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偏置电压对 Cr/CrAlN 多层涂层的摩擦学性能及残余应力的影响 *

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摘　要：为了解工艺对多层涂层性能的影响，针对偏置电压对涂层中残余应力以及其相应摩擦性能的影响进行了研究，并通过更改工艺参数来制备优良的涂层系统并调整其残余应力。通过磁控溅射装置利用-75～-150 V 的偏置电压把 Cr/CrAlN 多层涂层系统沉积到热作模具钢 H11 上。除对涂层进行了金像分析外，还使用 X 射线衍射来分析了其残余应力。通过扫描电子显微镜测定涂层的结构和形态，采用纳米压痕实验和球盘摩擦实验来验证来工艺参数对力学和摩擦性能的影响。结果表明，残余应力随着偏置电压的增加而增长，并导致了更致密和更无序的微观结构。由于涂层的致密，涂层的硬度和涂层的杨氏模量也急剧增加。摩擦学性能也随着偏置电压的增高进一步受到涂层表面形态以及高残余应力和高硬度组合的综合影响。

关键词：多层涂层；偏置电压；残余应力；摩擦学性能；热锻压模具
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Influence of Bias Voltage on Tribological Behavior and Residual Stresses of Cr/CrAlN Multilayer Systems

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Abstract: The influences of the bias voltage on the residual stresses, as well as on the tribological properties, were investigated within the scope of this work in order to understand the operational behavior of the graded multilayer system used. The Cr/CrAlN multilayer systems were deposited on hot working steel substrates by magnetron sputtering with varying bias voltages between -75 V and -150 V. In addition to the metallurgical phase analyses, residual stress evaluations were performed using X-ray diffraction. The structure and morphology investigations of the coatings were determined by scanning electron microscopy. Furthermore, a nanoindenter and a ball-on-disk device were employed in order to characterize the mechanical and tribological properties and to clarify the effect of the process parameter on the service behavior of the PVD coating. It was shown that residual stresses increase with an increasing bias voltage, and resulted in a denser and more randomly orientated microstructure. Due to the refinement of the coating, both the hardness and Young's modulus increase drastically. The tribogological behavior was further affected by the change of the topography as well as by the combination of high residual stresses and a high hardess with a rising bias voltage.

Key words: multilayer coatings; bias voltage; residual stresses; tribological property; hot forming tools

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0 Introduction

Hard coatings have been widely studied owing to the raising importance of these in industry. Several coating systems have been investigated such as multilayer coatings, multicomponent solution hardened layer materials, metastable layer materials, nanocrystalline layer materials and superlattice films. Due to their versatility and good performance under complex loads, multilayer coatings have become an important goal in coatings industry[1]. Multilayer coatings present a better performance, increasing toughness and hardness and reducing wear and residual stresses as well as crack extension compared to monolayer systems[1-6]. The interfaces between single layers in PVD multilayers systems are sites for energy dissipation and thus could have positive effects on the tribological behavior of the coatings. Furthermore their constitution is sensitively dependent on the materials meeting together as well as on the fabrication parameters of the coating[1].

Traditionally, TiN has been used as protective layer, increasing lifetime and performance of cutting tools, but more recently has been reported that the addition of aluminium improves significantly its oxidation resistance and hardness[7-9]. Parallel to TiN development, CrN coatings have gained force in industry due to their excellent mechanical properties, combined with a high wear and corrosion resistance[10-12]. A remarkable property of CrN is that internal stresses are lower than in TiN, this permits to obtain coatings with thickness over 40 μm, in contrast with TiN coatings, which can be deposited up to 10 μm thickness through high internal stresses and consequent poor adhesion[9,12].

CrN properties have been enriched by adding Aluminium as a third component in its composition. CrAlN coatings promote the formation of aluminium and chromium oxides which surpress undesired diffusion of oxygen to the substrate, and subsequently grants better corrosion resistance which increases with increasing Al content[12-16]. Hofmann et al. state that the oxidation resistant of CrAlN is five times higher than for CrN, due to a complex (Cr, Al)-oxynitride layer which reduces the diffusion rate of Cr[16].

