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Investigation of high power impulse magnetron sputtering pretreated interfaces for adhesion enhancement of hard coatings on steel

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Abstract

In order to improve the adhesion of hard coatings such as CrN, a surface pretreatment by the novel high power impulse magnetron sputtering (HIPIMS) technique followed by reactive unbalanced d.c. magnetron sputtering deposition was performed using a Cr target. The HIPIMS plasma comprising a high metal ion-to-neutral ratio consisting of single- and double-charged metal species identified by mass spectrometry increased the metal ion flux to the substrate. When applying a negative substrate bias U_b the adhesion was enhanced due to sputter cleaning of the surface and metal ion intermixing in the interface region. This intermixing, resulting in a gradual change of the composition, is considered to enhance the adhesion of the hard coatings on steel substrates. The pretreatment was carried out in an inert gas atmosphere at a pressure of $p_{Ar} = 1$ mTorr, the duration was varied between 25 and 75 min, whereas the negative substrate bias was varied between 400 V and 1200 V. The adhesion was found to depend on the substrate bias as well as on the target power and, for low substrate bias, on the duration of the pretreatment. For CrN the critical load of failure determined by scratch test could be increased in comparison to the values reported for specimens pretreated by conventional Ar etching. The influence of the target peak voltage, the substrate bias as well as pretreatment time on the constitution and morphology of the interface after the pretreatment is discussed applying analytical transmission electron microscopy.

Keywords: Ionized PVD; Pulsed magnetron sputtering; Analytical TEM; Adhesion; Ion implantation

1. Introduction

Magnetron sputtering is a well-established physical vapor deposition (PVD) technique. It is used to deposit different coatings such as metallic, ceramic thin films and compounds for a wide range of applications. The main drawback of this techniques is the low ionization degree, especially of the sputtered material (a few percent) [1] often resulting in a porous microstructure of the films and low adhesion. Additionally, it is well-known that the coating–substrate interface plays a key role with respect to the general functionality of coated parts. Especially in demanding metal cutting applications, beside the microstructure, the adhesion is important for the performance of the coatings and it has been shown earlier [2,3] that the microstructure and microchemistry of the interface region is directly correlated to the tool life. Therefore, interface engineering is an important issue demanding ions for surface cleaning and modification [4-7]. The cleaned and/or modified surface due to pretreatment was given to increase the bonding strength and with a well-preserved crystalline structure to promote local epitaxial growth maximizing the interfacial adhesion of thin films. Arc evaporation providing a high degree of ionization of the sputtered metal forms defects due to droplet formation degrading the quality and performance of the coatings. High power impulse magnetron sputtering (HIPIMS) as a modification of the conventional d.c. magnetron sputtering has recently drawn much attention from industry and academia. Due to its high plasma density exceeding 10^{19} m^{-3} and ionization of a large fraction of the sputtered material [8,9] HIPIMS is in general seen as an alternative technique for ion assisted film growth and surface engineering. The increase in plasma density is achieved by increasing the applied power, which is limited by the thermal load of the target. The solution to this problem is to apply a high power in pulses with a low duty factor (ratio between pulse-on time and the total time). Since the thermal load of the target is limited by the average power rather than the peak power, the peak power during the active discharge can be very high. The applied peak voltage can be up to 2.4 kV, resulting in a peak discharge current of the order of A cm^{-2} on the target surface. The ionization fraction reaches values of 30–70% [10], and a peak value of over 90% for Ti are reported [11], but it is believed to be strongly material dependent. The high degree of ionization opens new opportunities, since the ions may be controlled by the use of electric and magnetic fields. In this work, HIPIMS was used to initially pretreat the substrate surface in a metal/argon plasma prior to the coating deposition using conventional d.c. magnetron sputtering (dcMS).

