Laser melt injection of ceramic particles in metals
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Chapter 5

Microstructural response on loading

5.1 Introduction

The objective of this study is to improve the surface properties, in particular the wear properties, by injecting ceramic particles in the top layer of metals. The formation of a Metal Matrix Composite (MMC) layer may be an elegant method to enhance the performance, without affecting the bulk properties [1]. The mechanical properties of metal matrix composites are, besides particle size and particle volume fraction, determined by the bonding between the ceramic particles and metal matrix. In addition, the reaction products that are present in the material are relevant [2]. In the case of MMC layers produced by the Laser Melt Injection (LMI) process, the microstructure is dominated by reaction products, both at the particle-matrix interfaces and in the melt pool matrix, as discussed in chapter 3 and chapter 4. Injecting SiC particles in Al results in the formation of Al₄C₃ and Al-Si eutectic areas, while injecting WC in Ti-6Al-4V results in the formation of W₂C, TiC and W.

The influence of these phases on the bond strength between the particle and resolidified matrix is of great interest for potential applications of the coatings. Quantitative measurement of the bond strength is difficult to access because in the coating many particle-matrix interfaces are present. Standard tensile tests are performed to obtain the global tensile strength of the complete coating. Although, in practice, the MMC coatings are exposed to compressive loads, the coatings have to withstand tensile loads just outside the compressive area. In
addition to the bond strength of the particles with the matrix, also the result of
the tensile test will be strongly influenced by the reaction products that are
present between the particles.

The response of microstructural features in the coatings on loading can be
analyzed by qualitative measurements. Therefore, it is chosen to perform so-
called in-situ tensile tests, i.e. deforming the coating by applying a tensile force
while simultaneously observing the deformation in the coating by using a
microscope. Crack nucleation and propagation can be observed in detail by
performing these tests inside a Scanning Electron Microscope (SEM) [3,4].

In this chapter, both standard tensile tests and in-situ tensile tests of both
materials systems (SiC particles in Al and WC particles in Ti-6Al-4V) are
discussed. Furthermore, fracture surfaces of the material systems are analyzed.
In addition, nano-indentation experiments are performed in the reaction zone
of the WC/ Ti-6Al-4V system. All these experiments are carried out to reveal the
strong and weak spots in the microstructure.

5.2 SiC particles in Al

5.2.1 Tensile testing

The SiC_{p}/ Al MMC coatings are studied by 'standard' tensile tests. The
dimension of the single laser tracks, which have a small width and depth, limits
the dimension of the tensile samples. The tensile samples have a square cross-
section area of about 1 mm x 1 mm, i.e. the sample consists of only the MMC
material. The gauge length of the samples is about 20 mm. The loading
direction corresponds to the moving direction during the laser process, i.e.
parallel to the longitudinal direction of the laser track. The tensile tests were
performed by an INSTRON 1195 tensile test machine. The strain rate was
0.01 s^{-1} and the sample deformation was measured by a non-contact video-
extensometer (Messphysik ME-46), which is briefly described in chapter 2.

As a substrate material an Al-Si cast alloy was used instead of pure (99.6%) Al
that was examined in chapter 3. The reason for this is to provide data for
industrial Al alloys instead of the model system. The strength of the latter is
much lower. The Al-Si alloy contains 10 at-% Si and 0.4 at-% Mn. The
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The microstructure of the SiCp/Al-Si MMC layer, produced by the laser melt injection process, is comparable to the SiCp/Al MMC layer that is described in chapter 3. The former one contains, of course, more Si in the melt pool matrix, i.e. between the SiC particles.

Three different kinds of tensile samples were prepared: samples of untreated substrate material, samples of laser melted substrate material and samples with the injected particles. The samples of the laser melted material are laser treated with the same laser parameters as used during the laser melt injection process but without injection of particles. These samples are studied to reveal the contribution of the changes in the microstructure of the substrate material due to rapid solidification during laser processing. Figure 5.1 shows the (engineering) stress-strain curves of the different kinds of tested samples. Pure Al (99.6 at-%) was measured as a reference sample. From these curves the ultimate tensile strength and ductility are obtained. The ultimate tensile strength is defined as the maximum stress that can be sustained during tension before fracture. The ductility is defined as a measure of the material's ability to undergo plastic deformation before fracture. The ductility (EL) is quantified as the percentage of elongation at the maximal tensile stress. The measured values of the tensile strength and ductility are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>Ductility (EL%, l₀= 20 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (99.6 at-%)</td>
<td>65</td>
<td>16.3</td>
</tr>
<tr>
<td>Al-Si (10 at-% Si)</td>
<td>125</td>
<td>6.1</td>
</tr>
<tr>
<td>Al-Si, laser melted</td>
<td>167</td>
<td>4.8</td>
</tr>
<tr>
<td>SiCp/ Al-Si MMC</td>
<td>140</td>
<td>2.3</td>
</tr>
</tbody>
</table>
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Figure 5.1: Stress-strain curves of different tensile tested samples. A pure Al sample, an Al-Si (10 at-%Si) alloy sample, a laser melted Al-Si sample and a SiC\_p/Al-Si MMC sample.

