.
During the laser experiments, the laser beam is focussed 6 mm below the substrate, which results in a spotsize of 2.4 mm at the substrate. Ar was used as a shielding gas to protect the lens as well as to reduce oxidation of the specimen. The SiC particles were injected into the melt pool at an angle of 35° with respect to the substrate surface normal. Important is the direction of the particle flow with respect to the moving direction of the substrate. In this case the so-called 'over-hill' direction is used, where the particles are travelling over the coating towards the center of the melt pool, corresponding to the schematic picture in Fig. 2.1 in chapter 2. To achieve injection conditions for the SiC particles into the Al melt, the upper carrier gas outlet of the cyclone is partially or fully closed with the aim to increase the speed of SiC particles. This also helps to reduce the interaction time between laser beam and SiC particles, which is important because SiC has a high absorption (~90%) of the laser radiation [3]. For the same reason the focus point of the laser beam lies 6 mm under the substrate surface, which results in lower beam energy densities just above the surface where injected particles come in contact with the laser beam.

An appropriate combination of process parameters for the production of a single laser track was found: laser beam power density $P = 310 \text{ MW/m}^2$, scanning speed $v = 8.3 \text{ mm/s}$, powder feeding rate $m = 8.3 \text{ mg/s}$, glass nozzle diameter of 1.7 mm and 60 ml/s carrier gas flow. During the laser melt injection process the substrate is preheated to 300 °C by a hot plate and kept at a constant temperature. An example of a typical cross-section of a single laser track is shown in Fig. 3.2.
The SiC volume fraction in the MMC track is about 35%, and the width of the track is about 1 mm. No cracks and holes are present, the surface is relatively flat (no material build-up) and the process is reproducible, which is a remarkable achievement. The injection process is sensitive to small changes in power density, preheating temperature, powder flow and particle velocity, which results in an extremely small operational window of laser and powder flow parameters. For this reason the process parameters can not be changed too much, which makes it impossible to obtain different track characteristics (for example a higher particle density or wider tracks).

The only coating characteristic that can be varied is the injection depth of the particles. This can be achieved by changing the preheating temperature. The temperature of the substrate can be measured before and during the laser experiment by a Sensys monochromatic optical pyrometer. The optical sensor is focussed on the center of the side of the substrate block. The temperature of the Al substrate increases about 30 °C after producing one track due to the absorbed beam energy. This provides the possibility of setting different preheating temperatures above 300 °C, which is the maximum temperature of the plate heater, by scanning the laser beam over an area close to the to-be-treated area.

The influence of the preheating temperature on the injection process is shown in Fig. 3.3. When the preheating temperature is lower than 300 °C, the particles are not able to penetrate into the melt pool, while at higher temperatures the
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particles are successfully injected. Therefore, preheating is of crucial importance for the laser melt injection process of SiC particles in Al. Increasing the preheating temperature results in more and deeper injected particles. In all experiments, the melt pool was wider than the area where SiC particles are injected.

The effect of the temperature of the melt pool on the injection depth is also shown in a longitudinal cross-section (Fig. 3.4). During the production of a laser track with a length of about 30 mm the substrate temperature gradually increases and therefore the particles are injected deeper near the end of laser track. The increase in temperature during a single laser track depends on the

Figure 3.3: SEM micrographs of cross-sections of single laser tracks that were produced at different preheating temperatures. Above 300 °C the SiC particles are injected, and at higher preheating temperatures the particles are injected deeper. The particles are only injected in the center area of the melt pool; not at the edges.
length of the track and the size of the substrate, which acts as a heat sink. In the case of Fig. 3.4, the increase of the substrate temperature is about 30 °C, measured on the side of substrate block. Besides an increase to a maximum injected depth near the end of a track, also local oscillations in depth of injected particles are observed. These depth oscillations, with a frequency of 5-10 Hz may be explained by the oscillatory kinetic behavior of the melt pool surface or by the oscillatory changes in the powder stream.

By processing multiple adjacent tracks it would have been possible to cover larger areas than the size of a single track with an MMC layer. A second laser track should be positioned next to a first track, preferably with some small overlap to avoid gaps between the tracks. Unfortunately, it is not possible to produce a second laser track with some overlap to a previously produced track, due to the small processing parameter window. The surface of a single laser track consists roughly of three regions. In the center, the surface consists of solidified Al with the injected SiC particles. At both sides of the central area a zone with only resolidified Al is present (remember that only particles are present in the center area). Finally, at the side of the track a heat affected zone, i.e. Al that is only heated and not melted, is present. Therefore, the substrate surface of the second track consists of four different areas, all having a different interaction with the laser light, and all having a different state of oxidation. Because the parameter window for successful injection is small, no injection conditions can be attained in the already treated areas and therefore no overlapping tracks can be produced.

The extremely small operational window of laser and powder flow parameters can be explained by the large difference in the absorptivity of laser light between Al and SiC on the one hand and the oxide skin of Al on the other hand. A high laser energy input is needed to create a melt pool in Al while the same energy input will heat up the particles enormously, when they pass through the laser beam, due to their high absorptivity for laser radiation. This will damage the particles.
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and lead to undesired Al$_4$C$_3$ formation [6,10] that may have a negative effect on the mechanical properties of the coating, which will be discussed in chapter 5. Another effect of the high absorptivity is that the powder flow shields the surface. Therefore, the feeding rate should be low in comparison to the standard cladding parameters [14].

Preheating the substrate will make the laser process much more efficient because the coupling between laser light and substrate increases with increasing temperature. Especially when Al is in the molten state the absorptivity increases rapidly. If the substrate is preheated to 300 °C, heating to the melting temperature (660 °C), where most of the laser light is reflected, is about halved.

Although these reasons explain that by using the same laser energy the melt pool temperature is somewhat higher when the substrate is preheated, it is hard to believe that this explains the reason that preheating is of crucial importance for the particle injection process. Why have small changes in pre-heating temperature, obtained with a hot plate, a tremendous effect on a high-power laser process? For example, the particles are injected to a depth of 500 µm in the case of pre-heating to 340 °C whereas they are hardly injected at 300 °C pre-heating, as Fig. 3.3 demonstrates. To understand this we focus on the second problem: the oxide skin.

To get an idea about the behavior of the oxide layer during the laser process, single laser tracks were produced with the same laser parameters as in the injection experiments, but without a particle flow. The surface of such a track displays two different appearances. In the center, there is a shiny strip with a width of about 1.1 mm, while at both sides rather dull strips are present with an approximate width of 0.2 mm. The borders between these areas are quite sharp. SEM micrographs taken on both the center and side areas are shown in Fig. 3.5. In the central area of the laser track about 50–55% of the surface is covered by a thick oxide layer. On the other hand, 80% of the surface is covered at the edge of the melt pool.

