4 Microstructure evolution of laser deposited clad tracks

This chapter is devoted to the characterization of the microstructure formed in thick laser deposited coatings composed of traditional hard facing powder alloys. In the first part, the microstructure of Co-based alloys, Stellite-like alloys, is thoroughly examined by various microscopy techniques and x-ray diffraction to describe the evolution of the microstructure as a function of depth, the influence of the processing speed and the effect of laser track overlap. In the second part, the feasibility of tool steel powder as clad material is evaluated in relation to the microstructure generated by the laser deposition technique.

4.1 Introduction

4.1.1 Cobalt based alloys

The commercial introduction of cobalt superalloys was set in the beginning of the twentieth century when the first patents were granted to the Co-Cr and Co-Cr-W systems developed by E.Haynes [1]. Registered as trademark under the name of Stellites, these materials became industrially important for cutlery, machine tools and wear-resistant hard facing applications [2].

Stellites are austenitic materials, hardened by a combination of carbide formation and solid solution strengthening of the matrix, the former of which being the most important mechanism [3]. The carbide former elements commonly found in the commercial Co-alloys are: niobium, tantalum, molybdenum, tungsten, chromium, zirconium and titanium. Chromium also plays an important role in the oxidation resistance of these alloys. Depending on the carbon content and the heat treatment various carbides can be formed in these alloys, such as: MC, M_5C_2, M_{23}Co_6 and M_7C_3; demonstrated in the phase diagram of the Co-Cr-C system shown in Figure 4.1.
Chapter 4

*Figure 4.1: Isothermal of Co-Cr-C phase diagram at 1073 K [4].*

The most important elements that promote solid solution strengthening are in order of solubility: molybdenum, niobium, tantalum and tungsten, *Figure 4.2*. Since these elements are also involved in the carbide formation their degree of effectiveness as a solid solution strengthener is not completely clear. W is most commonly utilized due to its high solubility in Co.

*Figure 4.2: Phase Diagram of Co-Cr-X system (X is a refractory metal= W, Mo, Ta, Cb) showing 1200 oC solid solution field boundaries [5].*

The original application of Co-Cr-W alloys for cutting tools has declined over the years whilst its use has been partially replaced by carbides. Nowadays it is mainly applied as hardfacing alloy when erosion resistance and high temperature properties are necessary. Usual techniques for manufacturing the coating layers are plasma or flame spraying and laser cladding. The latter has the advantages of the formation of layers free of pores, finer grained microstructures and supersaturated solid solutions due to the higher cooling rate involved in the solidification process.

### 4.1.2 Solidification of alloys in dynamical process

Solidification is by far the most important route in industrial processes of metals and alloys. It is able to determine in a single step the microstructure and physical properties of materials
that can be optimized since specific morphology can be tailored by special solidification conditions.

The driving force of solidification is strongly affected by the so-called undercooling of the process [6-7]. In general, solidification starts with heterogeneous nucleation either due to impurity particles or by contact of the liquid with a solid surface. When the solid phase becomes saturated, the solute will partition into the liquid forming a mushy zone ahead of the crystal column. This accumulation of solute promotes instability on the growth front that branches as secondary and tertiary dendrites along one of the <100> perpendicular directions. In the interface area with the solid surface several nuclei form reproducing the orientation of the grains of the wall and start to propagate towards the liquid phase. In bcc and fcc metals the preferential crystallographic growth direction is <100>. As consequence, the crystals that are oriented most parallel to the maximum temperature gradient will grow faster than less favorable oriented grains and will propagate as columnar structures, Figure 4.3.

![Figure 4.3: Schematics of competitive dendritic crystal growth on the chill zone.](image)

The size and shape of the crystals may reflect the local solidification conditions of the melt. Coarse grains grow due to lower cooling rates, once crystals have time to accommodate and orient themselves towards the heat source. Non-turbulent conditions keep the dendritic arms intact. Finer grained microstructures are facilitated when fast cooling rates are active and when high turbulence breaks the dendritic arms forming. Since the grain growth orientation of cubic metals coincides with heat flow direction, the morphology of the microstructure resembles the heat flow orientation of the melt. That is, in regions where the heat is directionally extracted the grains will grow with elongated shapes, while regions of isodirectional heat extraction give rise to equiaxial grains.

