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High-power Impulse Magnetron Sputtering, HiPIMS

Plasma Electrolysis and Dishcarge Deposition (Technology)

Plasma diagnostics in HiPIMS

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Abstract: In high power impulse magnetron sputtering (HiPIMS), very high instantaneous power densities to the magnetron are used, which result in a dramatic increase of charge carriers in front of the target during the discharge pulse. For the HiPIMS discharge the electron density in the ionization region close to the target surface is on the order of 1018-1019 m^3[1,2]. For an electron density around 1019 m^{-3} the ionization mean free path of a sputtered metal atom is about 1 cm, while for an electron density of 1017 m^{-3}, commonly observed in a direct current magnetron sputtering (DCMS) discharge, the ionization mean free path is approximately 50 cm for typical discharge conditions[3]. Thus, given the high electron density in the HiPIMS discharge a significant fraction of the sputtered material is thereby ionized, which also has been verified in a great number of publications[4-7].

An important parameter to understand is the ratio of ion to neutral deposition rates which gives insight into the ionized flux fraction. A retarding field analyzer with integrate quartz crystal microbalance design will be presented. This device can be configured to turn on and off the flow of ions to the crystal, thus enabling a measurment of the deposition rate due to ions compared to that due to neutral species. Sample data from various process applications will be presented along with comparisons against other diagnostic techniques.

Also, some results of a deposition tolerant Langmuir probe will also be presented. This probe continues to work when insulating layers are deposited on it. The probe can be synchronised with the HIPIMS pulse to time resolve the data capture through the pulse period. Results from a HIPIMS application will also be presented.

Keywords: HiPIMS, magnetron

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Effects of HiPIMS pulse-length on plasma discharge and on the properties of WC-DLC coatings

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Abstract: Protective coatings are often deposited on the rotating parts and friction pairs to improve their performances and erosive wear resistance during the operation of equipment under poor conditions, such as heavy load, high speed, high temperature. And WC-DLC nanocomposite coatings deposited via reactive magnetron sputtering featuring high hardness, low friction coefficient and high chemical inertness are highly preferred and widely applied in solid lubrication, corrosion resistance and erosive resistance of automobile, textile machinery and aircraft industry. However, in conventional reactive magnetron sputtering, target poisoning frequently leads to an instability that requires the reactive gas flow rate to be actively regulated to maintain a constant composition of the deposited coatings. As a newly developed sputtering technology, high power impulse magnetron sputtering (HiPIMS) is quite advantageous in terms of the deposition of many coatings. However, HiPIMS is a transient pulse discharge, many researches have evinced that during the discharge process the constituent particles (neutral atoms, electrons and ions) can be influenced by its parameters such as pulsed voltage, current, discharge gas pressure and so on. Although, to a certain extent it provides an opportunity to control element composition and mechanical properties of coatings by varying the sputtering parameters. The transient discharge process of HiPIMS can also cause the uncertainty of coatings' structure. So in order to better apply the HiPIMS technology, it is of vital importance to investigate the interrelationship between the discharge parameters and the microstructure and properties of deposited coatings.

In this regard, this article presents a systematic and comprehensive investigation of the influences of pulse length upon plasma discharge characteristic, target poisoning in the reactive HiPIMS process, and upon the chemical composition, microstructure, mechanical and tribological properties of the deposited WC-DLC coatings. While conducting the experiment, WC-DLC coatings were deposited using HiPIMS with the pulse length varying from 50 μs to 200 μs at constant frequency. The discharge current recorded by an oscilloscope (OSC) showed a significant drop at short pulses but a slow descent at long pulses during the deposition process. The optical emission peak intensity of W (target material) monitored by optical emission spectroscopy (OES) displays the same tendency. The deposition rate and cross-sectional morphology of WC-DLC coatings were investigated by scanning electron microscope (SEM). Surface morphology and roughness were detected by atomic force microscopy (AFM). The chemical composition, crystal structure and carbon phase were analyzed by means of energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy respectively. The glow discharge optical emission spectroscopy (GDOES) was used to demonstrate the depth profiles of the WC-DLC coatings. The results verify that the coatings deposited with different depths at longer pulse length exhibit better elemental concentration uniformity. The hardness obtained by nano-indentation tester also shows significant changes from 35 GPa at 200 μs to 18 GPa at 50 μs pulse length of the deposited coatings. The friction coefficients and wear rates of WC-DLC coatings measured by ball-on-disk test and laser scanning confocal microscope (LSCM) show a strong dependency upon the amorphous carbon composition of regions close to surface, which is influenced by the pulse length of HiPIMS.