2. Experimental details

2.1. Coating deposition

The depositions were performed in turbo-molecular pumped high-vacuum chamber with a diameter of 44 cm and a height of 75 cm. The chamber was evacuated prior to the depositions to a base pressure of $3 \cdot 10^{-4}$ Pa. The inert gas (Ar, 99.9997% purity) and reactive gas (N, 99.998% purity) were introduced through a leak valve so that the desired gas pressure and mixture of the sputtering gas was achieved. A Cr target (15 cm in diameter, 6 mm thick, 99.9% purity) was mounted on a weakly unbalanced magnetron cathode. The magnetron cathode was driven either by a pulsed power supply (Chemfilt R&D AB, Stockholm, Sweden) or a d.c. arc-quenching power supply for the pretreatment process and the deposition, respectively. For the substrate biasing two d.c. power supplies (mounted in series), each delivering a voltage up to 600 V, were used. The pulsed power supply is able to deliver pulses with up to 2.4 MW (2000 V and 1200 A) peak power at a repetition frequency of 50 Hz and a pulse width in the range of 50–100 μ s. Stainless steel (AISI 304 (Fe/Cr18/Ni10)) and high-speed steel (HSS) disks (30 mm in diameter, 6 mm in thickness) were used as substrate materials polished to final mirror finish using 1 μ m diamond paste. Stainless steel was used for TEM investigation and the high-speed steel samples for scratch test analysis. Prior to the plasma cleaning process the substrates were ultrasonically cleaned in isopropanol and then in acetone, for 15 min each. The substrates were placed 10 cm below the target and were heated to 400 °C prior to the pretreatment.

(i) *Adhesion enhancing pretreatment step by HIPIMS.* HIPIMS pretreatment was performed with a Cr target in Ar atmosphere at a pressure of $p_p = 0.13$ Pa (1 mTorr). The peak voltage loaded to the target was 1.5 kV. The substrates were negatively biased between 400 and 1200 V in order to sputter clean the surface and to implant Cr metal ions with a process duration t_p between 25 and 75 min.

(ii) *CrN(dcMS) coating deposition.* CrN deposition using d.c. magnetron sputtering was performed in a mixed Ar and N₂ atmosphere with a partial pressure ratio of $P_{Ar}/P_{N_2} = 1:3$ (total pressure of 0.53 Pa (4 mTorr)) and a negative substrate bias of 50 V was applied. The d.c. power applied to the target during the deposition was 1 kW.

The details of the surface pretreatment for the samples discussed in this work can be found in Table 1.

Table 1: Process parameters of the HIPIMS pretreatment and critical load determined in scratch test for the samples analysed in Section 3

U_T (kV)	U_b (V)	Time, t_p (min)	Crit. load, L_c (N)
1.5	400	75	45
1.5	700	25	28
1.5	1200	25	40

2.2. Plasma and coating investigation

A quadrupole mass spectrometer (PSM003, Hiden Analytical, UK) was employed to determine the time-averaged energy-resolved ion composition in the HIPIMS plasma. The instrument is capable to measure ion energies up to 100 eV with a resolution of 0.05 eV. The instrument was inserted from the side of the chamber, parallel to the target with a vertical distance of 5.5 cm away from the target surface. The opening of the spectrometer was situated about 10 cm away from the center axis. The time-averaged plasma ion compositions were determined over 5 pulses for Ar ($M = 40$, 99.6% natural abundance) and Cr ($M = 52$, 83.789% natural abundance). The film adhesion was evaluated by the critical load L_c values in scratch tests (CSEM Revetest).

A Tecnai G² TF 20 UT equipped with a field emission gun (FEG) operated at 200 kV for a point resolution of 1.9 Å was employed to investigate the surface modification of the steel substrate as well as the structure evolution of the coating especially in the interface near region. The microchemistry across the interface was investigated with energy-dispersive X-ray spectroscopy (EDX) by performing line scans in scanning TEM (STEM) mode. The lateral resolution of the chemical analysis using EDX spectroscopy is in principle given by the probe diameter (~ 0.5 nm). A low camera length (90 mm) was used recording the STEM images employing a high-angle annular dark field detector (HAADF) to obtain preferential mass-thickness contrast (incoherent scattering) and reduce the influence from the diffraction contrast (coherent scattering). Light elements appear therefore darker in these images.

