Characterization of nanostructured ceramic and cermet coatings deposited by plasma spraying

E. Sánchez (1), E. Bannier (1), M. Vicent (1), A. Moreno (1), M.D. Salvador (2), V. Bonache (2), E. Klyatskina (2), A. R. Boccaccini (3)

(1) Instituto de Tecnología Cerámica - Asociación de Investigación de las Industrias Cerámicas. Universitat Jaume I. Castellón, Spain.
(2) Instituto de Tecnología de Materiales. Universidad Politécnica de Valencia. Valencia, Spain.
(3) Department of Materials. Imperial College London, London SW7 2BP, UK
Contact e-mail: emilie.bannier@itc.uj.edu

ABSTRACT

Industry has a growing need of advanced coatings for a variety of applications (aerospace, special machinery, medicine ...). Nanostructured coatings have the potential of providing novel materials with enhanced properties. This paper describes the results of recent research on wear resistant nanostructured coatings. Cermet (WC-Co) and ceramic (Al₂O₃-TiO₂) coatings were obtained by atmospheric plasma spraying. Coating microstructure and phase composition were characterized using SEM, EDX and XRD techniques. Vickers microhardness (HV) of the coatings was also measured. The microstructure and properties of the developed nanostructured coating was compared with those of their conventional counterparts. The influence of the substrate on both microstructure and properties was investigated, as the coatings were deposited on two different steels. In the WC-Co coatings, significant decomposition of the WC particles occurred during spraying which is prejudicial to wear resistance. Nanostructured Al₂O₃-TiO₂ coatings exhibited a bimodal microstructure that retained
the initial nanostructure of the powder. The presence of these areas leads to better
tribological properties.

1. Introduction

Advanced coatings are needed in many industrial sectors to enhance the surface
characteristics of structural elements or to functionalize a surface. In the former case,
the purpose is usually to improve some given material’s properties in order to provide
protection against wear, corrosion, chemical attack, thermal shock and/or high
temperatures. In the latter case, the coating provides a surface with a new function,
such as self-lubricating, catalytic, bioactive or self-cleaning coatings. Much research
has been undertaken into nanostructured materials, which generally display better
physical or mechanical properties than their conventional counterparts [1,2]. As a
result, nanostructured coatings could lead to significant advances in the availability of
high-performance materials in various industrial sectors [3,4].

There are numerous techniques for producing coatings: physical vapour deposition,
chemical vapour deposition, thermal spraying, electrochemical techniques, sol-gel
methods. Among these techniques, thermal spraying is one of the most versatile for
depositing thick coatings. In such process, a feed material is fused and accelerated
until it impacts upon the substrate, where it is rapidly cooled, forming the coating [5].

Thermal spray techniques can be classified in two large families, depending
on whether the energy source is of chemical or electric origin (figure 2) [5]. The
different techniques differ in flame temperature and particles velocity.

The two most commonly used thermal spray methods are atmospheric plasma
spraying (APS) and high velocity oxy-fuel flame spraying (HVOF), in which the feed
material is in powder form [6]. As a result, in order to obtain nanostructured coatings
using these techniques, it should be convenient to use nanoparticles as raw material.
However nanoparticles cannot be sprayed directly owing to their small mass. Thus
sprayable nanostructured powders must be obtained in two stages [7,8]. First, the nanoparticles need to be synthesised. Then, they have to be agglomerated to form sprayable micrometric agglomerates. This second stage, which is critical for the success of the method, is known as reconstitution process.

Innumerable methods exist to produce nanoparticles [9-13] but spray drying is the most widespread process for reconstituting nanoparticles into appropriate micrometric granules for thermal spray deposition [7,14-16]. The process consists, basically, of spraying a suspension through a nozzle into a drying chamber where the solvent is removed, producing a highly flowable agglomerate powder as a result of the sphericity of the agglomerates.

It is important to point out that not all spray-dried powders are suitable for thermal spray coatings. The reconstituted powder must be dense enough and have a proper size distribution. A fine and porous powder can not be fed adequately into the flame, conducing to low deposition efficiency, poor adhesion and high coating porosity. Some researchers [17] have found that spray-dried powders with bulk density >1.7 x 10^3 kg/m^3 and mean particle size > 20 µm can be directly used for plasma spray coating.