Keywords: WC-DLC coatings, HiPIMS, target poisoning, microstructure, mechanical and tribological performances

High power impulse magnetron sputtering based on novel waveform configuration

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Abstract: High power impulse magnetron sputtering (HiPIMS) has attracted much interest in academic institutes and industries due to its many advantages including higher plasma density, capability for conformal deposition, denser film structure and better surface properties. However, lower deposition rate has limited its wide application in PVD fields since HiPIMS is featured by higher current and higher voltage. A power supply with two-step voltage waveform has been developed in which two voltage pulses are produced. The higher and shorter pulse (booster voltage) is utilized to ionize gas and achieve original plasma with higher density, then followed by the lower and longer pulse to maintain discharge with relatively larger current compared to conventional DC magnetron configuration even with the same target voltage. Consequently, high density plasma is gained using a lower average power. The power supply runs on Cr target. With square voltage waveform (conventional pulsed DC or HiPIMS), the discharge current rises slowly with a triangle or parabolic shape. If a booster voltage is utilized in the pulse voltage, a current peak rapidly appears and even a square current waveform is achieved. The averagely larger current is maintained even with a lower pulse voltage. This may lead to a lower voltage HiPIMS in which higher plasma and higher deposition rate may be speculated.

Keywords: HiPIMS, novel waveform configuration

Discharge characteristics of superimposed HiPIMS-MF and properties of as-prepared nitride nanocomposite coatings

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Abstract: The low deposition rate of the high power impulse magnetron sputtering somewhat limits its commercial applications in thin film and coating industries. In this work, different ways to improve the deposition rate of HiPIMS TiN film was discussed. Superimposition of HiPIMS and MF fabricated TiN films with relatively smooth surface. All samples were found to have a single phase TiN according to the chemical composition and crystallographic analyses. The highest film hardness of about 31 GPa, elastic modulus of 313 GPa, and a density of 5.35 g/cm^3 were obtained in the sample grown at a MF pulse duration of 150 μs in each superimposed cycle. The higher the deposition rate was achieved with longer MF pulse duration. This superimposition technique successfully improved the power- normalized deposition rate from 4.5 to 17.2 nm/kW·min without significantly declining the mechanical properties and adhesion quality of deposited films. The role of MF pulse duration and average MF power were further studied in this work. It can be concluded that the MF pulse duration played a more significant role and showed a dominant influence on the plasma characteristics and resulting properties of deposited TiN films. Another effective way to improve deposition rate of HiPIMS TiN is by combining HiPIMS and conventional magnetron sputtering deposition. The related study is undergoing.

Keywords: thin film, high power impulse magnetron sputtering, coating

Gas breakdown and discharge formation in high power impulse magnetron sputtering

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Abstract: Discharge behaviors of high power impulse magnetron sputtering with different targets were investigated. Distinct current-voltage curves and target current waveforms were observed. Breakdown voltage and maximum target current showed periodic dips with the increase in subgroup or period numbers. The target current density was found to be mainly affected by the secondary electron emission yield. Thus its magnitude couldn't directly reflect the ionization degree in sputtering process. The interactive influence of secondary electron emission, sputtering yield, and ionization energy on the ionization degree of sputtered materials was discussed through an analytical current model. According to the ionization degree, targets could be categorized into four sorts: 1) low ionization degree targets, such as Ag and C less than 10%; 2) intermediate ionization degree targets like Cr and Cu with 55% and 35%; 3) high ionization degree targets, such as Al and W with 86% to 80%; 4) Ti, Zr, Mo targets with second ionization processes. These results could provide institutive operation ranges for state of the art sputtering applications.

Keywords: high power impulse magnetron sputtering, gas breakdown, current waveform, ionization degree

Mass spectrometry diagnostics of the ion energy and ion flux during bipolar pulsed high power impulse magnetron sputtering of titanium nitride

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Abstract: Mass spectroscopy was used to analyze the energy and composition of the ion flux during bipolar pulsed high power pulsed magnetron sputtering (HiPIMS) of a Ti target. In the bipolar pulsed HiPIMS mode, the positive pulses with different voltage are immediately applied after the initial negative pulse to drive all ions to the substrate and make the ions energetic. The ion energy distribution functions were recorded in the time-averaged and time-resolved mode for Ar^+ , Ar^{2+}, Ti^+ , Ti^{2+}, N_2^+ and N^+ ions with different positive voltage. The effect of positive voltage on deposition rate, microstructure, cross-sectional morphology and residual stress of the titanium nitride (TiN) coatings were studied. The average energy of all ions was improved with the increase of positive voltage. The low energy ion flux of all ions was decreased and the high energy ion flux of all ions was increased with the increase of positive voltage. The total ion flux of the Ar^+ was dramatically decreased and the total ion flux of the Ti^+ was remarkably increased with the increase of positive voltage. The procedure was simulated by a PIC-Monte Carlo method and the experimental result is in good agreement with the simulation. The coating's columnar crystals structure was restrained with the increase of positive voltage. The residual stresses of coatings were increased from –2.08 GPa to –4.66 GPa.

