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Low friction CrN/TiN multilayer coatings prepared by a hybrid high power impulse magnetron sputtering/DC magnetron sputtering deposition technique

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ABSTRACT

High power impulse magnetron sputtering (HIPIMS) has gained increasing scientific and industrial attention as it allows high plasma densities without the drawback of droplet formation. Recently, we showed that by a combination of HIPIMS with dc magnetron sputtering the properties of the coatings are comparable to those prepared solely with HIPIMS, but with the advantage of increased deposition rate.

Here, we show that for CrN_{HIPIMS}/TiN_{DCMS} multilayered coatings the friction coefficient μ decreases from 0.7 to 0.35 (with an almost constant hardness H around 25 GPa, and modulus of indentation around 375 GPa) when decreasing the bilayer period λ from 7.8 to 6.4 nm, while keeping the CrN_{HIPIMS} layer thickness constant at 3.2 nm. A further reduction of the friction coefficient at room temperature dry-sliding testing to ~0.25 or 0.05 is obtained when an additional HIPIMS cathode equipped with a Cr or Ti target material, respectively, is added to the process. Contact angle measurements of distilled water drops on as deposited film surfaces were carried out to investigate their wettability. The measurements show, that with increasing contact angle from 70° to 90°, for the individual coatings prepared, also their friction coefficient increases from ~0.05 to ~0.8. The depositions of all coatings were achieved with two- and threefold substrate rotation, which meet the industrial requirements of uniform deposition on complex shaped specimens.

1. Introduction

Chromium and titanium nitride (CrN and TiN) thin films are well known for their excellent properties like high hardness and good wear resistance. Therefore, great attention has been paid on the interrelation between their microstructure, morphology and resulting mechanical properties [1–4]. In general, the coating's microstructure and morphology can be improved by applying substrate temperatures as high as 700 °C. The drawback by using high temperatures during deposition is the limited number of suitable substrate materials, which need to be thermally stable in the used temperature range. Reports for TiN films show that with increased bias voltage the energy of the ions, impinging at the substrate and growing film, increases and causes a densification and often a preferred (111) orientation [5]. The thereby obtained densification is generally connected with high defect densities and high residual stresses [5,6]. Detailed studies on TiN microstructure evolution during film growth yield optimized properties when using an ion bombardment of the growing film with a high ion/neutral ratio and low energy [7,8]. DC unbalanced magnetron sputtering (DCMS), which is a well established physical vapor deposition (PVD) technique, is generally characterized by a low ionization degree of sputtered species. This often results in formation of porous and underdense films with a high defect density if the deposition temperature is below 0.2–0.3 of the melting point of the films [8–13]. High power impulse magnetron sputtering (HIPIMS) allows a much higher ion to neutral ratio of the sputtered species due to the high power dissipation at the target. Ionization rates above 40%, where also multiple ionized sputtered species can occur, are reported for various target materials [14–16]. Due to the ability of implanting metal species into surface near substrate regions by applying a high bias voltage during HIPIMS etching, the adhesion between coating and substrate can be optimized. Compared to a corresponding cathodic arc pre-treatment, the HIPIMS pre-treatment has the advantage of an essentially zero-droplet-rate and therefore an even further improved adhesion [16–18].

Furthermore, the high metal-ion and plasma density of the HIPIMS process is extremely beneficial for the coating morphology and structure itself. Recently, we showed that CrN and TiN coatings prepared by HIPIMS have a much higher density than their corresponding DCMS counterparts [19]. Consequently, also the mechanical and tribological properties are increased for HIPIMS coatings compared to DCMS coatings. By a controlled combination of HIPIMS cathodes with DCMS cathodes the advantage of both processes can be combined, resulting in e.g., depositions with dense coating microstructure and high growth rates [20].

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Here we show that for CrN_{HIPIMS}/TiN_{DCMS} multilayered coatings the friction coefficient decreases from 0.7 to 0.35 when decreasing the bilayer period λ from 7.8 to 6.4 nm, while keeping the CrN_{HIPIMS} layer thickness constant at 3.2 nm. A further reduction of the friction coefficient to ~0.25 or 0.05 at room temperature (RT) dry-sliding testing is obtained when an additional HIPIMS cathode equipped with a Cr or Ti target material, respectively, is added to the process. These results were achieved with two- and threefold substrate rotation.

2. Experimental details

The depositions were performed in a Z700HPM PVD coating plant, manufactured by Systec SVS Vacuum Coating Technology Karlstadt, Germany. The substrates, steel disks and Si (001) strips, are mounted on substrate holders which allow planetary rotation and face the targets at a minimum distance of 8 cm. All depositions are performed in a mixed $Ar+N_2$ glow discharge with additional heating which results in a substrate temperature of approximately 400 °C. Four different CrN/TiN multilayer coatings have been developed by varying the power at the DCMS Ti cathode between 4 and 7 kW while the HIPIMS Cr cathode was fed with 5.5 kW, using a one-fold substrate rotation between these two facing cathodes. Two further variations are obtained by introducing a third cathode operating in HIPIMS mode, either equipped with a Cr or Ti target, using two- and threefold substrate rotation. For convenience and easier identification these multilayer coatings are abbreviated with CrN/TiN/CrN and CrN/TiN/TiN, respectively. The deposition time was adjusted to achieve a film thickness of approximately 2 µm. More details on the deposition parameters as well as deposition arrangement used are reported in [19,21].

Prior to all depositions, the substrates are thermally cleaned within the vacuum chamber at a base pressure below 1 mPa [22], and both targets are sputter-cleaned with Ar ions. The substrates are ion etched in an Ar atmosphere using the Cr target in HIPIMS mode and applying a substrate bias potential of −1000 V. To avoid cross-contaminations during this process, a constant sputtering potential of 180 V is applied to the Cr facing Ti target.

