Laser melt injection of ceramic particles in metals
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Chapter 4

Injection of WC particles in Ti-6Al-4V

4.1 Introduction

In 1791 titanium was discovered by William Gregor [1], who was interested in minerals. He recognized the presence of a new element, now known as titanium, in menachanite, a mineral named after Menaccan in Cornwall (England). A couple of years later, the element was rediscovered in the ore rutile by a German chemist M.H. Klaproth and he named it titanium [2]. The main advantage of titanium is its high strength-to-weight ratio. Titanium alloys are mostly used where lightweight strength and ability to withstand high temperatures are needed, for instance in the aerospace industry where it is used both in airframes and engines. The excellent corrosion resistance makes Ti a suitable material for propeller shafts, rigging, and other parts of ships exposed to salty water.

Although titanium alloys exhibit all these excellent material properties, surface properties like a high friction and poor wear resistance hamper many potential applications. A Metal-Matrix Composite (MMC) layer in the top layer of a Ti matrix may improve these properties, while keeping the advantageous bulk properties unaffected [3]. The Laser Melt Injection (LMI) process is an auspicious technique to achieve this [4,5,6,7].

The properties of the MMC layer produced by LMI depend, among other things, on the amount of injected powder, the microstructure of the melt pool matrix and the bonding between particle and matrix. Because the wetting properties between ceramic and metal materials are usually poor [8], the
bonding between particle and matrix may cause severe problems during applications. To circumvent this problem, it was decided to choose for tungsten carbide (WC) particles. Because of the high affinity of Ti for C, a chemical reaction between WC particle and Ti matrix occurs during the laser process, where TiC is formed [9]. The consequence is that reaction layers between the particles and matrix may be formed [10,11,12], which improves the wetting and may therefore improve the bonding [8,13]. The commercial Ti-6Al-4V alloy is chosen as substrate material because it is widely used.

In this chapter, the influence of the LMI processing parameters on the appearance of the laser track is described. In addition the microstructure of the WCp/Ti-6Al-4V MMC is analyzed using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Electron Back-Scatter Diffraction (EBSD) and (energy-filtered) Transmission Electron Microscopy (TEM).

### 4.2 Laser Melt Injection process

WC particles, with a typical diameter of 80 µm are injected in Ti-6Al-4V slices (40 mm in diameter and 5 mm thick) by using the Nd:YAG laser. Figure 4.1 shows a SEM micrograph of the WC powder before injection. The WC particles are granular and have approximately a spherical shape. X-ray diffraction measurements showed that WC is the only detectable phase in the powder.

**Figure 4.1:** SEM micrograph of the WC powder that is used for the laser injection process. The WC particles are granular and have a spherical like shape. The average diameter of the particles is about 80 µm.
During the laser melt injection process, the laser beam is focussed to a spot size of 3.6 mm by setting the focal point of the laser 9 mm out of focus. This focus point is set below the substrate surface to get a higher laser power density at the substrate surface than the power density above the substrate, where the particles are passing through the laser beam. After all, the laser power should be used to heat the substrate and not the particles. A argon gas flow of 5 l/min is used as the shielding gas to protect the lens and to prevent oxidation of the sample. The carrier gas, 1.5 l/min Argon, transports the powder into the cyclone, where the major gas flow escapes through the upper outlet, which is fully open. The injection direction is in the 'cladding direction' (pointed towards the already injected track along the scanning direction, i.e. the opposite direction of the depicted direction in Fig. 2.1 in chapter 2) with an angle of about 35° with respect to the surface normal of the sample.

Cross-sections of single laser tracks, produced with different laser and powder parameters are observed to obtain a suitable set of parameters. A successful combination of parameters is found to be: power density $P= 79 \text{ W/mm}^2$, scanning speed $v= 8.3 \text{ mm/s}$ and powder feeding rate $m= 125 \text{ mg/s}$. The corresponding cross-section is shown in Fig. 4.2. The width of a single laser track is about 1.8 mm, the maximum depth is about 0.7 mm and the volume fraction of WC inside the track lies in the range of 0.25 to 0.30. It is important to note that the particle distribution is homogeneous and that the particles are injected over the whole depth and entire width of the melt pool.