The thickness of the oxide layers of different areas is analyzed by a special small spot UHV scanning electron-scanning Auger microscope based on a JEOL JAMP 7800F, in which depth profiling was performed in-situ by 1 keV Ar$^+$-ion bombardment. Ar$^+$-ion bombardment removed the surface layer, while after each etching step the intensities of Al, O and C element peaks in Auger Electron Spectra (AES) are analyzed.
In this way, the thickness of the oxide layer can be estimated by recording the etching time that is needed to remove the oxygen from the spectra. The results are depicted in Fig. 3.6a, b and c, which represent the depth profiles measured at the locations defined in Fig. 3.5. It is clear, that the oxide layer from the uncovered area at the center of laser track is removed after 100-150 seconds of Ar⁺-ion bombardment, as shown in Fig. 3.6a. To remove the oxide layer from the uncovered edge region an etching time of about 800 s is necessary (Fig. 3.6b) and removal of the oxide layer from the covered edge region needs more than 5000 s (Fig. 3.6c). From these etching times an estimate of the thickness of the oxide layer can be made [15] if one knows the principal etching parameters and
Figure 3.6: Aluminium, oxygen and carbon element peak intensities in AES spectra as a function of Ar+ ion bombardment time, giving an element depth profile. The plots a, b and c show the depth profiles measured at the corresponding marked areas in Fig. 3.5.

the so-called sputtering yield [16]. Such estimates for all three characteristic places are marked in Fig. 3.6 by dashed lines. In the central area, the 'open' parts are covered with an approximately 3 nm thick oxide layer. In the side areas, the 'open' parts are covered with an approximately 20 nm thick oxide layer and the 'spongy'-looking parts in the side area correspond to an approximately 125 nm thick oxide layer.

It is necessary to emphasize that the measured fractions and thickness of the oxide surfaces after the laser process are probably not the same as that they were during the laser process on the Al melt. To a first approximation it is reasonable to assume that the areas where an oxide layer of 3 nm is detected were without oxide layer during the laser experiments. This is because a 3 nm thick oxide layer is typical for an amorphous oxide skin reported as a layer grown on the solid Al surface [17]. In addition, also the fraction of 'open' areas may be higher during the laser treatments. Nevertheless, the ex-situ experiments underline the behavior described by literature [13]. Kaptay [13] studied the behavior of this oxide skin, as a function of temperature. The oxide skin is present on the melt till about 850 °C. Above this temperature, chemical interactions between Al and its oxide at the interface occur, leading to the formation of gaseous sub-oxides. Consequently, the oxide gradually disappears and the Al surface, by growing Al islands, takes over with increasing temperature. At about 1100 °C the oxide is totally removed.
Analogous to the transition from non-wetting to wetting behavior, that was mentioned in the introduction of chapter 3, the transition from an oxidized to an unoxidized surface takes place in a relatively small temperature interval (800 °C to 1100 °C). This explains that more oxidized surface is present at the side areas of the melt pool than in the center, because the temperature of the side areas is lower during laser treatment. It is striking that the discrimination between the central area and side areas of the surface of the melt pool regarding the oxide skin, corresponds to the discrimination between the areas where SiC particles are injected during the laser melt injection process. In the central area, where less oxidized surface is present, particles are injected, while in the side areas, where a higher surface fraction of oxidized surface is present, no particles are injected. This indicates that the oxide layer on the Al melt is important for the results of the LMI process.

Before calculating the influence of the oxide layer on the injection process, it is worthwhile to know the velocity of the SiC particles in the particle flow. From this velocity the kinetic energy of the particles can be calculated, which is the energy the particles have in order break the oxide skin. A high-speed camera (Kodac 4540 Ektapro High Speed Camera) was used to monitor the flight of the particles after they leave the glass nozzle. The velocity can be measured and hence their kinetic energy can be calculated. Experiments with different glass nozzle diameters (Φ = 1.7 mm and 2.3 mm) and different carrier gas flows (25-70 ml/s) were recorded with a camera speed of 27×10^3 frames/s. Afterwards, the particle velocity was measured on the video screen with the standard frame speed of 25 frames/s by counting the number of frames that a particle needed to travel between two markers at a constant distance.

The velocities of more than 50 particles were traced in each experiment. The results are summarized in Fig. 3.7. The mean velocity of the particles shows a linear increase with the carrier gas flow rate. A nozzle diameter of 1.7 mm increases the velocity by a factor of about 1.5, with respect to a nozzle diameter of 2.3 mm. The variation in particle speed is about 15–20%. Distinction is made between particles travelling in the upper, center and lower part of the powder stream. The particles have the highest velocity in the center of the stream; at the higher and lower part of the stream the velocity is about 90% of the velocity in the center. From the particle velocity experiments we learnt that in the laser melt injection process of SiC particles, with a diameter of about 80 µm, the particle velocities vary in the range of 2.5-5 m/s.
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Figure 3.7: Particle velocity as a function of carrier gas flow for two different nozzle diameters. The velocity is measured by high-speed camera observations.

3.3 Calculations on particle penetration

3.3.1 Physical concepts and modelling approach

In this section, a simple but useful model is constructed to predict the penetration depth of the particles and to get a better understanding of the kinetics of the particle penetration process. The particle penetration process can be divided in two parts: penetration of the particle through the melt surface and the movement of a particle in a liquid. A schematic picture of the particle penetration process is shown in Fig. 3.8. The first part is basically a wetting problem, where the surface of the different interfaces in the system (solid-vapor, liquid-vapor and solid-liquid), change during penetration through the melt surface. The particle looses its kinetic energy when it penetrates through the surface, depending on the surface tensions (energies) of the different interfaces. The second part, movement of a solid particle in a liquid, is determined by the equation of motion given by two forces: the gravitational force ($F_g$), corrected by Archimedes' principle, and Stoke's force ($F_{Stokes}$), which takes into account the viscous friction.
To simplify the problem, several assumptions are made. Firstly, the shape of the particles is assumed to be spherical. Secondly, the viscosity of the Al melt is assumed to be constant. Finally, it is assumed that no convection is present in the melt pool. It is obvious that the first two assumptions do not fully agree with the experimental conditions. Fig. 3.1 shows that the SiC particles are not spherical, and the viscosity of Al depends on the temperature. Because the temperature of the melt is decreasing with the depth, the viscosity is increasing a little with depth. The third assumption seems to be valid because no signs of convection are found during the microstructure observations. Although the assumptions do not fully correspond to the experiments, it is still possible and useful to estimate the injection depth of the particles and more importantly, it is possible to reveal important process conditions/parameters from the calculations. Because in the laser melt injection process many parameters are involved, and especially the conditions in the powder flow (different shapes, different velocities) are even not constant during the same experiment, it makes no sense to calculate the injection depth very accurately.