Fracture cross-section scanning electron microscopy (SEM) investigations of coated Si (001) substrates were conducted in a Zeiss EVO 50 microscope using an operating voltage of 20 kV. Detailed studies on morphology and film structure are evaluated using a Phillips CM 12 transmission electron microscope (TEM) using an operating voltage of 120 kV. Structure and phase analyses of coated steel substrates are conducted by X-ray diffraction (XRD) in the Bragg–Brentano mode using a Siemens D500 equipped with a CuKα radiation source. Hardness (H) and modulus of indentation (E) of our coatings (evaluated on steel substrates) are obtained by nanoindentation with a Berkovich indenter using an ultra micro indentation system. The maximum loads are ranging from 10 to 35 mN to keep the indentation depth below 10% of the film thickness. The values for H and E were obtained from analyzing the loading and unloading segments of the indentation curves after the Oliver–Pharr method [23]. The time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed on a TOF-SIMS V instrument from IONTOF GmbH Muenster, Germany. The mass spectra were recorded by detection of positive secondary ions, generated by sample surface bombardment with 25 keV Bi^+ ions in high current bunched mode. Depth profiles were acquired by sequential sputtering with 2 keV O_2^+ ions in interlaced mode. In order to avoid crater edge effects, the Bi^+ and O_2^+ ion beams were scanned over 500 µm × 500 µm and 900 µm × 900 µm, respectively.

Dry-sliding tribological investigations are conducted at RT using a CSM ball on disk (BOD) tribometer equipped with an alumina ball (diameter of 6 mm) as counterpart. A normal load of 1 N and sliding distances from 500 to 3500 m were used. Experiments are performed in ambient atmosphere (relative humidity ~25%), dry nitrogen, argon and synthetic air atmospheres (relative humidity ~1%), and in distilled water. The relative humidity was measured by a Testo 608-H_2 hygrometer with an absolute error of 2% [24]. The sliding wear coefficients, of our multilayered coatings, are calculated after evaluating the wear track with a Wyko NT1000 optical profilometer.

3. Results and discussion

Fig. 1 shows the intensity for Fe, Mn, Cr, and Ti species versus the implantation depth of HIPIMS ion etched steel samples (see Experimental details section), without depositing the CrN/TiN multilayer films, obtained by ToF-SIMS measurements. The Cr HIPIMS etching of the steel substrates at −1000 V substrate bias resulted in an increased adhesion of our multilayer coatings, yielding a HF 1 value according to Rockwell adhesion testing [25]. The approximately 20 nm extension of the Cr signal within the region of Fe indicates that Cr was incorporated into the substrate, likely originating from implantation and surface near diffusion during the etching process. Cr incorporation in stainless steel substrates by HIPIMS etching at −1200 V substrate bias has already been reported by Ehiasarian et al. [10], who found an incorporation depth of approx. 40 nm by scanning transmission electron microscopy-energy dispersive spectroscopy analysis. Schönjahn et al. observed deposition of a 10 nm thick Cr coating at −600 V substrate bias in a cathodic arc plasma, however at −1200 V their XTEM-EDS profiles suggest selective Cr incorporation within a depth of approx. 10 nm [17]. With respect to the thickness of the Cr layer and the depth of the Cr incorporation zone it has to be stated that our values represent estimations based on comparison of the total O_2^+ sputter time with the depth of the sputter-craters as determined by white-light profilometry (Wyko NT1000 optical profilometer, see Experimental details section). Such a one-to-one conversion of sputter time and erosion depth can lead to significant deviations in thickness/depth for materials with differing erosion rates. The evaluation of the implantation depth was determined by appointing the bulk surface, which is the position of unchanging Mn and Fe content, and the maximum implantation depth, which is indicated by an unchanging Cr and Ti content, which corresponds to the bulk content. The profile also reveals a Cr and Ti film deposition of around 20 nm during the etching process. It is expected that this deposited layer is thinner when immediately after the etching process the deposition of the nitride layers start. The plot would also suggest diffusion of Fe and Mn into the Cr and Ti layer, but this effect is an artifact and mainly due to the high surface roughness of the HIPIMS etched steel substrate (R_a around 25 nm).

With decreasing the DCMS power at the Ti cathode from 7 to 4 kW at constant HIPIMS power of 5.5 kW at the Cr cathode the bilayer period λ decreases from 7.8 to 6.4 nm with a constant CrN layer thickness of 3.4 nm. These values are obtained after a simple estimation from the

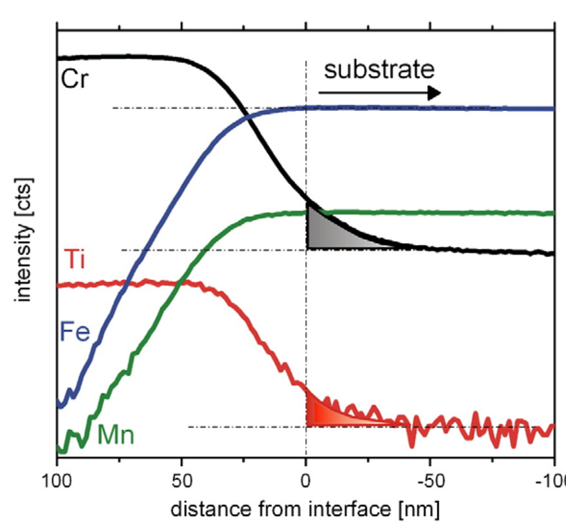

Fig. 1. SIMS analyses of the steel substrate surface near region after Cr HIPIMS etching.