PREPARATION AND CHARACTERIZATION OF MULTILAYER COATINGS ON TOOL STEEL

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Abstract
This work is focused on the design and preparation of ZrO2-, TiN- and TiAlN-based multilayer using a combination of different strategies. Films have been deposited onto stainless and tool steels with the aim of characterizing the coatings as well as analyzing their behavior in order to optimize service capacity, extend working life and minimize production costs. The results of the study revealed compatibility among the techniques through the optimal combination of layers in terms of thickness and densification thus leading to an optimization of the properties of multilayer coatings.

Keywords: Coatings, zirconia, mechanical characterization, tools.

1. Introduction

The use of materials in the form of thin films is undoubtedly a subject of great interest from both the scientific and technological points of view. (1) (2). The study and development of coatings and thin layers should be aimed at improving the design and performance of materials, as well as achieving continuous improvement and reduction of production costs.

Superficial protection by means of ceramic coatings can be the solution to many practical problems. Hence, the study and development of coating techniques with materials for some time now, have been an area of great scientific and technological interests (3) (4). Zirconia (ZrO2) is used in numerous technological applications such as cutting tools, thermal barriers, turbines and combustion engines, etc. In these and other applications, the material works under extreme conditions, being subjected to contact stresses, thermal shocks and chemical agents that can cause the catastrophic failure of a system. Surface engineering is important in the manufacture of numerous industrial products. For example, most components of an injection engine or any vehicle are treated by some technique related to surface treatments, heat treatments, coatings, etc. The use of coatings as thermal barriers in turbines, chambers and combustion engines is an idea that has been used for years and is becoming more embraced by the day (5) (6).

There are several procedures for the manufacture of ceramic coatings, among which CVD (Chemical Vapor Deposition), PVD (Physical Vapor Deposition), plasma spray soil sol-gel. (7) (8) (9) stand out. The suitability of each of the methods depends on the type of substrate, as well as the properties of the coating to be obtained.

For example, physical and chemical depositions in the vapor phase (PVD and CVD) constitute advanced coating techniques of wide diffusion and versatility, as well as being well-established at the industrial level (10) (11). These techniques allow the production of coatings by physical (ion bombardment, plasma, laser, etc.) or chemical (reactions of precursor gases inside a reactor), methods. They apply to a wide variety of substrates used in surface protection and materials that operate in aggressive environments (friction, wear, corrosion, etc.), and show extraordinary multifunctionality (high hardness layers, decorative layers, solar cells, microelectronics, etc.).

The sol-gel method is one of the most interesting alternatives for obtaining thin ceramic films and there are multiple examples in the literature that illustrates its versatility and simplicity (12) (13). Compared to other techniques, the sol-gel method exhibit certain advantages such as low processing temperatures and precise control of chemical composition among others (14). Currently, there is a wide variety of sol-gel coatings that have been developed for application in various areas such as optics, electronics, optoelectronics, mechanics, photonics, biotechnology and chemistry.

The current state of knowledge about the sol-gel technique is quite broad in relation to the basic aspects of this process (15) (16). In fact, there is a strong impetus in technological research motivated by the applications of the materials prepared through the sol-gel route (17) (18). The efforts of scientists and technologists in this methodology are justified, among other reasons, by the powerful advantages of this synthesis route, among which we can highlight the preparation of materials with unpublished compositions impossible to obtain by other methods, the synthesis of ceramic powders with specific surface and high reactivity, the synthesis of solid materials with controlled porosity, obtaining dense solids with thermal treatments at relatively low temperatures, as well as the synthesis of films on substrates of diverse nature or unsupported, and all with low relative costs.

However, there are certain basic aspects of the research and development of these coatings that need to be improved on. Specifically, in the coatings obtained by PVD, the adherence and the anchoring mechanisms of the layers to the substrates on which they are applied, as well as the study of the generated interfaces, require an exhaustive study and knowledge, since they will help us to understand, improve and avoid the adhesive failure of the layers to the substrates.

The sol-gel technique is presented as an ideal complement in these coatings, as it can provide films with strong chemical bonds between the substrate and PVD coatings that significantly improve the anchoring capacity of substrates. Similarly, the coatings obtained by CVD, in many occasions present a porosity and superficial roughness that, sometimes, constitutes a specific problem for certain applications. In most cases it is necessary to proceed with an additional polishing of the surface. The technique could constitute an ideal complement for the layers obtained by CVD, since with its application the roughness would be minimized, the surface sealing will be achieved and some extra surface quality would be communicated to the material. For example, coefficient of friction, increased protection against oxidation and chemical corrosion, etc.

