4.1 INTRODUCTION

In the actual tribological performance of PVD coatings, the adhesion of the coating to the metallic substrate turns out to be a crucial parameter. A first requisite is that the coatings adhere to the substrates after deposition. It was shown in chapter 2 that excessive buildup of compressive stresses during coating growth may result in the decohesion of the coating immediately after deposition (flake-off). A further requirement is that the coating is able to maintain its adhesion to the substrate, up to a certain extent, when the system undergoes elastic and plastic deformation during use. The ability of a coating to do so is known as load bearing capacity, which is of crucial importance for the final tribological performance. To enhance coating adhesion, the substrates need to be carefully cleaned with degreasing agents to remove surface contaminants and subsequently dried before being introduced in the vacuum chamber. After the vacuum chamber is brought to the desired base pressure, an ion cleaning step is performed using the glow discharge from the magnetrons or auxiliary plasma sources. The substrates are subjected to heavy ion bombardment under RF or pulsed-DC current to remove surface oxides. The pre-cleaning and ion-cleaning steps are crucial for a good adhesion, but the influence of these steps on the final adhesion was not studied in this work.

In PVD coating laboratories several tests are employed to monitor the variation of coating adhesion with the deposition parameters. The most commonly employed ones are the Scratch Test and the Rockwell adhesion test, regulated by the European norms (EN) 1071-3 and 1071-8, respectively. In both tests a Rockwell C indenter is used, the geometry of which is shown in Fig. 4.1a. In the former case, the Rockwell stylus is passed over the surface under a gradually increasing load, in the latter, after a pre-load step, a very high load of 150 Kg is applied to the stylus, and subsequently retracted. There is a large difference in the loads applied during the two different tests. Indeed, in the scratch test it is rare to encounter coatings whose critical loads are higher than 100 N, while the standard indentation load for the Rockwell adhesion test is about 1470 N, as depicted in Fig. 4.1b. For this reason, during the scratch test only the spherical end of the indenter is slid against the material, while in the Rockwell test the indenter penetrates into the material with the 120° aperture cone. Typical modes of failure observed in the scratch test and the Rockwell adhesion test are shown in Fig. 4.1c and d, respectively. In the scratch test, the load at which chipping of the coating material is observed with an optical microscope is defined as the optical critical load, Lc1. In the Rockwell adhesion test, the extent of chipping of the coating material is classified according to a scale ranging from 0 (perfect adhesion) to 3 (extensive delamination on the border and in the area around the indentation), and is generally observed with an optical microscope at 100× magnification.
As an initial approach to the optimization of the adhesion strength of DLC-based coatings a finite element model (FEM) of the Rockwell adhesion test was developed. FEM analyses usually allow the determination of optimal properties of the materials that may be tailored to reduce the peak stress or strain that causes failure. A second approach taken was to study the adhesion of a well developed commercial coating that is known to have extremely good adhesion to steel substrates. A statistical technique was applied to determine the most important parameter that determines its superior adhesion strength. Subsequently, the structure of a complex intermediate layer of graded composition was studied with the aid of bright-field (BF), energy filtering (EF), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HR-TEM) techniques.
4.2 ADHESION STRENGTH OF DLC COATINGS

4.2.1 FINITE ELEMENT MODELING OF ROCKWELL ADHESION TEST

The so-called Finite Element Method (FEM) technique as applied to materials development is a very powerful tool that is able to predict the influence of the performance of the material in actual applications. Through the technique a field quantity, such as the displacement field or the stress field, in the case of mechanical problems, is calculated. The technique can be applied to the calculation of thermal, electric and magnetic fields, fluid flow problems and coupling of different fields, for instance thermal-mechanical coupling. The technique is versatile and can be applied to study the behavior of structures of any shape and subjected to complex supports and loading conditions, where an analytical solution to the problem may not exist. The method provides a numerical, approximate solution to a specific problem. The most interesting results that may be obtained are generally the locations of peak values of the field quantity or its gradient. Therefore, the technique may be an aid in the optimization of the design of the structure so as to minimize or maximize the relevant peak values.

A brief description of the FEM technique as applied to a simple problem of elastic deformation will be presented. The deforming structure is meshed, i.e. it is divided geometrically in elements that contain a number of nodes, e.g. triangular or quadrilateral 2D elements. The field quantities are calculated at the various nodes and their value in the space between the nodes is interpolated using a linear polynomial (linear elements) or higher-order polynomial (e.g. 2nd order, quadratic elements). For instance a 2D rectangular structure may be meshed using linear quadrilateral elements each of which will contain four nodes that are shared with neighboring elements. Each node will contribute one row to the global stiffness matrix of the structure, where its interactions with neighboring nodes will be implemented by non-zero off-diagonal matrix values. In a load-controlled FEM model an external force is applied to certain nodes, and an unknown nodal displacement will be generated. The solution of the problem is based on the fact that the loaded structure in equilibrium will have a minimum potential energy. Therefore, the problem may be described in matrix form using the following equation:

\[
[K] \cdot \{U\} = \{F\}
\]

(4.1)

where \([K]\) is the stiffness matrix of the structure, \(\{U\}\) the column vector of unknown displacements and \(\{F\}\) the column vector of known applied nodal forces. Equation 4.1 may be solved by inverting the stiffness matrix \([K]\):

\[
\{U\} = [K]^{-1} \cdot \{F\}
\]

(4.2)

In actual applications this is never done since the stiffness matrices may contain too many elements. Various types of solvers may be employed to solve the problem in a computationally efficient way. The solvers may be divided in direct and indirect solvers. Direct solvers are based on a rearrangement of the stiffness matrix (such as a Gaussian
elimination) that produces, for instance, a triangular stiffness matrix based on which the various displacements may be computed recursively. Indirect solvers are more efficient for very large stiffness matrices and they are based on the iterative computation of trial displacements that may solve the problem within a certain tolerance.