As expected, the reference sample has the lowest strength (65 MPa) and highest ductility (16.3%). The tensile strength of the Al-Si alloy is increased by a factor 2, compared to the pure Al sample. The ductility decreased with a factor of 3 to about 6%. Laser melting and subsequent rapid solidification increases significantly the tensile strength to 167 MPa and decreases slightly the ductility to 4.8%. The increase in strength after laser melting is due to the change in microstructure after rapid solidification. The grain size will be much smaller after rapid solidification, which may result in an increase in tensile strength. In addition, the thermal stresses induced during the laser processing may increase the tensile strength. The SiC\_p/ Al-Si MMC, produced by the laser melt injection process, has a lower tensile strength than the Al-Si laser melted material, however, the tensile strength (140 MPa) is higher than the original Al-Si material. The ductility of the MMC is very low (2.8%).

From these results we can conclude that injecting the SiC particles increases the tensile strength with respect to the substrate material. Nevertheless, the increase
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of this strength is mainly due to the laser melting. The high dislocation density generated by the large difference (10:1) between the coefficients of thermal expansion of Al and SiC is another contribution to the strengthening effect [5]. The low ductility of the SiCp/Al-Si MMC is due to the brittle phases, i.e. SiC and Al4C3, that are present after laser melt injection. The (absolute) results strongly depend on the particle volume fraction [6]. In addition, it is known that small changes in the microstructure of the matrix of a metal matrix composite may have a significant contribution to the tensile strength and ductility [7].

The purpose of the MMC coating is to increase the wear resistance of Al workpieces. To achieve this, it is chosen to add hard wear resistant, but brittle particles. Therefore a decrease in ductility is inevitable. This decrease in ductility is not dramatic because the MMC material is only a coating. During applications the MMC coating is attached to a ductile substrate that is able to absorb more mechanical energy.

5.2.2 In-situ tensile testing

In-situ tensile tests on wear resistant coatings provide rather dynamic than static observations of the nucleation and propagation of cracks during straining. Single SiCp/Al MMC laser tracks were produced in a 99.6 at-% Al substrate, according the laser melt injection process described in chapter 3. The SiC volume fraction is about 35 %. The microstructure of the SiCp/Al MMC tracks is described in detail in chapter 3. Small and flat tensile specimens with a thickness of 1 mm, which is the thickness of the MMC coating, were cut from the Al substrate surface by spark erosion. V-type notches were made in the middle of the samples by laser cutting. The dimensions of the samples and the position and orientation of the laser track can be found in chapter 2, section 2.2.1. The direction of the specimen loading corresponds to the moving direction during laser injection, i.e. in the longitudinal direction. The surface of the specimens was mechanically ground and polished to observe the microstructure.

The in-situ tensile test samples were loaded by a special tensile-compression stage (Kammrath & Weiss) inside an environmental scanning electron microscope (FEG-E-SEM Philips XL30 (Field Emission Gun)), which enables us to observe deformation of the specimen surface simultaneously upon loading the sample. Elongation data as well as applied tensile force were recorded during loading. The working length of the sample, after clamping, is about
24 mm. The displacement velocity is set as 0.5 µm/ s, which gives a deformation rate of about $2.1 \times 10^{-5}$ s$^{-1}$. Besides observing the microstructure during loading, the loading can be halted to observe different parts of the sample or to record digital micrographs. It is possible to record the in-situ experiments on videotape as well.

The crack nucleation is observed by straining the sample to a macroscopic strain of about 0.4%. An SEM micrograph of such a strained sample is shown in Fig. 5.2. In this figure the tensile force is applied in the vertical direction. Of course, features perpendicular to the tensile axes are preferred to initiate cracks. Three favourable crack nucleation mechanisms are observed. These three types appeared simultaneously in different places near the stress concentrators, i.e. the notches. Decohesion of the Al$_4$C$_3$ plates, which are present in the melt pool matrix, from the Al matrix is one nucleation mechanism. Another common nucleation mechanism is brittle fracture of the injected SiC particles. A third, but much less frequently observed nucleation mechanism is decohesion of the SiC from the matrix. These three different nucleation modes are indicated by numbered arrows in Fig. 5.2.

![Figure 5.2: After elongating the sample 100 µm (0.4%) three types of crack initiation sites are visible: 1) Decohesion of Al$_4$C$_3$ plates and Al matrix, 2) Cracking of the SiC particles and 3) Decohesion of SiC particles from the matrix. The third type occurs less frequently. The tensile stress is applied in the vertical direction.](image)
The brittle fracture of SiC particles is shown in Fig. 5.3. The cracks, which are nucleated in the SiC particles, propagate through the Al$_4$C$_3$ reaction layers towards the matrix, and not along the Al$_4$C$_3$/ SiC or Al$_4$C$_3$/ Al interface. This is an indication that the bonding between particle and matrix is, in these cases, strong enough to transfer the load from the matrix to the particle. As showed in Fig. 5.2 in some cases decohesion between particle and matrix occurs, i.e. the crack propagates along the particle/ matrix interface. However, because the latter fracture phenomenon is not frequently observed, the bonding between particle and matrix is reasonable.

