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The effects of adding aluminum on crystal structure, mechanical, oxidation resistance, friction and wear properties of nanocomposite vanadium nitride hard films by reactive magnetron sputtering

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ABSTRACT

Vanadium nitride films exhibited excellent tribological properties due to the formation of Magnéli phases during the wear test, while the poor thermal stability, low hardness and high wear rate restricted it applied in cutting tool field. In this paper, aluminum was added into the vanadium nitride matrix in order to improve the thermal stability, mechanical and tribological properties. V-Al-N films with various Al content were deposited by reactive magnetron system and the effects of Al content on the micro-structure, oxidation resistance, mechanical and tribological properties of V-Al-N films were investigated. The results showed that V-Al-N films regardless of Al content exhibited a single face-centered cubic (fcc) structure. There was an increase in hardness when the content of Al was below 4.7 at.% with a corresponding decrease in room temperature friction coefficient (μ) and wear rate (WR). Rising Al content improved the oxidation resistance, while degraded the fracture toughness. The film at 4.7 at.% Al with highest hardness and lowest μ and WR was chosen to investigate its high temperature tribological properties. The rising temperature induced both the wear mechanism change and tribo-film vanadium oxides phase transition, and increased μ to 0.7 at 300 °C firstly and then dropped to 0.28 at 700 °C, while WR increased gradually. The film at 4.7 at.% Al was found to be optimized for cutting tool application.

HIGHLIGHTS

- Vanadium aluminum nitride films were deposited by magnetron sputtering.
- The maximum value of hardness was ∼24 GPa at 4.7 at.% Al.
- Oxidation resistance temperature of the V-Al-N films increased from ∼420 °C at 0 at.% Al to ∼790 °C at 38.8 at.% Al.
- The incorporation of Al into the VN film below 4.7 at.% improved the room tribological properties.
- The tribological properties of the film at 4.7 at.% Al were investigated.

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1. Introduction

Transition metal nitride films such as TiN and CrN systems have been widely applied in cutting tool since 1980s due to their excellent mechanical and stable chemical properties [1–6]. The remarkably comprehensive properties, especially, the thermal stability and tribological properties at elevated temperatures, are urgently demanded in the high-speed and dry-cutting fields with the development of the modern processing and manufacturing industries [7,8]. Thus, how to improve relevant properties of the materials has been an important

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Table 1
Elemental composition, residual stress, H/E and H^3/E^2 ratios of V-Al-N films as a function of Al target power.

Al target power (W)	Elemental composition (at.%)					residual stress (GPa)	H/E	H^3/E^2 (GPa)
	V	Al	N	O	Al/(V + Al)			
0	+51.0 ± 3	0	+47.3 ± 2.4	+1.7 ± 0.1	0	+2.3 ± 0.1	0.044	0.0213
30	+51.0 ± 3	+0.7 ± 0.04	+46.9 ± 2.4	+1.4 ± 0.1	+1.3 ± 0.1	+1.6 ± 0.1	0.05479	0.04182
60	+48.3 ± 2.4	+2.4 ± 0.1	+47.8 ± 2.4	+1.5 ± 0.1	+4.7 ± 0.2	+1.2 ± 0.1	0.07796	0.14701
100	+43.5 ± 2.2	+7.3 ± 0.4	+47.4 ± 2.4	+1.9 ± 0.1	+14.4 ± 0.7	+0.5 ± 0.03	0.0575	0.05489
140	+38.1 ± 1.9	+13.0 ± 1	+46.8 ± 2.3	+2.1 ± 0.1	+25.4 ± 1.3	−0.3 ± 0.02	0.04631	0.02843
200	+31.1 ± 1.6	+19.8 ± 1.0	+47.5 ± 2.4	+1.6 ± 0.1	+38.8 ± 1.9	−0.8 ± 0.04	0.03637	0.01358

challenge for material scientists.

