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Enhancing the wear resistance of magnetron sputtered VN coating by Si addition

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ABSTRACT

Although Si addition into transition metal nitrides has been long known to enhance hardness of coatings, relatively less evidence indicates that the hardness gain can be translated into a significant improvement of wear resistance as expected. The reported wear rates of TM–Si–N coatings are generally greater than 10^{-16} m^3/N m. Here, we prepared VSiN coatings by adding Si into VN coatings, and investigated the friction-wear behavior of the VSiN coatings which achieved wear rates on the 10^{-17} m^3/N m order of magnitude. The friction-wear behavior was studied by ball-on-plate sliding tests against Al_2O_3 balls (3 or 6 mm in diameter), followed by microscopic examination on the worn surfaces. For the VN coating mild wear transited to fatigue failure after $\sim 10^4$ sliding cycles with crack growth and propagation, whereas the VSiN coatings retained mild wear more than 10^5 cycles, in which the sliding wear proceeded predominately by tribo-oxidation removal mechanism. The enhanced wear resistance of the VSiN could be mainly attributed to their special nanocomposite structure that limited intergranular cracks, and then suppressed fracture-dominated wear. Based on the results, it was proposed that the resistance to fracture-dominated wear could be taken into account for developing low-wear transition-metal nitride coatings.

1. Introduction

Transition-metal nitrides have been widely used as wear-resistant coatings, to reduce high production cost of worn tools [1,2]. Recently, it has been known that Si addition into transition metal nitrides can lead to great enhancement of hardness, and even can achieve superhardness (> 40 GPa). Some Si-containing transition-metal nitride coatings, such as TiAlSiN and CrAlSiN, have been used in the field of cutting [3–5]. However, relatively less evidence indicates that the hardness gain can result in excellent wear resistance as expected. The reported wear rates of state-of-the-art Si-containing coatings are generally higher than 10^{-16} m^3/N m, presenting lower wear resistance than some superlattice coatings and C-based coatings [6–8].

Hardness that is a measure of the resistance against plastic deformation, has long been regarded as a primary parameter defining the wear resistance for most materials, metals in particular [9,10]. For the cases of ceramics, however, the wear resistance of ceramics is in fact governed by their fracture toughness and the hardness plays a much smaller role, as the wear of ceramics does not usually occur by plastic deformation, but by fracture [4]. Recently, theoretical and experimental studies have shown that the combination of a higher ratio of hardness to elastic modulus (H/E) and a lower (E) are desirable for high wear resistance, since high H/E and low E generally represents the improved toughness [11,12]. Excellent wear resistance of nanometer scale multilayered coatings is attributed to the limited crack propagation in the 2D structures [13,14]. Additionally, we observed in the VSiN coatings that mild wear transited to severe wear when cracking and spallation occurred [15]. Failure mechanisms of hard coatings can be roughly divided into two broad categories: fracture dominated failure or oxidation-induced failure. Since the wear loss due to oxidation is much less than that from fracture, it can be expected that the wear resistance of hard coatings can be greatly improved if their fracture can be suppressed. Improved fracture toughness could be vital in developing low-wear transition-metal nitride coatings, as the absence of significant fracture is prerequisite in the regime of mild wear for ceramics [16].

Generally, the monolithic binary transition-metal nitride coatings suffer from relatively high wear rates (typically $\sim 10^{-15}$ m^3/N m or higher) [6,17]. In dry sliding wear the monolithic binary coatings are subject to transversal crack propagation along the columnar grain boundaries, and then the peeling of coatings [13]. In our previous work, however, very low wear rate ($\sim 10^{-17}$ m^3/N m) is achieved in

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dense binary nitride coatings with highly oriented growth structure (VN and CrN), although those coatings exhibit moderate mechanical properties ($H < 30$ GPa, $H/E < 0.1$, stress < -2 GPa) [18]. We attribute the high wear resistance of the binary nitride coatings to the dense and highly oriented growth structure as a "strong boundary" case, suppressing all fracture-related wear mechanisms [18]. Subsequently, the wear rate of 10^{-17} m^3/N m magnitude is obtained in the VSiN coatings prepared by alloying the VN coatings with a small amount of Si [15]. TM-Si-N coatings have been characterized as multiphase nanostructure where nanocrystalline grains are encapsulated by SiN_x layers [19,20], which can be considered as another "strong boundary" case [21,22], giving rise to enhancing the fracture toughness of coatings.

In this work, we compared the wear behavior of two "strong boundary" cases, i.e. the dense and highly oriented VN coating, and the VSiN nanocomposite coatings. Friction-wear tests were performed for the VSiN coatings, as well as corresponding post-test characterization of the worn surfaces. Additionally, the effect of Si addition on microstructure, mechanical properties and deformation behavior for the coatings was investigated, as to develop a better understanding of the main factors for low-wear transition-metal nitride coatings.

