Adhesion improvement of carbon-based coatings through a high ionization deposition technique

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Abstract. The deposition of highly adherent carbon nitride (CN\textsubscript{x}) films using a pretreatment with two high power impulse magnetron sputtering (HIPIMS) power supplies in a master-slave configuration is reviewed. SKF3 (AISI 52100) steel substrates were pretreated in the environment of a high ionized Cr\textsuperscript{+}/Ar plasma in order to sputter clean the surface and implant Cr metal ions. CN\textsubscript{x} films were subsequently deposited at room temperature by DC magnetron sputtering from a high purity C target in a N\textsubscript{2}/Ar plasma discharge. All processing was done in an industrial-scale CemeCon CC800 coating system. A series of depositions were obtained with samples pretreated at different bias voltages (DC and pulsed). The adhesion of CN\textsubscript{x} films, evaluated by the Daimler-Benz Rockwell-C test, reaches strength quality HF1. Adhesion results are correlated to high resolution transmission electron microscopy observations confirming the formation of an optimal interfacial mixing layer of Cr and steel. The throwing power increase for HIPIMS coatings is associated to the higher ionization in the plasma discharge.

1. Introduction
During the last two decades, carbon-nitride (CN\textsubscript{x}) coatings deposited by physical vapor deposition (PVD) techniques have enjoyed a growing interest in several disciplines. Amorphous and fullerene-like films exhibit very attractive properties, such as low friction and wear, high hardness, good chemical stability, and high resiliency to deformation, which make them suitable for replacing diamond-like carbon (DLC) films [1]. The first successful industrial application of this material has been the use of very thin (~2-5 nm) amorphous CN\textsubscript{x} films for the protection of hard disk drives [2-3]. However, commercial use of thicker (1-5 µm) coatings on steel substrates has been difficult because of the development of high compressive intrinsic stresses during deposition, which causes adhesion failures with delamination of films from the substrate surface [4].

The common practice to increase the adhesion of carbon-based coatings on steel substrates is to make a pretreatment of the substrates and the use of a metallurgical glue layer interposed between the surface substrate and the film. In this paper we present the deposition of highly adherent CN\textsubscript{x} films on martensitic steel substrates using a high plasma ionization pretreatment [5-6]. The plasma-processing methods used for improving adhesion of carbon-based coatings are reviewed in Section 2. A description of our original pretreatment and the experimental techniques are considered in Section 3. Section 4 presents the results and discussions, and Section 5 gives the conclusions.
2. Review of plasma-processing pretreatments

2.1. Glow discharge cleaning

In-situ surface preparation is an essential step in vacuum coating processing and is critical to assure a good film-substrate adhesion. For example, air-exposed stainless steel is covered by a native oxide layer (from 1 to 5 nm thick) composed of metal oxides and hydroxides [7]. Despite of pre-cleaning processes, other contaminants like organic and water molecules will also be present on the metal surface. Without the elimination of the oxide and contaminants, it is likely that any coating deposited on the surface will delaminate.

For many years, it has been known that cleaning of substrates using plasma techniques prior to physical vapor deposition processes can significantly improve coating adhesion. Such bombardment is expected not only to remove unwanted contaminant layers at the substrate surface, but also to create active dangling bonds, which may promote adhesion of the deposited film [8]. The first in-situ plasma cleaning technique was developed in 1935 by Strong for the cleaning of glass surfaces used in astronomical telescopes [9]. The equipment for this technique, included nowadays in basic commercial coating machines, consists basically of a DC high voltage “glow bar” that allows the formation of plasma. The surfaces in contact with the plasma acquire a negative voltage (several volts) with respect to the plasma. This sheath potential accelerates positive ions to the surface. When an ion contacts the surface it combines with electrons and releases its energy of ionization (5-20 eV). This low energy bombardment and heating desorbs adsorbed contaminants such as water vapor. This “ion scrubbing” can be done using argon or reactive gases like oxygen, chlorine, and hydrogen, the later are used to clean contaminants like hydrocarbons. In this technique, also known as “glow discharge cleaning” because of the light generated by the plasma, there is no bias voltage applied to the substrate (figure 1). The technique was popular in the 1960’s and most of laboratory and commercial-scale PVD deposition systems commercialized in that decade were including this option [10].