Keywords: bipolar pulsed, HiPIMS, positive voltage, mass spectrometry diagnostics, TiN coatings, PIC-Monte Carlo

Hipims industrialization under high ionization applications

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Abstract: With the continuous developing of industrial upgrades, the advantages of Hipims power supplies in plasma surface treatment processes are gradually reflected. However, in practical applications, Hipims power supplies usually do not exist in isolation. How to deal with Hipims and other power supply problems in one system is a key issue for actual production.

Keywords: Hipims industrialization, high ionization applications

Study on the thermal stability of the Zr-B-O-N coatings fabricated by hybrid coating system

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Abstract: Preoxidation is an effective method to improve the heat resistance of the coatings. It was expected that doping oxygen into the Zr-B-N coating can improve the thermal stability and antioxidant capacity of the resulted coatings. In this work, a series of Zr-B-O-N coatings with different oxygen content were deposited on 304 stainless steel, super alloy GH4169, and single-crystal silicon wafers by combining high power impulse and pulsed DC co-sputtering techniques. Then, the coatings were heated isothermally 3 hours in air at 500, 600, 700, 800 ℃, respectively. The influence of heat treatment temperature on the microstructure and mechanical properties of the Zr-B-O-N coatings were investigated systematically. The chemical composition, microstructure, and phase constituents of the resulted coatings were observed and analyzed using electron probe microanalysis, scanning electron microscope (SEM) and X-ray diffraction (XRD); The hardness and residual stress of the coatings were tested by 402MVD Wilson type micro-hardness tester and FST150 film stress tester. The results indicate that the hardness of the Zr-B-O-N coatings was greatly improved after heat treatment, and decreased slightly with increasing heat treatment temperature in the range of 500-700 ℃, but the coating hardness increased again after heat treatment at 800 ℃. In the meanwhile, the internal stress increased gradually and adhesion between the coating and substrate became more and more inferior. As the heat treatment temperature is 500 ℃, the Zr-B-O-N coating with low oxygen possessed the highest hardness about 1840.5 HV. But the coating with high oxygen presented the better oxidation resistance, the microstructure was uniform and dense, and well adhered to the substrate. With increasing the heat treatment temperature, the preferred orientation of coating growth changed gradually and more ZrO_2 phases were formed in the coatings. As the heat treatment temperature reached 800 ℃, the cracks began to appear on the coating surface. With crack propagation, part of the coating peeled off and caused serious failure.

Keywords: HiPIMS, Zr-B-O-N coating, thermal stability, hardness, internal stress

Discharge and deposition of HiPIMS based on cylindrical-shape cathode

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Abstract: High-power impulse magnetron sputtering (HiPIMS) has been widely studied because of its high ionization, large coating density and good adhesion. However, the obvious disadvantages such as low deposition rate, unstable discharge, and different ionization rates for different materials hamper its industrial applications. To circumvent them, an optimized cylindrical-shape cathode has been developed and the special cathode shape introduces the hollow-cathodic effect which greatly enhances the discharge. By a modified time dependent global model and diffusion model, the plasma characteristics and transportation are studied. The discharge order and the diffusion routes of the different particles in the plasma are firstly observed by a homemade time-resolved optical emission and mass spectrometer with the resolution of 10 ns. The further simulation studies reveal the critical role of the ionization energy and ion mass to the plasma characteristics. At last, a nearly pure ion deposition is realized by Cr HiPIMS discharge in cylindrical-shape cathode in the Ar/N_2 atmosphere. Interestingly, high density nano-twins are discovered in the Cr_xN coatings, first observation in the ceramic materials, which increases the hardness to more than 35 GPa.

Keywords: cylindrical-shape cathode, HiPIMS, hollow-cathodic effect, plasma characteristic, nano-twins

Semi-condutivity ZnO film prepared by HiPIMS

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Abstract: In this report, the preparation the semi-conductuivity ZnO film is grown by reactive high power impulse magnetron sputtering (HiPIMS). We use sputtered metallic zinc (Zn) target reacting input oxygen for n-type ZnO depostion. When nitrogen is simultaneously flown into the chamber, the p-type ZnO is grown. In order to improve the reactive activity of nitrogen an inductively coupled plasma (ICP) is added in the HiPIMS. It is obtained the crystal ZnO grows in orientation with a high quality. The temporal resolution optical emission spectroscopy (OES) diagnosis is then employed to reveal the relationship of oxygen and nitrogen partial pressures with the ZnO structure and properties. It is found that at the ratio of O_2/Ar = 5/80 sccm, the small oxygen partial pressure, the line of atomic O I appears later than that of Ar II line; while at the ratio of O_2/Ar = 14/80 sccm, the large oxygen partial pressure, the line of atomic O I appears earlier than that of Ar II line, and the intensity of Zn II is increased. We then think the oxygen partial pressure can lead to Penning discharge in HiPIMS improving Zn species ionization. As a result, the mono-crystal ZnO can be grown, and the deposition rate is promoted.