The weakest features in the laser melt injected SiC$_p$/ Al MMCs are the Al$_4$C$_3$/ Al interfaces of the plates in the melt pool matrix. This becomes visible after straining the sample further to 150 µm (0.6%). Figure 5.4 shows that decohesion of the Al$_4$C$_3$ plates from the Al matrix, which are preferred nucleation sites for cracks, is important for crack propagation. This decohesion is the predominant fracture mechanism in the produced MMC coatings. The cracks propagate along the randomly distributed Al$_4$C$_3$ plates. Furthermore, brittle fracture of the SiC particles and, to a less extent, decohesion of the SiC particles from the matrix influence the crack propagation path. In other words, the crack propagation occurs by connecting of the three crack nucleation sites.

**Figure 5.3:** Failure initiation by brittle fracture of the SiC particles. The crack propagation through the Al$_4$C$_3$ reaction layer is also visible. The tensile stress is applied in vertical direction.
Figure 5.4: Crack propagation through the Al matrix along the Al₄C₃ plates. The sample is 150 µm (0.6%) elongated in the vertical direction.

It is difficult to separate the different stages of crack nucleation and propagation because during further straining many new cracks are initiated. Figure 5.5 shows the situation in the advanced stage of failure where the sample is strained 318 µm (macroscopic strain ~2%). Usually more than one predominant crack propagates through the sample, in the direction macroscopically perpendicular to the applied tensile stress. Finally, single crack fracture is caused by ductile fracture of the Al matrix.

Observation of the fracture surfaces confirms the four different types of failure mechanisms that are observed during fracture: decohesion of the Al₄C₃ plates from the Al matrix, cleavage of the SiC particles, decohesion of the SiC particles form the Al matrix and ductile fracture of the Al matrix. Figure 5.6 shows an SEM micrograph of a fracture surface where all four types are present. Decohesion of an Al₄C₃ plate is indicated by arrow #1 in Fig. 5.6. The surface of the Al₄C₃ plate is visible after fracture. Arrow #2 indicates the cleavage surface of a SiC particle. Decohesion of a SiC particle from the matrix is indicated by arrow #3. The original surfaces of the SiC particle are visible after fracture. The typical morphology (dimples) of ductile fracture of Al is indicated by arrow #4.
Figure 5.5: Crack propagation in the advanced stage of straining (elongation = 318 \( \mu \)m, i.e. strain = 2\%). Several cracks, approximately perpendicular to the applied stress, cause the final failure.

Figure 5.6: SEM micrograph of a fracture surface of SiC\(_{p}\)/Al MMC produced by the laser melt injection process. The white line indicates the edge between the fracture surface (lower part) and surface which was polished and observed during the in-situ tensile test (upper part). The four typical fracture mechanisms are indicated by arrows: 1) decohesion of an Al\(_{4}\)C\(_{3}\) plate, 2) brittle fracture of a SiC particle, 3) decohesion of a SiC particle and 4) ductile fracture of Al.
5.2.3 Discussion

The in-situ tensile experiments showed that the presence of Al\textsubscript{4}C\textsubscript{3} in the melt pool matrix of the SiC\textsubscript{p}/Al MMCs produced by the laser melt injection process, plays an important role in the crack nucleation and propagation mechanisms. Al\textsubscript{4}C\textsubscript{3} appears in two different kinds, as illustrated in chapter 3. Small Al\textsubscript{4}C\textsubscript{3} plates as a reaction layer between the SiC particles and Al matrix and larger Al\textsubscript{4}C\textsubscript{3} plates in the melt pool matrix (see Fig. 3.15).

That decohesion of the SiC particles from the matrix is not the most frequently observed crack nucleation and propagation mechanism is an indication that the relatively small Al\textsubscript{4}C\textsubscript{3} plates in the reaction layer may play a positive role in the strengthening of the MMC. These plates are (semi-) coherent with the SiC particles. This may be concluded because their crystal orientation is influenced by orientation of SiC, which is discussed in chapter 3. The adjacent plates form a high interface roughness at SiC\textsubscript{p}/Al interface, which causes relatively good mechanical bonding. Thus the reaction zone may form a good anchorage for the SiC particle in Al matrix. However, when the Al matrix is deformed, Al\textsubscript{4}C\textsubscript{3} plates transfer the tensile stress to the particle surface, which may lead to the failure of the SiC particle. Therefore, the surface roughness may also act as a local stress concentrator and due to the low fracture toughness of SiC the brittle fracture initiates and propagates through the particle by a cleavage mechanism.