2.2. Sputter ion cleaning

One of the most successful techniques for adhesion enhancement has been the pre-treatment of the substrate surface with a low energy (~500 eV) Ar+ ions bombardment, in-situ before vacuum vapor deposition of the films [11]. The first report of this technique is back to 1955, when Farnsworth et al [12] reported using sputter cleaning with Ar+ ions to prepare ultra-clean surfaces for low-energy electron diffraction studies. Later, sputter cleaning was adopted by D. M. Mattox [13] as a part of his “Ion-Plating” technique. Mattox’s process, with a filament used to evaporate a metal and a DC voltage used to accelerate ions toward a biased substrate, evolved rapidly with the introduction of the DC magnetron sputtering technique for the deposition of the films. Before deposition, the plasma cleaning is performed by ions generated in the cathodes, while the acceleration of the ions toward the substrate to be cleaned can be performed by a negative DC voltage applied to the substrate [14]. Figure 2 shows a typical process where the ions are generated by a magnetron cathode with a Cr target.
and the bias is provided by a negative DC voltage: the magnetron generates mainly Ar$^+$ ions because
the efficiency of Cr ion generation is very low. Radio frequency (RF) biasing has also been used since
the 1970s to induce the energetic particle bombardment of insulating substrates. RF bias supplies,
usually operating at 13.56 MHz, are connected to the substrates via a matching network [15].

In industrial production, where it is common to have a large deposition area, Ar$^+$ ions are usually
provided by external sources. The “plasma booster” technology, introduced at the beginning of the
1990’s by researchers from the company Leybold [16] has been evolving with the discovery of other
ion sources. Anders [17] has recently reviewed some of these ion sources, such as hollow cathode
discharges, linear sources of end-Hall type, and capacitively or inductively coupled plasma sources.

There are two drawbacks of this cleaning method. The first one is the substrate heating during ion
bombardment that can change, per example, the properties of some temperature sensitive substrates
like steels. Another disadvantage is the incorporation of the gas ions into the substrate. An inert gas
like Ar can occupy interstitial sites and induce increased strains in the substrate lattice. These high
strains can embrittle the substrate material by bringing it closer to its yield stress. Furthermore, when
heated during pretreatment or under use, Ar could diffuse and agglomerate into bubbles, introducing
porosity and weakening of the interface [18].

The use of unipolar pulsed substrate biasing in cathodic arc evaporation was introduced in 1991 by
Olbrich et al [19] to reduce thermal input associated with ion bombardment. With the advent of
pulsed-DC target sputtering, bias pulsing techniques with frequencies in the range 20-350 kHz become
more popular in the late 1990s because it was then realized that it could provide improved control of
substrate bombarding ion energy and flux, and be utilized to bias substrates during reactive deposition
of insulating films [20]. Unipolar pulsed-DC substrate biasing is often carried out in combination with
pulsed-DC target sputtering. In such situations, both target and substrate are pulsed at the same
frequency (usually 100 kHz) in a synchronous “master-slave” configuration [21-23].

2.3. Ion-metal implantation
An improvement in the adhesion of carbon-based coatings has been the pretreatment in metal arc
discharge environment. Bombardment with metal ions is known to provide cleaner interfaces [24]:
cathodic arc discharges produce a high flux of metal ions, which bombard the surface of the substrate
and remove oxide layers. That was the base for the development in the 1990’s of the so-called ABS
(Arc Bond Sputtering) technique where a cathodic arc is used to generate metal ions that are
accelerated by a DC bias voltage toward the substrate in order to produce an etching prior to the film
deposition by magnetron sputtering [25]. As it has been pointed out by many researchers, the multiply
ionized metal ions, which are produced in the vapor of the cathodic arc discharge, not only clean the
substrate, but also produce low-energy implantation promoting the formation of a graded interface
between the substrate and the coating. The formation of such interface provides a relief of film stress,
increasing the adhesion of the coatings [26-28].
The effects of DC bias voltage on the composition and structure of the graded interface for enhanced adhesion on steel has been the subject of many studies. For example, Schönjahn et al studied Cr arc etching of M2 mild steel, where an implantation/diffusion layer of Cr in the steel was observed at DC bias voltages of -800 to -1200V [29]. One of the problems of etching with cathodic arc is the production of molten particles which are deposited onto the surface to be cleaned. Münz et al investigated the generation of droplets by many target materials, including Cr [30]. They found that the number and size of the droplets depend on the melting point of the metal used during the ion etching, with a typical droplet size of 100 nm.