**Figure 3.8:** A schematic drawing of the particle penetration process. To estimate the penetration depth of spherical SiC particle, with a radius R and injection velocity $v_i$, in liquid Al, the penetration process can be divided in two parts. First, the penetration of a solid particle through the melt surface, shown in the magnified picture (right) is calculated. Secondly, when the particle is fully immersed in the melt ($x > 2R$), the movement of a particle in a liquid, which is determined by the gravitational force $F_g$ and Stokes’ (friction) force ($F_{Stokes}$), is calculated.
3.3.2 Part I: Penetration through the melt surface

The surface of the melt may act as a barrier for the penetrating particles. In this part the energy loss of a particle that penetrates through the surface barrier is determined. This energy loss is used to calculate the velocity of the particle when it is fully in the melt, by subtracting it from the initial kinetic energy. The initial kinetic energy of a SiC particle is:

$$E_{\text{kin}} = \frac{2}{3} \pi R^3 \rho_{\text{SiC}} v_i^2$$  \hfill (3.1)

where $R$ is the radius of the particle, $\rho_{\text{SiC}}$ is the density of SiC (3217 kg/m$^3$) and $v_i$ the initial injection velocity.

During penetration, the total interface energy changes because the areas of the different interfaces, which have different interface tensions, change. The total interface energy for a particle that is partially immersed in a melt at depth $x$, where the depth $x$ is defined in Fig. 3.8, is given by [18]:

$$G_{\text{interface}} = (R-x)^2 \pi \sigma_v + 2R \pi x \sigma_{lp} + 2R \pi (2R-x) \sigma_{pv}$$  \hfill (3.2)

where $\sigma$ is the interface tension between the phases indicated by the indices: $l=$ liquid Al, $p=$ solid SiC particle and $v=$ vapor. For a partially immersed particle holds $0 \leq x \leq 2R$.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Interface tension (mJ/m$^2$)</th>
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<tbody>
<tr>
<td></td>
<td>Al oxidized</td>
</tr>
<tr>
<td>$\sigma$(SiC, solid-vapor)</td>
<td>1920</td>
</tr>
<tr>
<td>$\sigma$(Al, liquid-vapor)</td>
<td>870</td>
</tr>
<tr>
<td>$\sigma$(liquid Al- solid SiC)</td>
<td>2480</td>
</tr>
</tbody>
</table>
Important is that $\sigma_{lv}$ and $\sigma_{lp}$ have different values for oxidized and unoxidized Al. The values of the interface tensions of the Al(l)/SiC$_p$ system, of both oxidized and unoxidized Al, are found in literature and given in table 3.1 [19]. The data in table 3.1 are based on calculations that agree with experimental data.

The interface energy as a function of depth for both oxidized and unoxidized Al, calculated by inserting the interface tension values in Eq. 3.2, and taking $R=40$ µm, is shown in Fig. 3.9. The difference between oxidized and unoxidized Al is clearly visible. The strength of the surface barrier ($E_{\text{barrier}}$) is defined as the difference in interface energy of a fully immersed particle and the minimal interface energy. It takes more energy for a SiC particle to enter an oxidized Al melt than to enter an unoxidized Al melt.

The equilibrium depth, $x_{eq}$, can be calculated from Eq. 3.2 by minimizing the interface energy:

$$\frac{dG_{\text{interface}}}{dx} = 0 \Rightarrow x_{eq} = \frac{R(\sigma_{lv} + \sigma_{pv} - \sigma_{lp})}{\sigma_{lv}}$$

\text{(3.3)}
From this, by using the definitions that are given in Fig. 3.8, the equilibrium contact angle $\Theta$ can be calculated:

$$\Theta = \frac{\pi}{2} + \sin^{-1}\left(\frac{R - x_{eq}}{R}\right)$$  (3.4)

This is basically the same as Young's equation for the equilibrium contact angle or the wetting angle. Substituting the data from table 3.1 in Eq. 3.3 and Eq. 3.4 the contact angle is 130° for oxidized Al and 50° for unoxidized Al. These values correspond to the values that are mentioned in the introduction of this chapter.

The strength of the surface barrier can be estimated by the amount of change in interface energy when a single particle is moved from the depth where the interface energy of the system is minimal, i.e. the wetting angle, to the depth where the particle is entirely inside the melt:

$$E_{\text{barrier}} = G_{(x=x_{eq})} - G_{(x=2R)} = \frac{(\sigma_{lv} + \sigma_{lp} - \sigma_{pv})^2}{\sigma_{lv}} \pi R^2$$  (3.5)

The kinetic energy of the particles should be larger than this energy loss to overcome the surface barrier and to be able to penetrate in the melt pool. Combining Eq. 3.1 and Eq. 3.4 gives the minimum vertical velocity of the particle that is required to overcome the surface barrier of the melt:

$$v_{\text{min}} = \sqrt{\frac{3}{2\sigma_{lv} R \rho_{\text{SiC}}} (\sigma_{lv} + \sigma_{lp} - \sigma_{pv})}$$  (3.6)

If the initial particle velocity is higher than $v_{\text{min}}$, the particle overcomes the barrier and may propagate further into the melt with the reduced velocity $v_r$, which can be calculated by subtracting the energy of the barrier from the initial kinetic energy. The reduced velocity is:

$$v_r = \sqrt{v_i^2 - v_{\text{min}}^2}$$  (3.7)

The energy barrier that the surface of the Al melt forms has two extreme cases: the energy barrier for a fully oxidized surface (strong energy barrier) and for a fully unoxidized surface (weak surface barrier). As both theory and
experiments indicate (Fig. 3.5), the surface of the Al melt may be partially oxidized, where a network of oxidized surface separates oxide free islands. It is therefore likely that in practice the strength of the energy barrier is between these two extreme cases. The surface energy of this partially oxidized surface may be estimated, realizing that the particles size (diameter = 80 µm) is much larger than the oxide free parts (diameter < 5 µm in Fig. 3.5), by applying a rule of mixture on Eq. 3.2:

\[
G_{\text{interface,partial}} = a(R-x)^2 \pi \sigma_{lv,ox} + a2R \pi x \sigma_{lp,ox} + \\
(1-a)(R-x)^2 \pi \sigma_{lv,al} + (1-a)2R \pi x \sigma_{lp,al} + \\
2R \pi (2R-x) \sigma_{pv}
\]  