The method may be easily applied to linear elastic problems. Nevertheless, considerably more sophisticated material behaviors may be implemented. In many cases the problem to solve is non-linear. In the case of mechanical problems, this occurs whenever the stiffness matrix varies as a function of the nodal forces or the displacements:

$$\begin{align*}
[K(U,F)]\cdot\{U\} = \{F\}
\end{align*}$$

In this case, a linearization of the problem must be performed. The linearization may be implemented in mechanical problems by dividing the total applied load in several smaller steps, and obtaining an approximate solution for each increment within a certain tolerance for the residual displacements and/or residual nodal forces, with an iterative procedure such as the Newton-Raphson technique.

The Rockwell adhesion test is a test where contact exists between the indenter and the coated substrate, and extremely high plastic deformations of the substrate occur. Contact problems are a class of highly non-linear problems, and for problems where high plastic deformation occurs remeshing of the structure during deformation may be necessary to avoid high distortion of the elements. The software used to model the problem is MSC.Marc, which is well suited to non-linear contact problems and has remeshing capabilities. In MSC.Marc, various remeshing steps may be applied during the incremental deformation of the structure to reduce the extent of geometric distortion of the elements. A new, undistorted mesh is applied to the deformed structure and the field quantities are transferred from the old mesh.

An axisymmetric geometry was employed for the simulation. An elastic-perfectly plastic substrate, a perfectly elastic coating and adhesion layer and a rigid Rockwell indenter were employed. The load was applied incrementally to the Rockwell indenter following the loading curve reported in Fig. 4.1b, in 150 steps. A Cr intermediate layer and a DLC coating were modeled on top of the M2 tool steel substrate, as shown in Fig. 4.2a. The adhesion layer and coating were considered as a single body in the simulation, which was glued to the underlying substrate, i.e. the relative displacements of the nodes in contact at the respective surfaces were coupled. Elastic Young’s moduli of 210, 280 and 115 GPa were employed for the steel, substrate, the Cr adhesion layer and the DLC coating, respectively, and a Poisson’s ratio of 0.3 was employed for all materials. A yield stress of 2 GPa was employed for the steel substrate. A Coulomb-type friction was implemented with a value of friction coefficient of 0.3 between the coating and the rigid indenter. Linear axisymmetric quadrilateral elements were employed. A direct multifrontal sparse solver and an iterative Newton-Raphson algorithm were employed to solve each loading step.

The 180° 3D expansion of the axisymmetric substrate at the end of the Rockwell adhesion test is reported in Fig. 4.2b. Two different zones where global remeshing was performed can be distinguished and are indicated by arrows. The final geometry of the modeled substrate is in good agreement with the geometry observed experimentally.
ADHESION AND INTERLAYER STRUCTURE

Figure 4.2 (a) Initial mesh employed for the substrate, the adhesion layer and the coating. (b) Deformed substrate and mesh at the end of the Rockwell test, arrows indicate two different areas where remeshing was employed; the box on the left indicates the scale over which the mesh stacking depicted in (a) could be observed.

The shape of the coated substrate and the calculated values of principal total strain maximum at various stages of the indentation are shown in Fig. 4.3. The maximum strain is observed in the substrate below the center of the indenter. A region of high strain is also observed in the substrate at the border of the indentation. This secondary strain peak in the substrate may be an explanation for the fact that the coating is generally observed to undergo chipping at the rim of the indentation. Nevertheless, the location of the peak is inside the crater and not on its rim, which may indicate that the model is not fully realistic. Indeed, the maximum level of strain observed approaches 0.25 in the substrate and 0.20 in the coating, and such a high value of strain in the coating is not realistic, since DLC coatings are brittle materials that can hardly sustain tensile strains higher than about 0.05. Cracking of the coating material could be implemented in the simulation, nevertheless, the experimental determination of the actual strain limits of Cr adhesion layer and DLC coating is a very challenging task due to the limited thickness of these materials and the inevitable influence of the substrate material in their determination. Furthermore, the real substrate will have a certain degree of roughness, which is difficult to implement realistically in the model, which considers a perfectly flat interface between substrate and coating, and the adhesion of the coating will also rely on the surface energies of the different materials, which are difficult to implement in the simulation and to measure experimentally. For these reasons, no optimization of the coating adhesion was performed based on the FEM model, whose function was to gain insight in the mechanism of deformation during the Rockwell test.
CHAPTER 4

Figure 4.3 (a) Initial configuration of the axisymmetric model, the rigid indenter approaches the coated substrate from the top of the figure, the coating can be observed between the indenter and the substrate (indicated). The substrate-coating system deforms as the load applied to the indenter is gradually increased, (b) after the pre-load step, (c) as the full load is applied and (d) after retraction of the indenter. The color-coding indicates the principal total strain maximum, which approaches 0.25 below the center of the indenter and at the edge of the indentation below the coating.

4.2.2 FACTORIAL ANALYSIS OF Cr-DLC ADHESION STRENGTH

The Cr-DLC coating that is investigated in the following section is a commercial product that is well established in the coating market, especially for its excellent adhesion to hardened steel substrates. It consists of Cr-doped H-free DLC obtained through magnetron sputtering ion plating of graphite and Cr targets. It is very hard (above 20 GPa) and therefore highly stressed, nevertheless a complex adhesion layer deposited between the substrate and the coating improves its adhesion. This is a very attractive feature for DLC coatings since their adhesion is usually rather poor. An investigation has been performed directed to identifying the most important factor that determines its superior adhesion strength.