2.4. HIPIMS technique

Recently, the use of high power impulse magnetron sputtering (HIPIMS) technology has been proposed to increase the adhesion of coatings on metal substrates [31]. HIPIMS produces a high flux of ions with high metal content similar to an arc discharge, but without droplets. The ions (gas and metals) are accelerated to the substrate by the use of a DC bias, producing a high rate of substrate etching and also the implantation of metal atoms like in arc discharges.

The metal ion etching by HIPIMS using a DC bias voltage has been first reported by Ehiasarian et al [32], as in the scheme shown in figure 3. The highly ionized plasma conditions of HIPIMS with 80% metal ions resulted in a more efficient ion bombardment, improving the etching of the substrate and increasing the adhesion of the coatings. It has also been claimed that the presence of a DC bias voltage facilitates the formation of a shallow metal implantation on the surface, promoting the formation of an adherent interface between the substrate and the coating [33].

![Figure 3. (a) Ion-metal cleaning and implantation; ions generated by a HIPIMS magnetron with a Cr target. A DC bias voltage is applied to the substrate. (b) Deposition of carbon nitride films after substrate pretreatment.](image)

Different ion metal etching prior to the deposition of coatings have been reported: Cr or Nb for CrN [18, 34, 35], V for TiAlCN/VCN multilayers [36], Cr for CrAlYN/CrN multilayers [37, 38], WC for W-DLC and C-DLC multilayers [39], and Cr for DLC and metal-DLC coatings [40]. Besides our previous work [5-6], to our knowledge there are not reports on the deposition of CNx (carbon nitride) coatings using the HIPIMS interface sputter cleaning, or on the use of two HIPIMS power supplies for etching (one connected to the cathode and one to the table) [41].

The most important problem to solve during the substrate pretreatment by HIPIMS for the cleaning and interface formation is the high current flowing from the cathode to the substrates. In some DC power supplies used for biasing, this high current is interpreted by the bias power supply as the presence of arcing, which causes the power supply to interrupt the operation. This problem has been partially overcome installing large capacitor-resistors banks or special power supplies with filters that can stand the current pulse arriving to the substrates [42, 43]. However, the constancy of the bias during the discharge will depend on the size of the capacitors and resistors. From an industrial point of view, the drawback is that this device occupies a vital space in the chambers, especially if a nearly constant bias voltage is desired.
Based on our innovation [5] we have recently reported results for the deposition of highly adherent CNx films on steel substrates using a novel HIPIMS pretreatment in an industrial production chamber [6]. During the pretreatment, the substrates were pulse-biased in the environment of a HIPIMS Cr plasma in order to sputter clean the surface and to implant Cr+ metal ions, as shown in figure 4. Subsequently, CNx films with superior adhesion to the steel substrates were obtained by DC unbalanced magnetron sputtering [6].

![Figure 4.](image)

**Figure 4.** (a) Ion-metal cleaning and implantation; ions generated by HIPIMS magnetron sputtering with a Cr target. A HIPIMS bias voltage is applied to the substrate in a master-slave configuration. (b) Deposition of carbon nitride films substrate after pretreatment.