(3.8)

where \(a\) is the area fraction of the surface that is covered with an oxide skin, and the indices 'ox' and 'al' indicate the interface tensions of the oxide and unoxidized case, respectively. In the same way as explained above the energy barrier and minimum velocity that is needed for the particles to overcome this energy barrier can be obtained:

\[
E_{\text{barrier,partial}} = \frac{(a \sigma_{lv,ox} + a \sigma_{lp,ox} + (1-a) \sigma_{lv,al} + (1-a) \sigma_{lp,al} - \sigma_{pv})^2}{a \sigma_{lv,ox} + (1-a) \sigma_{lv,al}} \pi R^2
\]  

(3.9)

\[
v_{\text{min,partial}} = \sqrt{\frac{3(a \sigma_{lv,ox} + a \sigma_{lp,ox} + (1-a) \sigma_{lv,al} + (1-a) \sigma_{lp,al} - \sigma_{pv})^2}{2 \rho_{\text{SiC}} (a \sigma_{lv,ox} + (1-a) \sigma_{lv,al})}}
\]  

(3.10)

3.3.3 Part II: Particle moving in a liquid

The second part of the injection process, i.e. a particle moving in a liquid, is straightforward and well known. There are two basic forces acting on a particle that is dropped in a liquid. The gravitational force \(F_g\) pointing downwards and Stokes friction force \(F_{\text{Stokes}}\) pointing upwards, in the opposite direction of the movement, as depicted in Fig. 3.8.

\[
F_g = \frac{4}{3} \pi R^3 g (\rho_{\text{SiC}} - \rho_{\text{Al}})
\]  

(3.11)
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In Eq. 3.11 denotes $R$ the radius of the particle (40 µm), $g$ the gravitational acceleration (9.81 m/s²), $\rho_{\text{SiC}}$ the density of SiC (3217 kg/m³) and $\rho_{\text{Al}}$ the density of Al (2702 kg/m³). The Stokes force is given by:

$$F_{\text{Stokes}} = -6\pi \eta R \, v(t)$$  \hspace{1cm} (3.12)

where $\eta$ is the (dynamic) viscosity of the melt, that is taken constant at 0.9 mPa s (the viscosity of Al at 927 °C [20]).

By solving the equation of motion of the system (Eq. 3.13), with boundary conditions $x(0)= 0$ and $v(0)= v_r$ (the starting velocity which is the reduced velocity obtained by Eq. 3.7), the velocity and depth of the particle as a function of time ($t$) can be calculated as follows:

$$\frac{4}{3} \pi R^3 \rho_{\text{SiC}} \ddot{x} = \frac{4}{3} \pi R^3 g (\rho_{\text{SiC}} - \rho_{\text{Al}}) - 6\pi \eta R \dot{x}$$ \hspace{1cm} (3.13)

$$v(t) = \dot{x}(t) = \frac{b + c e^{-ct}(v_r - \frac{b}{c})}{c}$$ \hspace{1cm} (3.14)

$$x(t) = \frac{bt}{c} - \frac{b - c v_r}{c^2} + \frac{e^{-ct}(b - c v_r)}{c^2}$$ \hspace{1cm} (3.15)

In Eq. 3.13 and Eq. 3.14, $b$ and $c$ are constants that are defined as:

$$b = g(1 - \frac{\rho_{\text{Al}}}{\rho_{\text{SiC}}}) \quad \text{and} \quad c = \frac{9}{2} \frac{\eta}{R^2 \rho_{\text{SiC}}}.$$

3.3.4 Results and discussion

After all the necessary calculations are made, they can be used to attempt to answer the main experimental question that is still open: How can small pre-heating temperature changes have tremendous effects on the laser melt injection process of SiCₚ in Al? Is the behavior of the oxide layer responsible for the sensibility of the laser melt injection process?
The oxide layer has a strong influence on the wetting behavior. The contact angle between SiC and Al with oxide skin is 130°, between SiC and Al without oxide layer 50°, i.e. when the surface of the Al melt is oxidized there is non-wetting behavior, while for a clean surface there is wetting behavior. Actually, the oxide skin prevents direct contact between the particle and Al liquid, at low temperatures, while when no oxide layer is present there is direct contact between the particle and Al liquid. This result in chemical interactions between the particle and Al melt that lower the energy of the particle/Al interface. The wetting behavior is therefore improved [13]. This explains the connection between temperature of the melt and wetting behavior. At lower temperatures (<850 °C) of the melt, an oxide layer is present and therefore there is non-wetting behavior, while at higher temperatures of the melt (>1100 °C), the oxide layer is disappeared, which lead to wetting behavior.

The consequence of the oxide layer on the injection process can be discussed on the basis of Fig. 3.10. Figure 3.10 displays the dependence of the minimum required velocity to overcome the surface barrier as a function of particle size for different percentages of oxide coverage (Eq. 3.10). Here, curves are depicted that characterize a surface that is fully covered, together with two experimentally observed partially covered surfaces (50% and 80%) and a surface that is free of oxide skin. In addition, the area corresponding to the particle velocities and sizes used in the injection experiments is marked in Fig. 3.10.

One may conclude, that for 50% coverage, which is characteristic for the area near the center of the laser track, a particle velocity of about 4 m/s, for a particle with a radius of 40 µm, is sufficient to penetrate through the surface layer. On the other hand, if 80% or more of the surface is covered with oxide layer, the particles with experimental sizes and velocities cannot be injected. This kind of behavior is observed in our experiments as well, where particles are injected only in the central part of laser track and not near the edges. The distribution of the injection depth as a function of injection position, with respect to the center of the track, observed in the cross-sections of the laser track (Fig. 3.2) is not controlled by the distribution of particle velocity across the particle stream, but is determined by the increase of coverage with oxide from the center of the laser track to its outer edges. Figure 3.10 clearly indicates that laser melt injection is not a suitable technique for preparation of SiC/Al MMCs with particles that are smaller than R= 20 µm. A pre-placement technique is reported to be successful for particles with a size smaller than 45 µm [8,21].
Figure 3.10: Calculated minimum particle velocity, required to overcome the surface energy barrier, as a function of SiC particle radius for different percentages of oxide coverage. The experimental window of the particle radius and minimum velocity is marked.