3. Results and discussion

3.1. Plasma investigation

The results of the time averaged and energy-resolved plasma ion composition for an Ar plasma ($p(\text{Ar}) = 1$ mTorr) and a peak voltage applied to the target of 1.5 kV using a mass spectrometer are shown in Fig. 1a.

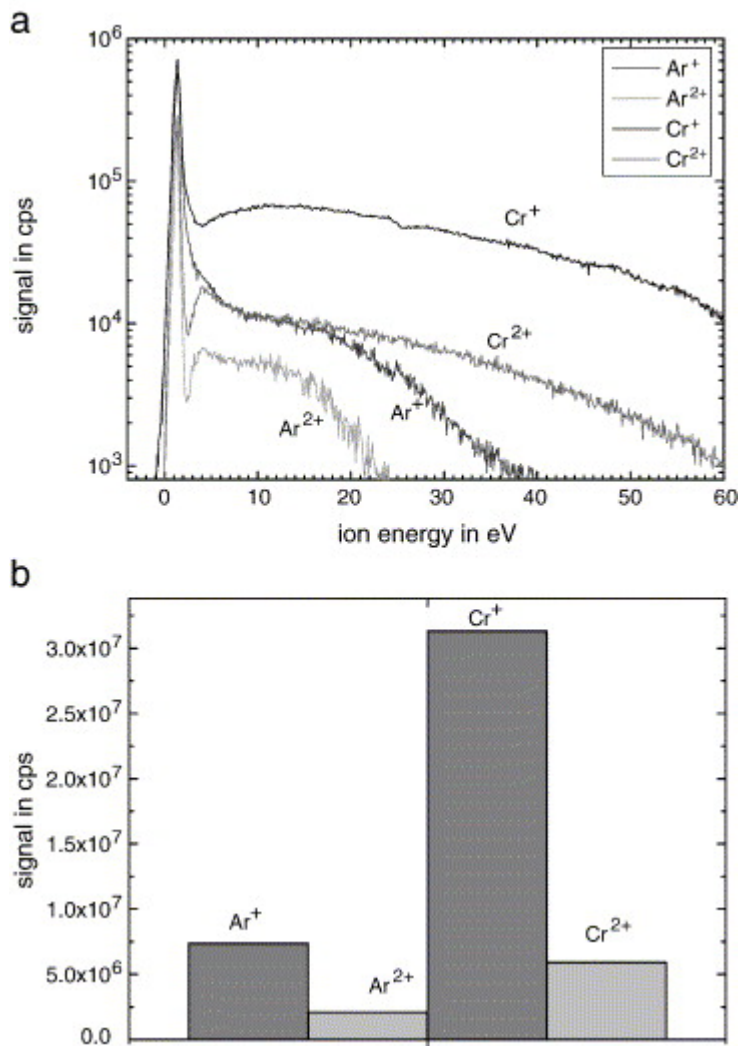


Fig. 1. Mass spectrometer measurement showing the amount of Ar^+ , Ar^{2+} and Cr^+ , Cr^{2+} and their energy distribution; $U_T = 1.5$ kV, $p(\text{Ar}) = 1$ mTorr. (a) Energy distribution of the $\text{Ar}^{1+,2+}$, $\text{Cr}^{1+,2+}$ ions. (b) Amount of the $\text{Ar}^{1+,2+}$, $\text{Cr}^{1+,2+}$ ions.

The HIPIMS plasma consists of single- and double-charged Ar and metal ions. Both Cr and Ar ions, independent of the charge state, show a maximum in the energy distribution at around 1.4 eV, which is correlated to the thermalized ions accelerated by the plasma potential at a late stage of the discharge or in the afterglow between the pulses when the plasma

potential is low [12]. A pronounced high-energy tail is observed in the case of the Cr ions. By integrating over all energies in Fig. 1a, the amount of Ar^+ , Ar^{2+} and Cr^+ , Cr^{2+} over 5 pulses was extracted (see Fig. 1b). From these results the ratio between the Ar and Cr ions was determined to be $\text{Cr}^+/\text{Ar}^+ = 4.3$ and $\text{Cr}^{2+}/\text{Ar}^{2+} = 2.8$. Further, the average charge state of the Ar and Cr ions was calculated to be 1.22 and 1.16, respectively. It has to be noted that the neutral flux is unknown and the ion flux and the metal neutral to ion ratio are strongly time dependent.