### 3. Experiments

The experiments were carried out in a CC-800/9 industrial system manufactured by CemeCon AG in Würselen, Germany. The chamber (85 x 85 x 100 cm) is equipped with four rectangular magnetron sputtering cathodes (50 x 8.8 cm) facing a table holder that can provide up to three-fold rotation to the substrates. Due to the nature of our experiments only two out of four cathodes mounted in the system were used. The system is equipped with DC magnetron power supplies Pinnacle 3000 (Advance Energy) and HIPIMS power supplies SINEX 3 (Chemfilt Ionsputtering AB, Linköping, Sweden). The targets materials were Cr and C (99.8% pure). The substrates used in the experiments were Si (100) wafers and SKF3 (AISI 52100) bearing stainless steel.

Cross-sectional specimens for transmission electron microscopy (TEM) investigations were made by gluing slices into Ti disks followed by mechanical polishing and grazing incidence (4°) Ar+ ion thinning at 10 kV to electron transparency using a Technoorg Linda IV6 ion milling unit. The ion energy was decreased in the final period of the ion milling procedure down to 500 eV to decrease the ion damage. The high-resolution TEM (HRTEM) investigations were made in a Technai G2 and a JEOL 3010 electron microscope operated at 200 and 300 kV, respectively. EDS line scans were recorded in the Technai G2 microscope. Cross-sectional scanning electron microscopy (SEM) experiments were made using a LEO SEM equipment operated at 5 kV.

#### 3.1. Substrate pretreatment and coating

The metal substrates were mirror polished by mechanical polishing with a sequence of 6, 3, and 1 μm diamond pastes, and then were cleaned using a sequence of ultrasonic washing stages with alkaline detergents (Decon-90 at 5%), de-ionized water rinsing and air-drying. Prior to loading into the chamber, all the substrates were ultrasonic cleaned with acetone and isopropanol, and blow-drying with nitrogen gas.

Different substrate pre-treatments were carried out prior to the deposition of the CNx films (see figures 2, 3, and 4):

- a first group of substrates (figure 2) were biased to a DC voltage of ~1200 V while the Cr target was operated in a DC mode at a pressure of 3 mTorr of Ar and a current of 1 A during 30 minutes;
• a second group of substrates (figure 3) were biased to a DC voltage of -600 V while a HIPIMS source was operated at a pressure of 3 mTorr, with a peak target voltage of 1100 V, a frequency of 150 Hz, and a pulse width of 100 s, during 30 minutes;
• the third group of substrates (figure 4) were biased to a HIPIMS source with peak voltages of in the range 400-800 V, a frequency of 150 Hz, and a pulse width of 200 s. The target was also connected to a second HIPIMS source operated at a pressure of 3 mTorr, with a peak target voltage in the range 500-1100 V, a frequency of 150 Hz, and a pulse width of 100 s, during 30 minutes. Both HIPIMS power supplies were synchronized, being the one in the target the “master” and the one in the substrate the “slave”. The voltage pulse in the target was programmed to start 10 s after the pulse in the substrate in order to assure the stability of the bias voltage (figure 5)

The coating step was carried out by DC magnetron sputtering of a C target in a reactive atmosphere of Ar and N₂ (partial pressure ratio of 84:16 and total pressure of 3 mTorr), target power of 1800 W, and a negative bias voltage of 25 V.

No heating treatment was used during the pretreatment or the deposition steps.

![Figure 5](image_url)

**Figure 5.** Target current (■), target voltage (□), and substrate bias voltage (O) waveforms recorded in one of the experiments of the configuration illustrated in figure 4.

3.2. Cathode current and plasma characterization
The target current was measured with a Tektronix CT-04 high current transformer together with a Tektronix TCP202 current probe mounted right at the connection to the vacuum chamber. A Tektronix P6015 high voltage probe was used to measure the cathode voltage. Current and voltage waveforms were recorded with the Picoscope 3000 real time digital storage PC oscilloscope from Pico Technology.