Keywords: HiPIMS, semi-conductuivity, ZnO, OES

Industrial use of HiPIMS with voltage reversal: high deposition rate of metal nitrides

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Abstract: Recently, it has been demonstrated for highly ionized discharges that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse gives rise to the generation of high fluxes of energetic ions. This effect allowed unprecedented benefits for the coating industry, where the key factor is the ability to tailor both the energy and flux of the high fraction of ionized material present in a HiPIMS discharge by controlling the amplitude of the positive voltage overshoot.

A description of this technology as well as different experimental results obtained in different industrial coating machines showing its benefits will be presented in this paper, such as:

1) Up to 30% deposition rate increase in hard metal nitrides such as TiN, ZrN or CrN. This result improves the productivity of industrial HiPIMS batch coating machines for applications such as cutting tools, molds, dies as well as metallization of decorative parts.

2) Ion-assisted deposition of films on glass substrates, such as aluminum metallizing with extraordinary reflectivity or hard DLC or oxide layers with enhanced mechanical properties. Hardness up to 22 GPa can be achieved for DLC layers on glass.

Low temperature deposition of hard coatings in temperature sensitive substrates, such as plastics for decorative applications or tempered steels for tribological applications such as the coating of bearings.

Keywords: HiPIMS, energetic ions

Composition depended ion extraction characteristics of cylindricalshape cathode assisted by the electromagnetic attractor

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Abstract: Cylindrical-shape cathode has been developed to circumvent the disadvantages of the high-power impulse magnetron sputtering (HiPIMS), such as unstable discharge and various ionizations for different target materials. To attract out the ions effectively from the cylindrical-shape cathode and improve the deposition rate, an electromagnetic attractor is developed and the ion extraction characteristics are studied by particle-in-cell/Monte Carlo collision (PIC/MCC) method and plasma diagnostics. The ion extraction routes and the distributions of N^+, Ar^+ and Cr^+ in the deposition space are revealed by the simulation, which shows a uniformly feature in the range of -5 cm to 5 cm with the symmetry axis as 0. With the increase of the ion mass and ion energy, the ion routes and the largest density centralize to the symmetry axis, in detail, the extraction position of Cr^+ is closest to the symmetry axis, while that of N^+ is the farthest. Ion spectrum measured by time-resolved spectrometer at different radial locations is in good agreement with the simulation. This special phenomenon suggests a good controllable in the deposition coating composition and structure by coating position selection and parameter applications.

Keywords: cylindrical-shape cathode, ion extraction, simulation, plasma diagnostics

Semi-condutivity ZnO film prepared by HiPIMS

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Abstract: In this report, the preparation the semi-conductuivity ZnO film is grown by reactive high power impulse magnetron sputtering (HiPIMS). We use sputtered metallic zinc (Zn) target reacting input oxygen for n-type ZnO depostion. When nitrogen is simultaneously flown into the chamber, the p-type ZnO is grown. In order to improve the reactive activity of nitrogen an inductively coupled plasma (ICP) is added in the HiPIMS. It is obtained the crystal ZnO grows in orientation with a high quality. The temporal resolution optical emission spectroscopy (OES) diagnosis is then employed to reveal the relationship of oxygen and nitrogen partial pressures with the ZnO structure and properties. It is found that at the ratio of O_2/Ar = 5/80 sccm, the small oxygen partial pressure, the line of atomic O I appears later than that of Ar II line; while at the ratio of O_2/Ar = 14/80 sccm, the large oxygen partial pressure, the line of atomic O I appears earlier than that of Ar II line, and the intensity of Zn II is increased. We then think the oxygen partial pressure can lead to Penning discharge in HiPIMS improving Zn species ionization. As a result, the mono-crystal ZnO can be grown, and the deposition rate is promoted.

Keywords: HiPIMS, semi-conductuivity, ZnO, OES

The construction of aminated diamond-like carbon coating onto polyetheretherketone with better osseointegration