3.2. Substrate–film interface investigations

The microstructure and microchemistry investigations of three samples pretreated with different ion energies and pretreatment durations are presented in Figs 2-4.

The XTEM image of the CrN(dcMS) coating in which the substrate was ion-etched with a negative pretreatment voltage of $U_b = 1200$ V including the interfacial region is shown in Fig. 2a. The ion-etched modified region of the steel is apparent due to the dark contrast in the CrN(dcMS)–substrate interfacial region indicating strain fields associated with a residual radiation-damage-induced defects within the matrix of the substrate grains as a result of the intense Ar and Cr ion irradiation. The strained interfacial region can be estimated from the TEM/STEM image in Fig. 2a, b to approximately 15 nm. The interfacial region is followed by a region of pronounced competitive growth of the CrN(dcMS) resulting in a columnar appearance with widths of about 40–50 nm. Fig. 2b shows the STEM image of the interfacial region. The line in the image marks the position and length of the STEM-EDX line scan and the associated chemical composition profile is shown in Fig. 2c. A transition region over which the Fe decreases and Cr signal increases with a width of approximately 15 nm is observed which correlates with the dark interfacial layer. The oxide layer naturally formed on the steel surface is completely removed which is demonstrated by the constant oxygen signal. The overall observed oxygen content is due to the oxidation of Cr and Fe, when exposing the prepared TEM sample to air and the plasma cleaning using an oxygen/argon plasma.

The measured compositional intermixing region is thicker than the intermixing depth calculated by means of TRIM calculations [13]. From TRIM calculations using an acceleration of 1.2 keV and an average charge state as given in Section 3.1, the estimated maximum projected range $R = 2.5$ nm and the straggle $S = 0.9$ nm for Ar^{2+} and Cr^{2+} gives a ballistic intermixing length ($R + S$) of 3.4 nm. With STEM-EDX a significant Cr signal can