The large Al\textsubscript{4}C\textsubscript{3} plates in the melt pool matrix play a negative role in the laser produced SiC\textsubscript{p}/Al MMC. The plates easily separate from the matrix by decohesion, forming the main crack nucleation and propagation mechanism in the MMC coatings. If the number of Al\textsubscript{4}C\textsubscript{3} plates in the matrix would had been smaller this negative effect on the strength would have been much smaller. However, the number of plates is so high, that the plates are almost linked. This makes it possible to form large cracks along the Al\textsubscript{4}C\textsubscript{3} plates. The way to postpone the failure initiation process towards a higher stress level lies in suppressing the formation of Al\textsubscript{4}C\textsubscript{3} phase in the matrix. Then only two predominant mechanisms of failure will be present, i.e. particle cracking and SiC\textsubscript{p}/Al interface debonding. Such behaviour was indeed observed in SiC\textsubscript{p}/Al MMC produced by extruding mixtures of Al alloy powder and SiC particles [8] as well as in layered SiC\textsubscript{p}/Al6061 MMC produced by spray atomisation and co-deposition [9].
Above outcomes on positive and negative effects of Al₄C₃ plates in the MMC coatings are based on the in-situ tensile tests. In addition, it is known from literature that Al₄C₃ formation has several undesirable effects for the MMC properties [10,11]. Al₄C₃ at the SiC/Al interface may degrade the interfacial strength due to the high brittleness. Another disadvantage is that Al₄C₃ can be susceptible to corrosive environments because Al₄C₃ is unstable in environments such as water, methanol and HCl [12].

The formation of Al₄C₃ is inevitable when SiC gets in contact with liquid Al [13]. In the SiC powder that is used for the laser melt injection process also free carbon is present, resulting in more Al₄C₃ plates in the melt pool matrix. In literature several suggestions to prevent Al₄C₃ formation are reported. Covering the SiC particles with a coating (for example SiO₂ by oxidizing the SiC particles) to avoid direct contact between SiC and liquid Al is one suggestion [10]. Another suggestion is addition of Si to the Al matrix to shift the following reaction to the left [13,14]:

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

Both suggestions are not helpful in the laser melt injection process. The strong interaction between the laser beam and the injected powder easily destroys such a protective layer around the particles. Adding Si is not preventing the Al₄C₃ formation as well. A Si content of about 7 at-% should be sufficient to suppress the Al₄C₃ formation [14], however laser melt injection experiments carried out on Al containing up to 20 at-% Si did still not result in less Al₄C₃ formation. The reason for this is that due to the rapid solidification during the laser process the chemical reaction is not occurring in equilibrium conditions. These conditions are needed to shift the equilibrium of the reaction to the left.

A third solution to prevent Al₄C₃ formation is adding another element, besides SiC, in the powder flow that has a higher affinity for C than Al. Ti is such an element that result in the formation of TiC instead of Al₄C₃. This is useful because the mechanical and chemical properties of TiC are better than the properties of Al₄C₃.

The formation of Al₄C₃ may be reduced by keeping the temperature in the melt pool as well as the temperature of the SiC particles as low as possible. Injection of the particles behind the center of the laser beam, to reduce the time during which particles are exposed to laser light, is not an option to reduce the
temperature increase of the particle. The small processing parameter window in which particle injection is successful only allows injection in the center of the laser beam.

5.3 WC particles in Ti-6Al-4V

5.3.1 Tensile testing

Standard tensile tests of WC_p/ Ti-6Al-4V MMCs [4] that are produced by the laser melt injection process are performed by the same procedure as described in section 5.2.1. The cross-section area of the tensile samples is 1.5 x 1.5 mm; the working length of the samples is 15 mm. Three different types of samples are tested: samples of the substrate material (Ti-6Al-4V), samples of laser melted substrate material and samples with the injected WC particles. The microstructure of the laser melt injected WC_p/ Ti-6Al-4V is extensively discussed in chapter 4.

Typical stress-strain curves are shown in Fig. 5.7. In this figure, one stress-strain curve of the substrate material, one stress-strain curve of the laser melted substrate material and three stress-strain curves of the laser produced MMCs are depicted. Laser melting and subsequently rapid solidification of the original substrate material, Ti-6Al-4V, slightly increases the tensile strength (from 1000 MPa for original Ti-6Al-4V to 1150 MPa for the laser melted samples) but strongly decreases the ductility from about 8% to 2.5%. This behaviour is expected because the microstructure of the commercially Ti-6Al-4V is optimized by accurately investigated thermal treatments to reach the best mechanical characteristics. The additional laser heat treatment changes the optimal microstructure to a microstructure that is typical for rapid solidification, which increases the strength but lowers the ductility. Another reason for the reduction of ductility may be the residual stresses that are present after laser treatment, due to the thermal gradients in the melt pool.

The stress-strain curves of the laser melt injected WC_p/ Ti-6Al-4V show that the tensile properties are much worse than the tensile properties of the original Ti alloy. The tensile strength is around 400 MPa and the ductility is about 0.5%, i.e. the material becomes very brittle. In the insert in Fig. 5.7 the stress-strain curves of the MMCs are magnified. In this insert a non-linear behavior at the beginning of loading is visible.
Figure 5.7: Stress-strain curves of different tensile tested samples. A untreated Ti-6Al-4V sample, a laser melted Ti-6Al-4V sample and three laser melt injected WC$_p$/Ti-6Al-4V MMC samples. The latter three are shifted from the origin to make them visible. A magnification of the MMC samples is shown in the insert.