When the second part of the model is included, i.e. the particle moving in a liquid, the injection depth can be estimated. Examples of such calculations are displayed in Fig. 3.11 and Fig. 3.12. In these figures, the particle velocity and depth of a particle with a radius of 40 µm, an initial velocity of 4 m/s and with 50% of the surface area covered by an oxide skin are plotted as a function of time. When the initial velocity is 4 m/s the vertical component, which is responsible for depth, is \(4 \cdot \cos(35^\circ) = 3.3\) m/s. After penetrating through the surface, the velocity is reduced to \(v_r = 1.0\) m/s due to the surface energy barrier (Eq. 3.7 and Eq. 3.10). By substituting this in Eq. 3.14 and Eq. 3.15, the velocity and depth as a function of time is obtained. The particle decelerates very quickly to its equilibrium velocity in about 4 ms (Fig. 3.11). The equilibrium velocity, that can be calculated by Eq. 3.14, is equal to \(b/c = 2\) mm/s. Therefore, the particle reaches its final injection depth within 10 ms, since this equilibrium velocity is very low compared to the velocity in the first couple of milliseconds. From this we may conclude that it is not useful to increase the lifetime of the melt pool, that is about 0.4 s, to achieve larger injection depths. Attacking the oxide layer, which lowers the surface energy barrier, and thus results in a higher starting velocity \(v_r\), is more useful, because a larger depth is reached within the important first milliseconds. The effect of this can be seen in Fig. 3.3.
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Figure 3.11: Velocity of the SiC particle in liquid Al as a function of time. The initial injection velocity is 4 m/s, 50% of the surface is covered with an oxidized skin and particle radius is 40 µm.

Figure 3.12: Injection depth of the particle as function of time. The initial injection velocity is 4 m/s, 50% of the surface is covered with an oxidized skin and particle radius is 40 µm.

From Fig. 3.12 can be seen that the injection depth of the particle is about 1.2 mm, which is reached in about 4 ms. The viscosity is taken constant in the calculations, belonging to Al liquid of 927 °C. This is valid for the temperature that is reached in the melt pool. However, the temperature gradient with respect to the depth results in an increase in viscosity as a function of depth, especially near the bottom of the melt, which promotes the deceleration effect due to the Stokes’ force. Therefore, the calculated final depths are somewhat overestimated.

In Fig. 3.13, the depth, at t= 0.01 s, is presented as a function of the injection velocity for different oxide percentages. The relative steepness of the graphs reveals that, provided the injection velocity is sufficient to penetrate through the surface, a relatively large depth can be reached. This explains why small changes in laser process parameters may result in a substantial change of injection depths. This is shown in Fig. 3.3, where a change in the pre-heating temperature from 290 °C to only 320 °C results in a very considerable difference in the actual injection depth. For preheating temperatures higher than 440 °C the particles with the lowest speed are able to reach relatively large depths, as Fig. 3.3 also shows.

From the results of the calculations we may discuss the injection process of SiC, in particular the influence of the oxide skin, in more detail. Without preheating, the temperature of the melt pool is probably close to 850 °C, at which the oxide
skin is still present and no particles can be injected. Pre-heating to 290 °C increases the temperature that is reached during the laser processing, but not enough to remove a sufficient part of the oxide. Upon increasing the temperature further to 320 °C, the oxide layer is sufficiently removed to allow particle penetration. This substrate temperature increase of 30 °C may lead to a much higher temperature increase in the melt pool because of the better coupling factor of the laser light at higher temperatures. In addition, the fact that we are in the temperature interval of 850-1100 °C, where small temperature changes result in a substantial change in wetting behavior, explains the impact of preheating the substrate.

The idea that the temperature of the melt pool lies in the interval 850-1100 °C is supported by the fact that the particles are only injected in the center of the melt pool and not near the edges. In the center the temperature is high enough, while at the edges the temperature is too low to make injection possible. Consequently, a transition temperature from wetting to non-wetting behavior is present in the melt pool, indicating that the temperature of the melt pool lies in the range of 850-1100 °C. The sharp transition from injection up to several hundreds of µm to no injection at all at the edges of the laser track is explained once more by the rather steep slopes in the graphs shown in Fig. 3.13.

The increase of injection depth during the laser processing itself (Fig. 3.4) is explained by the disappearance of the oxide layer as well. The decrease in
kinetic energy loss during the penetration of the particles through the surface, because of the higher temperature at the end of the laser track, makes that the particles penetrate deeper.

The question 'How can small pre-heating temperatures changes have tremendous effects on the Laser Melt Injection Process of SiC\textsubscript{p} in Al?' can be answered now. In the temperature interval 850 °C to 1100 °C small temperature changes have substantial effects on the oxide skin. An increase in temperature dissolves the oxide skin, which results in a change from non-wetting to wetting behavior. This transition results in a change from no injection to injection, for particles with a kinetic energy comparable to the experimental conditions.

The behavior of the oxide skin is confirmed by observations of the melt injection process of SiC particles in Al with a high-speed camera. In these recordings it was clearly visible that in the center of the laser track openings in the oxide skin appeared when the pre-heating temperature was above 300 °C. The opening and closing of the oxide skin was very dynamical, which might explain the oscillations in the injection depth. At the edges no opening of the oxide layer was visible. High-speed camera observations of laser experiments with pre-heating temperatures below 300 °C clearly showed that the oxide skin was unaffected.

Other apparent solutions to create better injection conditions, i.e. besides pre-heating the substrate, are increasing the laser power to increase the melt pool temperature and remove the oxide skin, or to enhance the particle velocity to increase the kinetic energy of the particles. Increasing the laser power is not advisable because this will lead to further damaging of the SiC particles and formation of unwanted Al\textsubscript{4}C\textsubscript{3} [6,10]. Increasing the particle velocity may result in damages or blowing away of the melt pool by the bombardment of the particles and the strong carrier gas flow. Therefore, pre-heating is an efficient and elegant method to inject SiC in Al.

The only experimental problem that cannot be solved is how to process a layer of more adjacent tracks. When the two adjacent tracks come too close, the change of the re-solidified melt pool in the first track affects the injection process of the second track so much, that no smooth layer can be formed. Overlapping results in a higher concentration of particles at the surface and a higher concentration of undesired Al\textsubscript{4}C\textsubscript{3}. Therefore, the surface area that can be reinforced is limited by the size of the laser beam.
3.4 Microstructure

The microstructure of the laser melt injected SiC/Al MMCs can be divided into two areas: the area where no particles are injected and the area where the particles are injected. The microstructure at the bottom of the melt pool, where no injected SiC particles are present, consists of simple Al grains with a grain size of about 50–100 µm. The grains contain large amounts of columnar dendrites with a length of about 5 µm. The longitudinal axes of individual dendrites are oriented in the radial direction with a small amount of Si and Fe based impurities located in the interdendritic area.