Moreover, thermal stability of CrN coatings is limited up to 600 ℃, but an addition of Al in the CrN matrix increases the thermal stability of ternary nitride up to 850 ℃[9]. This property, which guarantees the maintenance of coating properties even at higher temperatures, commonly reached at the different processes where coating have been used such as cutting tools and hot forming.

Besides the good mechanical characteristics, reduction of friction and wear leads to a significant improvement of the PVD-coatings. So Brizuela et al. performed ball on disc tests with a Ti6Al4V and a AISI 52100 steel ball where CrAlN coatings have exhibited a reduction of friction coefficient compared to CrN coatings under light load conditions. A good adhesion of the coatings was also reported with critical load values higher than 90 N for CrN and values above 60 N for CrAlN coatings, without a dramatic failure of the coating[12]. CrAlN coatings present a dense microstructure, with low amount of porosity and surface defects, and a high hardness attributed to several factors such as small interatomic distance, covalent nature, solution hardening and small crystallite size of coating[9]. During deposition, bias voltage enhances kinetic energy of the impacting positive ions in the plasma, changing drastically microstructure and residual stresses in the coating; and in turn affecting coating properties such as hardness, young′s modulus and friction and wear coefficients[16-17].

Based on previous studies about different coating designs of Crostack et al[18]. and Tillmann et al[19]. the main motivation of this study is to investigate the influence of the bias voltage on the residual stresses and tribological properties of the selected Cr/CrAlN multilayer system. Thus comprehensive data should be collected in order to optimize deposition parameters and improve coatings properties.

1 Material and methods

The Cr/CrAlN coatings were deposited on AISI H11 hot working steel substrates by means of an industrial magnetron sputtering device (Cemecon MLsinox800, Germany). The cylindrical samples (Φ 40 mm×5 mm) were grinded and polished prior to the coating deposition process. The surface roughness Ra of the polished substrates was determined by an optical 3D-surface analyzer (Alicona, Austria) and was measured to be (0.06±0.03) μm.

In this study, a graded coating design was investigated which based on the investigations of Tillmann et al[19]. It was shown that the graded coating system with 10 nm Chromium layer in Fig. 1 has the best mechanical and tribological properties. This multilayer system consists of ten alternating metal and ceramic layers. The chromium layers have a thickness of 10 nm, while the chromium aluminum nitride layers rise from 100 nm to a maximum of 500 nm in 5 nm×100 nm steps.

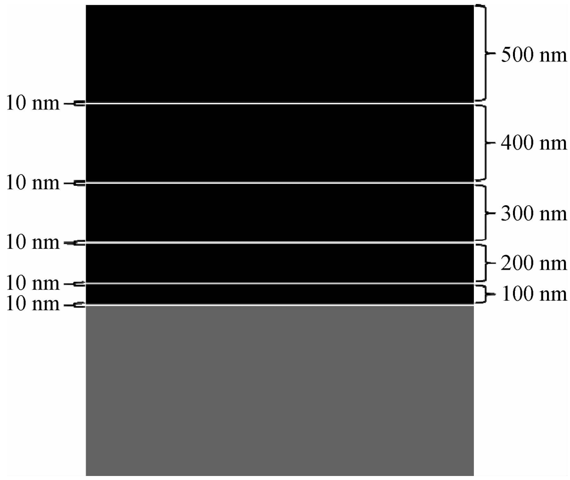

图 1 多层设计的 Cr/CrAlN 系统(陶瓷层-黑色,金属层-白色,钢基体-灰色)

Fig. 1 Multilayer design of the Cr/CrAlN system (ceramic layer - black, metal layer - white, steel substrate - grey)

During the deposition process the specimens rotated in the chamber, which was heated with a constant heating power of 8 kW for all coatings. Depending on the position of the samples in the chamber the process temperature is between 420 ℃ and 450 ℃. Furthermore, the target power of CrAl and Cr were also kept constant. The power of the CrAl and Cr target amounted to 3 kW and 4 kW. Argon and Krypton were used as inert gases and injected into the chamber with continuous gas flows of 250 cm^3/min and 50 cm^3/min. For all experiments the reactive gas nitrogen was used with a gas flow of 240 cm^3/min. In this study, the bias voltage was varied in order to analyze the effects on the mechanical and tribological behavior of this coating system. Four different bias voltages of -75, -100, -125, and -150 V were used for the deposition of the multilayer coating systems.