COATING STRUCTURE AND PROPERTIES

An SEM micrograph of a fractured cross-section of the coating is displayed in Fig. 4.4. The areas corresponding to the Cr adhesion layer, the Cr/C graded intermediate layer and the Cr-DLC coating are indicated. The mechanical properties of the coating are reported in table 4.1.
ADHESION AND INTERLAYER STRUCTURE

**Figure 4.4** SEM micrograph of the fractured cross-section of the Cr-DLC coating. The different portions of the coating are indicated.

**Table 4.1** Hardness ($H$), reduced Young’s modulus ($E^*$), $H/E^*$, $H^3/E^*^2$, scratch test optical critical load ($L_{c1}$) and Rockwell adhesion class (HF) of the Cr-DLC coating.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20.7 ± 4.4</td>
<td>259.9 ± 41.9</td>
<td>0.08</td>
<td>0.13</td>
<td>50.5</td>
<td>0</td>
</tr>
</tbody>
</table>

**FACTORIAL EXPERIMENT**

A $2^k$ factorial experiment with $n$ replicates (i.e. the number of repetitions of the same treatment) is able to investigate the influence of $k$ factors, varied over 2 levels, in an experimental run were $2^k$ treatments are performed in a random order. The random order of application of the treatments is employed to minimize variations in the experimental setup, and the experiment is said to follow a completely randomized design. The performance of $n$ experimental units produced with the same treatment is investigated, where $n$ is the number of replicates of the experiment. A powerful feature of this analysis is that it allows the investigation of interactions between the different factors. An $M$-order interaction is the joint effect of $M$ main factors. In our case we investigated the influence of $k=3$ factors, $A$, $B$ and $C$, over two levels, -1 and +1, performing $2^3=8$ treatments. The different factors and their levels are shown in table 4.2. While for factors $A$ and $B$ the two levels indicate the presence of the Cr adhesion layer and the Cr/C graded layer, respectively, for factor $C$ the two levels indicate the extent of polishing of the substrate material, so that -1 indicates coarse polishing, and +1 indicates fine polishing. The resulting roughness of the substrates was measured with a confocal microscope and its root-mean-square ($R_q$) value was 0.061±0.004 μm for $C=-1$ and 0.014±0.002 μm for $C=+1$.

The influence of factors $A$, $B$ and $C$ on the adhesion strength of the resulting coatings was investigated using the scratch test and the Rockwell adhesion test. Since it is known that the hardness of the base material has great influence on the results of both tests, this was measured with a Vickers microindenter for each substrate (Vickers Hardness, HV).
Table 4.2 Factors varied in the analysis and description of their respective levels.

<table>
<thead>
<tr>
<th>Factor/Level</th>
<th>-1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No Cr adhesion layer</td>
<td>Cr adhesion layer</td>
</tr>
<tr>
<td>B</td>
<td>No Cr/C graded layer</td>
<td>Cr/C graded layer</td>
</tr>
<tr>
<td>C</td>
<td>Coarse polishing</td>
<td>Fine polishing</td>
</tr>
</tbody>
</table>

Table 4.3 Hardness and roughness of the substrate material used in each treatment and respective factor levels.

<table>
<thead>
<tr>
<th>Treatment #</th>
<th>[HV]</th>
<th>Rq</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A×B</th>
<th>A×C</th>
<th>B×C</th>
<th>A×B×C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>868</td>
<td>0.06</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>965</td>
<td>0.06</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>965</td>
<td>0.07</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>949</td>
<td>0.06</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>891</td>
<td>0.01</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>940</td>
<td>0.02</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>7</td>
<td>934</td>
<td>0.02</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>934</td>
<td>0.01</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The average value of hardness for all substrates was 931±34 HV. As already mentioned, the factorial analysis allows the investigation of the interaction between different factors, so that additional combined factors are introduced: AB, AC, BC and ABC, which are also varied over two levels, -1 and +1, depending on the sign of the product of the contributing factors (e.g. sign(A×B) for factor AB) in the particular run. The hardness and roughness values of the substrate material used in each different treatment are reported in table 4.3, together with the respective factor levels. The performance of the coatings was tested in 4 different locations of each substrate, and assuming that the results of the treatment are uniform over the whole surface of the substrate, the repeated measurements of the adhesion strength can be considered replicates of the experiment. The values of each measurement for the scratch optical critical load Lc1 are reported in table 4.4.

A cube plot representing the experiment is reported in Fig. 4.5a. The 8 corners of the cube represent the 8 treatments, where the factor indicated along each side of the cube is varied between -1 and 1, as indicated. The average value of the response variable scratch resistance from the 4 replicates is reported on each corner of the cube. By considering as an example the C=-1 plane, it can be seen that an improvement of scratch resistance is observed when going from points where the A, B and C factors are negative, such as (A,B,C)=(-1,-1,-1) (2.250 N), to points where either factor is positive, such as (A,B,C)=(+1,-1,-1) (30.950 N), (A,B,C)=(-1,+1,-1) (38.875 N) and (A,B,C)=(-1,-1,+1) (22.250 N). It is clear that positive values of the factors A, B and C result in an improvement of the scratch resistance.