Another important aspect that currently focuses on research in the field of coatings is based on generating multilayer coatings, consisting of a succession of alternating layers (usually two materials of different nature) - with thickness ranging from 100 nanometers to several microns Multilayer coatings, obtained by dipping through the combination and alternation of sol-gel films of different nature, will allow better adaptation of elastic-plastic characteristics between the coating and the substrate, thereby improving its tenacity and resistance to fracture, while maintaining the hardness and wear resistance of the layer.

In the present work, new multilayer coatings was developed by combining sol-gel layers (ZrO2) with layers deposited by PVD (TiN) to improve the anchoring capacity of these layers to the substrate, and layers obtained by CVD (TiCN), TiN) to improve their surface quality in terms of roughness and sealing them. We have sought to optimize the thickness, compactness, microstructure and alternation or stratification of the layers, in order to establish the guidelines to be followed for the intelligent design of multilayer structures resistance, multifunctional and better adaptation to certain industrial requirements.

2. Materials and methods

2.1 Preparation and characterization of the substrate

The substrate AISI-D2 used in the present work was supplied by the company GGD metals. Said steel is characterized by its high content of carbon and chromium. Table 2.1 shows the data corresponding to its composition.

Table 2.1. Chemical composition of AISI-D2 steel

Composition	C	Mn	Si	Cr	Mo	V
(% Weight)	1.50	0.60	0.60	12.00	1.00	1.00

To facilitate its handling during the mechanical treatments to which the AISI-D2 stainless steel test pieces are going to be subjected, they were packed with a resin, TransOptic supplied by Buehler. The tableting process was carried out in a Buehler Simplimet 1000 press.

Once the previous process is finished, the substrates are sanded and polished. For this, a Buehler brand polisher, model Phoenix 4000, is used. The sanding of the sample is carried out with SiC discs, progressively increasing the number of grains from 240 to 400 and finally to 800 grains during 5, 8 and 10 minutes respectively. Distilled water was used as lubricant and polishing was carried out with a monocrystalline suspension of diamond particles (Buehler brand) in three phases, using in each of the diamond paste of 9, 6 and 3 microns respectively, for 15 minutes each Subsequently, the samples were despatched.

The AISI-D2 steel was characterized by a Dataview rugosimeter model TR-200. The parameter Ra was determined, which represents the arithmetic mean of the absolute values of the profile deviations with respect to the mean line.

2.2 Preparation and characterization of the solution

The solutions were prepared by adding zirconium n-propoxide (ZNP) in 1-propanol with nitric acid (HNO3). These solutions were mixed with another solution of yttrium acetate (YAc-4H2O) in propanol (PrOH) and HNO3, to obtain the precursor solutions of ZrO2-3mol% Y2O3. After one hour of stirring, distilled water was added to each solution without stopping the stirring. After an additional 1 hour of agitation, the final solution with a pH of 0.5 and a molar ratio of ZNP / alcohol / H2O / HNO3 of 1/15/6/1 is obtained.

The solutions prepared were characterized by means of density, viscosity and pH measurements at room temperature. The density (ρ) is determined with a Lussac pycnometer for liquids of 10 ml (± 0.1) and the masses with a Sartorius analytical balance, model BP 121S, with a deviation of 0.1mg. The viscosity (η) of a liquid is determined with the Ostwald viscometer. Finally, we proceeded to measure the pH of the solution with a Hanna HI 3220 peachimeter.

2.3. Coatings

2.3.1. Coatings by PVD and CVD

The PVD and CVD coatings were deposited by means of a multi-cathode arch deposition system and in an industrial deposition unit at atmospheric pressure respectively, by the company Tratas Térmicos Carreras (TTC-Spain). The coatings prepared by PVD consist of layers of TiN produced by vapor deposition from metallic cathodes of titanium with a mixture of argon gases and reactive nitrogen. The CVD process was carried out using precursors $TiCl_4$, N_2, H_2 and Ar. More details about deposition processes can be found in previous works of various authors (5) (10).

2. 3.2. Coatings sol-gel

The ZrO_2 coatings were prepared from sol-gel precursor solutions. To carry out the ZrO_2 coatings by dip-coating, a computer, KSV NIMA controlled by software, was used. This equipment is used to control the extraction speed, as well as the residence time in the sol-gel solution.