This behavior indicates that the formation of local cracks and plastic deformation starts already at the beginning of straining. At an external stress level in the range of 250-300 MPa, small kinks appear in the curves, which is an indication of the formation of a macro crack. The macro crack leads to final failure at a stress level of about 400 MPa. It is observed that fracture occurs randomly along the sample length, however, by dividing the sample into 3 to 5 segments by markers that can be observed by the video extensometer, fracture is always localized inside the segment in which the kinked stress-strain curve is observed. The macro crack that is initiated first is responsible for final failure. The fracture surface is macroscopically oriented perpendicular to the tensile axis.

The route to increase the wear resistance of the coating by adding hard but brittle particles suffers from a high loss in ductility. Besides the brittle WC particles, brittle reaction products as W$_2$C and TiC are present in the MMC that results in the formation of a hard but brittle coating. This does not necessarily
lead to a deleterious effect on the quality of the MMC under wear conditions because the MMC is attached on top of a ductile substrate. The formation of local cracks in an early stage of straining may imply that high internal stresses are present in the MMC coatings. This will be discussed in the next two sections.

5.3.2 In-situ tensile testing

To know more about the fracture behavior and to couple the observed fracture effects during the standard tests to microstructural features, in-situ tensile experiments in SEM are performed. The same experimental procedures (sample size, equipment and analyzing methods) as the in-situ tensile experiments on the SiCp/Al MMC are used.

The first striking result is that before straining small cracks are present in WC particles that are close to the notch. These cracks probably arise due to the high internal stresses in the samples. The notches, which act as stress concentrators, may therefore initiate cracks inside the WC particles. An example of an area near a notch of an unstressed sample is shown in Fig. 5.8a. The internal stresses will be discussed in section 5.3.3. The cracks in the WC are often branched and are temporary delayed at the particle/matrix interface. Applications of a small external load leads to cracking of the WC particles, as shown in Fig. 5.8b.

Figure 5.8:  a) Area near notch before straining showing some cracks in the WC particles. b) Area near notch after minor straining 0.3% (elongation of 56 µm) showing the crack propagation at the initial stage of failure.
Two distinguishable modes of failure of the particles are observed: intergranular brittle fracture in the center of the WC particles and brittle fracture along the WC/W₂C interface. An SEM micrograph of in-situ observed failure along the WC/W₂C is shown in Fig. 5.9a. Observation of the fracture surfaces confirmed the two modes of particle failure, which is shown in Fig. 5.9b. If the TiC reaction layer around the particle is relatively thick, brittle fracture in this layer is occasionally observed. Decohesion between W₂C and TiC is never observed. The most frequently observed fracture mechanism, in an early stage of failure, is the intergranular brittle fracture inside the WC particles. Therefore, the granular WC particles are an important source of crack nucleation.

After cracking of the WC particles, cleavage of TiC dendrites in the melt pool matrix is the main failure process. Although the cracks are macroscopically propagating perpendicular to the applied stress, the orientation of the TiC may redirect the cracks locally, as demonstrated in Fig. 5.10a. Many longitudinal cross-sections of TiC dendrites are observed on the fracture surfaces. This indicates that the failure process minimizes the work of deformation by cleavage of TiC dendrites along their trunks. An example is shown in Fig. 5.10b. In the areas around the TiC dendrites ductile fracture of the Ti-6Al-4V occurs, which is shown by the dimpled areas in Fig. 5.10b.

**Figure 5.9:** a) In-situ observation of failure by decohesion along the WC/W₂C interface. b) Fractographic observation of the two types of failure inside the WC particles: intergranular cleavage (I) and decohesion along the WC/W₂C interface (II).
Further elongation of the sample results in the formation of even larger cracks. The tips of these cracks form stress concentration fields that induce cracks in embedded WC particles in the neighborhood of these tips, as was the case for the notches. Between these particles, the cracks propagate through the TiC dendrites, followed by the Ti alloy, which elongates the large crack. Stress concentration fields at the new tip induces failure of the particles in the surrounding area. These processes repeat, which results in a jerky type of crack propagation. Usually, two or a few main cracks propagate in the sample, as is demonstrated in Fig. 5.11. The main cracks follow the path with a high density of WC particles. Final failure occurs when two opposite cracks join or one crack reaches the opposite side of the sample.

Figure 5.10: a) In-situ observation of crack propagation by cleavage of TiC dendrites (dark features). b) Fractographic observation of the cleavage of TiC dendrites and ductile fracture of the Ti alloy matrix.