The results of the factorial experiment can be analyzed in a quantitative way through an analysis of variance (ANOVA) procedure, which will be outlined below. For a generalized $2^k$ factorial experiment with $n$ replicates, the contrast of a single or combined factor will equal the sum of the $2^{k-1} \times n$ measurements performed when this factor is positive, minus the sum of the $2^{k-1} \times n$ measurements performed when this factor is negative.
ADHESION AND INTERLAYER STRUCTURE

Table 4.4 Values of optical critical load $L_{c1}$ [N] for each treatment and replicate. The mean value and its standard deviation are also reported for each treatment:

<table>
<thead>
<tr>
<th>Treatment #</th>
<th>value 1</th>
<th>value 2</th>
<th>value 3</th>
<th>value 4</th>
<th>Mean</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.9</td>
<td>3.4</td>
<td>2.0</td>
<td>1.7</td>
<td>2.2</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>32.2</td>
<td>30.5</td>
<td>29.4</td>
<td>31.7</td>
<td>30.9</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>40.7</td>
<td>43.1</td>
<td>33.0</td>
<td>38.7</td>
<td>38.9</td>
<td>7.0</td>
</tr>
<tr>
<td>4</td>
<td>46.4</td>
<td>51.7</td>
<td>40.5</td>
<td>36.0</td>
<td>43.6</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>22.9</td>
<td>22.6</td>
<td>20.8</td>
<td>22.7</td>
<td>22.2</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>30.0</td>
<td>31.3</td>
<td>29.6</td>
<td>33.1</td>
<td>31.0</td>
<td>3.6</td>
</tr>
<tr>
<td>7</td>
<td>47.5</td>
<td>46.7</td>
<td>44.3</td>
<td>45.1</td>
<td>45.9</td>
<td>2.1</td>
</tr>
<tr>
<td>8</td>
<td>51.9</td>
<td>50.6</td>
<td>49.3</td>
<td>50.1</td>
<td>50.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 4.5 Degrees of freedom (dof), Contrast, sum of squares (SS), mean square (MS), $F$ value, % contribution to the sum of squares and $P$ value for all the factors:

<table>
<thead>
<tr>
<th>Factor</th>
<th>dof</th>
<th>Contrast</th>
<th>SS</th>
<th>MS=SS/dof</th>
<th>$F$=$MS/MS_E$</th>
<th>% SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>187.2</td>
<td>1095.5</td>
<td>1095.5</td>
<td>80.8</td>
<td>16.5</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>369.8</td>
<td>4273.7</td>
<td>4273.7</td>
<td>267.4</td>
<td>54.6</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>135.8</td>
<td>576.0</td>
<td>576.0</td>
<td>60.1</td>
<td>12.3</td>
</tr>
<tr>
<td>AB</td>
<td>1</td>
<td>-112.6</td>
<td>396.4</td>
<td>396.4</td>
<td>26.2</td>
<td>5.3</td>
</tr>
<tr>
<td>AC</td>
<td>1</td>
<td>-80.3</td>
<td>201.6</td>
<td>201.6</td>
<td>11.7</td>
<td>2.4</td>
</tr>
<tr>
<td>BC</td>
<td>1</td>
<td>-24.9</td>
<td>19.3</td>
<td>19.3</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>ABC</td>
<td>1</td>
<td>79.0</td>
<td>195.2</td>
<td>195.2</td>
<td>10.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td></td>
<td>223.2</td>
<td>$MS_E=9.3$</td>
<td></td>
<td>6.5</td>
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<tr>
<td>Total</td>
<td>31</td>
<td></td>
<td>6980.9</td>
<td></td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5 (a) Cube plot describing the variation of factors and resulting average scratch resistance. (b) % contribution to the total sum of squares of the single factors $A$, $B$ and $C$ for the Rockwell and scratch test.
The average effect of each factor will be given by the contrast/(2^{k-1} \times n). The sign of the contrast and average effect indicates the direction of variation caused by the factor. The contrast of each factor allows the simple calculation of the sum of squares (SS) for that factor. In 2^k design with n replicates, the sum of squares for any factor is:

$$SS = \frac{\text{contrast}^2}{8n}$$ \hspace{1cm} (4.4)

The total sum of squares $SS_T$ can be computed from:

$$SS_T = \sum_{y=1}^{2^k} \sum_{x=1}^{n} y_{yx}^2 - \frac{\left(\sum_{y=1}^{2^k} \sum_{x=1}^{n} y_{yx}\right)^2}{4n}$$ \hspace{1cm} (4.5)

where $y$ is the treatment number, $x$ is the replicate number and $n$ is the number of replicates. The sum of squares due to errors $SS_E$ can be computed from the difference between the total and each single factor:

$$SS_E = SS_T - SS_A - SS_B - SS_C - SS_{AB} - SS_{AC} - SS_{BC} - SS_{ABC}$$ \hspace{1cm} (4.6)

By dividing each sum of squares by its degrees of freedom the mean square is obtained. The mean square of the error is an estimate of the variance $\sigma^2$. By computing the ratio of the mean square of each factor and the mean square of the error the $F$ parameter is obtained, whose value is an indication of the significance of the interactions with respect to the error. The ANOVA table for the various factors relative to the scratch test is reported in Table 4.5.

The $F$ value of each factor at 95% confidence level for the present problem ($F_{0.05, 1, 24}$) is 4.26, therefore all factors are significant within this confidence interval except the factor $BC$, whose effect seems negligible as compared to the error. The % contribution of each factor is also reported in Table 4.6, and is calculated from the ratio of $SS$ for each factor with respect $SS_T$. The residuals in the model contribute to an error of 6.5 %, which is low considering the numerous sources of error in the experimental setup. The $R^2$ value of the model is given by:

$$R^2 = \frac{SS_A + SS_B + SS_C + SS_{AB} + SS_{AC} + SS_{BC} + SS_{ABC}}{SS_T}$$ \hspace{1cm} (4.7)

The value of $R^2$ is an indication of how well the model fits the data. Nevertheless, the value of $R^2$ depends on the number of factors introduced in the model. A value of $R^2$ that is independent of the number of factors is $R^2_{adj}$, which can be calculated using:

$$R^2_{adj} = 1 - \frac{SS_E / \text{dof}_E}{SS_T / \text{dof}_T}$$ \hspace{1cm} (4.8)
The two values of $R^2$ will differ substantially when the model is neglecting important terms. For the analysis of the scratch test results, $R^2=0.9680$ and $R^2_{adj}=0.9587$. These values are indicative of a satisfactory statistical model.