![Figure 4.2: SEM micrograph, obtained in the SE mode, of a cross-section of a single laser track produced with $P= 79 \text{ W/mm}^2$, $v= 8.3 \text{ mm/s}$ and $m= 125 \text{ mg/s}$. The WC particles are the bright features in the image.](image-url)
An interesting and advantageous point is that this particular material system allows a certain variation of the processing parameters, in order to obtain different track characteristics. In general, the following parameters range result in suitable tracks: \( P \) ranging between 39 and 84 W/mm\(^2\), \( v \) in the range from 5.0 to 11.7 mm/s and \( m \) varying from 83 to 167 mg/s. The influence of a single processing parameter on the track characteristics is shown in Fig. 4.3. An optical micrograph of a cross-section of a laser track produced with an average set of processing parameters \((P= 59 \text{ W/mm}^2, v= 8.3 \text{ mm/s}, m= 125 \text{ mg/s})\) is shown in Fig. 4.3a. The other images are taken from cross-sections produced with different processing parameters. Only one parameter is changed for the connected images. This parameter is given in the box between the images, where an arrow indicates if this parameter is increased (up) or decreased (down). Figure 4.3b shows a micrograph of a cross-section obtained with the same laser power and powder feeding rate but with the scanning speed increased to 11.7 mm/s. Because of this higher speed the heat input is less, which results in a less thick composite layer. In addition, the volume fraction of WC particles in the resolidified melt pool is decreased, because an increasing scanning speed decreases the number of injected particles per unit area. Figure 4.3c shows a cross-section produced with an increased powder feeding rate, with respect to the cross-section of Fig. 4.3b, resulting in an higher volume fraction of particles compared to Fig. 4.3b and less thick than the layer of Fig. 4.3a. Figure 4.3d shows a cross-section of a laser track with the same processing parameters as the cross-section of Fig. 4.3a, only the powder feeding rate is decreased. It is obvious that the volume fraction of WC particles decreases compared to the laser track shown in Fig. 4.3a. The cross-section of Fig. 4.3e is produced with an increased power density that results in a thicker and wider laser track.

To cover larger areas with an MMC layer, more adjacent laser tracks can be produced. An example is shown in Fig. 4.4. The parameters of the single tracks are \( P= 59 \text{ W/mm}^2, v= 8.3 \text{ mm/s and } m= 83 \text{ mg/s} \). The five tracks, with a distance of 1.6 mm between the centers of two adjacent tracks apart, have an overlap of about 10%. This overlap region is treated twice but shows, nevertheless, no distinct difference with the regions that are treated only once. This makes it therefore possible to cover larger areas than the widths of the laser beam and powder flow with a constant MMC layer, which is important for applications.
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When a second track is laid partially over an already produced track, the substrate surface of the latter track consists of three different areas. The surface of the area to be treated consists partially of a previously injected track, partially of a heat affected zone of the previously track and partially of the unimpaired substrate. Therefore, the laser interaction with the substrate surface is changing over the width of the laser track. However, the margins in the processing parameter window, as mentioned above, make the LMI process still successful and relatively constant within the whole treated area. This is the key to cover areas that are larger than laser beam and powder beam dimensions, which is important for potential applications.
Figure 4.4: SEM micrographs, obtained in the SE mode, of five adjacent laser tracks. The process parameters of each single track were $P= 59 \text{ W/mm}^2$, $v= 8.3 \text{ mm/s}$ and $m= 83 \text{ mg/s}$. The distance between the centers of two neighbour tracks is 1.6 mm, which results in an overlap of about 10%. In the overlap regions the LMI process is still successful, and does not differ much from the center areas of the individual tracks.

It is striking that it is relatively easy to inject WC particles in Ti by the LMI process, i.e. the processing parameter window for successful laser processing is large. The main reason that this parameter window is relatively large is the ease to create a melt pool in the Ti substrate. Despite of the quite high melting temperature of Ti-6Al-4V (1650°C [14]), a relatively modest laser power density is needed to generate this melt pool. The reason is the relatively low reflectivity of Ti for laser light with a wavelength of 1.06 $\mu$m, compared to Al for instance [15]. The relatively large parameter window makes it possible to adjust the laser track dimensions and particle volume fraction by changing the processing parameters. This is in contrast to SiC$_p$ injection in an Al substrate, where the parameter window is too small to allow for large variations in the processing parameters (see chapter 3).

The thermal conductivity of Ti is relatively low (20 W/m°C at room temperature compared to 237 W/m°C for Al [26]). Therefore the lifetime of the melt pool is relatively long. After the passage of the laser beam the melt pool is not resolidified yet. The distance that the melt pool protrudes after the laser beam depends on velocity of the laser beam, provided that the laser power corrects for the loss in energy density by increasing the beam velocity. This extended melt pool makes it possible to inject the powder in the melt pool fully or partially outside the laser beam as is illustrated in Fig. 4.5. Kloosterman et al [5] used this successfully to control the amount of reaction products in the melt pool and to control the reaction layer thickness around the particles. When the particles are not, or less, illuminated by the laser beam the temperature of the particles is much lower, and therefore they dissolve less in the melt pool matrix. Besides, the particles are injected in Ti that is already cooling down, which also contributes to oppose the reaction between WC and Ti. The feasibility to inject
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Figure 4.5: Schematic pictures of the influence of the laser beam velocity \(v\) on the length of the melt pool. The beam velocity in \(b\) is larger than the beam velocity in \(a\) \((v_b>v_a)\). The laser energy density is kept the same by adjusting the laser beam power. Extending the melt pool gives the possibility of injecting the particles outside the laser beam.

The particle behind the laser beam, and thus control the amount of reaction products, makes Ti suitable for laser processing. It should be noted that the results that are discussed in this thesis are obtained by injecting the particles in the center of the laser beam, unless it is explicitly mentioned that the particles are injected behind the laser beam center.