Figure 5.11: Overview of crack propagation during testing close to final failure. Two main cracks are visible.
5.3.3 Discussion

According to the observations of cracks in the WC particles near the notches before straining indicates that internal stresses, induced during the laser melt injection process, play an important role in the fracture behavior. There are two different causes for internal stresses in MMCs produced by the laser melt injection process. The laser process itself induces stresses in the laser treated areas because the thermal gradients induced by the laser treatment result in residual stresses, both in the laser produced coatings [15] and laser surface melting treatments [16]. Besides this, the mismatch in the thermal expansion coefficients between the metal matrix and ceramic particle induces stresses in the particles and the surrounding area after cooling [17,18].

Residual stresses induced by laser treatment due to the thermal gradients can be either compressive or tensile. X-ray measurements on laser melted Ti-6Al-4V showed that the stresses are in the order of ±200 MPa [16], tensile in the center area of a laser track and compressive near the edges. It should be noted that the laser experiments were carried out with a CO₂ laser, which has a Gaussian energy distribution instead of the top-hat distribution of the YAG laser that is used in our experiments. The top-hat energy distribution induces less thermal gradients. However, those measured stress values are an indication for the stresses in our laser experiments. Phenomenological analyses of residual stresses in laser coatings showed that the longitudinal and transverse components of the residual stresses are nearly equal both in the laser track as in area close to the laser track [15].

To estimate the amount of stress that is induced by the mismatch in the thermal expansion coefficients, a misfitting sphere model [17], based on the method described by Eshelby [19] is used. In this model stress and strain are obtained for a spherical precipitate in a matrix, by the absence of plastic relaxation, i.e. under purely elastic conditions. For simplicity, the reaction layers (TiC and W₂C) are ignored. A spherical particle, with a radius of a(1+ε) in the absence of constraints, a shear modulus Gₚ and Poisson ratio νₚ, is placed into a spherical hole, with a radius a, in an infinite matrix with shear modulus Gₘ and Poisson's ratio νₘ. ε is the difference between the thermal expansion coefficients times the temperature difference during cooling, i.e. ε=(αₚ-αₘ)ΔT. Supposing that the effective radius of the precipitate is a(1+βε) under the constraint imposed by the matrix and by fitting the particle in the hole, the displacements can be calculated by applying the correct boundary conditions. From the
displacements the strains can be obtained and by using Hooke's law, the stresses are calculated. The calculations are described in the appendix at the end of this chapter. The radial, \( r \), and tangential, \( \theta \), stress components in the particle and matrix are:

\[
\sigma_r^p = \sigma_\theta^p = 2G^p \left( \frac{1+\nu^p}{(1-2\nu^p)} \right) (\beta - 1) \epsilon, \\
\sigma_r^M = -2\sigma_\theta^M = -4G^M \beta \epsilon \left( \frac{a}{r} \right)^3
\]

where \( r \) is the distance from the center of the particle that is chosen as the origin of the spherical coordinate system. The constant \( \beta \), which is a function of \( G^p, \nu^p, G^M \) and \( \nu^M \), can be calculated by using the fact that the matrix and particle are in equilibrium. Therefore, the radial stress component of the matrix (\( \sigma_r^M \)) must be equal to the hydrostatic stress of the particle (\( \sigma_r^p \)) at the particle-matrix interface (\( r = a \)). Inside the particle, a hydrostatic compression is present. The magnitude is independent of the particle size. It depends on the material properties and linearly increases with the temperature misfitting. Outside the particle both radial and tangential stresses rapidly decrease (1/\( r^3 \)). The material properties that are needed to calculate the stresses in the WC/\( p/ \) Ti-6Al-4V system are given in Table 5.2 [20,21].

The radial and tangential stress components, as a function of distance from the center of the particle with a diameter of 40 \( \mu m \), are plotted in Fig. 5.12. The temperature range in which the thermal expansion coefficients induce elastic stresses is estimated to be from around 1000 \( ^\circ C \) to room temperature. The thermal expansion coefficient for Ti-6Al-4V is taken constant at 9.5·10^{-6} \( ^\circ C^{-1} \). The expansion coefficient of WC is taken as the average of the coefficients of the

| Table 5.2: Material properties that are needed for the stress calculations. |
|-------------------|-------------------|
| Ti-6Al-4V          | WC               |
| Thermal expansion coeff. (\( \cdot 10^{-6} \)  \( ^\circ C^{-1} \)) | 8.5 at 0 \( ^\circ C \) | 5.2 for (0001) planes |
|                     | 10.5 at 800 \( ^\circ C \) | 7.3 for (10\( \bar{1} \)0) planes |
| Young's modulus (GPa) | 110              | 700 |
| Poisson's ratio     | 0.33             | 0.20 |
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(0001) and (1010) planes (6.3 \times 10^{-6} \, ^{\circ}C^{-1}). The calculated hydrostatic compression in the particle is therefore about -350 MPa. Because the stress in the particle is hydrostatic compressive, the cracking of the WC particle can not be explained.