The statistical model describes the scratch test results with an equation where each factor contributes to the value of scratch resistance. The intercept of the equation is the average value of scratch resistance, the $x_f$ variables are the values assumed by the single or combined factors and their respective coefficients equal half the value of the average effect defined above, since the two values each factor may assume, -1 and +1, span a numerical interval equal to 2. For the present model this equation is:

$$Lc_1 = 33.2 + 5.8 \cdot x_A + 11.6 \cdot x_B + 4.2 \cdot x_C - 7.0 \cdot x_{AB} - 5.0 \cdot x_{AC} - 1.5 \cdot x_{BC} + 4.9 \cdot x_{ABC}$$

(4.9)

It can be seen from table 4.6 and Eq. 4.9 that the contrasts and average effects of factors $A$, $B$, $C$ and the combined factor $ABC$ are positive, indicating that they result in a positive variation of the response parameter scratch resistance. On the other hand, the sign of the contrasts of the combined factors $AB$, $AC$ and $BC$ are negative. This does not necessarily mean that a positive value of these combined factors has a negative impact on the scratch resistance, because these factors are not dominant with respect to the combined single factors. Considering a general case where the $A$ and $B$ effects are dominant with respect to the combined factor $AB$, if the contrast of the $AB$ factor was equal to 0, the single effects of factors $A$ and $B$ would add-up linearly to the final value of scratch resistance. If the contrast of $AB$ was positive, a synergistic effect of the factors would be observed, where the respective contribution would add-up over-linearly, and in the case of negative contrast, the two effects would not be independent and would add-up under-linearly, as is observed in the present case for the combined factors $AB$, $AC$ and $BC$.

The results of the Rockwell adhesion test are reported in table 4.6. In this case the results of the measurements were measured on a discrete scale (the Rockwell adhesion scale), therefore large errors are expected in the ANOVA analysis, reported in Table 4.7. Indeed, it can be seen that the error contributes to 31.8 % of the total sum of squares, resulting in low $F$ values, an $R^2$ value of 0.6820 and a $R^2_{adj}$ value of 0.5892. Indeed, within a 95 % confidence only factors $A$ and $B$ are significant. They are both negative, indicating that they contribute to achieving lower Rockwell adhesion scale values, increasing the adhesion, and factor $B$ is the dominant factor. The high error does not allow further investigations of the interaction between factors.

Considering that the single factors are dominant with respect to the combined factors, a graph of the % contribution of the single factors to both the scratch and Rockwell adhesion can be drawn as shown in Fig. 4.5b. It is clear from Fig. 4.5b that the dominant factor than enhances the adhesion of the Cr-DLC coatings is the graded Cr/C layer. It can be concluded that improvements of the adhesion of DLC coatings should be sought in the development of an appropriated graded adhesion layer between substrate and coating.
4.3 TEM ANALYSIS OF A GRADED INTERLAYER

It has been shown in the previous section that the most important parameter enhancing the adhesion of the commercial Cr-DL coating is the compositional gradient realized along its thickness, and that an initial Cr adhesion layer is also beneficial to the final adhesion strength. This result has been implemented in our nanocomposite TiC/DLC coatings, where a complex interlayer scheme was employed. A Cr adhesion layer was deposited first. Two compositional gradients were subsequently introduced between substrate and coating. The first is a gradual compositional variation from Cr to Ti, obtained through a corresponding gradient of the power applied to the relative metallic targets. The second gradient is a variation from Ti to Ti-DLC achieved by varying the flow rate of acetylene in the chamber, from 0 up to the level used for coating deposition. The following analysis investigated the interfacial structure of coating 100V80.

4.3.1 BF AND EF-TEM

Cross-sectional TEM was employed to study the structure of the coating. A bright field (BF) image from the cross-sectional specimen is shown in Fig. 4.6.
Figure 4.6 Cross-sectional BF-TEM image of the coating. From the bottom: steel substrate, Cr adhesion layer, Cr/Ti mixed layer, TiC interlayer, coating. DP insets show that the TiC interlayer is (111)-textured (bottom inset, (111) reflections indicated by arrows), whereas the coating is not (top inset, TiC diffraction rings). The microstructure of the coating is columnar, indicated by an arrow.
In the lower part of the micrograph the SS substrate is visible. On top of the substrate a Cr interlayer is present, then a mixed Ti-Cr layer, followed by a 150 nm thick TiC layer, and finally the coating. The bottom inset in Fig. 4.6 shows an SAED pattern from the area circled in the figure, i.e. the TiC interlayer. This portion of the interlayer is clearly textured, as the TiC (111) planes preferentially orient parallel to the substrate surface. The observed (111) texture is common to several fcc compounds grown by PVD. More specifically, such texture has already been reported by Hultman et al. for TiN coatings, and it is due to kinetic-limited crystal growth. TiN and TiC have the same crystallographic structure, the only structural difference being a more covalent bond between Ti and C than between Ti and N. The lowest energy surface for both crystals is the (002) plane, and this corresponds with the texture that would be expected for thermodynamical equilibrium. Hultman et al. have observed that a (111) texture develops instead for depositions performed with low ratio of ion flux to neutrals flux ($J_i/J_a$, ion number). When the coating is deposited under weak ion bombardment the equilibrium structure cannot form, and a kinetic-limited (111) texture develops instead. At higher values of $J_i/J_a$ the situation is reversed, prevailing the thermodynamically favored (200) texture. It is not clear yet if the same mechanism may apply to TiC columns, but small areas of (200)-textured TiC were also observed in the present case, while the overall texture is predominantly (111).