In the WC\(_p\)/Ti-6Al-4V system the oxide layer, which may be present at the surface of the liquid Ti forming a barrier for the penetrating particles, does not play a significant role compared to the oxide skin in the SiC\(_p\)/Al system (see chapter 3). There are two reasons for this. Firstly, the temperature during the laser process is much higher because of the lower reflectivity, which probably lead to dissolving the oxide skin. Secondly, the kinetic energy of the WC particles is higher because of the higher density of WC (15630 kg/m\(^3\) [26]) compared to SiC (3217 kg/m\(^3\) [26]), which makes WC particles less sensitive to energy barriers that may exist in the penetration process. In addition, the high density of the WC particles results in a high density difference between the particle and the melt and thus in a relatively high particle velocity in the melt pool (chapter 3, Eq. 3.14). The WC particles are therefore less sensitive to small changes in the viscosity of the Ti melt. Although the viscosity can be assumed constant in the high temperature ranges in the melt pool, it increases when the temperature reaches the melt temperature, i.e. at the bottom and at the back of
the melt pool. Therefore the WC particles can be injected to relatively deep regions in the melt pool. Injecting the WC particles behind the center of the laser beam, where the temperature of the Ti melt is lower (close to the melt temperature), and thus the viscosity of the liquid Ti melt is somewhat higher, is therefore less complicated than injection of more light-weighted particles.

4.3 Microstructure

4.3.1 Phases

During the laser melt injection process, high temperatures of the order of 2000 °C to 3000 °C may be reached. Liquid Ti is likely to react with the particles, which may also have a high temperature when they have passed through the laser beam. Reaction products may therefore dominate the microstructure of the produced MMC layers. Before analyzing the microstructure in more detail, it is worthwhile to know which phases are present in the coatings. Therefore, X-ray diffraction measurements are performed on polished surfaces of single laser tracks to obtain the crystal structures of the phases that are present. An X-ray database (Powder Diffraction File™) is used to identify the peaks with the corresponding phases. Figure 4.6 shows a typical XRD spectrum of a laser track, using Cu-Kα radiation. Besides the expected α-Ti and WC peaks W2C, TiC, W and β-Ti peaks are identified. An overview of the crystal structures and lattice parameters of the phases that are present in the specimen is given in Table 4.1 [16,17,18].

The composition of the coatings can be predicted by the thermodynamics of the chemical reactions between the metal and ceramic materials [19]. If the free energy change ($\Delta G^0$) of a reaction is negative then the reaction is favorable, if $\Delta G^0$ is positive the reaction will not occur. The free energy changes were calculated on the basis of the thermodynamic data taken from [9]. The calculations were performed in the temperature range of 1600 °C to 2200 °C, in which Ti is liquid and WC solid. When both phases are liquid the reactions will be more favorable. In this range the results were qualitatively identical, and therefore values of the free energy change will be given for a typical temperature of 2127 °C.
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Figure 4.6: XRD spectrum, obtained with Cu-Kα radiation, of a laser track. α-Ti, WC, W₂C, TiC and β-Ti peaks are identified.

Table 4.1: Crystal structures of the phases that are present in the WC/Ti-6Al-4V layers.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>Hex.(P6m2)</td>
<td>a₀=2.91, c₀=2.84</td>
</tr>
<tr>
<td>W₂C</td>
<td>Trig.(P3m1)</td>
<td>a₀=2.98, c₀=4.71</td>
</tr>
<tr>
<td>TiC</td>
<td>Cub.(Fm3m)</td>
<td>a₀=4.31</td>
</tr>
<tr>
<td>W</td>
<td>Cub.(Im3m)</td>
<td>a₀=3.16</td>
</tr>
<tr>
<td>α-Ti</td>
<td>Hex.(P63/mmc)</td>
<td>a₀=2.95, c₀=4.67</td>
</tr>
<tr>
<td>β-Ti</td>
<td>Cub.(Im3m)</td>
<td>a₀=3.31</td>
</tr>
</tbody>
</table>

The chemical reaction where TiC is formed out of WC and Ti is favorable because the change of free energy is negative:

\[
WC + Ti \rightarrow TiC + W
\]

\[
\Delta G_{2127}^0 = -116 \text{ kJ}
\]
W₂C formation is also observed in previous research, for instance after high temperature processing of WC powder in an oxygen environment, where CO and CO₂ formation degrades WC to W₂C [20,21,22]. The extraction of C from WC due to the TiC formation may also degrade WC to W₂C [23]:

\[
2\text{WC} + \text{Ti} \rightarrow \text{W}_2\text{C} + \text{TiC} \quad (4.2)
\]

\[
\Delta G_{2127}^0 = -222 \text{ kJ}
\]

Because the change of the free energy of this reaction is negative, this reaction is possible as well. It is also reported that WC dissociates directly, i.e. without the presence of Ti or any other element, into W₂C and C in the temperature range of 1800 °C - 2500 °C [24]. W₂C in contact with Ti is not stable because they may react to form TiC and W:

\[
\text{W}_2\text{C} + \text{Ti} \rightarrow \text{TiC} + 2\text{W} \quad (4.3)
\]

\[
\Delta G_{2127}^0 = -11 \text{ kJ}
\]

Reaction 4.1 is the sum of reactions 4.2 and 4.3 divided by two. The negative free energy change of this reaction 4.3 is quite small. Above a temperature of about 2250 °C the free energy difference becomes even positive, making this reaction impossible. However, the calculations are based on a stoichiometric TiC. Non-stoichiometry of TiC may affect the thermodynamic values. A rather experimental argument that W₂C is stable in the coating is that locally no Ti is available around the W₂C grain, for example when WC and TiC surround W₂C. This will be discussed in section 4.3.3.