In dynamical processes, like welding or laser cladding, a clear analysis of microstructure morphology formation can be complicated due to the variation of the local solidification conditions discussed above, the 3-D aspect of the shape of the solidification front and the influence of the processing speed. In these processes the direction of the maximum temperature gradients changes continuously because the heat source keeps moving. Therefore, the crystals try to follow the maximum temperature gradients, while keeping their <100>
favorable growth direction. This will result in a change of crystal growth direction as a function of the position in the solidification front as illustrated in Figure 4.4. Assuming a single laser clad track, or a weld line, a change in the solidification conditions will alter the shape of the pool shape and therefore the crystal growth behavior. The speed of the process is the most important parameter because it determines the solidification rate of the melt pool.

Figure 4.4: Schematics of solidification front of the melt pool in a weld from [6]. A) Top view of the melt pool where \( v \) is the speed of solidification and B) is the longitudinal view.

4.2 Microstructure characterization of cobalt based laser deposited clad layers

The microstructure of the cobalt based laser clad tracks and layers deposited on iron based substrates were characterized by optical microscopy, scanning (SEM) and transmission (TEM) electron microscopy techniques. The phase analysis was performed by diffraction of lab and synchrotron x-rays. Electron backscattered diffraction (EBSD) patterning microscopy was used to complement the microstructure description by revealing the global distribution of grains and crystallographic texture.

Three Co-based alloys, similar to alloys of the Stellite family, were used for laser cladding deposition on substrates of the medium carbon steel, C45, and a gray (US spelling throughout) nodular cast iron, GGG60. These materials and their chemical compositions are listed in Table 4.1.

Table 4.1: Chemical composition of alloys in wt% given by commercial providers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Co</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Mo</th>
<th>C</th>
<th>Fe</th>
<th>Si</th>
<th>V</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stellite 20</td>
<td>45</td>
<td>33</td>
<td>-</td>
<td>18</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eutroloy 16006</td>
<td>58.7</td>
<td>29</td>
<td>-</td>
<td>8.5</td>
<td>-</td>
<td>1.6</td>
<td>1.0*</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eutroloy 16012</td>
<td>58.7</td>
<td>29</td>
<td>-</td>
<td>8.5</td>
<td>-</td>
<td>1.6</td>
<td>1.0*</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C45</td>
<td>-</td>
<td>0.40</td>
<td>0.40</td>
<td>-</td>
<td>0.10</td>
<td>0.46</td>
<td>bal.</td>
<td>0.40</td>
<td>-</td>
<td>0.65</td>
</tr>
<tr>
<td>GGG60</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>3.4</td>
<td>bal.</td>
<td>2.1</td>
<td>-</td>
<td>0.4</td>
</tr>
</tbody>
</table>
4.2.1 Characterization of clad/substrate interface

The integrity of interface coating/substrate is checked by examining the presence of cracks or pores. When the heat input is high enough to melt both the clad material and the substrate an interface without those defects can be formed as presented in Figure 4.5.A. At this magnification the interface is planar and free of defects. It is well defined by the chill zone created in the early solidification stage of the melt pool. A strong metallurgical bonding is created in the interface and intergranular melting of the substrate can be observed, Figure 4.5.B.

![Figure 4.5: A) Optical micrograph of faultless interface between Eutrolloy 16006 clad track and C45 substrate. B) Backscattered electron micrograph showing intergranular melting of the clad material into the substrate.](image)

The interface is composed by fine crystals that nucleate in contact with the “cold” substrate and reproduce specific crystallographic directions of the solid phase, Figure 4.6.A. The crystallites with the $<001>$ direction aligned with the heat flow will grow faster leading to the formation of columnar dendritic grains that propagate inside the melt pool to form the microstructure of the clad, Figure 4.6.B.

![Figure 4.6: A) Backscattered electron micrograph shows metallurgical bonding on clad/substrate interface and apparent growth relation between HAZ and chill zone grain. B) EBSD patterning characterization presented as [001] Inverse Pole Figure (IPF). The interface is defined by the ribbon of fine dendritic crystals. Above this interface the grains propagate in a columnar dendritic morphology.](image)
Chapter 4