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Abstract: As a new kind of bone implant materials, polyetheretherketone (PEEK) is outstanding for the mechanical properties, especially for that its elastic modulus is close to natural bones. Nonetheless, pristine PEEK still suffers from insufficient osseointegration due to the intrinsic bio-inertness, it should be further improved for better in vivo performances. In this study, gas plasma immersion ion implantation (PIII) is proposed to modify biomedical PEEK samples with better osteogenic capability. A dual process containing diamond-like carbon coating and amination treatment is involved. At first, C_2H_2/Ar PIII is employed to fabricate diamond-like carbon (DLC) coating. Guaranteed by the synergistic effect of plasma deposition and ion implantation, the integration of DLC coating and PEEK is very well. The micro scratch test shows that DLC coating cannot be detached from polymeric substrates even when the loading force is as high as 100 N. In the next step, NH_3 PIII is conducted to modify the DLC coating on samples with some N-containing functional groups. The characterizations by X-ray photoelectron spectroscopy and water contact angles measurements indicate that the N content on DLC coating after NH_3 PIII treatment is as high as 17%, and the N-containing functional groups also contribute to the better hydrophilicity. Various in vivo assays demonstrate that the PEEK samples with DLC coating and N containing functional groups are much better than the pristine PEEK for the adhesion, proliferation and osteogenic differentiation of mesenchymal stem cells. Further animal experiments reveal that the in vivo osseointegration of PEEK samples is significantly improved after functionalizations. It is our belief that the PEEK samples processed by dual PIII treatments combine the advantages of DLC coating, N-containing functional groups and polymeric substrates, which is more suitable for bone or joint replacements.

Keywords: polyetheretherketone, surface functionalization, diamond-like carbon coating, amination, osseointegration

Oxidation behaviour of chromium-aluminium-nitride coatings deposited by HiPIMS

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Abstract: In physical vapour deposition (PVD) addition of aluminium to chromium nitride (CrN), resulting in chromium aluminium nitride (CrAlN) coatings enhances oxidation resistance. This phenomenon is well-known from the system titanium nitride (TiN) and titanium aluminium nitride (TiAlN). Besides arc evaporation and different variants of magnetron sputtering High Power Impulse magnetron Sputtering (HiPIMS) is a new method to enhance the coating properties towards higher density and smoother surface quality.

For our experiments we used a semi-industrial PVD unit (Pro China Ltd.) equipped with Hüttinger magnetron sputtering sources: Two bipolar power supplies (TruPlasma 4020), a high pulse power supply (TruPlasma 4002 G2) and a dc bias supply (TruPlasma Bias 3018). Substrates of high speed steel and a stainless steel were deposited with CrAlN coatings at 400 ℃ with an interlayer of CrAl. For comparison we also produced CrN coatings with an Cr interlayer. The as-deposited coatings were characterized by scanning electron microscopy (SEM), scratch test, Vickers hardness and X-ray diffraction (XRD).

Oxidation experiments took place in an argon-oxygen atmosphere between 800 and 1000 ℃. Temperature rise was kept at 5 K/min and holding time was 2 hours. Afterwards weight difference measurements and again XRD and SEM examinations were used to characterize the samples. In addition to the oxidation experiments also a vacuum heat treatment at a pressure of 7×10^{-2} Pa was performed. For comparison reasons the temperature regime was the same as for the oxidation experiments (5 K/min, 2 h). It could be shown that oxidation of the CrAlN coatings start at higher temperatures compared to the CrN coatings. The oxygen intake results in significant aluminum diffusion towards the surface and the formation of an aluminium-rich oxide layer. As both types of coatings show a dense and smooth surface significant oxidation occurs at higher temperatures known from such coatings produced by arc evaporation.

Keywords: CrN, CrAlN, magnetron sputtering, HiPIMS, oxidation resistance, vacuum heat treatment

Influence of Si content on structure and mechanical properties of TiAlSiN coatings deposited by HiPIMS

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Abstract: TiAlSiN have attracted many researchers' interests because of their unique properties including higher hardness, higher adhesion strength, lower friction and better high temperature oxidation resistance. It is now widely accepted that TiAlSiN nanocomposite coatings are composed of crystalline TiAlN (c-TiAlN) phase and amorphous Si_3N_4 (aSi_3N_4) phase, and the c-TiAlN is likely to be surrounded by the a-Si_3N_4. This unique structure has a significant effect on their desirable mechanical and thermal properties. There is an important relationship between the volume fraction of a-Si_3N_4 and the Si content. Therefore, the microstructure evolution, mechanical and thermal properties of TiAlSiN films are sensitive to the silicon content in film. In order to obtain the TiAlSiN coatings with excellent performance, it is imperative that a deposition technique is capable of controlling the coating growth process and subsequently controlling their microstructure. Although direct current magnetron sputtering (DCMS) is widely used for TiAlSiN coatings deposition, the main drawback of DCMS is its limited the quite low ionization degree of plasma particle.

High power impulse magnetron sputtering (HiPIMS) is a promising technique for improving magnetron sputtering today being used in many industrial processes for thin film deposition. It has received extensive interest from researchers because of its high level ionization degree of sputtered target material. For HiPIMS technique, low duty and frequency power applied to the target in pulse can lead to pulse target power densities of only several kW/cm^2. That unique design not only makes it possible to deposit coatings with increased density, reduced roughness, and improved crystallinity, but also enables more direct control over the deposition process.