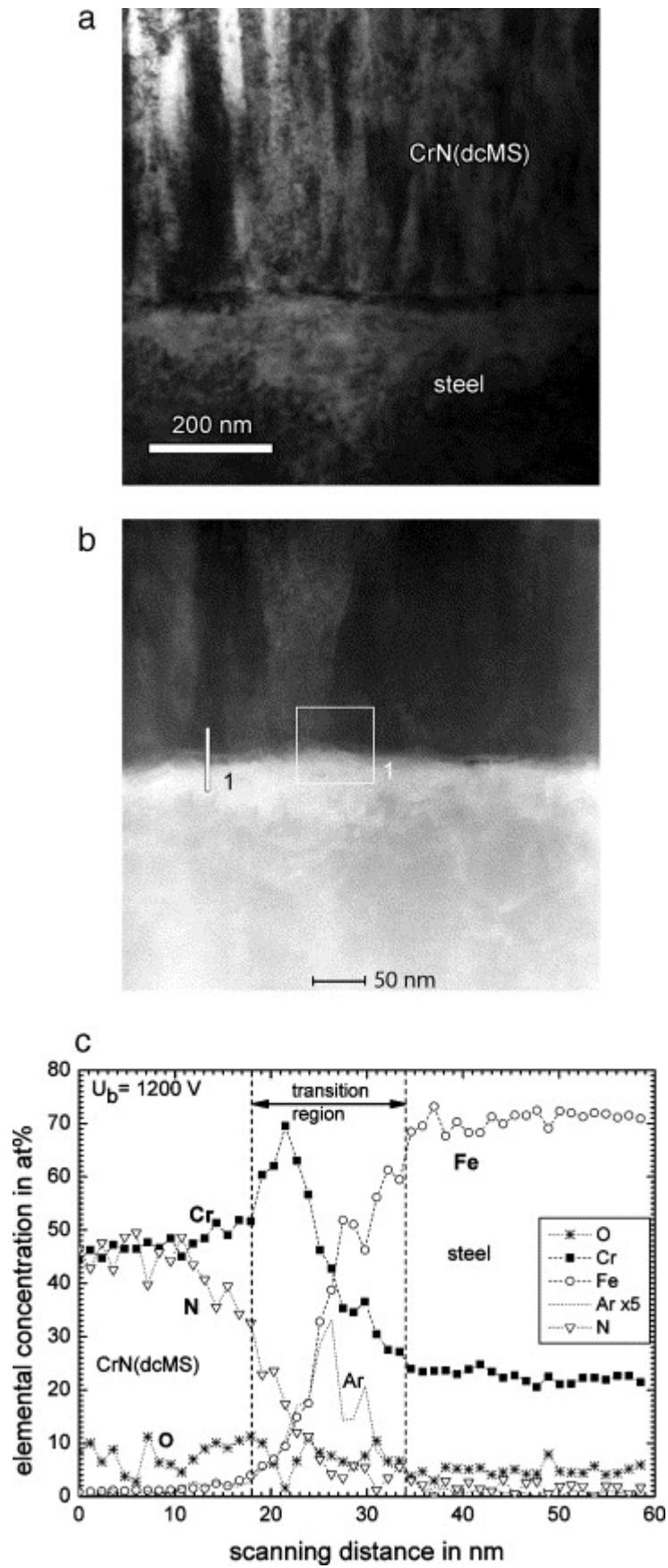


Fig. 2. (a) TEM image of the interface region showing the modified steel and the CrN film, (b) STEM image of the interface region, (c) depth profile across the interface region; $U_b = 1200$ V, $p_p(\text{Ar}) = 1$ mTorr, $t_p = 25$ min.