4.2.2 Phase analysis and characterization of bulk microstructure

Detailed phase analysis is carried out for the Eutrolloy 16012 alloy and laser deposited clad layer. The analyses are done first with lab. x-rays by means of the 0-2θ diffraction scan of Cu-Kα radiation with wavelength = 1.5405 Å. The powder diffractometer used is a Philips PW1830 with a graphite monochromator placed in the incident beam. The measurements are realized in reflection mode from irradiated areas that cover largely the polished surface of the coatings. The analysis was complemented by a synchrotron radiation diffraction experiment carried out at the European Synchrotron Radiation Facility (ESRF) on beamline ID-31 with a beam energy equals to 60 keV, i.e. $\lambda = 0.206762$ Å, and a line detector with precision of $10^{-5}$. The synchrotron experiment was done in transmission mode through an irradiated area of 50 x 1500 μm$^2$ located at the center of a 1 mm thick perpendicular cut from a single laser track. The diffraction patterns from the powder and the coating indicate the presence of $\gamma$-Co phase and formation of $M_7C_3$, $M_{23}C_6$, and $Co_6W_6C$ carbides as recognized from the JCPDS data files, Figure 4.7.A. It is verified that the phases present on the original powder are not changed due to laser deposition. Further analyses were done to compare the formation of phases in Stellite 6, 12 and 20 coatings deposited on C45 steel substrates by 0-2θ diffraction of Cu-Kα radiation, Figure 4.7.B. In accordance with literature [2,3,5] and the previous experiments all coatings presented the $\gamma$-Co and carbide phases, $M_7C_3$, $M_{23}C_6$, and $Co_6W_6C$. The fcc lattice space shifts from the pure $\gamma$-Co has been determined for all coatings and the results are summarized in Table 4.2.

![Figure 4.7: A) XRD spectra of Eutrolloy 16012 powder and coating analyzed by lab Cu-Kα x-ray, $\lambda = 1.5405$ Å, and synchrotron at 60 keV, $\lambda = 0.206762$ Å. B) XRD spectra of Eutrolloy16006, Eutrolloy16012 and Stellite 20 clad layers analyzed by lab Cu-Kα x-ray diffraction. In both plots it is given the position of the peaks indicating the phases found according to the JCPDS databank: $\gamma$-Co, $M_7C_3$, $M_{23}C_6$, and $Co_6W_6C$.](image)

Co-Cr-W alloys were developed based on the formation of an austenitic lattice, $\gamma$, strengthened by hard precipitates, where the main precipitation mechanism is the formation of carbides by the addition of carbon to the alloy. Assuming the typical Stellite composition where the Cr concentration does not exceed 35%, it is predicted by the Co-Cr-C ternary phase diagram, Figure 4.1, that $M_7C_3$ is preferentially formed while $M_{23}C_6$ precipitation is favored.
Microstructure evolution of laser deposited clad tracks

when the carbon concentration is low. The mechanisms of $\text{M}_2\text{C}_6/\text{M}_7\text{C}_3$ formation are quite complicated and the relative amount of carbide phases will depend on the properties like the solubility and stability of the carbides, but also on the processing parameters that define the thermodynamics of the system. Since laser cladding has a broad operational window, a big variation of composition is achieved caused by the dilution with the substrate and the solidification rate defined by the processing speed. For these reasons the carbide content may vary a lot when different processing parameters applied or different substrates are used. For instance, Figure 4.8.A shows the microstructure of Eutroloy 16012 deposited on C45 and Figure 4.8.B the microstructure of the Eutroloy 16006 deposited on grey cast iron, both at scanning speed of 5 mm/s.

Table 4.2: Lattice parameters of fcc lattices from pure $\gamma$-Co according JCPDS data files, Stellite coatings determined by x-ray diffraction.

<table>
<thead>
<tr>
<th>a$_0$ ($10^{-10}$m)</th>
<th>a ($10^{-10}$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Co (JCPDS)</td>
<td>Eutroloy 16006</td>
</tr>
<tr>
<td>3.545</td>
<td>3.451</td>
</tr>
</tbody>
</table>

Figure 4.8: SEM micrographs A) Eutroloy 16012 deposited on C45 steel. The white spots reveal the high amount of the heavy element W. and B) Eutroloy 16006 deposited on GGG60 substrate.

In both microstructures fine $\gamma$-Co rich dendrites are observed with typical size of 5-10 µm and the carbide rich eutectic area is located in between the fine interdendritic spaces. It is clear that even though the original Eutroloy 16012 powder contains more carbon than Stellite 6, Table 4.1, the influence of GGG60 dilution into the laser track is reflected by the higher amount of the carbides formed.

The eutectic structures formed in the interdendritic spaces are characterized by TEM to confirm the results of XRD phase identification and to quantify the local chemical compositions. Electron transparent thin foil samples of Eutroloy 16012 are prepared from the overlap region between adjacent tracks of a coating where the highest amount of carbide
Chapter 4

phases was observed. The TEM analysis reveals that the eutectic phase is composed of lamellar shaped carbides and stacking faults can be observed [8-10], Figure 4.9.

Figure 4.9: Bright field image showing the microstructure of the eutectic phase in Eutroloy 16012 coating and the associated orthorhombic diffraction pattern from the carbide marked by the circle. Stacking faults are observed as well.

