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Aluminum-rich HPPMS $(Cr_{1-x}Al_x)N$ coatings deposited with different target compositions and at various pulse lengths

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ABSTRACT

Target properties and pulse configuration are important factors in high power pulsed magnetron sputtering. The present work deals with analyses of the effects of the pulse length, i.e., duty cycle on the HPPMS process and on the properties of Al-rich $(Cr_{1-x}Al_x)N$ coatings deposited with plugged targets in an industrial scale unit. The results showed that the peak power density increased from 0.32 kW/cm^2 to 0.86 kW/cm^2 as the pulse length decreased from t_{on} = 200 µs to 40 µs. $(Cr_{1-x}Al_x)N$ coatings with a high aluminum content between x = 68 at% and x = 76 at% were produced. The deposition rate reveals a constant behavior using different Al-rich targets at the same pulse length. A mixture of cubic and hexagonal $(Cr_{1-x}Al_x)N$ phases was found for each coating. Furthermore, a finer and denser morphology as well as a smoother surface were observed at reduced pulse length compared to large pulse configuration due to the high peak current and power density. The maximum hardness of H_U = 30.0 GPa and a moderate elastic modulus of E_{IT} = 421 GPa were achieved for the $(Cr_{0.30}Al_{0.70})N$ coating deposited at a pulse length of t_{on} = 40 µs, i.e., duty cycle of 2%.

1. Introduction

$(Cr_{1-x}Al_x)N$ is an important hard transition metal nitride as protective coating that has gained importance due to its mechanical and chemical properties, which makes this coating system a promising candidate for different tribological applications, e.g. cutting, forming operations, plastic processing, machine components [1–9]. Therefore, $(Cr_{1-x}Al_x)N$ deposited by high power pulsed magnetron sputtering (HPPMS, also known as HiPIMS) was chosen to be investigated in this study. HPPMS is a physical vapor deposition (PVD) technology, which corresponds to an advancement of pulsed magnetron sputter ion plating (MSIP). In HPPMS process high power is applied to the magnetron in short pulses, with a duty cycle below 10%. A detailed description of HPPMS technology and its advantages can be found by Sarakinos et al. [10] and Lundin et al. [11].

A great advantage of the HPPMS discharge is that it provides high plasma densities and a high grade of ionization in the coating chamber. The variation on pulse on/off time configuration, i.e. pulse energy, in HPPMS process, permits a control of the high energetic ions [12,13]. It gives an opportunity to influence the coating properties such as microstructure, roughness, phase composition and mechanical properties. Investigations in HPPMS CrN processes have shown that high frequency leads to nano-sized grain structure and suppression of columnar growth [14]. In previous works, we have analyzed the influence of HPPMS pulse length t_{on} on the properties of Cr-rich monolithic $(Cr_{1-x}Al_x)N$ coatings for x = 0.21–0.24. It was shown that short pulse lengths result in a densification of the coating microstructure, so that and a hardness of H_U = 32.4 GPa was achieved for x = 0.24 [15]. Recent analysis of HPPMS $(Cr_{1-x}Al_x)N$ monolithic coatings deposited at different frequencies and duty cycles reveal that particularly the hardness increased with increasing frequency [16]. These coatings were deposited using a 3″ diameter $Al_{0.70}Cr_{0.30}$ alloy target at various frequencies and the duty cycles in the range of 1250–500 Hz and 2–5%, respectively. Through the variation of the mentioned pulse parameter, coatings with Al content between x = 72 at% and 75 at% were produced [16]. A maximum hardness of H_U = 39.9 GPa was achieved for x = 0.75 at a frequency of 1250 Hz and a duty cycle of 2% [16]. In contrast to [16], the focus of the present contribution is to analyze the effects of the HPPMS pulse length on the properties of Al-rich $(Cr_{1-x}Al_x)N$ coatings (0.60 < x < 0.80) deposited at constant mean power and frequency using an industrial scale coating unit with large rectangular targets, where the expected peak power density is lower

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compared to lab-scale unit. Due to the variation of the pulse length the duty cycle was varied in a wide range from 2% to 10%. In this regard, the influence of the pulse length, i.e., duty cycle on the cathode current and power density as well as on the microstructure, crystalline structure and mechanical properties of Al-rich $(Cr_{1-x}Al_x)N$ coatings deposited in an industrial scale coating unit with two different plugged targets was investigated.

2. Experimental

2.1. Coating deposition

An industrial scale coating unit CC800/9 Custom by CemeCon AG, Würselen, Germany, with a chamber volume of 1000 m^3 was used for the coating deposition. The coating unit is equipped with a HPPMS power supply made by ADL GmbH. In a first step, an aluminum target with 20 chromium plugs with diameter of 15 mm (AlCr20 target) was applied for the coating production. In a second step, an aluminum target with 30 chromium plugs with diameter of 15 mm (AlCr30 target) was used. The mentioned targets had a purity of 99.5% for Al, of 99.9% for Cr. The size of all used rectangular targets was 88 mm × 500 mm. The HPPMS $(Cr_{1-x}Al_x)N$ coatings were deposited on cemented carbide (THM12) substrates at different pulse lengths (t_{on} = 40 μs, 80 μs and 200 μs). The mean power (P = 5 kW) and the frequency (f = 500 Hz) were fixed, so that the duty cycle was varied from 10% (t_{on} = 200 μs) to 4% (t_{on} = 80 μs) and to 2% (t_{on} = 40 μs). During all deposition processes one cathode was used and the samples were moved in a two-fold rotation with a dc bias voltage of U_B = −100 V. Further process parameters are shown in Table 1.