2.4. Characterization of the coatings

The composition and stratification of the coatings of PVD and CVD films was determined by optical emission spectrometry by light discharge (GDOES) (LECO, SA-2100) and scanning electron microscopy (SEM) (HITACHI S-3600N).

To study topography and microstructural evolution of the films, an atomic force microscope (AFM) (Park Scientific Instruments) and a scanning electron microscope were used and finally, the mechanical behavior of multilayer coatings has been investigated by performing micro and nanoindentation tests using an ultra-micro-durometer (Fischerscope, model H-100).

3. Results and discussion

In this section, we will discuss the most interesting results corresponding to the characterization of the substrate of solutions and coatings.

3.1. Characterization of the substrate

AISI-D2 steel has a high carbon content which gives it a high hardness, as well as chromium which gives it good resistance to oxidation (Table 2.1).

This steel is dimensionally stable with excellent cutting performance and wears resistance. Its most important applications are in the metal industry and especially in the manufacturing of cutting tools.

Prior to the deposition process, the substrates were roughened and polished to an approximate surface roughness Ra = 0.5 µm.

3.2 Characterization of the dissolution

The solutions of ZrO2-3mol% Y2O3 were characterized by the measurements of pH, density and viscosity at a working temperature of 22º C. The results obtained for the solution were, pH 0.5, density 0.966 g • cm-3, viscosity 0.8904 cP for a molar ratio (ZNP-AcY) /alcohol/water/nitric acid are 1/15/6/1. The incorporation of Y2O3 in the preparation of ZrO2 solutions aims to improve the corrosion resistance of the ceramic coating.

3.3 Characterization of coatings

In a large number of practical applications, the properties of the surface layers and the coatings used to improve the performance and service life of the mechanical parts are closely related to the composition, structure and thickness of the treatment layers (19)(20).

In order to carry out these studies, the GDOES technique was used, as it allows for the performance of depth profiles quickly and accurately on ceramic coatings of metal surfaces (21) (22) (23) (24).

In Figures 1 and 2, the layer thickness and the depth profiles corresponding to the AISI D2 steel covered by CVD with TiC-TiNC-TiN and by PVD with TiN were studied by GDOES spectroscopy. In these figures you can see the distribution of the elements in the coatings, as well as the thicknesses reached in the deposition processes, being around 7 μm for the CVD and 3 μm for the PVD coatings.

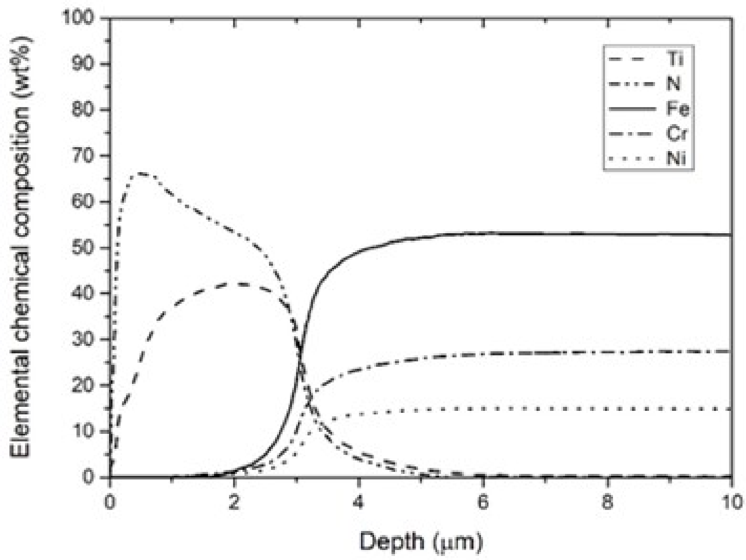

Figure 1. AISI D2 steel coated by CVD with TiC-TiNC-TiN.