It is known that cobalt-based solid solutions have low stacking fault energy and several slip systems are operative. When high thermal stresses are generated by the fast cooling of the laser cladding process, stacking faults are easily formed in the $\gamma$-Co phase. This effect is more pronounced in regions with a high amount of hard carbides, Figure 4.10, that are able to block the stacking faults forming obstacles for dislocations, consequently, contributing to the wear resistance of the cobalt-based alloys [8].

Figure 4.10: Bright field image of eutectics shows a high density of stacking faults in the cobalt-based phase located between hard chromium rich carbides.

The metallic content of the carbidic and the cobalt-based phases were determined by TEM EDS and are 71Cr-17Co-12W and 2Si-22Cr-2Fe-64Co-10W, given in wt%. These phases were also investigated by high resolution TEM, Figure 4.11, to reveal arrangement of the stacking faults and carbide streaks caused by the planar defects.

Figure 4.11: High resolution TEM A) of Co rich phase with composition 2Si-22Cr-2Fe-64Co-10W and B) lamellar chromium rich carbide phase with chemical composition 71Cr-17Co-12W. The compositions given in wt% were analyzed by EDS.
The diffraction patterns from the interface between the cobalt solid solution and carbide were observed, Figure 4.12. The cobalt diffraction pattern was observed with the beam along the [013] direction and revealed the (200) and (311) planes of the fcc lattice.

4.2.3 Microstructure dependence with processing speed

The effect of the cooling rate on the microstructure is directly related to the processing speed [7]. To investigate this effect, single tracks of Eutroloy 16006 on C45 steel substrates are deposited by side laser cladding setup under two different speed levels that differ from each other by a factor of 10, Table 4.3. The thickness of the slowest deposited track becomes about twice the thickness of the quickest deposition. It can be expected that much thicker tracks are formed when the speed is decreased 10 times, due to the increase in the powder feeding rate (F/S). However, in order to avoid an excessive dilution or formation of tracks with unwanted geometry for clad layer deposition, i.e. \( \alpha < 100^\circ \), the laser power is tuned for all speeds to achieve similar temperature conditions in the processing area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (W)</th>
<th>F (g/s)</th>
<th>S (mm/s)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow deposited</td>
<td>800</td>
<td>12.50</td>
<td>1.67</td>
<td>0.91</td>
</tr>
<tr>
<td>Fast deposited</td>
<td>1700</td>
<td>1.25</td>
<td>16.67</td>
<td>0.42</td>
</tr>
</tbody>
</table>

The understanding of the microstructure formation in laser cladding can be complex due to its actual three dimensional nature, while the samples produced for analysis are flat surfaces. For this reason, the samples are prepared for electron microscopy analysis by cross sectioning of the single tracks by spark cutting erosion along two planes: perpendicular and longitudinal to the process direction. It is important to note that the longitudinal cuts are made at the centre of symmetry of the track transversal width. The single tracks are investigated by...
EBSP technique and the data are characterized by Orientation Imaging Microscopy software (OIM) in terms of crystal orientation mapping, grain size distribution and texture plots.

Low processing speed.

Figure 4.13 shows the microstructure of the transverse and longitudinal cross sections of the sample processed at 1.67 mm/s speed, represented by the Inverse Pole Figure mappings of the [001] crystallographic direction ([001] IPF). The straightforward analysis of these pictures reveals that the clad track is composed of coarse grains despite the small sized dendrites showed on Figure 4.8. On both types of cross sections the grain size decreases from the top of the track towards the interface with the substrate. It is noted however, that despite the refinement of the microstructure through the depth the average morphology of the microstructure is quite constant in each sample. On the transverse cross section the grains take a more equiaxial aspect ratio, while the longitudinal section presents coarser and more elongated grains that are tilted with respect to the substrate.

The grains of the sample processed at 1.67 mm/s have an aspect ratio 10 times larger along the longitudinal cross section compared to the transverse view as revealed by the grain size distribution plots, Figure 4.14. The highest values of the plots indicate those grains that during the solidification of the melt pool are preferably oriented towards the heat source, and since the process is carried under slow speed, these crystals have the possibility to accommodate themselves in order to propagate via selective crystal growth. For instance, the coarsest grains of the transverse and longitudinal samples, with surface areas of 0.027 or 0.025 mm$^2$ and 0.25 mm$^2$ respectively, are identified by EBSP software treatment and indicated in the pictures of Figure 4.14.

Figure 4.13: IPF mappings of the normal direction (ND) projected on the transverse and longitudinal cross sections of Eutroloy 16006 single clad track samples processed at 1.67 mm/s speed. The laser process coordinate system is given in each picture. Relation between crystallographic directions and color is given in the insert in the upper picture.
Microstructure evolution of laser deposited clad tracks

Figure 4.14: Grain size distribution plot of transverse and longitudinal planar views of the Eutroloy 16006 single clad track samples processed at 1.67 mm/s speed. The smallest grains correspond to those closer to the substrate, while the coarser grains are located towards the top of the coating.