In addition to the determination of the layer thickness, the topography of the coatings was investigated as well using a scanning electron microscope (FE-JSEM 7001 JEOL, Japan).

In order to obtain more information about the mechanical properties of the coating, nanoindentation experiments (Agilent Technologies, USA) were performed. This device allows the determination of the hardness and the Young's modulus. A maximum depth-controlled penetration into the material of 10%-15% of the coating thickness ensured that the substrate material did not influence the measured values of the coating.

Tribological investigations in the form of ball-on-disk tests were performed by means of a tribometer (CSM, Switzerland). The determination of the friction coefficients was carried out at room temperature with a relative humidity of 30%. The ball used for the tests had a spherical diameter of 6 mm and consisted of cemented carbide (WC-Co). The normal force as well as the linear velocity were kept constant and set to 5 N and 0.4 m/s. No additional lubricants were used, thus ensuring dry conditions. The tangential force was recorded continuously during all tests till the ball-on-disk tests stopped automatically after 15 000 revolutions. Subsequently the wear volume was identified by means of an optical 3-D surface analyzer (Alicona, Austria) in order to calculate the wear coefficients.

X-ray diffraction (XRD) analysis was used to evaluate the crystal phases and residual stresses in the coatings. XRD measurements were performed by means of a four circle diffractometer (Bruker D8, Germany), polycapillary optics in the incident beam and using a wavelength of λ = 1.540 6 Å (Cu-Kα1 radiation).

The residual stresses in the coatings were evaluated by the conventional sin2ψ-method[20] measuring the reflection positions of (111) CrAlN peak in the ψ-mode at various ψ-tilt angles between 0° and ±45°. The positions were analyzed by PEARSON

VII curve fitting method after the correction of Lorentz- and Polarisation factor and substraction of the background intensities and the Kα2-portion, as well. The corrected d-values were plotted against sin2ψ and the stress values were calculated by the slope of the straight line. The error of the stress values is given by the standard deviation from this slope.

Since the X-ray elastic constants (XEC) of physical vapour deposited CrAlN are unknown, approximated values were calculated according to the method developed by Voigt[21] using the specific Young′s modulus (Table 1) of these deposited coatings measured by means of the nanoindenter. The Poisson ratio was constant at 0.22[22].

表 1 不同偏置电压的涂层性质和 X 射线数据

Table 1 Coating properties and X-ray data at different bias voltages

	Structure	Composition			X-ray data	Mechanical properties			Tribological properties	
Bias voltag e/V	Thickness/μm	Cr (w/%)	Al (w/%)	N (w/%)	2θ peak position of CrAlN (111)/(°)	Residual Stresses/GPa	Hardness/GPa	Young′s modulus/GPa	Friction coefficient μ	Wear coefficient k/(10^{-6} μm^3 · Nm^{-1})
-75	$1.52^{+0.10}_{-0.09}$	41.11	28.98	29.92	37.97	0.0±2.7	6.36±1.04	215.2±27.4	$0.78^{+0.00}_{-0.00}$	$2.02^{+0.67}_{-0.90}$
-100	$1.30^{+0.05}_{-0.06}$	21.66	14.32	64.2	37.57	-3.9±1.1	33.76±6.33	431.2±68.0	$0.72^{+0.03}_{-0.02}$	$1.92^{+0.48}_{-0.58}$
-125	$1.28^{+0.02}_{-0.03}$	19.43	12.95	67.63	37.46	-4.9±0.5	45.28±7.35	526.2±84.6	$0.72^{+0.01}_{-0.00}$	$5.53^{+0.74}_{-0.74}$
-150	$1.04^{+0.17}_{-0.12}$	28.35	18.95	52.70	37.60	-5.1±0.4	47.32±5.50	539.7±75.2	$0.71^{+0.01}_{-0.01}$	$5.35^{+1.85}_{-1.08}$