Recently, a solid lubrication known as Magnéli phases was found in the application of oxide materials with 'easy' crystallographic shear phases, and numerous related research activities have been carried out to investigate the formation and function mechanism of Magnéli phases in hard metal nitride films [4,5]. Vanadium oxide, tungsten oxide and molybdenum oxide are common Magnéli phases, while the V, W and Mo are usually considered as additional elements to introduce into some traditional metal nitride films [7]. Currently, in view of the poor thermal stability and high wear rate, V-N, W-N and Mo-N based films is comparatively much less applied in cutting tool field. As reported [3,6], alloying metallic/nonmetallic elements into metal nitride matrix to deposit ternary, quaternary and multicomponent hard films could combine the benefits of individual components. Addition of Al into hard metal nitride matrix has been considered as an effectively method to improve the oxidation resistance and wear resistance properties. For example, the incorporation of Al into TiN matrix to form substitutional solid solution Ti-Al-N could improve the mechanical, thermal stability and wear resistance properties [9]. A similar enhancement of comprehensive properties can also be observed in other films like Cr-Al-N [10], Zr-Al-N [11]and Nb-Al-N [12] systems. Based on above results, our group deposited a series of Mo-Al-N with various Al content and investigated the influence of Al content on the mechanical, oxidation resistance and tribological properties of the films [13]. The incorporation of Al into face-centered cubic Mo_2N was found to improve the oxidation resistance property and tribological properties at room temperature. Therefore, it can be reasonably expected that V-Al-N films should exhibit good oxidation resistance and tribological properties. P. Zhu et al. [14] synthesized the V-Al-N films with different Al content using magnetron sputtering and the result showed that the V-Al-N films exhibited higher hardness and lower wear rate at room temperature as compared with binary VN films. However, seldom effort has been made to investigate the fracture toughness, oxidation resistance and high temperature tribological properties V-Al-N films. In this paper, Al was introduced into the VN matrix in order to improve the thermal stability, mechanical and tribological properties, and V-Al-N hard films with various Al content were deposited using RC reactive magnetron sputtering system and the efforts of Al content on the film's crystal structure and mechanical, oxidation resistance and tribological properties were studied.

2. Experimental details

The vanadium aluminum nitride films with a thickness of ~1 μm on mirror polished stainless steel (AISI 304 SS) and silicon (100) wafer substrates were synthesized by magnetron sputtering. Vanadium (purity 99.99%) and aluminum (purity 99.99%) targets with a diameter of 7.5 centimeter were fixed on three independent RF powers, and the substrates were ultrasonically cleaned in acetone and alcohol respectively. The distance between the substrates and targets was 150 mm. Argon (purity 99.99%) and nitrogen (purity 99.99%) were introduced into the chamber simultaneously when the base pressure of the chamber reached below 6×10^{-4} Pa. Surface contaminant of the targets was removed through argon bombardment with the target power of 40 W for 10 min, and then a vanadium interlayer with a thickness of ~100 nm was deposited on the substrate before deposition the vanadium aluminum nitride films. The vanadium aluminum nitride films with different aluminum content were synthesized by fixing vanadium target power of 150 W and changing the aluminum target power from 0 to 130 W, meanwhile keeping the working pressure of 0.3 Pa, Ar:N_2 flow ratio of 10:7 and the substrate temperature of 200 °C. The substrates were not biased.

The elemental compositions of the films were characterized by Electron Probe Microanalysis (EPMA) of CAMECA SX-50. The crystal structure of the films was analyzed by X-ray diffraction (XRD, Shimazu-6000, Shimadzu, Japan) using Cu Kα radiation, operated at 40 kV, 35 mA. The crystallite size of the films was calculated by Scherrer formula and the lattice constant of the films was also calculated based on the XRD data according to the Nelson Riley function. The microstructure of the film was further studied by the transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) operated at an accelerating voltage of 200 kV. The thickness and curvature radii of the films were measured using Bruker DEKTAK-XT profilometer, and then the residual stress of the films with different aluminum content was calculated based on the Stoney's equation [15]. A nano indentation tester system (nano-indenter CPX + NHT + MST), equipped with a diamond Berkovich indenter tip was used to determine the hardness of the film. The indenter was calibrated using fused silica as a reference. A total of nine (9) indentations were made for each sample and the mean value taken. To avoid the influence of the Si substrate on the hardness of the film, a maximum load of 4 mN was applied to meet the criterion that less the 10% indentation depth. The Thermal Gravimetric Analyzer

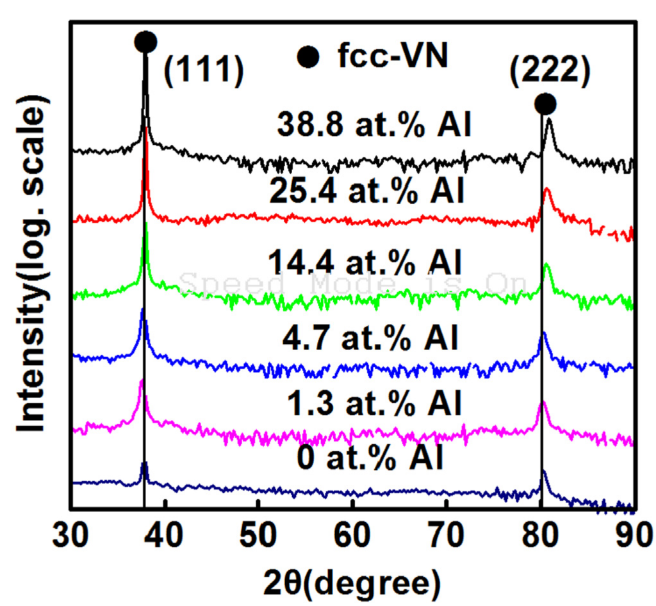

Fig. 1. The XRD patterns of VN and V-Al-N films with the different Al content.