There are two reaction products, Al₄C₃ and Si, present in the area where the SiC particles are injected. These two new phases are formed when SiC gets in contact with liquid Al according the reaction \([22,23]\):

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

Some SiC particles are partially dissolved during the injection process and Al₄C₃ plates are observed in the matrix of the melt pool (Fig. 3.14). The platelet shape is a common shape for Al₄C₃ formed when SiC gets in contact with Al [24].

![Figure 3.14: Optical micrograph of SiC particles and Al₄C₃ plates in the Al matrix.](image)

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An SEM micrograph of a deep etched sample is shown in Fig. 3.15. With this deep etching technique, i.e. intensive etching to remove large amounts of Al, a 3D view of the remaining phases can be obtained. The amount of Al₄C₃ formation between the SiC particles strongly depends on the temperature in the melt pool. Because of this, more Al₄C₃ is found in the top of the melt pool than in the bottom, where the temperature is lower. The formation of Al₄C₃ is accompanied by the formation of Si. Therefore, Si-Al eutectic regions are present between the plates (Fig. 3.15).

At the Al/SiC interface, reaction layers existing of Al₄C₃ plates are found. The main type of reaction layer consists of parallel Al₄C₃ plates pointing out of the SiC surface (Fig. 3.15 and 3.16). In general, the plates are parallel to one another, independent on the curvature of the SiC surface as Fig. 3.16 illustrates. In addition, reaction layers with some non parallel-plates are observed as well. The formation of the Al₄C₃ plates is straightforward. The Al₄C₃ plates nucleate at the SiC surface and grow into the Al melt. As can be seen in Fig. 3.16, there is also minor growth into the SiC particle. This occurs due to dissolution of the SiC interface by Al, which was also found by Janghorban [25].

**Figure 3.15:** SEM micrograph of a deep etched sample, where Al is removed, showing a corner of an injected SiC particle, the large Al₄C₃ (II) plates in the melt pool matrix, the Si from the Al-Si eutectic and small Al₄C₃ (I)plates at the SiC surface.
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**Figure 3.16:** TEM bright-field image of a reaction layer, showing $\text{Al}_4\text{C}_3$ plates pointing out of the SiC particle surface into Al. The $\text{Al}_4\text{C}_3$ plates are parallel to one another, independent of the SiC surface curvature.

**Figure 3.17:** Bright-field TEM image of an $\text{Al}_4\text{C}_3$ plate in a reaction layer, where SiC and $\text{Al}_4\text{C}_3$ are both in the $[11\bar{2}0]$ pole, with corresponding diffraction patterns. The (0001) planes of SiC and $\text{Al}_4\text{C}_3$ are parallel. The main growing direction of $\text{Al}_4\text{C}_3$ is along the (0001) planes. The white arrows in the bright-field image indicate the twin planes in $\text{Al}_4\text{C}_3$. 
It is observed, by electron diffraction experiments in Transmission Electron Microscopy, that the (0001) basal planes of SiC (hexagonal crystal structure with \(a_0 = 3.08\) Å and \(c_0 = 15.09\) Å) and Al\(_4\)C\(_3\) (Trigonal crystal structure with \(a_0 = 3.33\) Å and \(c_0 = 24.99\) Å) tend to be parallel. An example is shown in Fig. 3.17, where diffraction patterns of a SiC particle and an Al\(_4\)C\(_3\) plate, obtained in the [11\(\bar{2}\)0] zone axis, show that the (0001) planes of both phases are parallel. The basal planes in the Al\(_4\)C\(_3\) plates are also parallel to the long sides of the plates, indicating that the main growing direction is along the (0001) planes. From the diffraction pattern of Al\(_4\)C\(_3\) it can be seen that twin planes are present in the Al\(_4\)C\(_3\). These twin planes, in this case (0001) planes, are also visible in the bright field image.

In TEM, it is only possible to observe small areas, which makes it difficult to analyze the orientation of many grains in different reaction layers, to get better statistics. By using automated Electron Back-Scatter Diffraction (EBSD) [26] in SEM, so-called Orientation Imaging Microscopy (OIM), it is possible to analyze larger areas. The sample preparation method of the multiple phase SiC\(_p\)/Al system, which is not straightforward, is described in chapter 2.

Before analyzing the reaction layers, with the more complex Al\(_4\)C\(_3\) phase, a two phase scan (SiC and Al) is performed. Figure 3.18 shows the tilted (70°) SEM micrograph of the surface after ion polishing together with an OIM map, taken

![SEM micrograph of the ion polished SiC/Al surface of the 70° tilted sample](image)

**Figure 3.18:** SEM micrograph of the ion polished SiC/Al surface of the 70° tilted sample. The insert depicted on the left shows the OIM image quality image of a two phase scan, scanned with a step size of 1.1 µm, obtained from the marked area.
from the marked area. The insert in Fig. 3.18 represents the so-called Image Quality (IQ) map in which darker gray shades denote lower IQ values. The IQ parameter describes the quality of the EBSD pattern. The IQ factor depends on the material, the deviation from the perfect crystal (deformations, impurities etc.) and system factors such as resolution of the electron beam and video processing parameters. Elements with higher atomic numbers generally produce stronger patterns due to increased scattering. This is the main reason for the high contrast between the Al matrix and SiC particles. The IQ also depends on the local roughness, which results in deviation from the ideal 70°-sample tilt. This is the reason why different facets of the same SiC particle give different qualities of the patterns even though each SiC particle is a single crystal. A low quality signal is obtained from the boundaries between the individual Al dendrites as well as from the Al grain boundaries, because the EBSD patterns form these places is formed from two or more different oriented crystals. Finally Al\textsubscript{4}C\textsubscript{3} plates lying randomly in the Al matrix are visible on this OIM scan as darker lines with lower image quality. The different crystallographic structure as well as the small thickness of these plates is responsible for a low image quality.

