



## Adhesion failures on hard coatings induced by interface anomalies

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### A B S T R A C T

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In this work, the lack of adhesion occurred during the up-scaling of the deposition of tribological coatings in a semi-industrial apparatus is interpreted. The adhesion problems were detected for both hard and self-lubricant coatings from W–Ti–N and W:C systems, respectively, when they were deposited in a 4 cathodes TEER<sup>®</sup> chamber by reactive unbalanced magnetron sputtering. In spite of cleaning the substrates surface by ion bombardment prior to deposition, by establishing a discharge close to the substrate, insufficient adhesion critical load values were measured by scratch-testing. A powerful set of complementary techniques was used to the detailed analysis of the interfaces in order to understand and overcome the adhesion problems: RBS gave some insights on the nature of the problem by detecting composition anomalies in the substrate/coating interface; Auger spectroscopy was used for identifying the underneath chemical composition close to the interface; cross section TEM gave the final evidence of the presence of a contamination layer attributed to malfunctioning of the ion cleaning process, which was the cause of the lack of adhesion.

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### 1. Introduction

The up-scaling of the sputtering process from laboratory to industrial dimensions brings many times several problems not always completely identified. Probably, those which have required more concerns are the “adhesion failures”. The adhesion achieved in the laboratory development of tribological coatings is most of the times enough to assure the reliable characterization of their mechanical behaviour. However, from the moment that any coating reaches the interest to be implemented in the market, one of the challenges to overcome in industrial facilities is the improvement and optimization of the coatings adhesion. Extensive studies of the influence of cleaning solvents, type of water, in situ plasma surface erosion procedures and interlayers are carried out before the in-service use of the coatings.

The adhesion problems between thin films and substrates have been remarkably presented and reviewed by Mattox (see e.g. [1,2]). The importance of the contamination layers, as well as the different steps necessary to reach a good surface cleaning before the deposition, were discussed. Among these steps, the in situ surface

cleaning assumed special importance, the different methods possible to be applied in the deposition chambers for achieving a good final adhesion have been referred. Sputter cleaning was one of these methods and, probably, the most used in laboratory and industrial environments. By establishing a discharge close to the substrates holder, the ion bombardment of their surfaces permits to sputter the contamination layer and to obtain an atomic cleaned surface, essential for promoting good bonding between the film and the substrate.

In this paper, the problem of adhesion of hard coatings (from W–Ti–N and W-DLC:H systems) when deposited in a semi-industrial equipment, after having been developed in laboratory equipments, will be presented and discussed. The importance of the in situ plasma cleaning on the adhesion values and the way how to optimize this procedure will be referred.

### 2. Experimental methods

The coatings were deposited by d.c. reactive magnetron sputtering in a 4 cathodes (375 × 150 mm) semi-industrial equipment (the deposition chamber was from TEER Coatings Lda) working in unbalanced mode. Two different type of coatings systems were studied: W–Ti–N and W–C:H. In both cases the targets arrangement was similar, i.e. composite plates consisting of Ti or C base elements embedding several W pellets (see Fig. 1). A Ti target was

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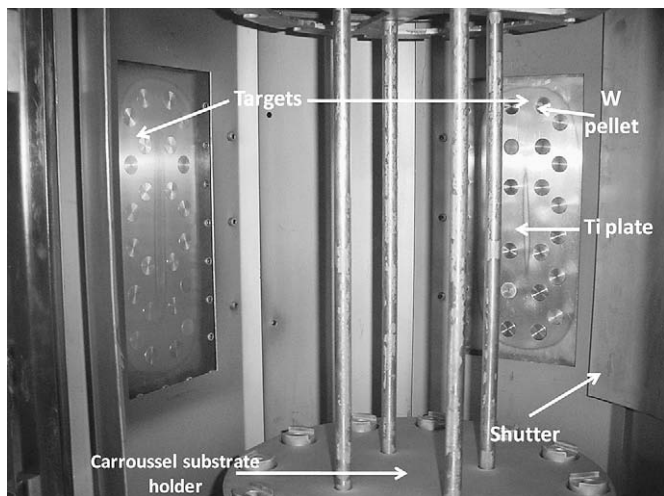


Fig. 1. General view of the semi-industrial deposition chamber showing the composite targets.

used for depositing an adhesion interlayer ( $\sim 200$  nm). It should be remarked that in the case of the previously developed W–C:H coatings in laboratory conditions, chromium was used as adhesion interlayer.