2.2. Process and coating characterization

Cathode current and voltage were recorded using an oscilloscope TDS3014B, Tektronix, Oregon, USA, during the HPPMS discharge. The cathode peak current and power density were calculated considering the whole target area. By means of the mentioned oscilloscope and a current probe connected to the substrate table the time evolution of substrate current (also called ion saturation current) was investigated, as shown in Ref. [17].

The coating morphology and the thickness were investigated using scanning electron microscope (SEM) ZEISS DSM 982 Gemini, Jena, Germany. SEM micrographs of fractured cross sections were taken using secondary electrons (SE) detector. The deposition rate was calculated by means of the coating thickness and the deposition time. The chemical composition was analyzed via energy dispersive spectroscopy (EDS). The surface roughness was analyzed by means of a confocal laser scanning microscope Keyence VK-X210, Tokio, Japan, according to ISO 4287 (line profile). Crystallographic phase analysis was carried out via X-ray diffractometry (XRD) with a grazing incidence X-ray diffractometer XRD 3003, General Electric, Munich, Germany. All measurements were performed with Cu-Kα radiation (wavelength λ = 0.15406 nm) operated at 40 kV and 40 mA using the following parameters: ω = 1°; 2θ = 30°–80°; step width: s = 0.05°; step time: t = 10 s. The ω was chosen to be very low in order to avoid a strong influence of the substrate on the interpretation of the XRD results. Universal hardness H_U and elastic modulus E_{IT} were determined using a Nanoindenter XP, MTS Nano Instruments, Oak Ridge, TN, USA. The indentation depth did not exceed 1/10 of the coating thickness. The evaluation of the measured results was based on the equations according to Oliver and Pharr [18]. A constant Poisson's ratio of ν = 0.25 was assumed.

3. Results and discussion

3.1. HPPMS process characteristics

The applied pulse shapes on the AlCr20 target during the HPPMS process for different pulse lengths t_{on} at constant mean power of P = 5 kW and frequency of f = 500 Hz are exemplary demonstrated in Fig. 1. In the present work industrial-size targets were used. Therefore, the shape of current and voltage curves is determined by the size of the capacitor bank in the power supply [12]. As shown in Fig. 1, the voltage is not constant during the whole pulse, but decreases from the peak value after plasma ignition. In Fig. 1a at t_{on} = 200 μs two different regimes can be identified: Between 0 μs and 100 μs the discharge operates in typical HPPMS conditions [12]. After 100 μs the current decreases gradually to a lower value. In contrast to t_{on} = 200 μs, the discharges in Fig. 1b at t_{on} = 80 μs and in Fig. 1c at t_{on} = 40 μs operate during the whole pulse time in HPPMS conditions. The measured peak current and the calculated peak current density of the investigated targets are exhibited in Fig. 2 as a function of the pulse length and duty cycle.

The peak current at the AlCr20 target increased from 224 A to 548 A and the peak current density increased from 0.51 A/cm^2 to 1.25 A/cm^2 when the pulse length is reduced from t_{on} = 200 μs to 40 μs (Fig. 2). The same trend can be observed for the AlCr30 target. The current raised from 223 A (0.53 A/cm^2) at t_{on} = 200 μs to 553 A (1.26 A/cm^2) at t_{on} = 40 μs. Considering that high peak currents can be associated with an increased plasma ionization degree [12,19], an increased ionization rate of metal atoms is expected specially at a reduced pulse length of t_{on} = 40 μs.

The correlation between the peak power, peak power density, duty cycle and pulse length are presented in Fig. 3. For the coatings deposited with an AlCr20 target the peak power increased from 149.1 kW to 195.6 kW and the peak power density increased from 0.34 kW/cm^2 to 0.44 kW/cm^2 as the pulse length decreased from t_{on} = 200 μs to 80 μs, i.e., the duty cycle decreased from 10% to 4%. Compared to that, the process with an AlCr30 target shows similar behavior. The peak power changes from 140.4 kW to 185.6 kW and the peak power density increases from 0.32 kW/cm^2 to 0.42 kW/

Table 1
Deposition parameters.

Process parameter		AlCr20 target	AlCr30 target
Deposition time t	min	120	120
Temperature at heaters T	°C	500	500
Argon flow F(Ar)	sccm	120	120
Krypton flow F(Kr)	sccm	80	80
Nitrogen flow $F(N_2)$ (pressure controlled)	sccm	39–40	36–41
Pressure p	mPa	450	450
dc bias voltage U_B	V	−100	−100
Mean cathode power P	kW	5	5
Pulse frequency f	Hz	500	500
Pulse length t_{on}	μs	200/80/40	200/80/40