The quantification of the crystallographic orientation on the transverse and longitudinal planes of the single tracks are given by the texture plotted as Pole Figures (PFs) of the Orientation Distribution Functions (ODF) calculated by the harmonic series expansion according Bunge formulation [11,12]. Figure 4.15 shows the [001] PFs that describe the texture formed in the slower processed sample. A multiple fiber texture is detected on the perpendicular cut of the single track that is caused by the 3D concentric temperature gradient profile of the melt pool as suggested by Figure 4.4. When the longitudinal cut is analyzed it is revealed that the preferential grain growth direction on this plane lies 45° tilted from the normal direction with the substrate, observed qualitatively in Figure 4.13.

Figure 4.15: Texture Pole Figures of [001] direction in the transverse and longitudinal planar views of the Eutroloy 16006 single clad track samples processed at 1.67 mm/s speed.

High processing speed.

Similar analyses were performed for the sample deposited with a laser beam velocity 10 times higher, i.e. 16.67 mm/s. Figure 4.16 shows the microstructure of the transverse and longitudinal cross sections of this sample represented by the normal direction IPF. Analogous to the previous case, refinement of the microstructure takes place from the top of the track.
towards the interface with the substrate. However, the transverse and longitudinal sections show grains that have similar aspect ratios and sizes. It is noted that the morphology of the grains varies over the depth of the track, which differs from the slowly deposited sample. Close to the interface and at the center of the coating the grains are quite elongated and the top of the coating is composed of equiaxial grains. The upper part, formed the latest in the clad track, undergoes isotropic heat extraction, whereas the bottom part is formed in a strongly directionally oriented solidification front. The transverse picture did not show the upper part of the track due to limitation of the scanned area and, therefore, not all grains are visualized.

Despite of the change in aspect ratio over the depth, the grains located at the center and top of the coating present similar surface areas as revealed by EBSP. The plots of the grain size distribution in Figure 4.17 confirm a similar grain size for both cross sections.

The texture analyses represented by the pole figures, Figure 4.18, reveal heterogeneity over the depth of the clad track. The perpendicular section presents a fiber texture that is preferentially formed along the rolling direction, even though, side grains with other orientations contribute to the disturbance of this picture. For the analysis of the longitudinal cross section the scanned area is divided in three parts marked in the figure as Interface, Centre and Top. The crystallographic coordinate system is rotated 90° around the RD axis so that the typical fiber texture along the normal direction with the substrate becomes evident. The texture develops through the depth of the track in the following way. Along the interface grains nucleate reproducing the orientation of the substrate grains, however only those crystals with the (100) direction oriented along the heat flow propagate leading to the formation of a fiber texture along this axis. A detailed microstructure picture of this area is the Figure 4.16. In the centre of the track the fiber texture becomes stronger which indicates the preferential heat flow of the melt pool along the ND axis. The texture of the Top grains shows a random orientation caused by the isoequiaxial solidification of the melt pool. The variation of texture through depth the track was not observed in the slowly processed sample.

Figure 4.16: [001]IPFs from the transverse and longitudinal cross sections of Eutroloy 16006 single clad track samples processed at 16.67 mm/s speed exhibit the change in the morphology over the depth of the track. The laser process coordinate is system is presented for each cross section.
Microstructure evolution of laser deposited clad tracks

Figure 4.17: Grain size distribution plot of transverse and longitudinal planar views of the Eutroloy 16006 single clad track samples processed at \(16.67 \text{ mm/s}\). The finest grains belong to the region close to the interface, while center and surface grains are coarser.

![Figure 4.17: Grain size distribution plot of transverse and longitudinal planar views of the Eutroloy 16006 single clad track samples processed at 16.67 mm/s.](image)

Figure 4.18: Texture Pole Figures of [001] direction on the perpendicular and longitudinal plane views of the Eutroloy 16006 single clad track samples processed at \(16.67 \text{ mm/s}\) speed. Heterogeneous texture formation is detected through the depth of the track.

4.2.4 Microstructure formation in the overlap area of laser clad layers

The investigation of the overlapping effect on the microstructure of a clad layer is evaluated in two Co-based samples of Eutroloy 16012 and Stellite 20 both deposited on C45 following the parameters provided on Table 4.3.