For getting N and H in the coatings composition,  $N_2$  and  $CH_4$  were used as reactive gases. Different discharge power and pressures, as well as substrate bias values, were used for the coatings deposition. The thickness of the coatings was in the range from 1.5 up to 3.0  $\mu\text{m}$ . Whenever relevant, specific information about these deposition parameters will be given.

Before deposition, the substrates were ion cleaned by establishing a discharge close to the substrate holder. Table 1 shows an example of the cleaning and deposition conditions. Pieces of (111) mono-oriented Si ( $15 \times 15$  mm) and M2 (AISI) steel (15 mm diameter) were used as substrates. M2 substrates were polished down with SiC paper of decreasing grain size (500, 1000 and 4000 grit) followed by 3  $\mu\text{m}$  diamond paste and, in both cases, before being placed in the deposition chamber they were cleaned in acetone and ethanol ultrasonic baths.

All comparisons which will be presented refer to the same type of coatings previously developed at a laboratory level. Details about the deposition procedures as well as on the basic characterization of the coatings can be found in previous papers from the present authors [3–8].

The characterization studies carried out specifically for this work included:

- (1) Analysis of the chemical composition through the film-substrates interfaces by depth profiling using Auger spectroscopy analysis. The Auger spectra were taken using a 10 keV,

Table 1  
Example of conditions for the coating procedure of the W–DLC:H system.

Parameters	Substrate cleaning	Ti interlayer	C–W deposition
Discharge pressure	0.3 Pa	0.3 Pa	0.5 Pa
$P_{CH_4}/P_{Ar}$	0	0	Variable
Discharge power ( $P_{dep}$ )	100 W/target	2000 W/target	Variable
Target current ( $I_A$ )	[0.3–0.5 A]	[6–6.5 A]	Variable
Target potential ( $V_A$ )	[200–250 V]	[300–350 V]	Variable
Substrate bias ( $-V_s$ )	500 V; 250 KHz,	50 V; 250 KHz	50 V; 250 KHz
plused current			
Deposition time ( $t_{dep}$ )	15 min	5 min	60 min

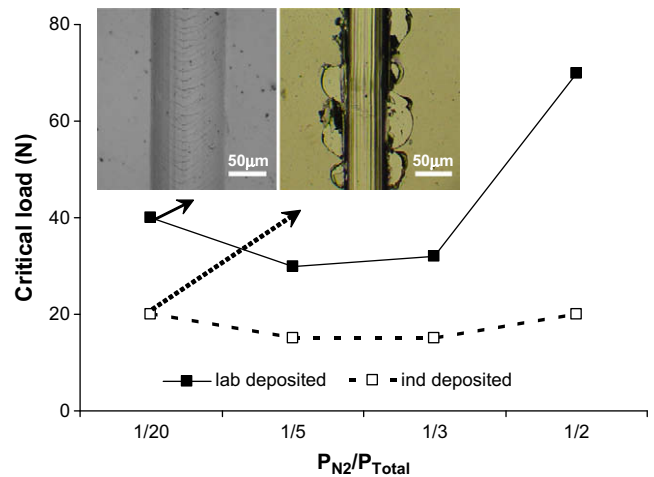


Fig. 2. Critical load values measured in scratch-testing of W–Ti–N coated samples deposited in laboratory and semi-industrial equipments.

100 nA primary electron beam. The angle between the primary beam and the normal was  $30^\circ$ . Before each analysis the sample surface was progressively eroded by  $Ar^+$  ion bombardment, permitting evaluating the underneath chemical composition.