The metastable β-Ti may be formed at higher temperatures (above 955 °C). This metastable phase can be retained after rapid cooling of Ti containing a higher amount (>14.2 at-%) of the β- stabilizer V [25]. Locally, the V content may be increased above this concentration due to the TiC formation that relatively lowers the Ti concentration in the melt.

The occurrence of all the phases that are detected in the coating by X-ray diffraction are explained. After inquiring the phase composition of the laser tracks, the different phases are localised and their microstructure is observed. Both EDX measurements in SEM (chemical composition) and Electron Diffraction in TEM (crystal structure and lattice parameters) are used to identify the phases of the different regions in the MMC layer.
4.3.2 Resolidified matrix

The melt pool matrix, i.e. the regions between the injected particles in the resolidified melt pool, can roughly be grouped in two regions: the bottom and center/top part. In the center and top part of the laser track many TiC dendrites as well as W cells and dendrites are present (Fig. 4.7a, Fig. 4.8a). A Back-Scatter Electron (BSE) detector is used in Fig. 4.7 to obtain phase contrast by the difference in atomic weight: the more heavy the atoms, the brighter the electron signal, i.e. W grains are bright and TiC grains are dark in Fig. 4.7. Ti grains, containing Al and V, are present as well, having a martensitic structure (Fig. 4.8b). In the bottom part Ti cells, containing also Al and V, and further TiC dendrites (Fig. 4.7b) are observed. However, the latter are less present than in the center/top part of the melt pool matrix.

There are two reasons that the microstructure of the melt pool matrix can be divided in two regions. The first reason is an obvious reason in laser surface engineering, namely that at the top of the melt pool the temperature is higher and the liquid state of the melt pool is longer retained and so reactions will develop more intensively. Therefore more TiC and W may be found in the center/top region of the melt pool than in the bottom region.

Another reason is the dynamic character of the laser melt injection process. It is possible that the surface layer of the WC particles (melting temperature of WC is 2870 °C [26]) is melted when the laser beam interacts with the particles during the laser melt injection. The surface temperature of the WC particles is probably ±3000 °C, which is still below the boiling point of Ti (3287 °C [26]). The top part of the liquid WC layer on the solid WC particle will have a higher temperature than the part that is closer to the liquid/solid interface, and therefore the viscosity will be higher at the surface of the WC particle. When the particle penetrates in the melt pool the top part of the melted WC may drip off the particle and be left in the upper parts of the melt pool, while the particle penetrates further in the melt pool. Therefore, we can distinct two different cases of reaction during the laser process: between small liquid droplets WC and Ti melt (mostly in top part of melt pool matrix) and between liquid WC, having a lower temperature than the droplets, at the solid WC particle and Ti melt.
Figure 4.7: SEM micrographs, obtained in BSE mode, of a cross section from two different regions in the melt pool. a) The center/top part of the melt pool matrix contains high amounts of TiC dendrites and W dendrites. b) The bottom region of the laser track contains less reaction products. The microstructure between the WC particles consists of TiC dendrites and Ti cells. The dotted line gives the approximate position of the bottom of the melt pool.
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Figure 4.8: TEM micrographs of the melt pool matrix showing: a) an area where TiC dendrites and W grains are present, b) martensitic structure of rapidly solidified Ti-Al-V alloy.

Liquid WC that is left behind will react with liquid Ti according reaction 4.1 to form TiC and W. The temperature of the reaction products will be ± 3000 °C, which is lower than the melting temperatures of W (3410 °C [26]) and stoichiometric TiC (3140 °C [26]), therefore W and TiC are rapidly solidifying. This is the reason why in the top part of the melt pool matrix many TiC and W dendrites are present (Fig. 4.7a). Ti that has not reacted with C rapidly solidifies, which explains the martensitic structures observed [27].

The liquid part of WC, which stays at the solid WC particle during penetration towards the bottom of the melt pool, will react with Ti to form the reaction layers, which will be discussed in the next section.

Another possibility is that the surface layer of the WC particles is not molten during exposure to the laser beam, but that the solid WC particles partially dissolve in the Ti melt pool and subsequently nucleate and grow TiC and W. Again, more reaction products are expected in the top region of the melt pool due to the motion of the particles, which result in traces of reaction products. When the particles are slowed down the dissolution of WC will result in the formation of reaction layers.
4.3.3 The particle reaction zone

The reaction zone, i.e. the transition area from particle to matrix, consists of different reaction layers. Figure 4.9 shows a typical particle surrounded by the reaction layers. Both EDX measurements in SEM (chemical composition) and Electron Diffraction in TEM (crystal structure and lattice parameters) were used to identify the phases of the different regions around the particles. A W\textsubscript{2}C layer surrounds the WC particle and next to the W\textsubscript{2}C a TiC reaction layer is present, which on its turn is surrounded by W and TiC grains.