In this work, TiAlSiN nanocomposite coatings were deposited onto cemented carbide (WC-10wt%Co) substrates by high power impulse magnetron sputtering (HiPIMS). The effect of Si content on plasma discharge characterization of HiPIMS, element concentration, deposition rates, microstructure, surface/cross-sectional morphology, hardness, adhesion strength and tribological properties of coatings were studied. The element content, cross-sectional morphology and thickness of the TiAlSiN coatings were measured by energy dispersive spectroscopy (EDS) and scanning electron microscope (SEM). The crystalline structure and the preferred orientation of the TiAlSiN coatings were obtained by XRD. The hardness and Young's modulus of the TiAlSiN coatings were obtained by nanoindentation. The adhesion strength was evaluated qualitatively by Rockwell indentation test. The tribological performance of coatings was evaluated by a HT-600 ball-on-disk tribometer. GCr15 bearing steel balls (6 mm diameter) were used as the counterparts. The wear tracks were investigated by a laser confocal scanning microscope. Depth profiles across the width of the track, perpendicular to the sliding direction, were also calculated.

Keywords: TiAlSiN, HiPIMS, Si content, microstructure, mechanical properties

Effect of substrate bias on microstructure and mechanical properties of Tungsten carbide coatings deposited by HiPIMS

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Abstract: The hardness and friction coefficient of the molding tools are the two key factors in influencing their performance during the cutting process. In this regard deposited by physical vapor deposition (PVD), Tungsten carbide (WC) nanocomposite hard coatings featuring high hardness and low friction coefficient are highly preferred to be used as protective coatings. As a newly developed PVD technology, high power impulse magnetron sputtering (HiPIMS) is quite advantageous in terms of the deposition of hard coatings. Substrate bias voltage exerts signicant influences on the discharge characteristic of HiPIMS, plasma energy, chemical composition and the microstructure of the deposited coatings, which subsequently affect the coating's mechanical properties and performance in production. This article aims at investigating the influences of bias voltage upon the deposition process and coating properties. For this reason my experiment made use of the oscilloscope (OSC) to measure the peak discharge current of HiPIMS when the substrate bias voltage changed from 40 V to 200 V. The hardness obtained by nano-indentation tester increased and the maximum hardness of 40 GPa appeared at 120 V bias voltage and then decreased as the bias voltage rose up further. Deposition rate and cross-sectional morphology of the deposited coating were investigated by scanning electron microscope (SEM). Surface morphology and roughness were detected by atomic force microscopy (AFM). Deposition rate dropped from 133.3 nm/min to 95.2 nm/min and surface roughness decreased from R_a 16.1 nm to R_a 9.2 nm as bias voltage increased. In order to figure out the connection between mechanical properties and microstructure of the coating, energy dispersive spectroscopy (EDS), Raman spectroscopy and X-ray diffraction (XRD) were used to demonstrate the change of element concentration, the carbon phase as well as crystal phase evolution of the coating. It is found that the carbon concentrations of deposited coatings decline and the composed phase of the coating is transformed from hexagonal α-WC at low bias voltage to equiaxial β-WC_{1-x} and then to hexagonal γ-W_2C accompanied by the rising bias voltage. In addition, there is a correlation among bias voltage, the grain size, the phase composition and the hardness of the coating. The minimum grain size of 6nm and the maximum hardness of 40 GPa appear at 120 V bias voltage when the coating is composed mainly of equiaxial β-WC_{1-x} phase. The friction coeffcient of the tungsten carbide coating measured by ball-on-disk test increased correspondingly with the increase of the bias voltage except that the wear rate reaches the lowest at 120 V bias voltage, indicating that the wear rate is related not only to friction coeffcient but also to coating hardness.

Keywords: tungsten carbide coatings, HiPIMS, microstructure, mechanical properties, tribological performance

Influence of annealing temperature on microstructure and erosive wear properties of the $Cr_xAl_yY_{1-x-y}N$ coatings

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Abstract: The $Cr_xAl_yY_{1-x-y}N$ coatings were deposited by closed field unbalanced magnetron sputter iron plating technique in this paper. The coatings were annealed in the vacuum and thermal oxidation environment. The performance and microstructure of the samples were analysed before and after annealed by the instruments such as XRD, SEM, AFM, XPS, TEM, micro-hardness tester, nano-indenter, and laser scanning confocal microscopy and so on. The effect of coating microstructure stability on wear properties were investigated, combines with the erosion abrasion experiment.