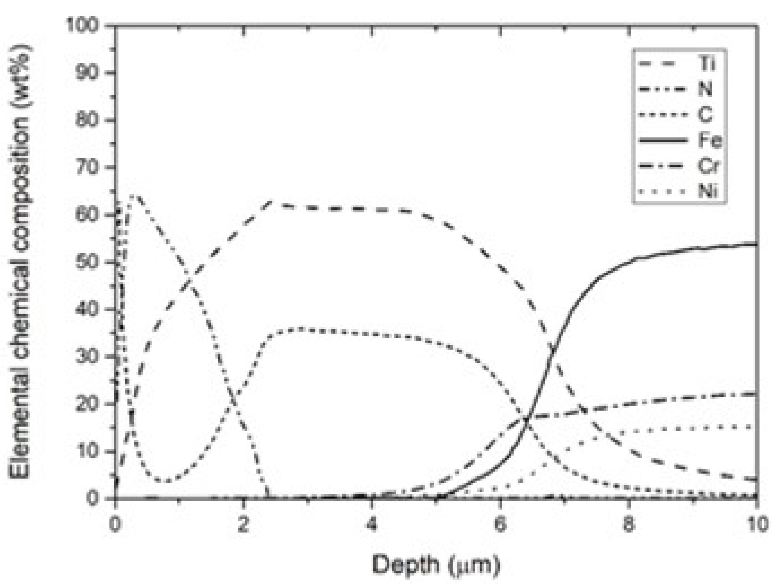

Figure 2. Steel AISI D2 coated with PVD with TiN.

Atomic force microscopy (AFM) is widely used to examine the surface of materials. The control and studies of the micro surface structure of thin films are currently directed towards topographical aspects in connection with other properties such as roughness analysis. (25) (26) (27)

Figure 3 shows some comparative results of the topographic images obtained by AFM on CVD and PVD coatings, before and after applying a sol-gel layer of zirconia on them using the dip-coating technique. The leveling effect on the surface that these sol-gel layers exert on the previous CVD and PVD coatings is observed by decreasing the surface roughness of about 180 nm (a) down to 150 nm (b), and 400 nm (c) down to 250 nm (d). At the same time, it also exerts a sealing effect on possible defects or superficial cracks, which will produce a beneficial effect on the fatigue and tribological work of these coatings. This effect could also prevent the frequency and cost of subsequent polishing operations on the coatings made by CVD, with the aim of improving the surface quality,required in certain technological applications.

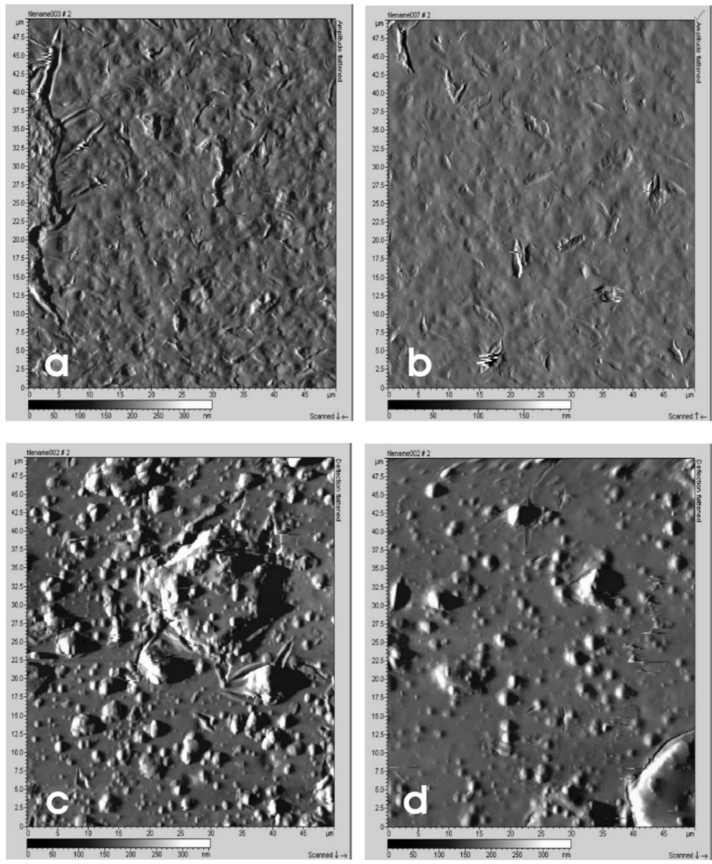

Figure 3. CVD coatings of TiC-TiNC-TiN (a) and TiC-TiNC-TiN + ZrO2 (b), and by PVD of TiN (c) and TiN + ZrO2 (d).

Through scanning electron microscopy, the morphology of the coatings were analyzed, as seen below..

Figure 4 shows micrographs made on sample profiles of TiC-TiNC-TiN + ZrO2 and TiN + ZrO2. In them, the arrangement and the thicknesses of the various layers deposited alternately on the stainless steel substrates can be appreciated. The coatings have, in general, a good bond to the substrate and the different layers between the, homogeneous and well-defined interfaces can be seen with good compactness of the assembly. We can deduce excellent compatibility between the layers and the substrates, which will result in a good structural and mechanical response of the obtained multilayers.