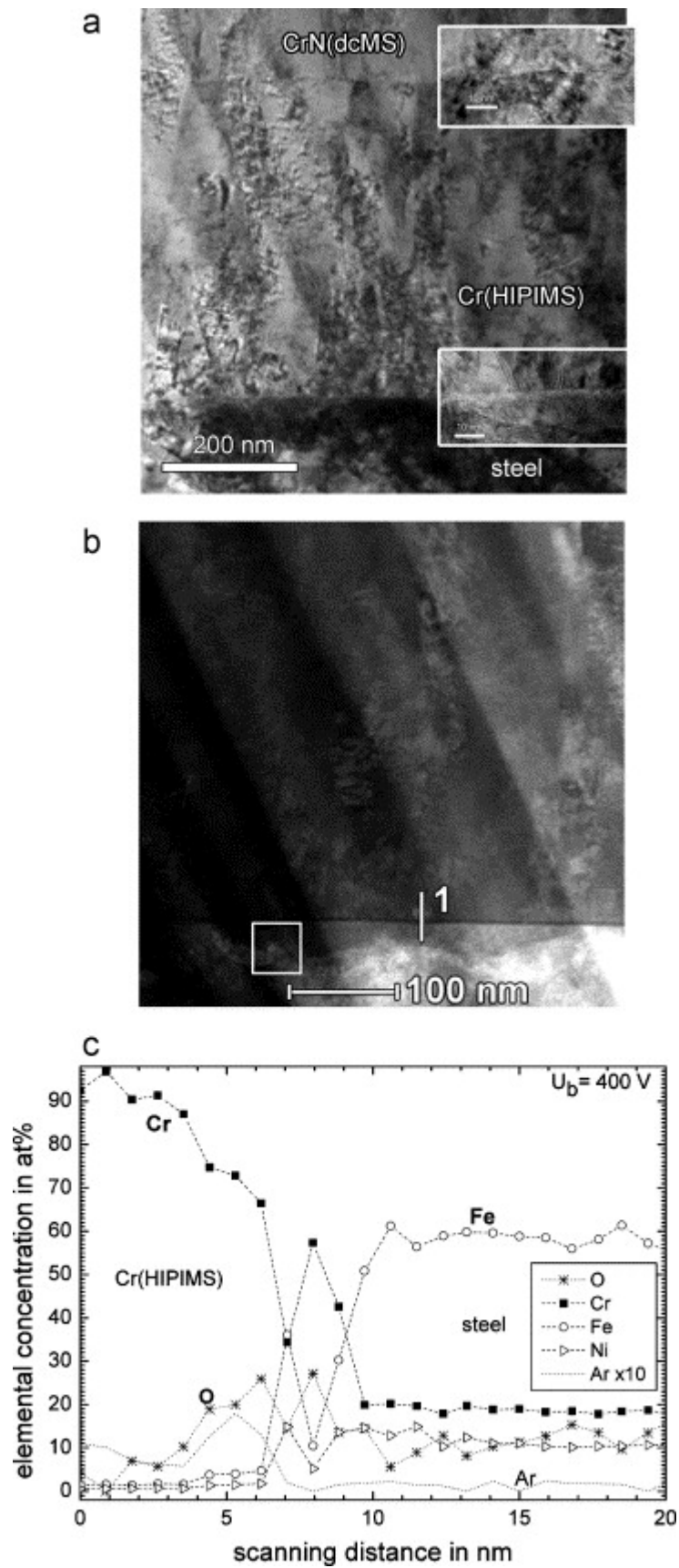


Fig. 3. (a) TEM image of the interface region showing the steel, a 540 nm Cr layer, and the CrN film, (b) STEM image of the interface region, (c) depth profile across the interface region; $U_b = 400$ V, $p_p(\text{Ar}) = 1$ mTorr, $t_p = 75$ min.

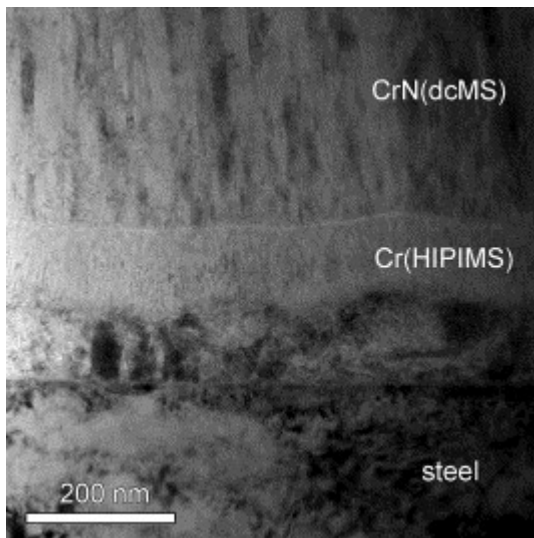


Fig. 4. TEM image of the interface region showing the steel substrate, the Cr(HIPIMS) layer, and the CrN(dcMS) film; $U_b = 700$ V, $p_p(\text{Ar}) = 1$ mTorr, $t_p = 25$ min.

be measured to a depth of up to 10 nm, before the level of the Cr content of the steel is reached, indicating radiation-enhanced diffusion due to intensive ion bombardment with a mixture of Ar and Cr ions of multiple charge leading to a broadening of the intermixing region.

The intermixing depth for the Cr is in good agreement with the results found for arc-etching where the Cr incorporation was measured to reach a depth up to about 15 nm [7].

The clean surface (no oxide layer) of the CrN(dcMS) film pretreated with a $U_b = 1200$ V (25 min) resulted in an enhanced adhesion in scratch test with a value of $L_c = 40$ N due to cohesive rather than adhesive failure.

The XTEM image of the film with $U_b = 400$ V applied during the pretreatment process in Fig. 3a shows a pronounced Cr(HIPIMS) layer deposited during the HIPIMS pretreatment with a thickness of about 540 nm confirmed by STEM-EDX analysis. The Cr(HIPIMS) layer as well as the CrN(dcMS) layer exhibits a dense columnar structure with a columnar appearance with widths in the range of about 150 nm. At a higher magnification (insert in Fig. 3a) at the substrate–Cr(HIPIMS) interface a sharp layer with a thickness of about 4 nm is observed corresponding to the naturally formed oxide passivation layer on steel in air. Fig. 3b presents the STEM image of the interface near region of this sample. The dark appearing line in the STEM image corresponds to a layer with lower mass indicating the oxide layer. The STEM-EDX chemical composition depth profile in Fig. 3c demonstrated significant Cr, Fe,