Once the reconstituted nanometric powder has been obtained, the process parameters need to be adapted to the characteristics of the new powder. In particular, heating of the agglomerates need to be closely controlled in order to preserve the nanostructure in the final coating without impairing adhesion to the substrate [18,19]. An intense research activity is being developed during this decade which deals with nanostructured powders to obtain different types of oxide and non-oxide coatings, such as alumina [20], titania [21,22], alumina-titania [23-25], stabilized zirconia [26-28], and cermets [23-31].

In this work alumina-titania ceramic coatings and cemented tungsten carbide cermet coatings were obtained by APS using commercial conventional micrometric powders and reconstituted nanopowders. Both materials are commonly used to form wear-
resistant coatings on metallic substrates and the use of nanostructured feedstock is expected to enhance their properties. This study is aimed to characterize the microstructure of the developed nanostructured coating and to compare the results with those of their conventional counterparts. Vickers microhardness (HV) of the coatings was also measured, as it is a highly relevant property of wear-resistant coatings. The influence of the substrate on both microstructure and properties was also investigated, as the coatings were deposited on two different steels.

2. Experimental techniques

2.1. Materials

Cermet (WC-Co) and ceramic (Al₂O₃-TiO₂) coatings were sprayed using commercial (conventional and nanostructured) thermal spray powders. The characteristics of the powders used are given in Table 1.

Two different steels coupons of dimensions 150x30x2 mm were used as substrates. Half of the coatings was sprayed on AISI 304 stainless steel samples. The rest of the layers was obtained on C45 (EN 1.11191) high grade steel coupons. Both substrates compositions are given in Table 2.

2.2. Coatings deposition

The coatings were obtained using a Sulzer Metco model F4-MB air plasma spray gun mounted on an industrial robot. Before spraying, the substrate was blasted with corundum grit and cleaned with ethanol to remove any dust or grease residue from the surface. In the case of alumina-titania coatings, a Ni-Al metallic alloy was sprayed between steel substrate and ceramic coating in order to improve adhesion. It was also necessary to hold the substrate temperature between 95 and 200 °C throughout the process in order to avoid spalling during the final cooling. In contrast, tungsten carbide coatings displayed very good adhesion without requiring the presence of a bond coat nor preheating of the substrate.
The main spraying parameters are given in Table 3. Tungsten carbide coatings were sprayed using Ar/H₂ or Ar/He mixtures as plasma-forming gases with a view to studying the effect of the nature of the secondary gas on the characteristics of the resulting coatings. In the case of the ceramic coatings, this paper describes only the influence of the feeding powder particle size and of substrate nature. The effect on some spraying parameters on coating microstructure and properties has been reported elsewhere [32].

### 2.3. Characterization techniques

Coatings crystalline phases were evaluated by X-ray diffraction (XRD) techniques (Bruker D8). Then coatings cross-sections were observed by scanning electron microscopy (FEI Quanta 200F Field Emission Gun-SEM or JEOL 6300) connected to X-ray energy dispersion microanalysis equipments (EDX). Vickers microhardness values were determined by realizing 10 indentations with a charge of 200 g for 15 s using a LECO M400 microhardness tester. All measurements were made on polished cross-sections.

### 3. Results and Discussion

#### 3.1. Characterization of WC-Co coatings

##### 3.1.1. Microstructure analysis

APS deposition is a high energy technique, as a consequence the initial WC-Co powder is not only fused during the process but also it may undergo reactions such as decarburization or oxidation which can lower the mechanical properties of the deposited coating [33-35]. The XRD analysis of as-sprayed cemented carbides coatings obtained with both conventional and nanostructured powders, sprayed either with Ar/H₂ or Ar/He, showed the presence of tungsten carbide (WC), ditungsten carbide (WC₂) and traces of cobalt oxide (Figure 1).
It was found that coatings sprayed on both types of substrates present similar phase composition but the layers deposited on C45 display a much lower decomposition, as visible through weaker W_2C and W peaks in XRD spectra (Fig. 1). This effect is more important in the case of the nanostructured powder. This lower decomposition is probably due to the higher thermal conductivity of high grade C45, which allows a quicker cooling of the as sprayed coatings.