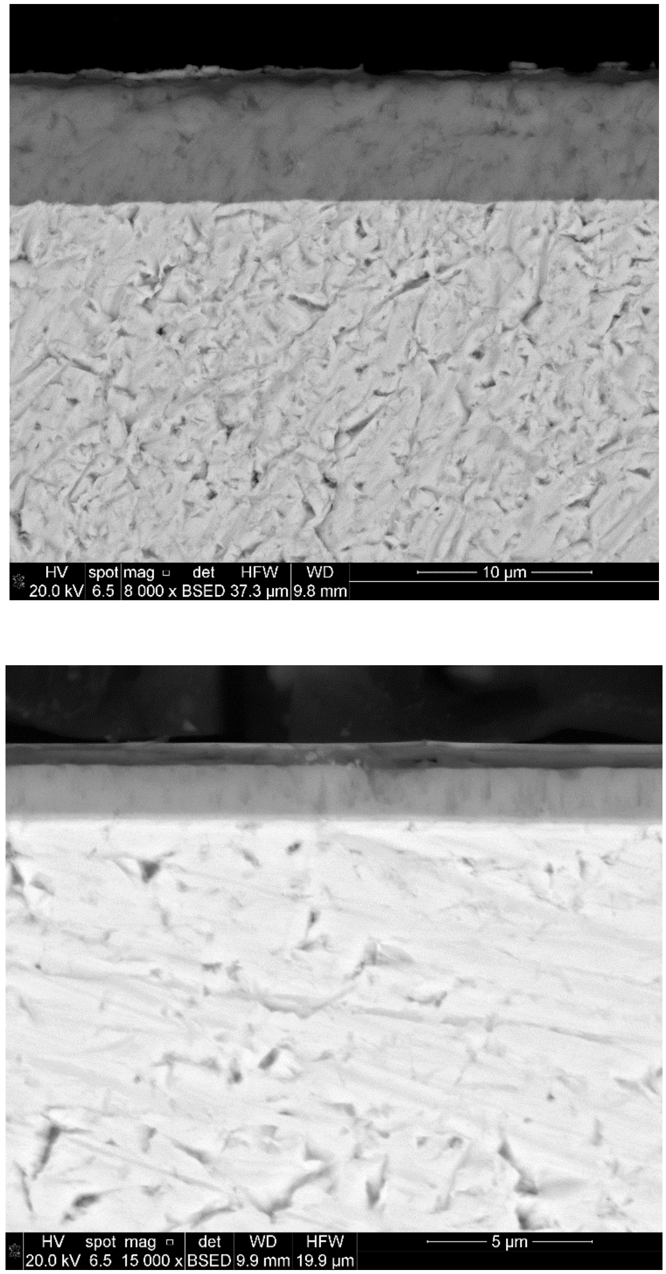

Figure 4. SEM micrographs with coatings formed by altérnate layers deposited by different techniques: TiC-TiNC-TiN + ZrO2 (a), and TiN + ZrO2 (b).

The nanoindentation technique is used to determine the hardness (H) and Young's modulus (E) of thin films.

In figures 5 and 6 it can be observed by the shape of the graphs that the AISI-D2 steel coatings have an elastoplastic behavior.

Figure 5 shows nanoindentation tests performed on the coatings deposited on the two types of substrates used in this study. It can be seen that for the same value of the load of 100 mN applied in the tests, the coatings deposited on substrates of AISI D2 steel have a more resistant mechanical behavior.