### Table 4.3: Processing parameters of laser clad double track and layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(P) (W)</th>
<th>(F) (g/s)</th>
<th>(S) (mm/s)</th>
<th>Overlap</th>
<th>No. of tracks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutroloy 16012</td>
<td>1500</td>
<td>9</td>
<td>5.0</td>
<td>25 %</td>
<td>2</td>
</tr>
<tr>
<td>Stellite 20</td>
<td>1500</td>
<td>9</td>
<td>5.0</td>
<td>25 %</td>
<td>9</td>
</tr>
</tbody>
</table>

67
Chapter 4

The Eutroloy 16012 double track is cross sectioned along the transverse direction and the Stellite 20 clad layer composed of nine tracks is ground and polished from the top until macro-roughness is removed. Both samples are characterized by the EBSP patterning microscopy to reveal the geometrical and microstructural details of the overlap area.

For analysis of the Eutroloy 16012 cross sections, the data of four scan sessions are combined, see Figure 4.19. The morphology of the overlapping area between two subsequent laser tracks is similar to the clad/substrate interface, that is the interface is straight, well defined, poreless but no substantial variation of chemical composition could be detected by SEM-EDS. For the deposition of the second track the laser needs to remelt part of the first track belonging to the overlap area and the substrate so that a metallurgical bond is created. The redistribution of energy absorption affects the dilution of the second track that becomes less diluted than the previous one. This processing setup generated a second track with 3 to 5% dilution, enough for metallurgical bonding with the substrate and conservation of the properties of the original alloy.

![Figure 4.19: EBSD patterning characterization of overlapped tracks represented by the [001] IPF of Eutroloy 16012 cross section double track layer.](image)

Relatively coarse grains compose the microstructure that can be divided into two regions. In the upper part of the laser tracks, equiaxial grains with size of the order of 0.28 mm² predominate. Towards the interface with the substrate the grains become finer and elongated. No preferential texture could be detected as indicated by the pole figure on the left upper corner of Figure 4.19.

The variation of grain size is also observed from the top view of the flat ground Stellite 20 coating. EBSP patterning analysis is performed in the middle of the 5th track of the clad layer to qualitatively characterize the grain size distribution of this surface, Figure 4.20. The remelting of the overlap area leads to grain coarsening and the creation of a texture due to directional heat flow in this region. The grains from the heated affected zone that are not remelted remain with the random crystallographic orientation typical of the isodirectional solidified structures.
Microstructure evolution of laser deposited clad tracks

Figure 4.20: A) Top view of grain size distribution by gray scale mapping on the centre of the 5th track of 9 tracks Stellite 20 coating shows grain coarsening on the overlap area between adjacent tracks. D) [001] PF of grains found on the overlap area.

4.3 Tool steel clad layer deposition

4.3.1 Introduction: Fe-C-V system of tool steels alloys

Vanadium was discovered for the first time in Mexico in 1801 by André del Rios [13] who named it “panchromium” due to the variety of colors of its many colored salts. The scientific community, however, did not believe his discovery and after some time even he gave up himself. The element was rediscovered in 1830 by the Swedish physician Nils Gabriel Sefström when he studied the ductility properties of an iron ore originated from the mine of Taberg (south of the city of Jönköping) and named it Vanadis in honor of the Scandinavian goddess of beauty. This discovery attracted the attention of the well known chemist Jöns Jacob Berzelius who announced Sefström’s discovery and started a large research program on the chemical properties of its compounds [14]. As a metal, vanadium was isolated for the first time by the English chemist Sir Henrey Roscoe in 1860, but before the end of the 19th century the main application of this element remained restricted to the field of chemical applications, such as pigments and catalysis. At the turn of the nineteenth century, motivated by the economical growth of metallurgical processes, the first processing unity was mounted in South Wales for the exploration of V as an alloying element in steels under the responsibility of Arnold of the Sheffield College. At the time it formed the base of a whole new range of mechanically resistant steels. In the Fe-C system the positive effects of vanadium is directly noticed by the increase of strength and wear resistance making these alloys suitable for cutting tools and die applications. Since then, the importance of vanadium in tool steels increased stimulated by modern metallurgical processes as powder metallurgy.

The improvement of the mechanical properties is caused by two main mechanisms: the formation of stable V-carbides and the refinement of microstructure [14,15]. In a steel melt the solubility of the vanadium is quite high [16] (on the order of 6% when the carbon amount is 2% at 1425°C) but it drops drastically in solid austenite (0.23% on γ-Fe at 727°C) and it becomes even worse when the ferritic phase is formed (<0.1% on α-Fe at 727°C). The strong
temperature dependence of V solubility indicates that the Fe-C-V austenitic system is subjected to a high amount of strengthening by dispersoids where V plays a very important role on the formation of carbides and carbonitrides in interdendritic spaces. The growth rate of the precipitates depends on the supersaturation of vanadium and the ratio of solute concentration in the matrix [17].