Moreover, coatings obtained using helium as secondary gas show lower decomposition than coatings sprayed with hydrogen: XRD spectra exhibit stronger WC peaks and lower W_2C and W peaks (Fig. 1). This can be explained by the lower energy of the plasma plume when helium is used as secondary gas and by the much higher gas flow rates which allow a higher plasma density and make difficult the entrance of oxygen inside the flame.

Finally, the substitution of conventional powders with agglomerated, nanostructured powders in APS process produced practically no changes in the XRD spectra, in most of the spraying conditions. However it was found that the nanostructured coating sprayed with helium on C45 high grade steel present a slightly lower decomposition than their conventional counterpart.

SEM micrographs have shown that all the coatings show a similar microstructure as can be observed in Figure 2 and 3 for conventional and nanostructured coatings respectively.

All coatings are highly heterogeneous with a porous splat-like structure. Three different zones were identified. First, the coatings have a matrix (referenced as A in Fig. 2 and 3) containing Co, W, and C in quantities that fluctuate throughout the layer, depending on temperature and decarburization levels. Furthermore, elemental tungsten phase is probably present in the vicinity of the splat boundary in areas of high W concentration (referenced as C). Finally fine dispersions of WC crystals in a cobalt-rich matrix are found in the zones referenced as B. Higher magnification of those areas are given in
Figure 4 in the case of the coatings deposited on C45 substrate using helium as secondary gas.

Although the microstructures of all coatings are quite similar, it was found that the WC crystals are much smaller when the coating is obtained from the nanostructured powders (figure 4). It was also observed that the coatings obtained from helium have a higher proportion of fine dispersion of WC crystals and contain less tungsten-rich white particles. These observations agree with the XRD results (Figure 1), which indicate a lower decomposition of the initial powder when spraying is done with helium.

Moreover, a recrystallization of small carbides from the melted matrix was observed in all coatings. This phenomenon becomes more important when the decomposition of the initial carbides increases. As can be seen in Figure 5, in the case of conventional coatings sprayed with hydrogen on C45 substrate, some of the initial WC crystals are partly melted in the surrounding matrix during the deposition process. Tungsten carbides (WC o and/or W2C) crystallized from the matrix, giving rise to the formation of nanosized crystals, as the cooling is fast enough to avoid the growth of the newly formed crystals. The presence of such nanocrystals may influence the coating properties.

### 3.1.2. Microhardness measurement

The Vickers microhardness measurement data are detailed in Table 4. They show that there are no great differences between the conventional coatings and those obtained from the nanostructured powder. In contrast, the coatings sprayed with helium exhibit higher microhardness than those obtained using hydrogen as a secondary gas. It can be seen that the coatings obtained on the high grade steel substrate seem to present slightly higher microhardness value. However, these differences are not significant, if the experimental error is taken into account.
3.1.3. Discussion

As mentioned in the introduction, WC-Co coatings are commonly used as wear resistant coatings. Although, further mechanical characterization comprising fracture toughness measurement and wear resistance determination is currently in progress, the microstructure characterization already give an idea of which coatings should give the best behavior.

First, microstructural characterization reveals an important decomposition of WC crystals during the projection with the appearance of new phases (W₂C and W). In fact, significant differences exist between the crystalline phases of the powder and the crystalline phases of the coating. During deposition, WC crystals undergo a partial decomposition, possibly as results of parallel reactions which involve both carbon and tungsten:

\[
\text{WC} \rightarrow \text{C} + \text{W} \\
\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \\
\text{W} + \text{WC} \rightarrow \text{W}_2\text{C}
\]

Such decarburization occurs in all coatings and does not depend on the powder particles size. However, it can be significantly reduced using an Ar/He mixture to form the plasma instead of the usual Ar/H₂ mixture, due to a lower plasma temperature and higher gas flow rates which reduce the quantity of oxygen present in the plasma plume. Moreover, it was found that coatings sprayed on AISI 304 stainless steel present a higher decomposition than layers deposited on C45 high grade steel, as a consequence of the much higher thermal conductivity of C45 substrate which allows higher cooling rate of the coating and reduces available time for decomposition.