The most interesting regions in the SiC/Al MMC are the SiC-Al interface regions. Special attention will be devoted to the orientation of the Al\textsubscript{4}C\textsubscript{3} grains with respect to the orientation of the SiC particle. To achieve this, three-phase scans (SiC, Al\textsubscript{4}C\textsubscript{3} and Al) were performed. Phase differentiation was achieved by automatic indexing a pattern according to the crystal structure parameters for each possible phase, i.e. SiC, Al and Al\textsubscript{4}C\textsubscript{3}. The indexing results were classified according to a ranking factor based on the number of votes [27] and the fit parameter. The votes give the most probable solution out of all possible solutions; the fit parameter is defined by the average angular deviation between all possible triplets of recalculated and detected bands. Because the phases have different crystal structures this procedure is sufficient to identify the phase and to obtain the correct orientation. In the case of the SiC phase, the set of diffracting planes based on intensities measured by X-ray diffraction was used as a first approximation to index the patterns. In principle the same diffraction planes are found for X-ray diffraction and electron diffraction, only the relative intensity of a diffraction set can slightly deviate. Therefore, manual tuning was applied to identify the right set of diffracting planes for electron diffraction. A trial and error method was performed to add new diffraction planes to recognize a band, which is not indexed, or to remove redundant one in EBSD patterns received for different SiC grain orientations.
Figure 3.19: Schematic picture of unit cell of Al$_4$C$_3$. The crystal structure of Al$_4$C$_3$ is trigonal, R$ar{3}$m (166).

Table 3.2: Electron diffraction planes for SiC and Al$_4$C$_3$ used to index the EBSD patterns.

<table>
<thead>
<tr>
<th>SiC based on X-ray database</th>
<th>Al$_4$C$_3$ calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal, P6$_3$mc(186), $a_0$ = 3.08 Å, $c_0$ = 15.09 Å</td>
<td>Trigonal, R$ar{3}$m (166), $a_0$ = 3.33 Å, $c_0$ = 24.99 Å</td>
</tr>
<tr>
<td>h  k  i  l</td>
<td>Intensity</td>
</tr>
<tr>
<td>1  0  T  2</td>
<td>100</td>
</tr>
<tr>
<td>1  0  T  1</td>
<td>40</td>
</tr>
<tr>
<td>1  1  $\bar{2}$  6</td>
<td>40</td>
</tr>
<tr>
<td>1  1  $\bar{2}$  0</td>
<td>35</td>
</tr>
<tr>
<td>1  0  T  3</td>
<td>20</td>
</tr>
<tr>
<td>1  0  T  9</td>
<td>15</td>
</tr>
<tr>
<td>0  0  0  12</td>
<td>7</td>
</tr>
<tr>
<td></td>
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For the Al\textsubscript{4}C\textsubscript{3} phase the X-ray diffraction data were not sufficient to index the EBSD patterns. This is probably because the IQ of the patterns from the reaction zone is relatively low. In addition, the crystal structure of Al\textsubscript{4}C\textsubscript{3} is somewhat complex. The combination of weak pattern, complex structure and the slightly deviating X-ray data makes automated indexing indecisive. Therefore, the diffraction intensities were calculated for electron diffraction, by introducing the atomic positions of the Al\textsubscript{4}C\textsubscript{3} unit cell [28] and using the kinematical theory [29]. The Al\textsubscript{4}C\textsubscript{3} unit cell is shown in Fig. 3.19. Table 3.2 shows all used sets of diffracting planes for both SiC and Al\textsubscript{4}C\textsubscript{3}. Because Al has a cubic structure the patterns could be indexed using four diffracting planes. These planes \{\{111\}, \{200\}, \{220\} and \{311\}\} were obtained from the TSL software database.

A typical three-phase area scan of a particle matrix interface region is shown in Fig. 3.20. The left part of Fig. 3.20 shows the SEM micrograph of the scanned reaction zone, the right part shows the accompanying phase map including the grain boundaries. The step size that was used during the automated scan is 0.13 µm. The system stores the orientation with respect to the sample reference frame, phase and image quality for every point inside the scan. Three axes define the sample reference frame. The Rolling Direction (RD) and the Transverse Direction (TD) are in the surface plane of the sample (RD) pointing downwards, TD pointing to the left in Fig. 3.20). The Normal Direction (ND) is perpendicular to the sample surface, pointing out of the surface. Fig. 3.20 shows that the SiC particle, Al matrix and Al\textsubscript{4}C\textsubscript{3} reaction layer can be distinguished, and the composition of the reaction zone corresponds with the previous observations on the microstructure. An Al\textsubscript{4}C\textsubscript{3} reaction layer is present between the SiC particle and Al matrix. In some cases SiC is identified outside the SiC particle, mainly positioned at the Al\textsubscript{4}C\textsubscript{3}/Al interface. These 'SiC grains' are indexed incorrectly, and falsely identified as SiC, which is underlined by the low confidence index of the points. Probably in these regions the EBSD patterns were a superposition of two EBSD patterns, one of the Al\textsubscript{4}C\textsubscript{3} grain and one of the Al grain. Therefore correct indexing is not possible.

The Al\textsubscript{4}C\textsubscript{3} reaction layer consists of many small grains. The crystallographic orientations of these grains can be reflected in pole figures as two-dimensional projections. These pole figures show the position of a pole, i.e. the normal of a lattice plane, relative to the reference frame. The (0001) pole figures of SiC and Al\textsubscript{4}C\textsubscript{3}, obtained from the data of the OIM scan in Fig. 3.20, are depicted in Fig. 3.21. The cluster of dots in the upper part of the SiC (0001) pole figure corresponds to the orientation of the SiC particle. The (0001) basal planes are
Figure 3.20: The left side shows an SEM micrograph of a tilted (70°) sample. On the right side, the corresponding phase map of the OIM scan, obtained from the marked particle/matrix interface in the SEM micrograph, is depicted.

Figure 3.21: 0001 pole figures of SiC and Al$_4$C$_3$, obtained from the OIM scan depicted in Fig. 3.20. The [0001] direction of the Al$_4$C$_3$ grains prefer to be parallel to the [0001] direction in the SiC particle. RD and TD are the reference directions in the sample.
about perpendicular to the SiC/Al\textsubscript{4}C\textsubscript{3} interface and the plane of paper. The other dots in the pole figure belong to incorrect indexed SiC grains. In the (0001) pole figure of Al\textsubscript{4}C\textsubscript{3}, a cluster of dots is in a comparable orientation to the SiC particle orientation. These pole figures indicate that there is a tendency that the Al\textsubscript{4}C\textsubscript{3} basal planes are parallel to the SiC basal planes. Remember that parallel SiC and Al\textsubscript{4}C\textsubscript{3} basal planes are also observed in transmission electron microscopy (TEM), as shown in Fig. 3.17. However, not all the Al\textsubscript{4}C\textsubscript{3} grains in the reaction layer of Fig. 3.20 have their (0001) planes parallel to basal planes in the SiC particle, because not all the dots are in this top area of the Al\textsubscript{4}C\textsubscript{3} pole figure. The other dots in the Al\textsubscript{4}C\textsubscript{3} pole figure are mostly close to the RD axis. This means that the basal planes of Al\textsubscript{4}C\textsubscript{3} are perpendicular to the SiC/Al\textsubscript{4}C\textsubscript{3} interface, but rotated by different angles around the TD direction, which is [11\textsubscript{2}0] in Al\textsubscript{4}C\textsubscript{3} in this case.