When a notch is created, which tip is located in or close to the laser track, the stress field induced by the notch destroys the approximately symmetric stress-state around the particles that are located close to the notch. Therefore the stress-state of these particles is not in hydrostatic compression anymore and the formation of brittle cracks inside the WC particles may occur at the weak grain boundaries. The macro crack that will develop will induce a stress field that destroys the symmetry of the stress field of the neighboring particles, which will induce cracks according the same process. This is confirmed by analyzing the percentage of cracked particles after fracture. In the crack surrounding 85% of the WC particles show cracks inside, while in the areas outside the crack only 20% of the particles are cracked.

Once a sharp crack is formed in the WC particle, further crack propagation through the surrounding TiC reaction layer does not need a substantial increase of external tensile stress. From the fracture toughness of TiC (2-3 MPa m^{1/2} [21])

Figure 5.12: Stress induced by the difference in thermal expansion coefficient between WC and Ti-6Al-4V as a function of distance from the center of a spherical WC particle with a radius of 40 µm.
and from the initial crack length in the WC particle, which is equal to the
diameter of the particle (~80 µm), a rough estimate of the a tensile stress can be
made. It predicts a lower bound of 190 MPa is required for cleavage of the TiC
layer or the TiC dendrites in the matrix. In practice, this value might be higher
because it is obtained from the most unfavorable case, i.e. when the initial crack
in the particle is straight, perpendicular to the external stress, and has
propagated through the whole WC particle. Therefore, higher tensile stresses
may be needed for cleavage of the TiC phase in the MMC layer. This
corresponds to results of the tensile tests where kinks are observed in the stress-
strain curves at an external stress of 250-350 MPa (Fig. 5.7).

The tensile tests showed that both strength and ductility of WC₆/Ti-6Al-4V
MMC coatings, which are produced according the laser melt injection process
described in chapter 4, may be improved by small adjustments. Exchanging the
fused granular WC powder by a single crystal powder will suppress the
formation of cracks in the WC particles. To initiate cracks in single crystal WC
particles higher stresses are needed than to initiate cracks along the weak WC
grain boundaries because of the high strength of non-fused WC (1550 MPa
[21]). A second adjustment is avoiding the formation of high amounts of TiC in
the melt pool matrix. This can be achieved by injecting the WC particles behind
the laser beam to minimize the temperature of the particles, as is discussed in
chapter 4. In this way, much less (brittle) reaction products will be present in
the MMC coating.

5.3.4 Nano-indentations

Hardness measurements on the MMC coatings are complicated because of the
high difference in hardness of the phases that are present in the coating. This
hardness of the MMC is difficult to quantify. Another problem is that during
conventional indentations a relative large area (~ 100 µm x 100 µm) is indented.
Because the size of phases that are present in the coating is of the order of µm,
conventional hardness measurements like Vickers hardness tests, will result in
the average hardness of several phases and will depend on the composition of
the indented area. Therefore it is chosen to perform nano-indentations to obtain
the hardness of the individual phases that are present in the coating. In this way
the properties of the reaction products can be tested.

The reactions during the laser treatments that impose high cooling rates are
likely to have occurred under non-equilibrium conditions. Therefore non-
Microstructural response on loading

stoichiometric phases may be formed, having slightly different properties than the stoichiometric phases. For instance questions remain whether the hardness of TiC in the reaction layer is comparable to that of the TiC dendrites in the melt pool, because they are formed under different conditions?

Because the optics in the nano-indenter do not allow to resolve the micro features in the melt pool matrix, i.e. it is not possible to direct the indenter in the phase you want, the following procedure is used to obtain the hardness of the individual phases. A polished sample is loaded into the nano-indenter (MTS Nano Indenter® XP). A matrix of 10 x 10 nano-indentations, using a Berkovich tip, are performed partially on a WC particle and partially on the surrounding melt pool matrix (the 80 µm sized particles can be distinguished by the nano-indenter optics). The nano-indenter software automatically calculates the hardness of each indentation from the data obtained from one cycle of loading and unloading [22]. The nano-indentation equipment is described in chapter 2. Afterwards, the locations of the indentations are observed in an SEM. Then the hardness values can be linked to the corresponding phase. By using an SEM useless nano-indentations can be selected and deleted from the results. The useless indentations are indentations in more than one phase or the indentation that are performed in an irregular surface (in crack or hole). In most cases the useless indentation can be selected by studying the load displacements curves of the indentations as well. By repeating this process for several samples enough correct single-phase indentations can be analyzed. The indentation force is experimentally obtained to be 15 mN. At this force, the size of the indentation is small enough to have a reasonable probability of indenting in a single phase. The step size between the indents is chosen to be 7 µm (both in x and y direction). With this combination of force and step size between the indentations, the neighboring indentations do not influence each other, i.e. the deformation zones of two indentations are separated by a deformation free zone.

An SEM micrograph of an indented area, containing 100 nano-indentations is shown in Fig. 5.13. On average 30% of the indentations are useful, i.e. in a single phase and on a flat surface. No clear dependence of the hardness as a function of distance from a particle is observed. The averages of the measured values are shown in Table 5.3. The literature values of the hardness are given in this table as well [20,21]. The average for each phase is obtained from 25-40 indentations. Only for W no value is mentioned because W is indented only twice. Indentations in this phase are not very probable to occur because this phase is
Figure 5.13: a) A matrix of 100 nano-indentations (10 x 10) in and around a WC particle, separated 7 µm. b) Magnification of the marked area in Fig.5.13a, showing in which phase the indentation is performed.