It is important to point out that the decomposition of the tungsten carbides during projection is highly prejudicial to the coatings properties. Actually, many investigators have studied this decomposition, and have tried to minimize it in order to obtain
coatings with enhanced mechanical and tribological properties [33-35]. In effect, the presence of W₂C and elementary W as well as the disappearance of the WC initial crystals is detrimental to the wear resistance of such layers. As a consequence, coatings sprayed with helium should present better tribological properties than coatings deposited with hydrogen as a result of their lower decarburization. For the same reason, the wear resistance is expected to be higher when the coatings are sprayed on C45 high grade steel instead of AISI 304 stainless steel.

Finally, no great differences were observed in the crystalline phases present in the coatings obtained from different powders. Nevertheless, SEM observation reveals that the main difference between nanostructured and conventional coatings resides in the size of the tungsten carbides crystals which are much smaller in the second case. It is expected that reducing the size of the carbides should enhance the coating wear resistance but it should be confirmed by tribological testing.

3.2. Characterization of Al₂O₃-TiO₂ coatings

3.2.1. Microstructure analysis

In the case of the ceramic coatings, XRD analysis (Figure 6) showed that the main phases were α-Al₂O₃ (corundum), γ-Al₂O₃, and TiO₂ (rutile) when the starting powders essentially contained α-Al₂O₃. When the powder is heated in the plasma flame, γ-alumina forms. Then, as the particles cool down, part of the γ-Al₂O₃ transformed back to corundum. In general, the layers deposited on C45 substrate present a lower α- to γ-alumina ratio than the coatings sprayed on AISI 304. This is probably due to a higher cooling rate of these coatings because of the higher thermal conductivity of C45 steel. Furthermore, the nanostructured coatings exhibited a larger α- to γ-alumina ratio than the conventional coatings, as shown in Figure 6. In fact the nanostructured powder is formed by porous agglomerates of nanoparticles [32] and, as a consequence has a low thermal conductivity, avoiding the complete fusion of the granulates. Actually, part of
the initial corundum does not transform to $\gamma$-alumina, and remains in the final coating, as confirmed by the SEM observations below.

Typical micrographs can be seen in Figure 7 and 8 for the conventional (left) and nanostructured (right) coatings in the case of AISI304 and C45 substrate respectively. EDX analysis was performed to determine the atomic composition of the different phases found in the coatings. Comparing these results with those of XRD analysis, the likely phase composition of each zone in the coating microstructure could be deduced. Both nanostructured and conventional coatings are confirmed to be formed by a completely melted matrix of $\gamma$-$\text{Al}_2\text{O}_3$ with dissolved Ti$^4+$ (marked A and D in Fig. 7 and 8) containing clear splat-like particles with high TiO$_2$ content (marked B and E). In the case of the nanostructured coatings, agglomerate-like particles (marked F), corresponding to partially melted starting agglomerates were observed. Due to these uncompleted melting zones, $\alpha$- to $\gamma$-alumina ratio is higher in the nanostructured coating as mentioned above. This microstructural description, which has been set out elsewhere [23,24] was observed on both substrates.

Finally, EDX analysis of the different phases showed a major difference between conventional and nanostructured coatings. Although both coatings have a similar matrix composition, conventional coatings present a segregation of titanium in the white zones which showed a lower aluminum content and much higher titanium proportion. In the nanostructured coating, however, the white zones have in general similar concentration of aluminium than the matrix with slightly higher titanium content. This segregation has been also pointed out in previous works [32,36].

3.2.2. Microhardness measurement

The results of the microhardness measurements are given in Table 5. When the error in the resulting values (5–10%) is taken into account, it appears that the nanostructured coatings display a higher microhardness than their conventional counterparts.
Moreover, it was found that the layers deposited on AISI 304 substrates present higher microhardness than the layers sprayed on C45.

3.2.3. Discussion

Microstructure characterization have shown that the main crystalline phases found in the coatings are $\alpha$-$\text{Al}_2\text{O}_3$ (corundum) and $\gamma$-$\text{Al}_2\text{O}_3$, whereas feeding powders are mainly formed by $\alpha$-$\text{Al}_2\text{O}_3$. The origin of $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ in plasma sprayed alumina coatings was explained by McPherson [37]. This author have shown that, when a particle is completely melted by the plasma plume, $\gamma$-$\text{Al}_2\text{O}_3$ nucleates preferably from the liquid phase. In fact, $\gamma$-$\text{Al}_2\text{O}_3$ has a lower interfacial energy with the liquid which compensates for the low driving force for crystallization resulting from the small free energy difference between liquid and crystalline phases. Occasionally, if the cooling rate is sufficiently slow, $\alpha$-$\text{Al}_2\text{O}_3$ may appear. However, most of the $\alpha$-phase present in the coating originates from unmelted or partially melted particles. In the later case, unmolten $\alpha$-$\text{Al}_2\text{O}_3$ acts as a nuclei for crystallization, favoring the formation of corundum during cooling.