A side effect of the enhanced carbide precipitation promoted by vanadium is that the microstructure becomes finer. Further refinement is promoted if a small amount of N is added, on the level of ~ 0.003%, which causes the formation of carbonitrides that slow down the austenite-ferrite transformation and promotes nucleation to happen in place of grain coarsening [14].

![Polythermal section of Fe-C-V system at fixed carbon content of 2.3 wt%](image)

Figure 4.21 shows the polythermal section of the Fe-C-V phase diagram, with the carbon amount fixed at 2.3 wt%. The primary parameters controlling the size of the grains in austenite/ferrite transformations are the cooling rate and the amount of precipitates formed in the interdendritic spaces. If the solidification process undergoes a low cooling rate, phase diagram tells that the resulting microstructure will be composed of ferrite, cementite and vanadium carbides. When the melt is rapidly cooled austenite does not have the time to transform in ferrite and due to oversaturation of carbon, a diffusionless transformation takes place resulting in martensite [18]. The resulting microstructure for high cooling rates is then composed of martensite, retained austenite and carbides.

The laser cladding technique can be used for the deposition of thick layers of tool steel alloys on the surface of workpieces [19]. Because of the high solidification rates the microstructure consists typically of fine grains, supersaturation and non-equilibrium phases. Undesirable effects as low hardness, low wear resistance and changes in microstructure during service may happen when the amount of retained austenite created in the matrix becomes very high. When this is the case, the portion of austenite can be affected by appropriate heat treatments. The application of the laser cladding technique to the formation of wear resistant
thick coatings composed of a commercial Fe-C-V based alloy powder system is evaluated by the analysis of the austenite content.

4.3.2 Microstructure analysis of a Fe-based clad layer

A clad layer of the Fe-based tool steel type AISI M3:2/W, Table 4.5, commercially known as Vanadis 23, deposited under the parameters: P: 1700 W; and S: 5 mm/s and F: 0.15g/s, is characterized in terms of phase analysis, microstructure and chemical composition by lab and synchrotron XRD, EBSD patterning microscopy, SEM and EDS.

Phase analyses of the AISI M3:2/W tool steel alloy is performed by XRD in the powder, clad layer and 2 mm thick cross section forms. The first two samples are analyzed with lab x-rays by θ-2θ diffraction scans with the same apparatus and conditions applied for the analysis of the Stellites. The transverse cross section of the clad is investigated by synchrotron x-ray diffraction in transmission mode at the beamline ID-11 with beam focus area of 20 x 30 μm² and energy of 80 keV, or λ = 0.15422 Å. A 2D CCD detector with 10 x 10 cm and 48 μm pixel resolution is used for the capture of the Laue diffraction patterns. Figure 4.22 shows the x-ray diffraction patterns of this investigation.

It is possible to identify the ferritic, austenitic, martensitic and vanadium carbide phases in the material. The similarity of the powder and the clad lab XRD spectra suggests that the phase composition of the original alloy is conserved. The spectrum of the clad cross section is constructed from the treatment of the image on Figure 22.B by the Fit2D computer program provided by the European Synchrotron Radiation Facility [20]. The high monochromaticity of the synchrotron beam is able to split the peaks due to the different phases with similar lattice parameters. The Laue pattern is acquired from a volume of 1.2⋅10⁻³ mm² equals to the size of the synchrotron beam through the thickness of the sample. The diffraction circles originating from this small volume suggest that the material must be fine grained with randomly oriented crystals.

The microstructure of the clad layer is observed by backscattered electron SEM and it confirms a fine dendritic morphology, Figure 4.23A. The microstructure is homogenously distributed through the whole coating and the overall composition of the clad alloy measured by SEM-EDS is 4Cr-5W-3Mo-85Fe-3V, in wt%. On Figure 4.23B subgrain microstructures can be observed inside the dendrites and the white phases on the interdendritic spaces point to heavy elements, likely the carbide phases.