- (2) Elemental in-depth composition studies with ERDA/RBS. RBS (Rutherford Backscattering Spectrometry) spectra were obtained with two Schottky barrier detectors placed in IBM geometry at  $140^\circ$  and  $180^\circ$  scattering angles, using a 2.0 MeV  $He^+$  beam. To detect hydrogen, ERDA (Elastic Recoil Detection Analyses) spectra were acquired with a Schottky barrier detector placed at  $24^\circ$  scattering angle in IBM geometry. All spectra obtained for the same sample were simultaneously analysed with NDF [9] and a unique solution was found.
- (3) Interface film-substrate examination in cross section by TEM. A Philips CM 30 microscope equipped with a field emission gun at an accelerating voltage of 300 kV was used. The samples were prepared by mechanical polishing and Ar ion milling.
- (4) The cohesion/adhesion of the coated samples was accessed by scratch-testing under standard conditions [8]. The critical load,  $L_c$ , was determined by the first failure (adhesive or cohesive as referred in the text) detected in the scratch channel.

### 3. Results and discussion

#### 3.1. Adhesion analysis

The deposition work carried out in the semi-industrial equipment followed a previous development of the studied systems in laboratory equipments [3–7]. Fig. 2 shows, for the case of W–Ti–N coatings deposited in both types of equipments, comparative values of the scratch-test critical loads as a function of the partial pressure of the reactive gas ( $N_2$ ). Industrially deposited coatings present much lower  $L_c$  values, particularly taking into account that  $L_c$  is referred to spalling or flaking of the coatings in contrast with the cohesive failure used for ranking the laboratory deposited ones (see examples in inset of Fig. 2). Similar differences in the  $L_c$  values were found for W–DLC:H coatings. For example for the coating shown in Fig. 3, the difference in  $L_c$  is from 82 N down to 15 N for laboratory and industrially deposited coatings, respectively. SEM/EDS analysis was used to identify the chemical elements in the spalled zones after scratch-testing. Fig. 3(a) and (b) shows the micrographs of the scratch channels, as well as the EDS spectra