2 Results and Discussion

2.1 Microstructure and morphology

The substrate bias voltage has a strong influence on the microstructure and the morphology of the Cr/CrAlN coatings. In order to correlate these parameters with the phase composition of the coatings, XRD measurements were carried out. The diffraction patterns of the coatings (Fig. 2) show the presence of crystalline CrAlN films with a mixed orientation of the crystal planes (111), (200), (220), (311) and (222) of a rock-salt structure in accordance with the theoretical lattice constant of CrN, a=4.14. Additional reflections of steel substrate were found, but Cr-oxides were not found. The patterns are influenced by variation of the bias voltage. In films grown at a low bias value of -75 V, a significant high intensity of the (111) reflection was found, which is much higher than the theoretical intensity ratio of 0.80 for (111)/(200) indicating a strong preferred {111} orientation. A slightly favored {111} orientation was also found for coatings deposited at higher voltages up to -125 V.

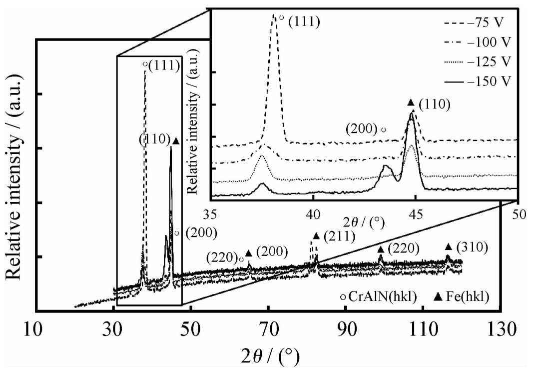

图 2 不同偏置电压沉积 Cr/CrAlN 多层涂层衍射图

Fig. 2 Diffraction patterns of Cr/CrAlN multilayers systems deposited at different bias voltages

In contrast to that, the intensity of (111) reflection decreases at a high bias voltage of -150 V and a small preferentially oriented peak (200) occurred (Fig. 2). The (111) peak position of the coating deposited at −75 V is shifted slightly to a higher value and a asymmetric peak shape with higher intensity at the left background occurred giving hints for a second phase. It is assumed that also a CrAlN solid solution phase with a higher Al content also exists. In contrast the position of the coatings deposited at higher voltages are nearly constant (Table 1) and the (111) peaks are symmetrical. Thus no hints for a further change in the Al concentration are expected.

Fig. 3 demonstrates the coating thickness depending on the bias voltage in the range between −75 V and −150 V. With an increasing voltage the coating thickness decreases from 1.52 μm at −75 V to 1.04 μm at −150 V. This decline is attributed to the growing attraction between the positive ions in the plasma and the substrates, so that more high energetic ions impinge on the substrate surface. Due to this peening effect by the ion bombardment, the surface atoms are re-sputtered and the deposition decrease[23-25].

In order to gain more information about the layer structure, the morphology of the coatings was analyzed.

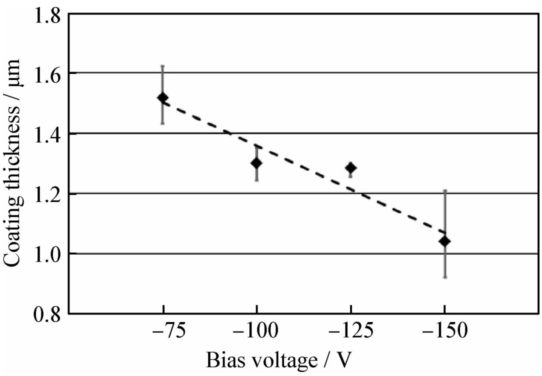

图 3 不同的偏置电压下 Cr/CrAlN 涂层的厚度

Fig. 3 Thickness of Cr/CrAlN coatings at different bias voltages

The different cross-sections of the fractured surfaces at different bias voltages are shown in Fig. 4. Even here the correlation between coating thickness and bias voltage could be also clearly observed. Moreover, it was found that the crystalline structure of the coatings is much denser with increasing bias voltage. The film at −75 V possesses a preferentially oriented columnar microstructure, while the other coating at bias voltages of 100 V and −125 V have grown randomly oriented. At −150 V any kind of columnar formations vanish and a dense coating structure can be observed.