Table 4.5: Chemical composition of tool steel in wt% given by commercial provider.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Mo</th>
<th>C</th>
<th>Fe</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI M3:2/W</td>
<td>4.2</td>
<td>-</td>
<td>6.4</td>
<td>5</td>
<td>1.28</td>
<td>bal.</td>
<td>3.1</td>
</tr>
</tbody>
</table>

It is possible to identify the ferritic, austenitic, martensitic and vanadium carbide phases in the material. The similarity of the powder and the clad lab XRD spectra suggests that the phase composition of the original alloy is conserved. The spectrum of the clad cross section is constructed from the treatment of the image on Figure 22.B by the Fit2D computer program provided by the European Synchrotron Radiation Facility [20]. The high monochromaticity of the synchrotron beam is able to split the peaks due to the different phases with similar lattice parameters. The Laue pattern is acquired from a volume of 1.2⋅10⁻³ mm² equals to the size of the synchrotron beam through the thickness of the sample. The diffraction circles originating from this small volume suggest that the material must be fine grained with randomly oriented crystals.

The microstructure of the clad layer is observed by backscattered electron SEM and it confirms a fine dendritic morphology, Figure 4.23A. The microstructure is homogenously distributed through the whole coating and the overall composition of the clad alloy measured by SEM-EDS is 4Cr-5W-3Mo-85Fe-3V, in wt%. On Figure 4.23B subgrain microstructures can be observed inside the dendrites and the white phases on the interdendritic spaces point to heavy elements, likely the carbide phases.
Chapter 4

Figure 4.22: A) XRD spectra of AISI M3:2 powder and clad analyzed by lab Cu-K\(\alpha\) x-ray, \(\lambda = 1.5405\ \text{Å}\), and synchrotron at 80 keV, \(\lambda = 0.15422\ \text{Å}\). B) Laue diffraction pattern of the AISI M3:2 captured by 2D CCD detector.

Figure 4.23: A) Fine dendritic microstructure of the AISI M3:2/W coating and B) subgrain microstructure investigated by backscattered electron SEM.

The subgrain phases are a suitable object of study for EBSD microscopy. Polishing with soft cloves and diamond and/or silicon carbide suspensions, produces a rough surface due to the difference in hardness between dendritic and interdendritic phases, Figure 24A. This generates a shadowing effect for the EBSD detector and it makes indexing impossible over a large area. The shadowing effect decreases intensively when the surface is smoothened by argon ion milling [21,22], Figure 4.24B, with the exception of some remaining valleys from the concave shaped surface that does not allow the complete diffraction pattern to be acquired by the detector. The martensite and austenite phases are indexed and the subgrain phase distribution is clear, Figure 4.24C, and IPF mapping reveals the random orientation of these subgrains, Figure 24D and E.

The analyzed area is composed of 40% of retained austenite and 60% martensite. This steel powder shows good fluidization properties during processing and entrapment by the melt pool (probably due to the similar melting temperature of the substrate and the alloying
Microstructure evolution of laser deposited clad tracks

powder). Most importantly the thick layers did not exhibit any propensity to cracking that arise due to the high residual stresses.

Figure 4.24: Secondary electron SEM images shows A) rough surface of the as polished AISI M3:2/W clad material and B) smoothened after argon ion milling. C) Phase distribution map shows subgrain microstructure inside the dendrites. Red color corresponds to austenite and green to martensite. Normal direction IPF mappings of D) austenite and E) martensite indicate random orientation distribution.

4.4. Conclusions

Co-based clad layers.

The microstructure of Co-based laser deposited clads is coarse grained with fine dendrites inside the grains. Four kinds of Stellite alloys were used to build clad layers on the surface of C45 or gray cast iron substrates, and the phases present in the coatings were $\gamma$-Co based matrix and carbide precipitates ($M_7C_3$, $M_{23}C_6$, and Co6WC) in the eutectic area located in the interdendritic spaces.

The morphology of the microstructure varied with the laser beam velocity. The fast deposition shows a homogenous microstructure more than in the slow deposition. Overall, refinement took place from the top towards the interface with the substrate. Slowly deposited tracks presented grains 10 times bigger in the longitudinal cross section plane than in the transverse cross section. In contrast, under high speed the grain sizes were comparable in the longitudinal and the transverse planes.

A texture dependence on speed was observed. Low speed deposited samples presented a multiple fiber texture when observed in the transverse cross section. In the case of fast
Chapter 4

depositions the samples show preferential fiber textures along the axis of the processing direction. A strong fiber texture was found on the longitudinal cross sections of both single clad track samples. The texture was normal to the surface in the slow case and tilted 45° in relation to the substrate in the case of fast deposition.

Grain coarsening in the overlap area is registered and characterized by EBSD patterning microscopy.

Fe-based (tool steel) clad layers.

The microstructure of the laser deposited tool steel clad layer is fine grained and dendritic, with the presence of subdendritic grains of martensite and retained austenite on the rate of 60 to 40%, respectively. It was not observed cracking problems during the deposition of the tool steel clad layer, nevertheless, post-heat treatment may be necessary.
Microstructure evolution of laser deposited clad tracks

References