The optical emission from the plasma was measured in the light-of-sight geometry through a port window of the chamber and the probe was directed towards the race track. A spectrometer (Mechelle Sensicam 900) connected to a collimator via an optical fiber was used to record the emission from the plasma. The spectral range of the spectrometer was 300-1100 nm. The optical emission spectra were acquired at argon gas pressures ranging between 0.5 and 10 mTorr and for different target voltages (implying different peak power levels). The shutter speed of the spectrometer was set to 100 ms, meaning that all data were time-averaged over ca. 30 pulses (the pulsing frequency was fixed at 300 Hz).
3.3. Throwing power
The throwing power of the Cr sputtered atoms was evaluated on Si substrates oriented at five different angles with respect to the cathode surface: 0°, 45°, 90°, 135°, and 180° from the horizontal. The Cr films were deposited by DC magnetron sputtering and HIPIMS, as shown in figure 2(a) with a DC bias of 60 V, and figure 4(a), using a HIPIMS bias of 60 V. After deposition, the coating thickness was measured by SEM on cross-sectional samples. The throwing power was calculated as a % of the film thickness relative to the film deposited in front of the surface cathode (0° from the horizontal).

3.4. Adhesion test
The adhesion was measured by the Daimler-Benz Rockwell-C adhesion test. Developed by the Union of German Engineers (Verein Deutscher Ingenieure, VDI [44]), it uses a standard Rockwell hardness tester fitted with a Rockwell C-type diamond cone indenter with an applied load of 150 kg. The result is obtained by using an optical microscope and classifying the adhesion as HF1 to HF6 according to the level of cracking and coating delamination around the indent (figure 6). Only indents classified as HF1 and HF2 correspond to adequate adhesion [45].

Figure 6. The Daimler-Benz Rockwell-C adhesion test chart (adapted from reference 44).

4. Results and discussion

4.1. Plasma chemistry during pre-treatment
The chemistry of the ion flux during the HIPIMS pretreatment was studied by optical emission at different energies. In figure 7 the optical emission intensities of the strongest lines are plotted for Cr⁺ ions and Cr neutrals, respectively, versus energy per pulse at an argon gas pressure of 3 mTorr [6]. The emission lines chosen for comparison are Cr-I at 399.2 nm and Cr-II at 336.9 nm. It is observed that there is a nearly linear relation between the intensity of optical emission of both Cr⁺ ions and Cr neutrals and the energy per pulse. Especially, the slope of the linear function for Cr⁺ ions is much larger than that of Cr neutrals. The detail quantification of the optical emission spectra is, however, complicated due to the dynamic nature of the discharge, lack of thermodynamic equilibrium (unknown electron temperature), and experimental setup (line-of-sight geometry), etc [6].

4.2. Interface characterization
The microstructure of the interface between CNₓ films and steel substrates was studied by cross-sectional TEM in samples deposited with the HIPIMS biased substrate method of figure 4. Figure 8 shows the formation of a modified Cr layer between the steel substrate and the CNₓ film prepared by this method. The layer is characterized by a polycrystalline structure of approximately 100 nm thick.
The transition between the substrate and the modified layer, which appears to have more contrast, has been previously analyzed by HRTEM; a ~5 nm amorphous transition layer was found between the Cr and the steel [6]. The overall structure of the interface is dense, with no formation of bubbles or voids, pointing to a strong bonding between the steel substrate and the CNx coating.

The modified layer is formed during the pretreatment stage where Ar+ and Cr+ ions generated by the HIPIMS discharge on the Cr target bombard the substrate biased by the second HIPIMS power supply. Two counteracting processes compete during the formation of the polycrystalline layer: (a) the Cr concentration decreases due to sputter removal; and (b) the Cr concentration increases due to condensation on the surface.

Figure 7. The dependence of emission intensity from Cr-I (339.1 nm) and Cr-II (336.8 nm) lines on the energy density per pulse.

The effective sputter removal effect of Ar+ plus Cr+ ions bombardment was evaluated by a simple experiment on two Si(100) substrates using the configuration of figure 4(a). The Cr target was operated during 30 minutes at a pressure of 3 mTorr of Ar, with a peak target voltage of 1100 V, a frequency of 150 Hz, and a pulse width of 100 s. These conditions are similar to the sample shown in figure 5, however, one of the Si substrates had a floating bias. After the experiment, cross-sectional SEM observations of the Si substrates revealed a Cr layer of 1.2 µm thickness for the substrate held at floating bias, in contrast to the 0.1 µm of the biased sample grown under HIPIMS Ar+ + Cr+ ion bombardment.