It is important to point out that nanostructured coatings display a greater relation of $\alpha$- to $\gamma$- alumina than the conventional layers, independently of the substrate. Actually, in the nanostructured case, SEM observation have shown a bimodal microstructure formed by partially molten agglomerates embedded in a completely fused matrix.

Indeed, during the deposition of nanostructured powders, it is important to achieve a partial fusion of the initial powder in order to avoid excessive grain growth and to preserve part of the nanostructure in the coating. $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ nanostructured feedstock is formed by porous agglomerates, with a low thermal conductivity. Therefore, particles are not completely molten during spraying and part of the initial $\alpha$-$\text{Al}_2\text{O}_3$ is retained in the deposited layer.
A typical application of Al$_2$O$_3$-TiO$_2$ coatings are wear resistant layers. Wear resistance of the coatings sprayed on AISI 304 stainless steel have been reported elsewhere by the authors [32]. The results showed that the nanostructured coatings present better properties than their conventional counterparts, as a consequence of the main microstructural differences existing between both coatings.

First, the presence of partially fused agglomerates in the nanostructured layer can slow down the propagation of cracks inside the coating as they should present higher fracture toughness than that of the matrix [38]. Then, in the case of conventional coatings, segregation of titanium at the splats boundaries was observed whereas a uniform repartition of titanium was found in the nanostructured coating. As titanium segregation leads to greater delamination, it reduces the wear resistance of the conventional layers [23]. As a consequence, nanostructured coatings exhibit better tribological properties.

Tribological characterization is still in progress on the coating sprayed on C45 steel. It is important to point out that the microstructure is quite independent of the substrate nature. As a consequence, it is expected that the nanostructured layers display better wear resistance than their conventional counterpart. However, XRD analysis revealed differences in the $\alpha$- to $\gamma$-alumina ratio. Thus, the tribological behavior may be slightly different.

4. Conclusions

In order to obtain nanostructured coatings by thermal spraying, reconstituted nanostructured powder (agglomerates made up of nanoparticles) is needed. Though different methods for obtaining nanoparticles are available, effective nanoparticle agglomeration is mainly performed by spray drying.

In this study, WC-Co and Al$_2$O$_3$-TiO$_2$ coatings were obtained by atmospheric plasma spraying using reconstituted nanostructured powders. In the WC-Co coatings,
significant decomposition of the WC particles occurred during spraying and new phases (W\textsubscript{2}C and W) appeared. This decarburization which is prejudicial to wear resistance, decreased when helium was used as spraying gas.

At microstructural level, the nanostructured Al\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} coatings exhibited a fused matrix of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} and Ti\textsuperscript{4+}, which contained partly fused areas that retained the initial nanostructure of the powder. The presence of these areas may explain the higher microhardness of these coatings compared with that of their conventional counterparts obtained from micrometric powders and leads to better tribological properties.

**Acknowledgements**

This work has been conducted by support of the Spanish Ministry for Sciences and Innovation (Project: MAT2006-12945-C03).

**References**


Tables

Table 1. Commercial feeding powders characteristics (supplier data).

<table>
<thead>
<tr>
<th></th>
<th>WC-Co</th>
<th>Al₂O₃-TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Nanostructured</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Sulzer Metco</td>
<td>Inframat Advanced Materials</td>
</tr>
<tr>
<td>Reference</td>
<td>METCO 72F NS</td>
<td>Infralloy™ S7412</td>
</tr>
<tr>
<td>Composition</td>
<td>WC-Co (weight ratio 88:12)</td>
<td>Al₂O₃-TiO₂ (weight ratio 87:13)</td>
</tr>
<tr>
<td>Additives</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Particle size</td>
<td>50–500 nm</td>
<td>50–500 nm</td>
</tr>
<tr>
<td>Agglomerate size</td>
<td>15–45 µm</td>
<td>5–45 µm</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the steel substrates.