Ni and O concentration changes below the Cr(HIPIMS) layer indicating the existing oxide layer. A slightly increased Ar concentration in the EDX analysis just above the interface was observed giving a maximum concentration of about 2 at.% and indicated that the sharp layer is the unaffected oxide layer formed on the steel substrate in air. The results reveal that the ion energy is too low and the growth rate of the Cr(HIPIMS) layer is too high, thus, covering the oxide layer immediately and disabling the removal of the oxide from the steel surface. Despite of the still existing oxide layer the adhesion of this film is with a value of about 45 N comparable to the CrN coating pretreated with $U_b = 1200$ V. This may be explained by the locally promoted epitaxial growth of the CrN(dcMS) on Cr(HIPIMS) leading to a strong interfacial bonding due to structural coherence. On the steel–Cr(HIPIMS) interface, the fact that the increase of the pretreatment time from 25 to 50 and to 75 min resulted in a linear improvement of the adhesion from $L_c = 30$ N to $L_{cv} = 45$ N, the pretreatment might be explained as an annealing process enhancing the diffusion of oxygen away from the oxide passivation layer and Fe into Cr(HIPIMS) (see Fig. 3c) strengthening the interfacial adhesion. Due to the low accuracy of the quantification of oxygen together with the overall existence of oxides in the TEM sample, a diffusion of oxygen is difficult to confirm.

In Fig. 4a the XTEM image of the interface region of the film pretreated at a negative substrate bias of $U_b = 700$ V for 25 min is presented. Even at the substrate bias of $U_b = 700$ V applied during the pretreatment process a net Cr(HIPIMS) layer is deposited on the top of the steel surface confirmed by EDX analysis. This layer is characterised by pronounced nanocrystalline structure resulting in a strong competitive columnar growth of the subsequently grown CrN(dcMS) film reducing the adhesion to $L_c = 28$ N and showing adhesive failure. This failure mechanism is comparable to that of films grown on pure Ar-etched steel leading to a low density interface region and competitive columnar growth.

4. Conclusions

The in situ cleaning of the substrate surface by ion etching prior to the deposition in physical vapor deposition was shown to be essential for the coating adhesion and therefore the coating performance. In many PVD processes, inert gas ions like Ar are used to clean the substrate surface. Besides its inefficient etching rate of oxides, the incorporation of a high concentration of Ar gas in the interface is disadvantageous. Consequently, the critical load L_c of failure values in scratch tests are rather low ($L_c < 40$ N) [7].

In this work, HIPIMS plasma containing a mixture of single- and double-charged metal and Ar ions was used to pretreat the surface of stainless and high-speed steel substrates using different ion energies and pretreatment durations. The adhesion of the films pretreated with a negative substrate bias U_b of 400 V (for 75 min) and 1200 V (for 25 min) during the HIPIMS pretreatment showed good adhesion with an average critical load of failure of 45 N and 40 N, respectively. The film pretreated with $U_b = 700$ V during the HIPIMS process, in contrast, had a low critical load of failure $L_c = 28$ N due to cohesive failure. These results can be understood due to two different mechanisms increasing the adhesion strength confirmed by the TEM investigations and STEM-EDX analysis. It was shown that high ion energies ($U_b = 1200$ V) during the cleaning process caused resputtering and ion implantation and removed the oxide passivation layer with subsequent competitive growth of the CrN(dcMS) whereas low ion energies ($U_b = 400$ V) result in a net metal deposition with columnar structure rather than sputter cleaning the substrate, promoting local epitaxial growth. For $U_b = 700$ V, the intense ion bombardment led to a nanocrystalline metal interfacial layer and the subsequent competitive growth of the CrN(dcMS) film resulted in a cohesive failure at lower loads in the scratch test. The values achieved with HIPIMS pretreatment are comparable with arc bond sputtering (ABS) or filtered arc-unbalanced magnetron sputtering (arc-UBM) processes where values of 40–65 N are achieved, but no defects due to droplet formation is apparent in the HIPIMS pretreated interface region.

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