We have previously shown that the amorphous transition layer is a mixture of Cr and Fe [6]. The presence of this mixed amorphous interface can be explained by the magnitude and composition of the ion flux. The introduction of Cr into the substrate is initiated by the direct physical implantation of Cr extracted from the plasma and accelerated by the high bias voltage. Additionally, the retention of Cr is facilitated by the high affinity of the metal ion, which could be incorporated at lattice sites of the substrate. In the system Cr-Fe there is a complete thermodynamic solubility and there is no limit to the expected concentration that can be incorporated [18, 35]. Recently, Ehiasarian et al [18] have simulated the depth of Cr incorporation resulting from implantation using the TRIDYN code. Assuming a steel substrate and bombarding ion flux concentration of 50 at. % Cr3+, 30 at % Cr4+ and 20 at. % Ar+, he obtained maximum range of implantation of 7 nm for a DC bias voltage of 600 V, similar to the depth profile we have measured previously [6]. This result contrasts with the ones from other authors [18, 35] where a mixed interface of 15-20 nm has been observed. The difference can be associated to thermal diffusion of Cr into the substrate. While these authors have been using substrate...
temperatures in the range 250-500 °C, our samples have been deposited at room temperature. It is well known that during DC bias cleaning of the substrates the surface temperature increases. In our case, we know the maximum substrate temperature during the dual-HIPIMS plasma etching (figure 4) was below 200 °C because we did not observe a change in the HV hardness of our SKF3 steel substrates [46].

Cross-sectional and plan-view SEM images of the CN_x films (not shown here) have revealed a coating with a dense microstructure, similar to that observed in amorphous CN_x films deposited in laboratory-scale chambers [1, 47].

4.3. Throwing power

Figure 9 compares the throwing power of films deposited by DC magnetron sputtering and HIPIMS as a function of the substrate angle with respect to the surface of the cathode. It clearly shows that the films are more uniform when they are deposited by HIPIMS.

It is well known that in the vapor evaporation technique the transport of the vapor atoms is almost strictly line-of-sight and follows the Knudsen’s cosine law \( \cos \theta / r^2 \), where \( r \) is the radial distance from the source and \( \theta \) is the angle between the radial vector and the normal to the receiving surface. The main reason to be a line-of-sight deposition is due to the low mean free path of the evaporated atoms, in the order of the distance between the evaporating source and the substrate [48].

In the case of DC magnetrons sputtering, like in figure 3(a), Cr atoms are ejected from the target following “under-cosine” or “over-cosine” distributions for low and high bombarding energies, respectively. Two additional differences with vacuum evaporation will appear, originated from the higher deposition pressure and the substrate biasing possibility. For working pressures in the order of millitorrs, the mean free path of the evaporated atoms will be shorter than the distance between the cathode and the substrate. A large portion of these atoms will be deflected by the series of collisions with gas molecules and many of them will reach surfaces, which are not in the line-of-sight of the cathode. In addition, if the substrate is biased, the small amount of ionized Cr atoms generated in the discharge will be accelerated towards the substrate along the electric field lines produced by the bias and will also be deposited in non-line-of-sight regions of the substrate. Due to these two effects, dc magnetron sputtering is considered to have higher throwing power than vacuum evaporation [48].

When considering the case of HIPIMS magnetron sputtering, like in figure 4(a), the higher ionization in the discharge will increase the influence of the substrate bias: a higher amount of Cr ions...
will follow the electric field lines of the substrate and as a result, we will get a higher throwing power than DC magnetron sputtering, as shown in figure 9.

![Figure 9](image.png)

**Figure 9.** Throwing power of CrN films as a function of the angle between the surface of the target and the surface of the substrate for DC magnetron sputtering and HIPIMS magnetron sputtering. Both depositions have been done at the same pressure.