<table>
<thead>
<tr>
<th>C wt%</th>
<th>Mn wt%</th>
<th>Si wt%</th>
<th>Cr wt%</th>
<th>Ni wt%</th>
<th>P wt%</th>
<th>S wt%</th>
<th>Mo wt%</th>
<th>Al wt%</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI 304</td>
<td>0.08</td>
<td>2</td>
<td>0.75</td>
<td>18</td>
<td>10</td>
<td>0.045</td>
<td>0.03</td>
<td>-</td>
<td>balance</td>
</tr>
<tr>
<td>C45</td>
<td>0.458</td>
<td>0.717</td>
<td>0.02</td>
<td>0.059</td>
<td>0.062</td>
<td>0.008</td>
<td>0.01</td>
<td>0.003</td>
<td>0.051 balance</td>
</tr>
</tbody>
</table>

Table 3. Main plasma spraying parameters.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ar (slpm)</th>
<th>H₂ (slpm)</th>
<th>He (slpm)</th>
<th>Intensity (A)</th>
<th>Spraying distance (mm)</th>
<th>Flow rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co</td>
<td>65</td>
<td>3</td>
<td>-</td>
<td>750</td>
<td>130</td>
<td>50</td>
</tr>
<tr>
<td>Ni-Al (bond coat)</td>
<td>45</td>
<td>11</td>
<td>-</td>
<td>600</td>
<td>140</td>
<td>80</td>
</tr>
<tr>
<td>Al₂O₃-TiO₂</td>
<td>35</td>
<td>12</td>
<td>-</td>
<td>600</td>
<td>120</td>
<td>45</td>
</tr>
</tbody>
</table>

slpm = standard litre per minute

Table 4. Vickers microhardness of WC-Co plasma-sprayed coatings.

<table>
<thead>
<tr>
<th>Substrate nature</th>
<th>WC-Co coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AISI 304</td>
</tr>
<tr>
<td>Plasma gas nature</td>
<td>Ar/H₂</td>
</tr>
<tr>
<td>HV GPa</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>6.6 ± 0.7</td>
</tr>
</tbody>
</table>
Table 5. Vickers microhardness of $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ plasma-sprayed coatings.

<table>
<thead>
<tr>
<th>Substrate nature</th>
<th>Al$_2$O$_3$-TiO$_2$ coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV GPa</td>
<td>AISI 304</td>
</tr>
<tr>
<td>Conventional</td>
<td>7.6 ± 0.3</td>
</tr>
<tr>
<td>Nanostructured</td>
<td>8.4 ± 0.4</td>
</tr>
</tbody>
</table>
Figures captions

Figure 1. Coating formation by thermal spraying [6].

Figure 2. Classification of thermal spray techniques [5].

Figure 1. XRD diffraction patterns of WC-Co coatings sprayed a) on C45 steel with Ar/He, b) on C45 steel with Ar/H₂, c) on AISI 304 steel with Ar/He, d) on AISI 304 steel with Ar/H₂.
Figure 2. SEM micrographs of WC-Co conventional coatings sprayed a) on C45 steel with Ar/He, b) on C45 steel with Ar/H₂, c) on AISI 304 steel with Ar/He, d) on AISI 304 steel with Ar/H₂.
Figure 3. SEM micrographs of WC-Co nanostructured coatings sprayed a) on C45 steel with Ar/He, b) on C45 steel with Ar/H\textsubscript{2}, c) on AISI 304 steel with Ar/He, d) on AISI 304 steel with Ar/H\textsubscript{2}.
Figure 4. SEM micrographs of WC-Co conventional (left) and nanostructured (right) coatings sprayed on C45 steel with Ar/He at high magnification (areas referred as B in figure 4 and 5).

Figure 5. SEM micrographs of WC-Co conventional coatings sprayed on C45 steel with Ar/He at high magnification showing the nanocrystals formed during cooling.
Figure 6. XRD diffraction patterns of Al$_2$O$_3$ coatings sprayed a) on C45 steel, b) on AISI 304 steel.

Figure 7. SEM micrographs of conventional (left) and nanostructured (right) Al$_2$O$_3$ coatings sprayed on AISI 304 steel.
Figure 8. SEM micrographs of conventional (left) and nanostructured (right) Al₂O₃ coatings sprayed on C45 steel.