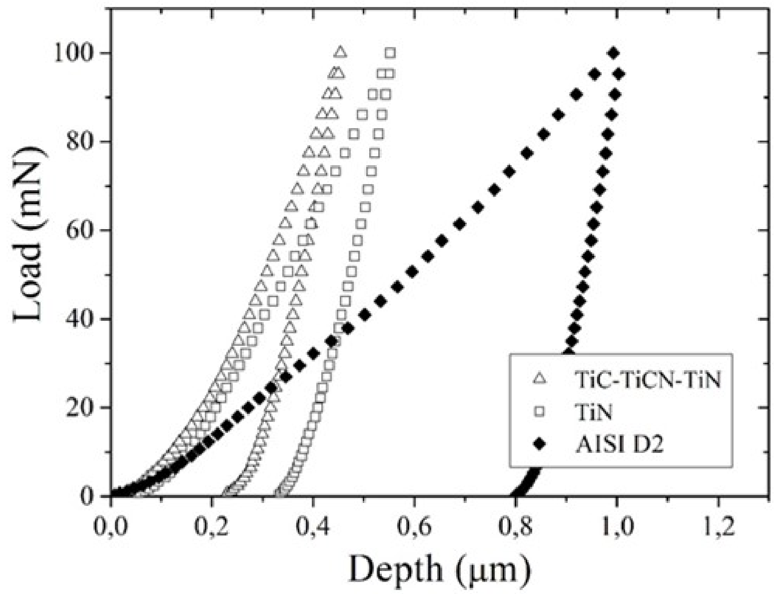

Figure 5. Nanoindentation tests carried out on the coatings deposited on the two types of substrates used in the work.

Figure 6 shows nanoindentation tests carried out on coatings of TiN and TiN + Sol-Gel deposited on the same type of substrate. It can be seen, that the layer of ZrO2 deposited on the TiN layer has a very little influence on the resistant characteristics of the coating. that is, it was only appreciated that the final layer of sol-gel has an influence on the visual appearance, irregularities and surface roughness of the base coat, aspects already shown and commented on previously through the AFM images.

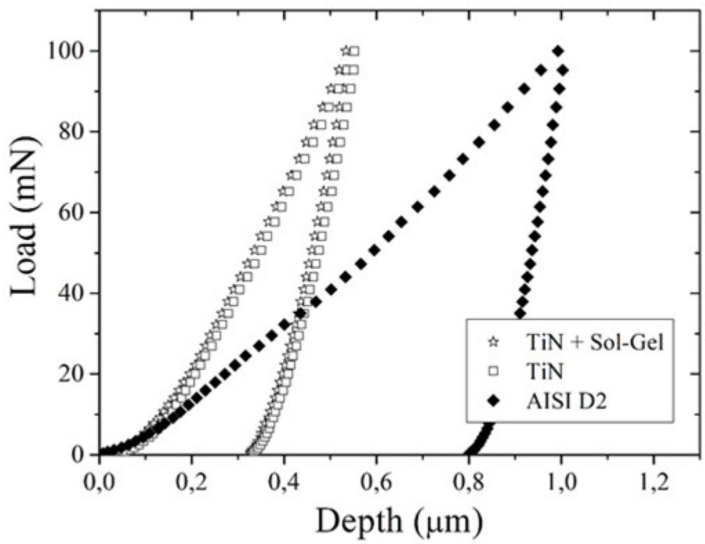

Figure 6. Nanoindentation tests carried out on coatings deposited on the same type of substrate.

Likewise, Table 3.1 shows the average values of hardness (H) and Young's modulus (E), calculated from the nanoindentation tests indicated above. For low loads, the values are in agreement with those referenced in the scientific literature on these materials (28). For relatively high loads (100 mN), where the depth of penetration of the indentor exceeds 1/10 of the thickness of the coating, the contribution of the substrate to the mechanical response of the coatings becomes noticeable. Finally, it is also worth mentioning that the application of a sol-gel layer of ZrO2 on top of the PVD and CVD coatings, has contributed to improving the surface finish of the samples while there is hardly any reduction in the mechanical resistance values of the coatings multilayers

	2 mN		20 mN		100 mN	
	H(GPa)	*E* (GPa)	*H* (GPa)	*E* (GPa)	*H* (GPa)	*E* (GPa)
D2 + TiN (PVD)	25 ±2	320 ±10	24 ±2	320 ±10	20 ±2	300 ±10
D2 + TiC-TiCN-TiN (CVD)	24 ±2	310 ±10	24 ±2	320 ±10	23 ±2	310 ±10

Table 3.1. Mean values of hardness (H) and Young's modulus (E), obtained in the coatings deposited by PVD and CVD on AISI D2 steel.

4. Conclusions

From the results shown in the previous section, the following conclusions can be drawn:

- The sol-gel films show very good compatibility with films of different nature, thereby allowing subsequent application of layers with different processing techniques. Likewise, in some cases, it supposes a considerable improvement in the superficial quality of the coatings obtained by means of other deposition techniques, mainly for the CVD.
- The mechanical behavior of multilayer coatings is affected by the nature of the substrate on which they are deposited, depending obviously on the depth of penetration of the indentation and the loads applied to the coating, since the greater the penetration in the coating, the greater the contribution of the substrate.

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