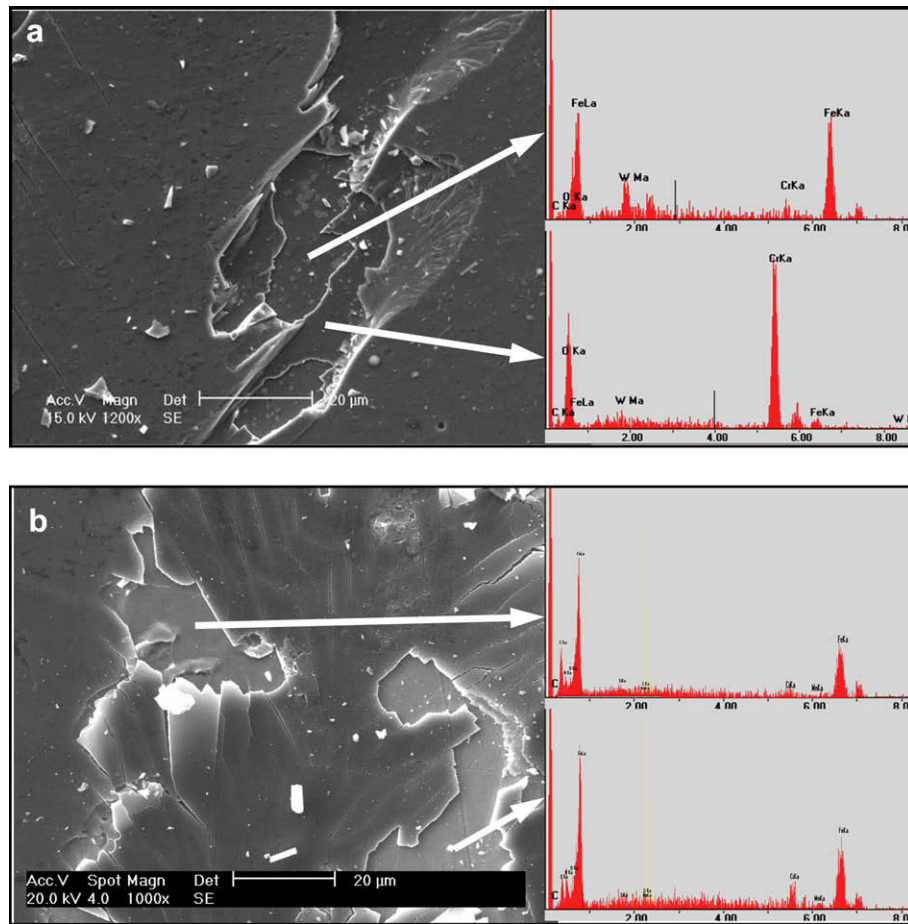


Fig. 3. SEM micrographs and EDS spectra taken from flaked zones of W-DLC:H coated samples deposited in (a) laboratory and (b) semi-industrial equipments.

taken in different spalled zones, of both W-DLC:H coatings deposited in laboratory and industrial machines. In laboratory deposited coatings (Fig. 3a) flaking occurs indistinctly in the interface between the coating and the interlayer or between the interlayer and the substrate. In fact, Cr is detected in several spalled zones suggesting that the interlayer is still adhered to the substrate. On the other hand, in industrially deposited coatings flaking occurs always through the substrate/interlayer interface as shown by the absence of any signs of Ti in the EDS spectra taken in any of the spalled zones (Fig. 3b). Such a result suggests unequivocally that the adhesion problems come from the first moment that the substrate starts to be covered. In conclusion, in the industrial machine the coating's failure during scratch-testing is due to extensive spalling being the lack of adhesion occurring in the interface with the substrate.

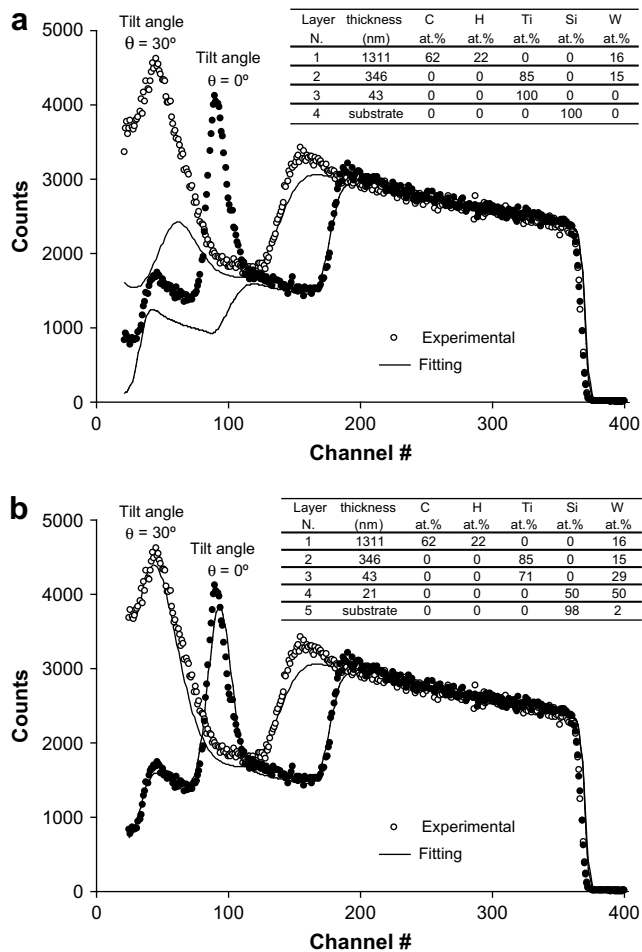
### 3.2. Evidence of anomalies in the substrate/interlayer interface

Two independent results helped to identify the adhesion problems above described: (1) the RBS/ERDA experimental spectra of a W-C:H film showed the presence of an unexpected element in depth; (2) the measurement of the in-depth chemical composition of a W-Ti-N deposition, close to the interface substrate/interlayer, using Auger spectrometry verified the presence of a W accumulation between the Ti interlayer and the substrate.