### 4.4. Adhesion tests

Figure 10 illustrates typical results from the Rockwell-C tests on samples deposited by the three different substrate pretreatment methods of figures 2, 3, and 4.

Figures 10(a) and 10(b) illustrate the resulting indentation when the samples were biased to a DC voltage of -1200 V and the Cr target was operated in a DC mode, like in figure 2(a). The indent can be identified to the adhesion strength quality HF5 shown in the chart of figure 6. The CNx coating shows radial cracks and large delaminations around the crater caused by the piling up of the substrate, and can be related to the poor adhesion of the film to the substrate.

Figures 10(c) and 10(d) show the resulting indentation of coatings when the samples were biased to a DC voltage of -600 V while the Cr target was operated with a HIPIMS source, like in figure 3(a). In this case the CNx coating has a typical failure that can be related to the adhesion strength quality HF3: cracks in the indentation area with small delamination in the vicinity of the crater.

Figures 10(e) and 10(f) show no visible delaminations around the indentation crater, and the presence of very few fine cracks, typical of adhesion strength quality HF1. This excellent adhesion was obtained when both substrate bias and Cr target were connected to two synchronized HIPIMS power supplies, as shown in figure 4.

The results of figure 10 can be correlated to the different pretreatments. We have shown [6] that at the optimum conditions of 1100 V Cr cathode voltage and 600 V bias voltage, a gradual interface between Cr and steel is formed (figure 8) that can withstand the high stresses of the CNx films. As we have discussed in section 4.2, at the beginning of the plasma pretreatment, the Ar⁺ + Cr⁺ ion bombardment have enough time to clean the substrate from oxides and other contaminants, and tends to sputter away the exposed steel substrate and implant Cr ions. As a result, the film adhesion with an optimal intermixing at the interface becomes very strong, with a high HF quality in the adhesion test (figure 10).

### 5. Conclusions

Carbon nitride films were deposited onto SKF3 (AISI 52100) bearing stainless steel substrates in an industrial chamber by DC magnetron sputtering with various interfacial treatments. A novel plasma HIPIMS pretreatment is employed where two HIPIMS power supplies are used in a master-slave configuration: one establishes the discharge in the cathode and the second produces a pulsed substrate bias. This configuration provides a more stable bias voltage during HIPIMS plasma pretreatment,
resulting in an alternative way to achieve excellent results without the use of specially designed DC power supplies.

![Figure 10](image)

Figure 10. Adhesion strength HF of CN$_x$ films deposited by DC magnetron sputtering. Each optical micrograph represents a sample deposited by a different substrate plasma treatment. (a) & (b): HF6, when gas ions are generated by a DC magnetron cathode and the bias is provided by a negative DC voltage, like in figure 2. (c) & (d): HF3, when the gas and metal ions are generated by an HIPIMS discharge in the cathode and the bias is provided by a negative DC voltage, like in figure 3. (e) & (f): HF1, when two HIPIMS power supplies are used in a master-slave configuration, like in figure 4.

The throwing power of films deposited by DC magnetron sputtering and HIPIMS has been compared. We show that the higher throwing power of HIPIMS coatings can be associated to the higher ionization in the plasma discharge.

Adhesion of CN$_x$ films evaluated by the Daimler-Benz Rockwell-C and the scratch tests was remarkably increased to maximum value by our pretreatment through the formation of an optimal interfacial mixing layer of Cr and steel.

We demonstrate the feasibility of depositing thick (1-3 µm) adherent CN$_x$ coatings on steel substrates in an industrial scale chamber, opening the possibility for new tribological applications of carbon nitride films. The findings of this study are also expected to be of general validity and applicability in the industrial scale deposition of carbon-based coating materials.

Acknowledgements
E.B acknowledges the support from the Swedish Government Strategic Research Area Grant in Materials Science. Dr. G. Greczynski from Linköping University (Sweden) and Dr. Zs. Czigány from MFA (Hungary) are acknowledged for the help in acquiring the data for figures 7 and 8, respectively.

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