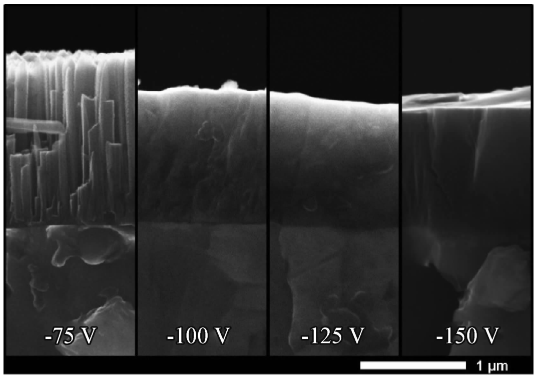

图 4 不同偏置电压下制备的 Cr/CrAlN 涂层的形貌

Fig. 4 Morphologies of Cr/CrAlN deposited at different bias voltages

This phenomenon can also be explained by the increasing ion bombardment with an increasing bias voltage. Furthermore, defects in the layers or in the interfaces between the substrate and the coating could not be detected[23].

2.2 Hardness, Young's modulus and residual stresses

The bias voltage obviously affects the mechanical properties of the coatings. Fig. 5 presents the hardness, Young's modulus and residual stresses of the coatings against the bias voltages at which they were produced. All curve progressions have a clear tendency towards higher values at increasing bias voltages. At −75 V the coating has low hardness and Young's modulus values of 6.4 and 215 GPa, respectively, which increase rapidly to 36.8 and 431 GPa at −100 V and 45.3 and 526 GPa at −125 V, respectively, and reach their respective maxima of 47.3 and 540 GPa at −150 V. The reason for this behavior lies in the structural changes of the coatings due to increasing bias voltage. As already described in the morphology section, the −75 V sample shows a preferentially oriented columnar microstructure. This leads to a high grain size to density ratio, which decreases with increasing bias voltage and results in a fine crystalline and dense structure at −150 V.

These properties are responsible for high hardness values, because, according to the well-known Hall-Petch-relation, smaller grains enforce the effect of dislocation blocking and thereby strengthen the coating[23,26].

Since the investigated PVD-coatings are too thin to absorb the incident X-ray radiation, the reflections with high 2θ angles are too weak for a stress evaluation. Furthermore the Cr-layers are also too thin to provide reflection intensities strong enough for a stress measurements, because the evaluation on the (200) reflection is very complex due to the partial overlapping by the (110) peak. On that account the sin2ψ-method was carried out at the intense (111) CrAlN peak only. For the stress evaluation the XEC were calculated by the experimental analyzed Young's modulus given in Table 1.

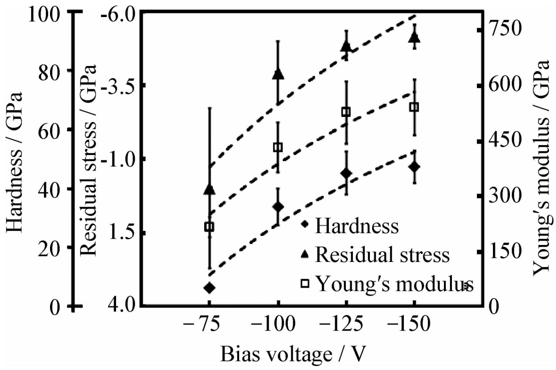

图 5 Cr/CrAlN 涂层对应于偏置电压的硬度,杨氏模量及残余应力

Fig. 5 Hardness, Young's modulus and residual stress of Cr/CrAlN coatings as a function of the substrate bias voltages