The results show that the coating mechanical properties increased with the rising annealing temperature. Before 450 ℃, oxidized had little effect on the thermal stability. After 450 ℃, oxidized was the main influence factor. The temperature less than 500 ℃, the slower coating grain growth, the smaller degree of recrystallization, the smaller coating phase structure changes, the better stability of the coatings microstructure. When the temperature is 400 ℃, $Cr_{0.768}Al_{0.15}Y_{0.082}N$ coating crystallite size increased 20%, N elements reduced 8.55%, $Cr_{0.636}Al_{0.10}Y_{0.264}N$ coating crystallite size increased 45%, N elements reduced 13.52%. $Cr_{0.768}Al_{0.15}Y_{0.082}N$ coating microstructure stability was stabler than $Cr_{0.636}Al_{0.10}Y_{0.264}N$ coating. $Cr_{0.768}Al_{0.15}Y_{0.082}N$ hardness and fracture toughness fell by 13.3% and 29.4%, respectively. $Cr_{0.636}Al_{0.10}Y_{0.264}N$ hardness and fracture toughness fell by 21% and 41.2%, respectively. The stabler the coating microstructure, the good mechanical properties.

The erosive wear experiment shows that the coatings erosive wear performance all decreased with the annealing temperature increase. $Cr_{0.768}Al_{0.15}Y_{0.082}N$ coating wear depth increased 20% and 60%, erosive wear rate increased 11.5% and 38% at 300 ℃ and 500 ℃, respectively. $Cr_{0.636}Al_{0.10}Y_{0.264}N$ coating wear depth increased 36% and 80%, erosive wear rate increased 35% and 43.3% at 300 ℃ and 500 ℃, respectively. That coating erosive wear properties at 300 ℃ was better than at 500 ℃. The $Cr_{0.768}Al_{0.15}Y_{0.082}N$ and $Cr_{0.636}Al_{0.10}Y_{0.264}N$ coatings erosive wear occurred non brittle peeling and cracking.

Keywords: $Cr_xAl_yY_{1-x-y}N$ coating, microstructure, thermal stability, erosive wear

Linker-free covalent immobilization of heparin, SDF-1a, and CD47 on polytetrafluoroethylene after plasma pre-treatment for antithrombogenicity, endothelialization and anti-inflammation

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Abstract: Small-diameter vascular grafts made of biomedical polytetrafluoroethylene (PTFE) suffer from the poor long-term patency rate originating from thrombosis and intimal hyperplasia, which can be ascribed to the insufficient endothelialization and chronic inflammation of the materials. Hence, biofunctionalization of PTFE grafts is highly desirable to circumvent these disadvantages. In this study, a versatile "implantation-incubation" approach in which the biomedical PTFE is initially modified by plasma immersion ion implantation (PIII) is described. After the N_2 PIII treatment, the surface of biomedical PTFE is roughened with nanostructures and more importantly, the abundant free radicals generated underneath the surface continuously migrate to the surface and react with environmental molecules. Taking advantage of this mechanism, various biomolecules with different functions can be steadily immobilized on the surface of PTFE by simple solution immersion. As examples, three typical biomolecules, heparin, SDF-1a, and CD47, are covalently grafted onto the PTFE. In addition to retaining the bioactivity, the surface-functionalized PTFE exhibits reduced thrombogenicity, facilitates the recruitment of endothelial progenitor cells, and even alleviates the inflammatory immune responses of monocytes-macrophages and is thus promising to the development of small-diameter prosthetic vascular grafts with good long-term patency.

Keywords: polytetrafluoroethylene, plasma immersion ion implantation, covalent immobilization, multi-functionalizations

The effect of titanium interlayer thickness on mechanical properties of TiAlSiN/Ti multilayer coatings

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Abstract: To explore mechanical properties of multilayer coatings consisting of alternating hard/soft layers, TiAlSiN/Ti multilayer coatings with a series of Ti layer thickness (0-150 nm) were deposited by using HiPIMS technique. The hardness, elasticity modulus, plasticity, microstructure, residual stress, toughness and wear resistance of those coatings are measured. It is demonstrated that the property of coatings were affected by Ti interlayer evidently. The hardness and elasticity modulus were reduced with increasing of Ti layer thickness. Meanwhile, the multilayer structure results in an increase of both toughness and plasticity of TiAlSiN coatings, and the one with Ti thickness of 25 nm (sample 2) shows the highest toughness without sacrificing hardness too much, from the data of nanoindentation, it can concluded that the enhanced toughness is not due to increase in the strain capacity (H/E), brought about by mutilayering.