Table 5.3: Hardness of the different phases in laser melt injected WC$_p$-Ti-6Al-4V MMC coatings. The hardness is obtained by nano-indentations and compared with values from literature.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Hardness (GPa) measurements</th>
<th>Hardness (GPa) literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>32 ±2</td>
<td>22 (for 0001) planes</td>
</tr>
<tr>
<td>$W_2C$</td>
<td>25 ±6</td>
<td>21</td>
</tr>
<tr>
<td>TiC (reaction zone)</td>
<td>26 ±5</td>
<td>28.5</td>
</tr>
<tr>
<td>TiC (matrix)</td>
<td>25 ±4</td>
<td>28.5</td>
</tr>
<tr>
<td>Ti alloy</td>
<td>7 ±1</td>
<td>1.2</td>
</tr>
</tbody>
</table>
not present much, and when it is present it has a small surface area. The errors in the table are obtained from the standard deviations. The relatively high errors are not due to measurement method, but are most likely due to the fact that the hardness value are sensitive to the presence of a second phase in the surrounding of the indentation. Although every indentation is analyzed in SEM before the result is taken in to account, it is in most cases impossible to select indentations that are completely independent, i.e. not influenced by the neighboring phase.

There is no difference between the hardness of TiC in the reaction zone and TiC dendrites in the melt pool matrix. Therefore, the mechanical properties of TiC formed in the reaction zone around the WC particle are the same as the TiC dendrites in the melt pool matrix, formed without the constraints of the solid WC particle. The measured values do not differ much from the literature value. It should be mentioned that the literature value is obtained from macro-indentations, which may result in smaller hardness values than the values obtained from nano-indentations. In addition, the measured values of the hardness of W₂C agree with the literature value. The increase in hardness of the Ti-alloy with respect to the literature value is due to the change of microstructure, like a different Al and V content and the transformation $\alpha$-Ti to $\beta$-Ti. This high hardness with respect to untreated Ti-6Al-4V goes together with a loss in ductility, which is shown above in Fig. 5.7, when Ti-6Al-4V is laser melted.

The somewhat striking result is the high difference between the measured hardness of WC (32 ± 2 GPa) and the value obtained from literature (22 GPa). Of course, because of the anisotropy of WC, the hardness depends on the crystallographic orientation. However, the reported value is for (0001) planes, and the values for other planes are even lower. The argument that the literature value is obtained from macro-indentations, and is therefore too high, is still valid but can not explain the high difference. The fact that the WC particles are in hydrostatic compression may also increase the hardness with respect to the literature values. High compressive stresses decrease the shear stress. These shear stresses drive the indentation plasticity beneath the indenter and therefore hardness impressions should be smaller when the sample is in compressive stress state [23]. However, the hydrostatic compression state may be changed at the surface of the sample. Probably the combination of the mentioned arguments causes the difference in the measured and reported hardness.
Chapter 5

5.4 Summary

The SiCp/Al MMC coatings produced by the laser melt injection process have a higher tensile strength than the untreated material. This increase in strength is mainly due to the change in microstructure due to the rapid solidification during laser processing and residual stresses caused by the laser processing rather than due to the injected SiC particles. The decrease in ductility after injecting brittle particles is not surprising. The weakest features in the produced MMC coatings are the Al₄C₃/Al interfaces of the Al₄C₃ plates that are present between the particles in the melt pool matrix. These interfaces easily decohere, making them predominant for crack nucleation and propagation along the plates that are randomly distributed in the matrix. Cleavage of the SiC particles is the second most important crack nucleation and propagation mechanism. The Al₄C₃ plates in the reaction zone form a good bonding between particle and matrix because decohesion of the SiC/Al interface does not frequently occur. However, the existence of Al₄C₃ plates in the Al matrix should be minimized to enhance the performance.

The tensile strength and ductility of the WCₚ/Ti-6Al-4V MMC coating produced by the laser melt injection process decrease dramatically with respect to the substrate material properties. Intergranular brittle fracture inside the WC particle and decohesion along the WC/W₂C interface are the two predominant failure initiation mechanisms. The pre-cracks are formed at low external stress or even induced by the internal stresses that are introduced during the laser process. The failure proceeds by cleavage of the TiC dendrites that are present in high amounts in the melt pool matrix, these dendrites are randomly distributed. The tensile properties can be improved by using powder that consists of single WC grains, to avoid intergranular fracture. Injecting the particles behind the laser beam will minimize the presence of brittle TiC in the melt pool matrix, which will improve the performance of the coating.

Nano-indentations on the WCₚ/Ti-6Al-4V MMC coating showed that the TiC in the reaction layer has the same hardness as the TiC dendrites that are present in the melt pool matrix.
5.5 References