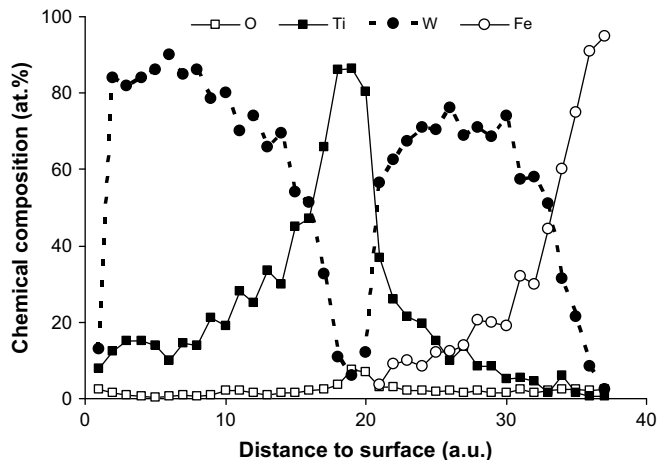
Fig. 4 shows the RBS spectra of a W-DLC:H sputtered coating. The dots correspond to the experimental spectra taken at two different tilt angles on the same sample. The lines correspond to the

simulation presented in the table inserts. Fig. 4(a) shows a simulation considering nominal in-depth composition. The accordance between spectra and simulation is good except in the region around channel number 90, where an unexpected peak appears in the experimental spectrum. A second measurement with a higher tilt angle results in the peak shifting to a lower channel number, i.e. lower energies, thus indicating that it originates from an element present in depth. RBS cannot unambiguously identify an element present in depth in the sample, as a heavier element at a higher depth would produce the same signal as a lighter element closer to the surface of the sample. A tentative simulation is shown in Fig. 4(b), including a W accumulation at the substrate/Ti interlayer interface. Note that the RBS identification of W at the interface is not conclusive and a second independent analytical technique is necessary.

Frequently, the problems related with coatings adhesion are due to the contamination of the interface by the presence of oxygen in the residual atmosphere of the deposition chamber [1,2]. In order to enlighten if this could be the origin of the bad adhesion, a special coating of the W-Ti-N system was prepared with very low thickness to allow the in-depth step analysis by Auger spectroscopy after progressive etching of the sample surface by ion bombardment. In a first phase, the deposition run was reproduced exactly as in normal procedure, i.e. the substrates were pre-cleaned with acetone and ethanol before being placed in the deposition chamber. Afterwards, they were ion bombarded by establishing the discharge close to the substrate holder. The changes in the procedure were related to the deposition times of



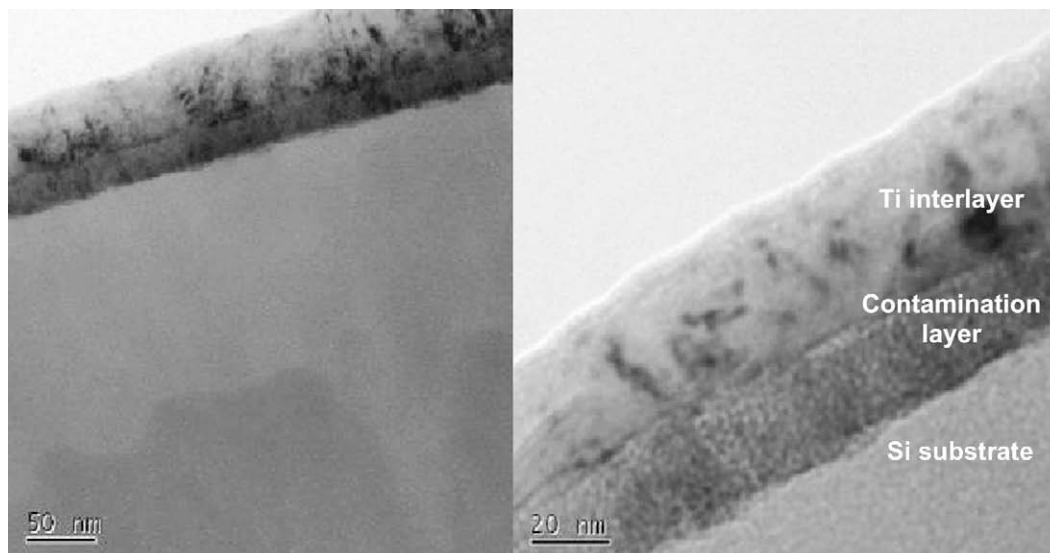
**Fig. 4.** RBS spectra of a W-DLC:H sputtered coating. The dots correspond to the experimental spectra taken at two different tilt angles on the same sample. The lines correspond to the simulation presented in the table insert, considering a succession of layers from 1, at the surface, going in depth progressively until the last number corresponding to the substrate. (a) Simulation considering nominal in-depth composition. (b) Simulation including a W accumulation in the substrate/Ti interlayer interface.