Keywords: multilayer coatings, fracture toughness

Corrosion resistance of HiPIMS-TiAlN coatings sealed by ALD-layers with and without N^+ pre-ion-implantation

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Abstract: PVD-TiAlN coatings with excellent properties, including high hardness, high oxidation resistance, excellent corrosion resistance, and low thermal conductivity, have been widely used as protective materials on various cutting tools. However, the PVD coatings usually suffer from many intrinsic defects, such as pinholes, columnar structures, pores and macro particles or clots atomic, may contribute to weaken theirs properties. Atomic layer deposition (ALD) as an advance deposition technology can be utilized to solve these problems, due to its excellent conformality and uniformity or precise thickness control. Plasma immersion ion implantation (PIII) is a method of surface modification can not only change the arrangement of surface atoms, but also form nanocrystalline or amorphous layer, or form a mixed interface, may improve the adhesiveness of ALD-sealing layers attach on PVD coatings.
In this research, TiAlN coatings deposited on 304 stainless steel substrates by high power impulse magnetron sputtering (HiPIMS), then modified by PIII using Nitrogen ions or not before the sealing ALD-Al_2O_3 layers were deposited. The pure TiAlN coatings, TiAlN/Al_2O_3 hybrid coatings with and without N^+ pre-ion-implantation were compared, the morphology, microstructure, element distribution were investigated by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometer(EDS), X-ray diffraction (XRD) and atomic force microscopy (AFM). The corrosion behaviors were researched by potentiodynamic polarization measurements in 3.5% NaCl solution at room temperature, and the SEM, EDS, XRD, and AFM have been brought to analysis these tested and untested specimens.

Keywords: PVD, PIII, ALD, HiPIMS, hybrid coatings, corrosion behaviors

High rate deposition of Cr_xN coatings using a new cylindric high power impulse magnetron sputtering system

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Abstract: High power impulse magnetron sputtering (HiPIMS) has shown great advantages compared to the conventional magnetron sputtering techniques. However, the deposition rate is much smaller than that of convention magnetron sputtering with the same average power, especially for the reactive sputtering. This paper proposes a cylindric HiPIMS system and the deposition rate of Cr coating increases apparently by an electromagnetic extractor. For reactive sputtering, a Cr_xN coating for example is fabricated on the high speed steel substrates using this cylindric HiPIMS system. The results show the deposition rates of Cr_xN coatings are 2-3 times compare to that of the conventional planar sputtering source. And it decreases with increasing the N_2 flow due to the target poisoning. The Cr_xN coatings are composed of Cr_2N and CrN, which are density and smooth without any "metallic droplets". Time-resolved mass spectrometer is used to trace the evolution of Cr^+ in a pulse. The system achieves a high ionization of the Cr and low ion energies which exhibits low peak ion energy in the range of 2-6 eV.

Keywords: Cr_xN coatings, high power impulse magnetron sputtering system, high rate deposition

The influence of superimposed DC current on electrical and spectroscopic characteristics of HiPIMS discharge

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Abstract: The electrical characteristics and spectroscopic properties have been comprehensively investigated in a DC superimposed high power impulse magnetron sputtering (DC-HiPIMS) deposition system in this paper. The influence of superimposed DC current on the variation of target and substrate current waveforms, active species and electron temperatures with pulse voltages are focused. The peak target currents in DC-HiPIMS are lower than in HiPIMS. The time scales of the two main discharge processes like ionization and gas rarefaction in DC-HiPIMS are analyzed. When the pulse voltage is higher than 600 V, the gas rarefaction effect becomes apparent. Overall, the ionization process is found to be dominant in the initial 100 microseconds during each pulse. The active species of Ar and Cr in DC-HiPIMS are higher than in HiPIMS unless that the pulse voltage reaches 900 V. However, the ionization degree in HiPIMS exceeds that in DC-HiPIMS at around 600 V. The electron temperature calculated by modified Boltzmann plot method based on corona model has a precipitous increase from 0.87 to 25.0 eV in HiPIMS, but varies mildly after the introduction of the superimposed DC current. Additionally, the current from plasma flowing to the substrate is improved when a DC current is superimposed with HiPIMS.

Keywords: HiPIMS discharge, DC current, electrical properties, spectroscopic characteristics

Effect of ignition pulse on microstructure and properties of CrN/TiN films using multi-pulse HIPIMS

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Abstract: As one of high power magnetron sputtering (HIPIMS) technologies, a new type of multi pulse high power magnetron sputtering technique is present. High voltage ignition multi pulse excites high density plasma, and low voltage work pulse maintains plasma discharge, at the same time reducing the effect of target attracting ions.

The new multi pulse high power magnetron sputtering power source is connected with the Cr target, and the DC magnetron sputtering power source is connected with the Ti target. CrN/TiN films are fabricated. Effect of ignition multi pulse on the microstructure, chemical composition and phase of CrN/TiN films have been researched by various techniques, including atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). At the same time, the mechanical and tribological properties of the CrN/TiN films characteristics under different ignition pulse parameters are also studied, such as hardness, indentation, and friction and wear.

Compared with conventional methods, the CrN/TiN films prepared by multi-pulse HIPIMS are dense without defects, and the surface composed many dendritic islands with a little surface roughness but no macroparticles. The deposition rate increases obviously. The results demonstrate that the hardness and adhesion strength increase with the increase of the number of ignition pulses.

Keywords: multi pulse, HIPIMS, ignition pulse, CrN/TiN, deposition rate