The phase identification agrees with the grey levels in the SEM BSE micrograph of Fig. 4.9, where the order of intensity is W\textsubscript{2}C > WC > TiC, according their atomic numbers. In some cases, a small layer, with a thickness of the order of 100 nm, of W is found to be present between the W\textsubscript{2}C and TiC reaction layers. A transmission electron micrograph of such a small W grain is shown in Fig. 4.10.

The reaction layers are formed according the chemical reactions 4.1, 4.2 and 4.3. The W\textsubscript{2}C layer is likely to be formed from the liquid state of WC or from solid WC, which is dissolved in the Ti liquid. This is because the W\textsubscript{2}C reaction layer consists of a rather smooth layer without a second phase between the W\textsubscript{2}C grains. If W\textsubscript{2}C had been formed directly from the solid state WC should have been dissociated into W\textsubscript{2}C and C grains. However, no C or TiC grains are present in the W\textsubscript{2}C reaction layers. The argument that during dissociation in the solid WC, C is diffused along the W\textsubscript{2}C grain boundaries towards the liquid Ti to form TiC is contradicted by analyzing the crystallographic orientations of the W\textsubscript{2}C grains, which will be discussed later.

Therefore, the W\textsubscript{2}C layer it is likely to be formed from a liquid, either the melted WC layer that remained at the surface of the WC particles or dissolved WC on the Ti liquid around the particles. The Ti melt will attract C to form a TiC layer and because of the lower C content, WC will transform to a W\textsubscript{2}C layer. In some cases, the C content is that low that a small W layer is formed. The formation of TiC is slowed down because the TiC layer is shielding the WC particle, which increases the distance between Ti and WC. After rapid solidification, the final composition of the reaction layers is fixed.
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Figure 4.9: SEM micrograph, obtained in BSE mode, of an injected WC particle and accompanying reaction zone. The WC particle is surrounded by a W\(_2\)C layer, which on his turn is surrounded by a TiC layer. Next to this TiC layer W grains are present, alternated by TiC grains.

Figure 4.10: TEM micrograph of a W\(_2\)C/TiC interface in the reaction zone where a small W grain is present between the two reaction layers.

The particles at the top of the melt pool matrix, which are injected later (or with a lower injection velocity) and meet the solidification front at a higher position in the melt pool, will have the same reaction layer structure. However, their reaction layers are thicker because less WC has been lost during their short passage in the melt pool. In addition, the thickness of the reaction layers depends on the laser processing parameters and on the position in the melt pool.
due to temperature and time interval reasons. An increasing power and decreasing scanning velocity result in a thicker reaction layer. In the top region the reaction layer becomes thicker than in the areas at the bottom. For example, for $P= 79$ W/mm$^2$, $v= 8.3$ mm/s and $m= 125$ mg/s the thickness of the W$_2$C reaction layer decreases approximately linearly with the depth of the particle (thickness is 3.2 µm at the top and 0.6 µm at a depth of 0.7 mm).

The opposite behavior is found when the particles are injected behind the center of the laser beam. In that case the reaction layers in the bottom of the resolidified melt pool are thicker than at the top. This is because the particles that are injected more towards the center of the laser beam are injected in liquid Ti with the highest temperature and thus Ti that has the lowest viscosity. These particles are therefore injected to deep regions in the melt pool. Particles that are injected behind the center of the laser beam are injected in Ti that has a lower temperature, i.e. more close to the melting temperature because it is more close to the liquid/solid boundary. At this position the viscosity of Ti is higher, therefore, the particles that are injected behind the center of the beam are injected less deep. According this reasoning the particles that are injected deep, are injected close to the center of the laser beam. These particles are exposed to the laser beam and thus have a higher temperature. Besides the high temperatures, which enhances the reaction layer formation, they travel a longer time in the melt pool that leads to the formation of thick reaction layers. The particles that are trapped in the top of the melt pool are injected behind the center of the laser beam, and are therefore not or less exposed to the laser beam. In addition to the lower temperatures of the particles, the particles have had a short path in the melt, which explains the thin reaction layers in the top of resolidified melt pool.

The relative C content in the reaction zone is analyzed with Energy Filtered Transmission Electron Microscopy (EFTEM). This technique makes use of the fact that the electrons of the electron beam in TEM may, besides elastically, scatter inelastically with the electrons of the atoms in the specimen. Because the energy-loss of the primary electrons, which is an ionization loss, is characteristic for each element to which they interact, these losses contain information about the chemical composition of the specimen [28]. Filtering electrons with a specific energy-loss, corresponding with an ionization loss characteristic for an element present in the specimen, and use them to make an image, makes it possible to produce an elemental map. To achieve this, an energy window with a width of 20 eV was used to select an energy range of core-loss electrons,
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associated with C to form an elemental map of C. The C K-edge at 283 eV was used to obtain a C map of a WC-W$_2$C-TiC reaction zone (Fig. 4.11a). The zero-loss image is also given (Fig. 4.11b) to show the corresponding microstructure. The C intensity profile divided by the zero-loss intensity, which is an attempt to correct for the difference in amount of electrons that are transmitted through the three phases, and integrated over the marked width across the reaction zone is shown in Fig. 4.11c. Figure 4.11c shows that the C content in WC gradually decreases when the distance from the WC/W$_2$C interface becomes small. In the W$_2$C layer the C content decreases further with increasing distance from the WC/W$_2$C. At the W$_2$C /TiC interface the C content abruptly increases. These results may confirm that attracting C from the WC particle, which degrades partially to W$_2$C or even to W, forms the TiC layer.