The coating starts to grow over the TiC interlayer up to a thickness of about 1.4 μm. Within the coating no texture of the TiC phase is present, as rings form in the diffraction pattern corresponding to TiC lattice spacing (see top inset in Fig. 4.6), indicating a random orientation of the TiC nano-crystals. Within the nano-composite layer columns develop of a width around 150 nm. They run through the whole coating thickness and are separated by brighter areas (indicated by arrows in Fig. 4.6), the composition of which is further detailed below.

Three-window EF-TEM was employed to characterize the composition variation that is obtained by the graded interlayer deposition scheme. The squared area near the bottom of Fig. 4.6 has been examined, and the results are shown in Fig. 4.7. The BF image indicates that a change of contrast accompanies the change of composition detected in the Cr, Ti and C maps. The elemental mappings indicate that on top of the Cr interlayer a thin area exists where both Ti and Cr are present, while C is absent. On top of this a Ti-rich area develops with the C content gradually increasing towards the side of the coating. Finally the composition stabilizes. Columns and columnar boundaries are visible (indicated by arrows). The elemental mappings show that the columnar boundary areas are enriched in C as compared to the columns. The columnar structure of the coating is a consequence of shadowing effects that occur during growth, and originates from the TiC intermediate layer. In the present case it was observed that C-enriched columnar boundaries in the coating seem to follow the columnar boundaries of the interlayer itself. As already introduced in chapter 3, this can be understood considering that columns typically grow with a spherical front that can shadow the material around the column by the incoming atomic flux in PVD deposition. This will result in the formation of a compositional discontinuity and the formation of columnar boundaries. The shadowing effects are caused by the roughness of the surface over which the coating is growing. If the columnar features within the TiC intermediate layer could be reduced, a reduction of columnar growth of the coating would
be expected. It is interesting to notice a contrast variation inside the mixed Cr-Ti zone, i.e. clearly phase transitions occurred as will be analyzed in section 4.3.2.

An attempt was made to determine the compositional gradient within the interlayer quantitatively, relating the integrated EELS signals to the coating composition. A two-window method was employed in this case to reduce thickness effects. Jump ratio images of the Cr, Ti and C EELS signals were integrated within 156.8 nm, along the 400 nm-long area shown on top of Fig. 4.8, where the pixel size in the maps is 0.8×0.8 nm.

Figure 4.7 Magnification of the square area in Fig. 4.6. BF image, Cr map, Ti map and C map, as indicated. Arrows indicate a columnar boundary.
Figure 4.8 BF image of interlayer area (top). Compositional profile measured from the same area (center). Power applied to the targets and reactive gas flow as a function of time during the interlayer deposition (bottom).
The Cr content was set equal to 100 at. % within the Cr interlayer and 0 at. % within the nanocomposite coating, respectively, whereas the Ti and C contents were set equal to 0 at. % within the Cr interlayer and equal to the coating composition, as measured through EPMA, within the nano-composite coating. The integrated signals were scaled to the compositions indicated above, so as to indicate a compositional variation within the graded part of the interlayer, see Fig. 4.8. It must be pointed out that the abscissa in Fig. 4.8 is in units of time, whereas the compositional variation in the middle graph is plotted as a function of the position within the interlayer. Consequently, to relate the two graphs the variation of the growth rate within the different portions of the interlayer must be considered. The change of power applied to the magnetrons results in a graded Cr-Ti compositional gradient, as expected. Subsequently, acetylene is introduced in the chamber. The presence of acetylene in the sputtering gas has two effects on the deposition process. The first effect is that it can change the degree of ionization in the plasma, as it has a different ionization potential, different mass and a complex dissociation behavior. This may affect the deposition process, as lighter C2H2-based ions do not bombard the growing film with the same momentum as Ar ions. The relative fractions of the different ions in the plasma and the plasma characteristics may be altered by a change in gas composition. The second effect concerns possible poisoning of the target that occurs during reactive sputtering deposition. For a recent review about this complex phenomenon reference is made to Berg et al. Under the currently employed conditions, we observed that the voltage applied to the Ti cathodes increases as a function of the relative flow rate of C2H2 gas, as already reported for depositions performed under the same conditions. Because the deposition is carried out by keeping the power to the cathodes constant, it implies that the ion current to the targets decreases, which is an indication of the progressive poisoning of the target. The progressive poisoning of the target results in a variation of the flux of atoms sputtered away from the target surface. In fact this will be gradually enriched in carbonaceous phases as the degree of poisoning increases. Furthermore, the plasma-enhanced chemical vapor deposition (PE-CVD) of C2H2 is a considerably faster process than magnetron sputtering of Ti from the cathodes. Indeed, the C content increases slowly at the beginning of the Ti/C graded area, and afterwards it increases much faster until the acetylene flow rate stabilizes at the end of the interlayer deposition. The observed target poisoning effect together with the higher relative rate of C2H2 deposition can explain why the profile of C concentration within the Ti/TiC intermediate layer does not exhibit a linear increase, as would be expected by observing the linearly increasing C2H2 flow rate at the bottom of Fig. 4.8.

4.3.2 HR-TEM

HR-TEM analysis was performed on the interlayer area. The initial Cr adhesion layer is crystalline, having a bcc A2 structure, as confirmed by the indexed atomic planes in Fig. 4.10. Cr has a bcc crystallographic structure, and when introduced as alloying element in Ti alloys it acts as a β-stabilizer, allowing the metastable formation of the β-Ti bcc phase, which is retained at room temperature if the Cr concentration is higher than 7.4 at. %.