Fig. 5 demonstrates that compressive stresses were observed in almost all investigated CrAlN coatings. Only in the coating deposited at -75 V no residual stresses were found. Due to the significant (111) orientation of coatings deposited at -75 V, the peak intensities diminish rapidly with increasing tilt angle and result in a high deviation of the stress value. In contrast to that the preferred (111) orientations diminish with increasing voltage and result in reduced deviations of stress values. At a bias voltage of -150 V, the {111} orientation changed to a {200} orientation. With increasing voltage the failure of the stress evaluation decreases and is attributed to a more homogenous stress state. With increasing bias voltage the morphology and the preferred {111} orientation of the coating changed. At -100 V and -125 V a denser morphology and a preferred {111} orientation was found. The very dense morphology at -150 V (Fig. 4) stress evaluation results in a higher stress value. This effect correlates with the increase of hardness (Fig. 5).

Comparing the thicknesses of the deposited coatings (Fig. 3) with the stress values, a significant correlation is detected. With increasing voltages, the coating thickness decreases and the density rises, which implies that the growth of the compressive stress values arises from the increasing density. The comparison of the stress and the hardness values at the respective bias voltages shows also a good correlation (Fig. 5). With increasing bias voltage the residual stresses follow the curve progression of the hardness and Young's modulus results. Besides the influence of the densification of the coating, changes of the solid solution represent an additional effect on the residual stresses. The peak shift of the (111) reflection to higher 2θ angles was observed in coatings deposited at -75 V which hints at a second crystalline phase, a Al rich CrAlN phase. This effect was also discussed by other authors[27].

As already mentioned, the increasing residual stresses are attributed to the micromorphology. The strong texture observed in the samples deposited at -75 V relieves a sliding of the columnar crystals. Therefore it is assumed, that the significant {111} orientation allows a relaxation mechanism. This phenomenon was also observed by Leonie[28]. In contrast a more statistical deviation of the interplanar lattice spacing in the coatings deposited at higher bias voltages (> -75 V) hinders a relaxation and leads to higher residual stresses.

2.3 Tribological behavior

The friction coefficients of the differently biased Cr/CrAlN coatings are illustrated in Fig. 6. Although all tested samples have the same CrAlN top layer and the coefficients are all in the same range, there is a slight tendency of decreasing values with increasing bias voltage. Starting with a maximum of 0.78 at −75 V, the friction coefficient decreases and ends at a minimum value of 0.71 at −150 V. Furthermore Fig. 6 presents the micrographs of the surfaces related to the respective friction values, which expose that the influence of the bias voltage on the morphology of the samples is also transformed to their topography. Comparing the different surfaces, it can be noted, that only on the surface of the −75 V sample small knolls are formed. These knolls are the hood-shaped endings of the columns, seen in the Fig. 4, which are responsible for this rough structure. According to literature[5,29] the structured surface results in increasing the micro contact surface between the sample and the counterpart during the tribological tests, which rises the tangential force, and hence the friction coefficient. In conjunction with their similar topographies, the other samples, produced at bias voltages between −100 and −150 V, have also similar friction coefficients.

The influence of the surface appearance on the wear behavior is superimposed by other effects. Fig. 7 presents the wear rates of the Cr/CrAlN-coatings, in which the results are divided into two groups. In the first group the −75 V and −100 V samples show low wear rates of 2.0×10^{-6} and 1.9×10^{-6} $\mu m^3/Nm$ while the second group consists of the −125 V and −150 V samples which have much higher wear rates of 5.5×10^{-6} and 5.3×10^{-6} $\mu m^3/Nm$, respectively. The reason for these high wear coefficients are large areas of chipping in the wear tracks, which represent a major portion of the wear volume and affect the wear coefficients drastically. The chippings are caused by a disadvantageous combination of high compressive residual stresses and a big difference between the hardness of the substrate and of the coatings. The ability of a high elastic and plastic deformation of the unhardened substrate limits a good wear performance of the very hard Cr/CrAlN-coatings produced at −125 and −150 V and results in adhesive eggshell-like failure at an early stage[30-31]. In addition to that, compressive residual stresses affect also the wear behavior of the coatings. Although compressive residual stresses may have a beneficial effect on the crack propagation and fatigue of the coated systems[32], high compressive residual stress values result in premature failure of the coating[33] and therefore deteriorate the tribological performance.