![Figure 4.11: a) Energy Filtered Carbon map of a WC-W$_2$C-TiC reaction zone. In the brighter regions more C is present. b) The zero-loss image of the same area. c) Integrated C intensity profile divided by the zero-loss intensity across the reaction zone, corresponding to the marked areas in a and c.](image-url)
To learn more about the reaction layer formation during the laser process, the crystallographic orientation of the different reaction zones is studied using Electron Back-Scatter Diffraction (EBSD) [29] by automated Orientation Imaging Microscopy (OIM) [30] in SEM and electron diffraction in TEM. OIM is an adequate technique to study larger amounts of reaction zones because larger areas than in TEM can be analyzed. Because the phases in the reaction zone (WC, W₂C, W and TiC) have different crystal structures (see Table 4.1), it is possible to obtain both the phase and orientation of the scanned grains.

Figure 4.12a shows a phase map, with depicted grain boundaries, of an area scan of a part of a WC particle with accompanying reaction layers. Look-up tables of WC, W₂C, TiC and W were used to index the Kikuchi patterns. Several WC grains are inside the scanned area. The W₂C and TiC reaction layers consist of many grains. The areas outside the TiC reaction layer are indexed as W (dark grains in Fig. 4.12a), however because W has a similar crystal structure and lattice constant as β-Ti also β-Ti grains should be indexed as W. Nevertheless, since we are interested in the reaction zone it is not necessary to distinguish between this two phases using OIM. At some places W is indexed between the W₂C and TiC layer. This is likely to be W and not β-Ti on the basis of TEM observations (see Fig 4.10). From the observation that the W₂C layer consists of many small grains that have different orientations and extend over the whole width of the layer confirms the supposition that this layer is formed from the liquid state. If the layer was formed in the solid state, by dissociating of the WC grain into W₂C and C and subsequently diffusion of C towards Ti to form TiC, the mutual orientations of W₂C grains should be related because they originate from the same WC crystal.

A general result concerning the orientation of the W₂C reaction layer is that most W₂C grains tend to have the [0001] direction perpendicular to the WC/W₂C interface, which is illustrated in the Inverse Pole Figure (IPF) in Fig. 4.12b. An IPF shows which crystal direction is aligned to a chosen sample reference direction. Figure 4.12b shows which crystal direction in the W₂C crystal lattice is parallel to the Transverse Direction (TD), which is defined along white arrow depicted in Fig. 4.12a. In this case, the TD is roughly about perpendicular to the WC/W₂C interface. The [0001] direction in W₂C is in most cases more or less parallel to the experimentally defined TD. And therefore perpendicular to the WC/W₂C interface. This preferred orientation is observed in all performed OIM measurements, both area scans and single point measurements.
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Figure 4.12: a) Phase map and grain boundaries of a reaction zone, which is more or less perpendicular to the TD direction (white arrow). b) Inverse Pole Figure of the WC grains, with respect to the TD direction, showing that [0001] direction in the WC crystals tend to be parallel to the TD direction, and therefore perpendicular to the WC/WC interface.

Occasionally an orientation relation between WC and W$_2$C is observed. An example is shown in Fig. 4.13a. It shows a phase map, with grain boundaries, of an area scan of a corner of a WC particle with its reaction layers. The SEM micrograph of the 70° tilted sample is shown Fig. 4.13b. Two WC grains are inside the scanned area. Again, at some places W is indexed between the W$_2$C and TiC layer. The grains that are indexed as W outside the TiC reaction layer may also be β-Ti according the reasoning above. The 3D hexagonal unit cells of the WC and W$_2$C grains are schematically depicted in the measured orientation, i.e. by 2D axonometric projections, in order to visualize the orientations of the WC and the W$_2$C grains. The upper left WC/W$_2$C interface shows an orientation relationship where the basal planes are parallel. It is striking to see that this W$_2$C grain and accompanying TiC grain are much larger and more regularly shaped, than the other W$_2$C and TiC grains. For these other smaller W$_2$C grains in Fig. 4.13b this orientation relation does not hold. However, it can
be noticed that again most W₂C grains tend to have the [0001] direction perpendicular to the WC/W₂C interface.

The orientation relation that is observed by using OIM is also found by electron diffraction analysis in TEM. With this technique, the orientation relation can be studied in more detail because of the possibilities to tilt the specimen in different directions. An example is shown in Fig. 4.14, where a bright field TEM image of a reaction zone with corresponding diffraction patterns is shown.