**Fig. 5.** Auger in-depth profile chemical composition results of a W-Ti coating after progressive erosion of the surface with ion bombardment.

either the Ti interlayer or the W-Ti (no reactive gas was used) coating: only a few seconds deposition time was used for each layer to allow thicknesses of approximately 20 nm (based on the calculated deposition rates for thicker coatings). Fig. 5 shows the evolution of the chemical composition with depth starting from the top going through the different layers down to the substrate. As can be concluded, no significant increase in the O signal was registered close to the substrate interface. Only at the Ti interlayer a small increase in this element was detected, probably related with the very high affinity of Ti for O. However, unexpected W and Ti counts were detected close to the substrate forming a sub-layer between the adhesion interlayer and the substrate.

These two analyzing techniques, RBS and Auger Spectrometry, undoubtedly demonstrated the existence of a contamination layer between the adhesion interlayer and the substrate independently of the system under study. The presence of this interlayer was later confirmed by HR-TEM for a W-DLC:H coating as it is shown in Fig. 6. This interlayer was amorphous and had a uniform thickness of about 25 nm. The EDS analysis showed that this layer contained high amounts of C and W; Ti and O could also be detected. These



**Fig. 6.** HR-TEM micrographs of the interface substrate/interlayer zone of a W-DLC:H coated sample.

elements could only be present if the targets are being sputtered, previously to the Ti interlayer deposition, during the ion cleaning process. The oxygen content of this layer is relatively high (more than 4 at.%), if compared to Ti-layer or DLC-layer (about 1 at.% O in both). It is interesting to point out that in this interlayer the presence of Ar atoms is not detected as in the DLC-layer.

### 3.3. Problem solution

After identification of the source for the lack of adhesion, the next step was to find the reason for the problem and its solution. The presence of the contamination layer before the interlayer deposition had to occur during the plasma cleaning procedure of the substrate surface. This step is performed by establishing the plasma close to the substrate. However, to ignite the plasma and to improve the plasma density in that zone, it is necessary to switch on the cathodes with very low power (see Table 1). Contrary to the expectable, the sputtered species from the targets, even with so low discharge powers, supplant the resputtering effect caused by the ion bombardment of the substrate giving rise to the net formation of a layer impeding the efficient cleaning of the normally contaminated surface.

Placement shutters in front of the cathodes permits not only avoid the passage of the sputtered species but also helping in establishing the plasma close to the substrate. With this system, coatings of the W–Ti–N system were deposited following the same procedure as before, excepting putting shutters in front of the targets. The test was carried out for the coating shown in Fig. 2, deposited with  $P_{N_2}/P_{total} = 1/2$ . The critical load was now higher than 70 N, contrasting with the 20 N achieved previously. Furthermore, again no flaking of the coating was observed being the Lc value attributed to the first cohesion failure observed in the scratch track, similarly to what occurred when testing the laboratory deposited coatings.

## 4. Conclusions

After the deposition of W–Ti–N and W–DLC:H coatings in a semi-industrial deposition, it was found with the help of RBS, Auger and TEM techniques, that a contamination layer was formed during the ion cleaning of the substrates prior to deposition. This layer was responsible for the much lower adhesion critical loads of those coatings when compared to the ones previously achieved in similar coatings deposited in laboratory conditions. The power applied to the targets to ignite the discharge during the ion cleaning process was enough to sputter the targets and promote the deposition of species onto the substrate with a rate higher than the one achieved by the ion bombardment. Placing shutters in front of the targets during the in situ substrate cleaning process allowed solving the adhesion problems.

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