2. Experimental details

The V–Si–N coatings were reactively deposited on Si substrates in a magnetron co-sputtering chamber including two cathodes, the schematic of which was reported previously [19]. Key deposition parameters for the VSiN coatings are listed in Table 1. A vanadium target on the right cathode was driven by a mid-frequency pulsed-DC power supply (AE Pinnacle Plus + 5/5). And a silicon target on the left cathode was hooked up in parallel to a DC power supply and a radio frequency (RF) power supply (Comdel CV-1000, 81 MHz). Fixing the RF power at 200 W, the Si content in coatings was adjusted by changing the DC power on the Si target in the range of 0–200 W. A DC bias voltage of -50 V was applied to substrate holder that was heated to 773 K. The thicknesses were 1.4 ± 0.1 μm and 1.2 ± 0.1 μm for the VN coating and the VSiN coatings, respectively.

The microstructure of coatings was investigated by transmission electron microscopy (TEM) and atomic force microscope (AFM). The cross-sectional and surface morphologies were examined by an FEI Tecnai F20 system and an AIST-NT SmartSPM™ 1000 AFM, respectively.

Mechanical properties were measured by an MTS Nanoindenter G200 tool with a sharp Berkovitch diamond tip. The maximum indentation depth was set about 150 nm. The load–displacement curves were analyzed with the Oliver–Pharr method [23]. Residual stress was determined from the substrate curvature method, in which Si(100) pieces, $40 \times 3 \times 0.42$ mm^3 in size, were used. The stress was calculated by the Stoney equation from the curvature change as scanned by a laser beam. Vickers indentation tests were performed on a MVS-1000D1 Automatic digital micro hardness tester with three normal loads (1 N, 2 N, and 3 N). In order to obtain a cross-section of indentation, we specially made an array containing about dozens of indentations, along a pre-remarked line. Then, the sample was broken off manually along the pre-remarked line, which could form coincidentally the cross-sections of several indentations. Postmortem microscopic examination of the Vickers indents was made on an FEI QuantaTM 250 FEG SEM.

Tribological behavior was evaluated by ball-on-plate dry sliding tests against alumina balls (Al_2O_3, diameter of 3 or 6 mm, surface finish of Ra ~0.04 μm) on a UMT-3 tribometer (CETR, USA). Alumina has been used widely as counterpart material in wear tests [7,8,24,25], due to its high hardness and chemical inertness which can reduce transfer of counterpart material to coating surfaces and avoid additional chemical reactions. All tests were conducted at the ambient temperature (~298 K) and a relative humidity of 50–60%. A fresh Al_2O_3 ball was used for every sliding test. A normal load of 5 N was applied during the sliding tests, and the sliding mode was reciprocating with a track length of ~5 mm and an average speed of 50.0 mm/s. Morphology of the wear tracks was examined by the FEI QuantaTM 250 FEG SEM. A KLA-Tencor Alpha-step IQ surface profiler was used to scan profiles of the cleaned wear tracks. Then, based on the profiles of the cleaned wear track at several locations, volume loss was calculated, from which specific wear rates were obtained by normalizing the wear volume with the total sliding distance and the applied load.

Table 1
Deposition parameters for VSiN coatings.

V target power	500 W (100 kHz, 80% duty)
Si target power	200 W (RF) + 0–200 W (DC)
Work pressure	1.0 Pa
Ar partial pressure	0.7 Pa
Ar/N_2 flow rate	32/24 sccm
Deposition temperature	773 K
Bias voltage	−50 V (DC)
Substrate holder rotation	10 rpm

3. Results

3.1. Microstructure

Previous studies have verified that the Si addition modifies the microstructure of coatings significantly [19]. More details on microstructural changes of the coatings were revealed by cross-sectional TEM studies, taken from the VN coating and the VSiN coating with the 5.5 at% Si. Fig. 1a is a bright-field (BF) image of the VN coating, in which large columns were densely packed with well-defined boundaries. The large columns that were estimated ~100 nm in width, were extending almost throughout the coating. A representative high resolution TEM (HRTEM) image is shown in Fig. 1b. Along the boundary (as denoted by a dotted line), the adjacent columns were both (200)-oriented with respect to the growth direction. The interface seemed slightly disordered, although there was almost no misorientation between the adjacent columns. In accordance with similar magnification, the BF (Fig. 1c) of the 5.5 at% Si coating presents a refined columnar structure with diffused boundaries. As precisely identified by HRTEM shown in Fig. 1d, the 5.5 at% Si coating was composed of nanocolumns, separated by thin disordered or amorphous phase. The distances of lattice fringes in the nanocolumn regions, were close to the interplanar spacing for VN (111) or (100) planes. Further combining the result of XRD [19], the nanocolumns could be believed to be cubic VN, and the disordered phase being SiN_x rich phase in amorphous state. Thus, it could be identified that the VN coating exhibited the dense and highly-oriented columnar structure, whereas the 5.5 at% Si coating exhibited the nanocomposite structure in which nanocrystalline VN grains were encapsulated by SiN_x layers.

The surface morphologies of the coatings are shown in Fig. 2. As a function of increasing the Si content, the grains became smaller and the surfaces became more smooth. The surface of VN coating consisted of round grains with ~100 nm in diameters ($Ra = 4.1$ nm, Rms = 4.9 nm), while the 5.5 at% Si coating appeared extremely smooth surface almost without any visible grain ($Ra = 0.7$ nm, Rms = 0.9 nm). It is generally recognized that Si