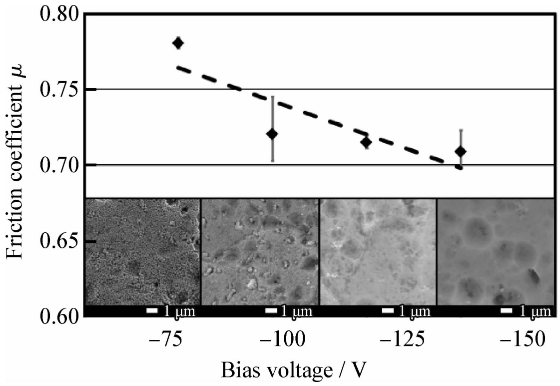

图 6 偏置电压对 Cr/CrAlN 涂层摩擦系数的影响

Fig. 6 Influence of the bias voltages on the friction coefficient of Cr/CrAlN coatings

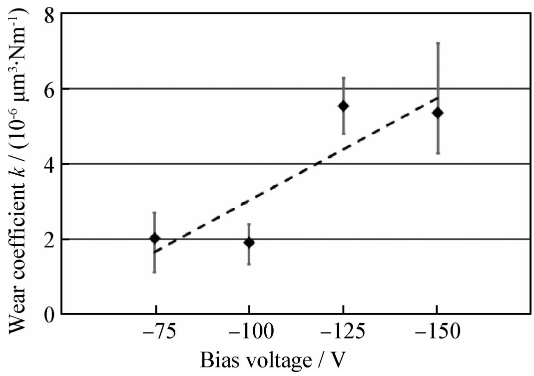

图 7 偏置电压对 Cr/CrAlN 多层涂层磨损因数的影响

Fig. 7 Influence of the bias voltages on the wear coefficient of Cr/CrAlN multilayer systems

Comparing these results with the wear coefficients of the −75 and −100 V samples, it is noticed that the hardness is not the only crucial factor for the wear behavior under these test conditions. Even if the −100 V sample has a high hardness value of over 33 GPa, there is hardly any chipping or buckling seen on the wear tracks. This may mean on the one hand, that this hardness value is not critical to adhesive failure of the coating in the wear track and on the other hand the lower residual stresses of this sample, compared to the −125 and −150 V samples, plays also an important role for the wear behavior. The −75 V sample has the lowest hardness (6.4 GPa) and residual stress (0.0 GPa) by far of all tested samples, has also no chipping in the wear track and achieves nearly the same low wear rate as the −100 V sample. However, this implies that the wear performance of the differently biased Cr/CrAlN-samples can be significantly reduced by adjusting hardness and residual stresses within a range from 6.4 to 33.7 GPa and 0 to −3.9 GPa respectively.

3 Conclusions

In this present work, Cr/CrAlN multilayer systems were deposited on hot working steel substrates by magnetron sputtering with varying bias voltages between −75 and −150 V. The studies showed, that the bias voltage has a strong impact on the structural, mechanical and tribological properties of the coatings. The results of this work are as follows:

(1) Combined with the change of morphology and the decrease of texture the compressive residual stresses increase and become more homogenous with increasing bias voltage.

(2) While the coating thickness decreases with increasing bias voltage their hardness and Young's modulus increase drastically.

(3) The friction coefficient is mainly affected by the topography of the coatings. While a bias voltage of −75 V generates disadvantageous surfaces and increase the friction coefficient, the values between −100 V and −150 V show small improvements.

(4) High hardness values in combination with high compressive stresses found out be detrimental for the wear behavior of the Cr/CrAlN coatings, while lower hardness and stress values promote low wear rate.

Further investigations will focus on the determination and separation of the intrinsic and thermal residual stress portions, since the increased stress states are attributed to a change of the ratio intrinsic/thermal residual stresses inside the coatings. Therefore the correlation of thermal and intrinsic stresses, hardness and wear will be investigated at elevated temperatures, to improve the coating process parameters for hard Cr/CrAlN multilayer coatings.

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