The multi-phase area scans are time consuming. Indexing takes about 5 s per point for our material system. Analyzing a few points per grain is sufficient to obtain a reliable orientation. Especially for the SiC particle, which is a single crystal, it is not necessary to scan the full area of the particle. Therefore, besides the area scans, line scans, starting in the SiC particle and pointing perpendicular to the SiC/Al\textsubscript{4}C\textsubscript{3} interface, through the Al\textsubscript{4}C\textsubscript{3} grain until Al is detected, are also performed to analyze more Al\textsubscript{4}C\textsubscript{3} grains in order to get better statistics. In this way over a hundred of SiC/Al\textsubscript{4}C\textsubscript{3} interfaces, from different SiC particles, are scanned. 25% of the cases fulfil the relation {0001}\textsubscript{SiC}//{0001}\textsubscript{Al\textsubscript{4}C\textsubscript{3}}. In this relation a rotation of a multiple of 30° around the [0001] axis of Al\textsubscript{4}C\textsubscript{3} is allowed. Whether the relation arises depends on the SiC orientation because the Al\textsubscript{4}C\textsubscript{3} plates prefer to grow with their basal planes parallel to the temperature gradient. Because the temperature of the particles is in general higher than the Al liquid, due to the difference in the reflectivity of the laser light, the temperature gradient is perpendicular to the SiC/Al\textsubscript{4}C\textsubscript{3} interface. Therefore, the more the basal planes of the SiC particle are perpendicular to the SiC/Al\textsubscript{4}C\textsubscript{3} interface the more the mentioned relation is found. For example, in the OIM scans that are depicted in Fig. 3.20 and Fig. 3.21 the SiC particle has the ideal orientation, with respect to the SiC/Al\textsubscript{4}C\textsubscript{3} interface, to allow {0001}\textsubscript{SiC}//{0001}\textsubscript{Al\textsubscript{4}C\textsubscript{3}}. In this reaction layer about 60% of the neighboring Al\textsubscript{4}C\textsubscript{3} grains have their basal planes parallel to basal planes of SiC. However, since not all the grains in this reaction layer have this relation, the growth direction parallel to the (0001) planes is preferred but not very strict.
Peteves et al [23] reported an orientation relation between SiC and Al$_4$C$_3$, found on SiC/Al interfaces prepared by putting a liquid Al droplet on solid SiC and heat it for 60 to 100 minutes at 850 °C. The orientation relation is:

\[ [0001]_{\text{SiC}}//\langle 0001\rangle_{\text{Al}_4\text{C}_3}, \quad (10\overline{1}0)_{\text{SiC}}//(10\overline{1}0)_{\text{Al}_4\text{C}_3} \]

This relation corresponds with our observations, however it is stricter and more frequently observed. This is due to the longer time of the Al$_4$C$_3$ formation process compared to our experiments.

The microstructure at the SiC/Al interface is important for revealing the strength of the coating because the mechanical properties of composites are determined by the interface between the metal and ceramic material. The reaction product Al$_4$C$_3$ at the SiC interface takes care of the bonding between SiC and Al. The fact that the orientation of the SiC particle influences the growth direction of Al$_4$C$_3$ indicates that SiC and Al$_4$C$_3$ are connected. However the mechanical and chemical properties of Al$_4$C$_3$ makes this phase unfavorable in the SiC/Al MMC coatings [6,10]. The consequences of the presence of Al$_4$C$_3$ in the MMC coating will be discussed in chapter 5.

### 3.5 Summary

In this chapter, it has been shown that it is possible to produce a SiC$_p$/Al metal matrix composite layer on an Al substrate by using the laser melt injection process. However, the processing parameters should be carefully tuned since the parameter window for which the process is successful, is small. This small parameter window for laser processing of an SiC$_p$/Al layer is caused by a large difference between the laser light absorptivities of SiC and Al as well as the presence of an oxide skin on the Al melt. The first one limits the laser power density that can be used to heat the Al melt, because a high power density will damage the exposed SiC particles, which have a high absorptivity.

The second drawback, the oxide skin on the Al melt, blocks the SiC particles, so the particles cannot propagate in the melt pool. This is because the kinetic energy of the particles is lower than the energy that is needed to overcome this surface energy barrier, which magnitude can be estimated by the surface tensions. The oxide skin dissolves by increasing the melt pool temperature. The dissolution of the oxide starts at about 850 °C by the appearance of Al islands without oxide skin. At 1100 °C the oxide skin fully disappears. By the increase
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of unoxidized Al surface area the wetting process improves. Therefore, the energy loss, caused by the surface penetration, decreases. This makes it possible for the SiC particles to penetrate further into the melt pool. Therefore, the final injection depth of SiC particle in Al melt is mainly controlled by the fraction of surface covered with oxide, i.e. by the temperature of the melt pool.

Preheating the substrate over 300 °C is an effective method for the successful injection of SiC particles into the Al melt. In this way, the necessary high temperatures of the melt pool are reached at which the oxide skin is fully or partially dissolved and the use of high laser power that leads to overheating the SiC particles is avoided. Because of the transversal gradient of the temperature in the melt pool, SiC particles are only injected in the central area of the melt pool. The two outer areas are almost fully covered by a relatively thick oxide layer. This is a serious obstacle for the preparation of a continuous layer by a superposition of adjacent laser tracks.

The particle volume fraction in the produced coatings is about 35%. An important achievement is that no cracks and holes are present and that the surface of the coating is relatively flat. During the process two new phases are formed: Al₄C₃ and Si. These are products of the reaction between SiC and liquid Al. Al₄C₃ appeared in platelet shape both in the melt pool matrix and at the interface between SiC and Al. Si is found in Al-Si eutectic regions between the Al₄C₃ plates. At the SiC/Al interface the Al₄C₃ plates form a reaction layer. Although the preferred growing direction along the temperature gradient plays a role in the appearance and crystal orientation of this reaction layer, it is observed that Al₄C₃ plates prefer to grow parallel to the basal planes of SiC. This indicates that there is an interaction between SiC and Al₄C₃.

3.6 References