**Figure 4.13:** a) Phase map and grain boundaries of a reaction zone. The orientation of the WC and some W₂C grains is visualized by plotting the axonometric projections of the hexagonal cells. The WC/W₂C interface shows an orientation relation (O.R.) in the left upper corner. b) An SEM micrograph of the tilted sample.
Besides the orientation relation between WC and W₂C, also an orientation relation between W₂C and TiC is present. The orientation relations can be described as follows:

\[
\begin{align*}
[1\bar{1}0]_{\text{TiC}} & \parallel [1\bar{2}10]_{\text{W}_2\text{C}}, (111)_{\text{TiC}} \parallel (0001)_{\text{W}_2\text{C}} \\
[1\bar{2}10]_{\text{W}_2\text{C}} & \parallel [1\bar{2}10]_{\text{WC}}, (0001)_{\text{W}_2\text{C}} \parallel (0001)_{\text{WC}}
\end{align*}
\]

The relation between W₂C and TiC is a common orientation relation between hexagonal (close-packed) and cubic structures [31]. In this orientation relation the close-packed directions and planes of both phases are parallel.

Whenever an orientation relationship is observed the [0001] direction in W₂C is about perpendicular to the WC/W₂C interface (and it holds that (0001)_{WC} \parallel (0001)_{W₂C} \parallel WC/W₂C interface). For the W₂C grains which do not satisfy the orientation relation, the [0001] direction is in general tending to be perpendicular to the WC/W₂C interface as well. From these observations we

\[250 \text{ nm}\]

**Figure 4.14:** TEM bright field image, with corresponding diffraction patterns, of a reaction zone with WC and W₂C in the [110] and TiC in the [110] zone axes. In this reaction zone an orientation relation between WC particle, W₂C layer and TiC layer is present.
may conclude that W2C prefers to grow with the [0001] direction perpendicular to the WC/W2C interface. If the orientation of WC allows an orientation relation, without disturbing the preferred growing direction too much, an orientation relation will be present. The orientation of the W2C layer with respect to the WC particle may be imposed by different reasons, for example interfacial strain (lattice misfits), heat flux (thermal conduction) and interfacial free energy.

The interfacial strain between WC and W2C may be a reason for a certain orientation. The lattice parameter mismatches for both lattice parameters, i.e. $a_0$ and $c_0$, between WC and W2C are:

$$\delta_a = \left| \frac{a_{0,W2C} - a_{0,WC}}{a_{0,WC}} \right| = 0.03 \quad \text{and} \quad \delta_c = \left| \frac{c_{0,W2C} - c_{0,WC}}{c_{0,WC}} \right| = 0.68.$$

Because the lattice mismatch in $a_0$ is that low, the (0001) interplanar distances of WC and W2C are almost similar. Therefore, it is favorable for W2C to have the (0001) (basal planes) planes attached on the (0001) of WC. In this configuration a coherent interface with minor coherency strains or a semicoherent interface with a low density of misfit dislocations may be formed (1 misfit dislocation every 30 planes). The (011̅0) planes (first order prism planes) of WC are extended by the (011̅0) planes of W2C. A schematic picture of this configuration is shown in Fig. 4.15a, where the Bravais unit cells of WC and W2C are illustrated. In Fig. 4.15a, the mutual $c/a$ ratios of both unit cells are according the literature values, but the relative atom sizes are taken much smaller to make all the atoms in the unit cell visible.

The next reaction layer, TiC, minimizes the lattice misfits when the (111) planes are fitted on top of the (0001) planes of W2C. The atomic configurations of the (111) planes in fcc based crystal structures are similar to the basal planes in hexagonal structures. The atomic distances in the (111) planes of TiC are 3.05 Å, which is close to the atomic distances in the (0001) planes of W2C (= $a_0$= 2.98 Å). Therefore, the misfit is only 0.02 when (111) planes of TiC are fitted on top of the (0001) planes of W2C.

The experimentally observed orientation relations, both between WC/W2C and W2C/TiC (Fig. 4.13 and Fig. 4.14), agree with the configurations based on minimal lattice mismatches, which is an indication that the mismatch plays a role in the formation of the reaction layers. This is a commonly known effect in
Injection of WC particles in Ti-6Al-4V growing processes in equilibrium conditions, but a somewhat surprising in a non-equilibrium process like the laser process where the reaction layers are formed in a relatively short time (the order of milliseconds).

However, because this orientation relationship is not frequently observed this is not the main mechanism that determines the W\textsubscript{2}C orientation. If the crystallographic configuration of the WC surface allows the orientation relation without changing the growing direction from [0001] too much, i.e. the WC/W\textsubscript{2}C interface should be close to (0001), W\textsubscript{2}C will minimize the lattice

Figure 4.15: a) Schematic drawings of the Bravais unit cells of WC and W\textsubscript{2}C. b) Schematic drawings of two typical W\textsubscript{2}C/WC interfaces. In the left drawing the crystallographic orientation of WC allows no matching of the (01\textbar{}10) planes and simultaneously obeying the preferred growing direction of W\textsubscript{2}C ([0001]). Therefore no orientation relation is present. In the right image the orientation of WC allows both matching and growing in the [0001] direction of W\textsubscript{2}C, therefore an orientation relation will be present.
misfits by nucleation of the basal planes on top of the basal planes of WC. If this fit is not possible, the orientation of the W₂C grain is solely determined by preferred growing in the [0001] direction, which appears to be the strongest requirement during growth of W₂C. The interface is incoherent in this case. The orientation of the W₂C grains is not very strict, which results in many small W₂C grains compared to the large W₂C grains where the orientation relationship is fixed by both growing direction and minimal lattice misfit. The mechanisms that determine the orientation of the W₂C grains are visualized in Fig. 4.15b, where the left drawing the imposed growing direction does not allow the minimal lattice mismatch, therefore no orientation relation will be present. In the right image the preferred growing direction and the minimal lattice mismatch can both be satisfied. Therefore, an orientation relation may be present.