A thorough theoretical study of the stability of the Cr-Ti solid solution has been presented by Sluiter et al. A bcc A2 substitutional solid solution (β-phase), a metastable B2 phase and a C15 Laves phase are expected in the compositional range. Nevertheless,
CHAPTER 4

Ti-Cr solid solutions were observed to undergo inverse melting (solid state amorphization, SSA) after high temperature annealing of mechanically alloyed samples\textsuperscript{9} and sputtered films\textsuperscript{10}. For the Ti-Cr system, a metastable phase diagram was formulated\textsuperscript{9}, which indicates that when varying the composition from Cr-rich to Ti-rich Ti-Cr solid solutions phase transitions are expected to occur as follows: Cr-rich $\beta \rightarrow$ amorphous $+\beta \rightarrow$ amorphous $\rightarrow$ amorphous $+\beta \rightarrow$ Ti-rich $\beta$, where the pure amorphous phase was predicted around 50 at. % Ti concentration, as shown in Fig. 4.9. Within the A2 crystal, a progressive variation of the lattice constant is observed in areas gradually richer in Ti, and finally the interlayer loses its crystallinity at the location indicated by a mark in Fig. 4.10. The EELS analysis indicates that crystallinity is preserved until concentrations of Ti around 60 at. %. Nevertheless, the determination of the concentration of the elements, as performed through EF-TEM, is only qualitative, and is expected to yield a reliable estimate of the relative variation of atomic composition, rather than giving the real values. Another approach to determine the composition to which the solid solution extends is based on the measurement of the lattice constant of the A2 phase. A careful study of the variation of lattice spacing with the composition for this phase has been performed\textsuperscript{9}, suggesting that the concentration dependence of the lattice constant can be described by Vegard’s law, and more specifically by the equation:

$$a = 0.328 \text{ nm} - 0.0398 \text{ nm} \cdot x_{\text{Cr}} \quad (4.10)$$

where $a$ is the final lattice constant and $x_{\text{Cr}}$ is the atomic fraction of Cr in the solid solution. The observed A2 (110) spacing prior to amorphization is 0.216 nm, as indicated in Fig. 4.10, instead of 0.204 nm expected for pure Cr or 0.234 nm for pure $\beta$-Ti. The corresponding lattice constant indicates a Cr concentration of 56.6 at. %, according to equation (1), which can be considered as a more reliable value than the one provided by the EELS analysis.

Figure 4.9 Metastable phase diagram calculated using the CALPHAD method for equilibrium between the liquid, bcc and amorphous phase only, from Ref. 9.
The substitutional Ti-Cr $\beta$ phase is based on an A2 bcc lattice. The lattice spacing indicates a Ti concentration of 43.4 % at. (see text). An amorphous/nanocrystalline phase forms as the Ti content increases beyond the point indicated by the arrow.

Figure 4.10
In the present case it was observed that the Cr-rich $\beta$ phase is stable in the 100-56.6 at. % Cr range, whereas in the metastable phase diagram,$^9$ at the presently employed deposition temperature of 185 °C, its decomposition is expected at very low Ti content to give a dispersion of $\beta$ phase crystals in the amorphous matrix. It must be stressed that PVD is a highly non-equilibrium technique, and off-stoichiometric compounds are likely to be formed. Nevertheless, the enhanced stability of the Cr-rich A2 phase can be partially explained by noticing that the underlying Cr layer may act as a template, stabilizing the growing A2 crystal in an extended range, until the thermodynamically favored amorphous phase forms. Further increasing the Ti content results in the formation of a dispersion of nano-crystals in the amorphous matrix, as shown in Fig. 4.11. This area is too small for SAED investigations, but the diffuse halo obtained from the fast Fourier transform (FTT) of the image of the amorphous phase is reported as an inset in Fig. 4.11. The formation of A2 Ti-Cr $\beta$ phase crystals is expected from the metastable phase diagram. The phenomenon of SSA has been mostly studied on multilayered structures (diffusion couples), where various suitable elements are stacked in layers with a periodicity of 10-60 nm.$^{11}$ Upon annealing the structures are observed to undergo an amorphization process that relies on diffusion, as confirmed through TEM investigations$^{12}$ and Rutherford Backscattering Spectrometry.$^{13}$ Furthermore, it was observed that by reducing the periodicity of the multilayer in the nm range, suitable elements undergo SSA during the deposition, without the application of any additional annealing step.$^{14}$ From the processing parameters-composition relation presented in Fig. 4.8, and taking into account the rotation speed of the substrate holder, we derive that in the amorphous area the interlayer grows about 1.5 nm after exposure to each target while the substrate holder rotates in the chamber. It is therefore expected that the periodicity of the compositional variation due to the alternating exposure to the different Cr and Ti targets is less than 1.5 nm. The growing film is bombarded by Ar ions during growth, which favors intermixing of the elements. The influence of defects generated by ion irradiation on the nucleation of the amorphous phase were investigated by Blatter et al.;$^{15}$ the authors determined that ion irradiation influences the alloy amorphization, and suggested that a minimum defect concentration is required for the amorphous phase nucleation, but too intense ion bombardment results in the nucleation of the thermodynamically stable TiCr$_2$ and $\alpha$-Ti phases. Indeed, the authors showed that a dose of $10^{12}$ cm$^{-2}$ He$^+$ ions accelerated at 500 keV towards the surface of a $\beta$-Cr$_{40}$Ti$_{60}$ alloy favored its amorphization upon annealing, due to the generation of vacancies that enhance diffusion and favor the nucleation of the amorphous phase. In the present case the Ar ion dose integrated over the whole Cr-Ti graded layer deposition is of the order of $10^{17}$ cm$^{-2}$, with an energy per ion of about 50 eV.