Because the heat flux is, just as the [0001] direction in W₂C, perpendicular to the particle interface, it is reasonable to ascribe the preferred growing direction to this heat flux. However, according to thermal conductance in the W₂C crystal, growth perpendicular to [0001], i.e. [1 1 0 0] or [1 1 2 0], is expected. We may therefore conclude that the heat flux is not responsible for growing in the [0001] direction.

A third possible reason for the preferred growing direction might be the interfacial free energy. W₂C is growing in the [0001] direction because the formation of (0001) planes is, due to lower interface energy, favorable. These planes consist of mono-atomic C and W layers (1 layer of C followed by two layers of W) and have a minimal number of broken bonds at the solid/liquid interface [32].

The presence of such an orientation relation may have a positive effect on the bonding between the layers because only small lattice misfits are present. These small misfits result in interfaces with a limited number of irregularities. From the fact that the orientation relations between the WC/W₂C and W₂C/TiC reaction layers will be present if the surface of WC is a (0001) plane, it is preferable to use powder that is consisting of particles with (0001) surfaces. Therefore, it is advisable to use powder that is, for example, produced by cleavage of larger WC pieces, since (0001) planes are cleavage planes of WC. Most particles will therefore have one or more (0001) surfaces.
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Laser melt injection experiments of a single grain powder produced by cleavage are carried out as well and indeed many (0001) surfaces with the corresponding orientation relations were found. In these cases the particles are injected behind the center of the laser beam to minimize the reaction between particle and matrix. An example of an OIM measurement is shown in Fig. 4.16, where the phase map with grain boundaries of such an injected particle is shown.

Figure 4.16: Phase map and grain boundaries of a reaction zone around a single crystal particle. The orientation of the WC and some W2C and TiC grains is visualized by plotting the axonometric projections of the cells. At the left and right reaction layers the orientations relations ([0001]_{WC} // [0001]_{W2C} // [111]_{TiC}) are present because the WC surfaces are the (0001) planes. At the top reaction layer no orientation relation is present.
Look-up tables of WC, W$_2$C and TiC were used. Ti and W are not used because only orientation of the particle with the reaction layers are of interest and adding look-up tables slows the indexing process down. For this reason the area outside the TiC layer in the phase map is not indexed correctly because the phases of that area (W and Ti) were not included in software. The surface quality of the W$_2$C layer is rather poor due to sample preparation. Therefore the quality of Kikuchi patterns is in many cases too low to index properly. However, there are enough suitable patterns to obtain the correct orientation. Scratches on the surface of the WC particle result also in incorrectly indexed points, as can be seen by the lines in Fig. 4.16.

The axonometric projections of the crystal cells of some grains are shown in Fig. 4.16. The WC particle is a single crystal particle and has two (0001) surfaces, one on the left side and one on the right side. The orientation relations with [0001]$_{WC}$ // [0001]$_{W2C}$ // [111]$_{TiC}$ are present on these surfaces. The upper surface of the WC particle is not a (0001) plane and therefore no orientation relations are present here. At this side the W$_2$C consists of more grains. The [0001] direction in these grains is for all grains approximately perpendicular to the WC/W$_2$C interface, as observed before. The subsequent TiC layer is a single grain with the [001] direction about parallel to the W$_2$C/TiC interface.

4.4 Summary

Laser melt injection is a suitable technique to form a WC$_p$/Ti MMC in the top layer of Ti-6Al-4V. The laser processing window allows a certain variation of the laser track dimensions and volume fraction of WC$_p$. In addition, it is possible to coat a larger surface area by producing multiple adjacent tracks with an overlap of about 10%. An important finding is that the particle distribution is homogeneous and that the particles are injected over the whole depth and entire width of the melt pool.

During the laser process, new phases are formed: TiC, W and W$_2$C. In the top of the resolidified matrix large amounts of TiC and W dendrites are present because of the reaction between liquid or dissolved WC, which is dripped off the WC particle during penetration in the melt pool, and the Ti melt. The liquid or dissolved WC that stays at the particle during penetration reacts with the Ti melt to form a W$_2$C and TiC reaction layer around the WC particles.
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$W_2C$ tends to grow in the [0001] direction. When the surface of the WC particle is close to the (0001) planes, $W_2C$ minimizes the misfits at the $WC/W_2C$ interface by growing according an orientation relation. This occurs when the [0001] growth direction is preserved and the (0001) planes of $W_2C$ fit on top of the (0001) planes of WC. In addition the (111) planes of TiC fit on top of the (0001) planes of $W_2C$. The presence of orientation relations between the reaction layers indicates there is some interaction between the layers, which is positive for the bonding. Therefore, it is advisable to use powder that consists of WC particles with preferred (0001) surfaces during the laser melt injection process. Powder produced by cleavage is, for example, a suitable powder for the laser melt injection process.

4.5 References

Chapter 4