In our case a considerably higher ion dose is employed but with much lower energy and with heavier ions. The difference of ion energy and mass does not allow a direct comparison of the two experiments, but it should be mentioned that ion-irradiation induced amorphization has been observed for many materials systems under energetic ion irradiation. The mechanical properties of the amorphous phase were investigated by Blatter et al.;$^{16}$ the comparison between the Ti$_{60}$Cr$_{40}$ $\beta$-phase and the amorphous phase of the same composition revealed that a hardness increase of about 40 % and a decrease in Young’s modulus of about 20 % (assuming a constant Poisson’s ratio) accompany the amorphization of the alloy.
On the top of the thin amorphous layer, crystalline $\alpha$-Ti columns start to grow; a column is depicted in Fig. 4.12a. In this area of the interlayer a gradual transition from Ti to TiC is expected as acetylene gas is gradually introduced into the sputtering chamber. A clear contrast modulation is observed at the bottom of the column, and it gradually decreases towards the top of the column. This moiré contrast is due to the periodic presence of stacking faults.

TiC bears a very high stacking fault energy, which varies as a function of the C/Ti ratio\(^{17}\), so that the formation of these defects occurs only as a consequence of the presence of impurities\(^{18}\) or during growth at low C content. Indeed, the crystallographic difference between hcp $\alpha$-Ti and fcc TiC is AB stacking versus ABC stacking. The transformation of

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Figure 4.11 Nano-crystalline/amorphous Ti/Cr phase. Nano-crystals (circled) are observed dispersed in an amorphous matrix. The FFT from this area is reported on the top inset.
Figure 4.12 (a) TiC column from the intermediate layer. (b) HR-TEM micrograph from the area indicated at the bottom of the column, the arrow indicates the location where the crystalline column starts growing on top of the amorphous phase. (c) HR-TEM micrograph from the area of the TiC column indicated in the middle of the column. Ti and TiC domains can be clearly distinguished, separated by horizontal lines and indexed crystallographically.
an fcc lattice into an hcp lattice along the close-packed (111) fcc direction occurs via the operation of Shockley partial dislocations. Such stacking faults increase the internal energy of crystals, but in the present case their formation indicates that locally the C content is not sufficient to stabilize the TiC fcc structure, and instead the hcp Ti phase with C in solid solution becomes favored. For low C content, it will be natural for the material to form stacking faults and produce a stacking of Ti followed by TiC domains. Indeed, the density of stacking faults decreases gradually as the column grows (i.e. as the C content increases). The transition region between the amorphous phase and the crystalline column (indicated by the bottom box in Fig. 4.12a) is investigated by HR-TEM in Fig. 4.12b. The location of the transition is indicated by an arrow, and the nucleating crystalline phase is \( \alpha \)-Ti, as indexed in the micrograph. Subsequently, certain areas are observed where it is possible to distinguish clearly the Ti and TiC, as indexed in the HR-TEM micrograph in Fig. 4.12c. The phases are identified through the inter-planar spacing and the angles between the different planes. It was observed that the stacking faults result in repeated switching between hcp Ti and fcc TiC crystallographic structures, which occurs every few atomic planes and within large domains; TiC forms in the lower half of the column, i.e. at low C concentrations (from the compositional profile in Fig. 4.8). The column eventually starts growing as defect-free TiC. At a composition of 50 at. % C, segregation of C occurs and C-enriched column boundaries develop, as is evident from the elemental maps in Fig. 4.7 and the compositional profile in Fig. 4.8. Finally the processing parameters stabilize and the coating starts to grow. The columnar boundaries observed in this coating (Fig. 4.7) grow in correspondence to the columnar boundaries present within the interlayer. The coating has a nano-composite TiC/DLC structure, with TiC crystals of size around 4 nm homogeneously dispersed within the DLC matrix, as will be described in chapter 5. The scratch test optical critical load \( L_c \) was measured at 32 N.

### 4.4 Conclusions

The factorial analysis of the Cr-DLC coating adhesion strength indicated that the most important factor determining its superior adhesion strength is the presence of the Cr/C graded interlayer. A graded interlayer scheme was applied for the deposition of the nanocomposite TiC/DLC coatings, resulting in a satisfactory composition gradient. The graded interlayer consists of two different parts, namely the Cr-Ti and Ti/TiC graded structures, the former of which gave the most promising results. The results point to the existence of a nano-crystalline/amorphous Cr-Ti phase. While the use of Cr interlayers is very common in several classes of PVD coatings no gradual interlayer schemes were proposed so far for Cr interlayers, that may improve their performance by allowing gradual matching between the Young’s modulus of the coating (ideally below 150 GPa) and the one of Cr (248 GPa) or of a steel substrate (typically 200 GPa). An increase of the Ti content above 45 at. % results in the formation of a Cr-Ti amorphous/nanocrystalline phase that was observed over a wide compositional range (55 to 5 at. % Cr). The variation of its mechanical properties is expected to follow the variation in composition, presumably with a gradual increase in compliance occurring as the Ti concentration increases. This would allow to begin the interlayer deposition with a composition that results in a perfect match between the Young’s moduli of the substrate and interlayer and subsequently the composition could be graded towards the coating side, until the Young’s modulus matches...
the one of the coating, to result in a perfect functional gradient of elastic properties at the coating/substrate interface. Furthermore, the formation of the amorphous/nano-crystalline phase is interesting because of the increasing importance of coatings with a “glassy” microstructure, as will be discussed further in Chapters 5 and 6. By starting the growth of the coating from an amorphous phase the columnar structure will be likely reduced, as no discontinuities would be present in the interlayer that may propagate within the coating. Nevertheless, while the structure of the interlayer influences the formation of columnar features in the coating, it has been shown in chapter 3 that the composition of the coating is the dominant parameter determining the creation of columnar boundaries. A final consideration is that the possibility of employing an amorphous interlayer for amorphous carbon coatings is attractive in that this solution would greatly decrease the diffusion of C atoms towards the substrate and the possible evolution of Kirkendall porosity in crystalline phases near the interlayer area. This aspect would be especially important in coated steel substrates designed for high-temperature applications, and for coated Al substrates. In fact the formation of Al carbides should be avoided because of their very poor mechanical properties.

References