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Structural and mechanical evolution of TiAlSiN nanocomposite coating under influence of Si_3N_4 power

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ABSTRACT

In this study, we have reported the microstructural and mechanical properties of nanocrystalline Titanium Aluminum Nitride (TiAlN) embedded in amorphous Silicon Nitride (Si_3N_4) nanocomposite films. The films were deposited on Si substrate by using DC\RF reactive magnetron co-sputtering of TiAl and Si_3N_4 targets by varying power to the Si_3N_4 target. The films were investigated using grazing incident X-ray diffraction (GIXRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), stylus profiler and nanoindentation. GIXRD shows the formation of crystalline cubic Ti_3AlN phase in the films. With the increase in Si_3N_4 power, crystal growth of TiAlN diminishes. FESEM micrographs showed the uniformly distributed, well developed, sharp-edged, irregular shaped grains on the surface of the films. The silicon-rich region was observed at inter-grain boundary region and the micrographs visualize the presence of amorphous Si_3N_4 on the edge of crystal grains. The amorphous content increases with Si_3N_4 power. EDS confirms the presence of all elements in the films. The optimum mechanical properties were observed at 70 W Si_3N_4 target power. Hardness, elastic modulus, elastic recovery and resistance to plastic deformation of film rises from 40 W to 70 W target power and then reduces at 90 W.

1. Introduction

The interest in thin films of metal nitrides is rising rapidly for its diverse uses, such as wear resistant coatings on cutting tools, diffusion barriers in integrated circuits and as selective transmission coatings on architectural glass. The bond structure in transition metal nitride consists of a mixer of covalent, metallic and ionic components [1]. This bond structure is responsible for high hardness, excellent wear resistance, chemical inertness, good electrical conductivity and superconducting properties [2]. Traditional transition metal nitride coatings, such as TiN, played an important role in first periods of protection of tool surfaces. The main drawback of TiN is its limited oxidation resistance at high temperatures (500 °C) [3]. Oxidation of coating results the crack formation and delamination of brittle oxide layer. Properties of simple TiN can be significantly enhanced by the addition of other elements, such as Al or Si. Incorporation of Al in FCC-TiN structure leads to the development of TiAlN coatings which characterizes high hardness and high oxidation resistance (up to 800 °C) [4].

Nanocomposite coatings composed of nanocrystalline (*nc*-) transition metal nitrides (*nc*-MeN, Me = Ti, W, V, Mo, or Ta) embedded in amorphous (*a*-) matrices (*a*-Si_3N_4, *a*-BN, etc.) have been developed. Mainly three kinds of coatings can be obtained, i.e. the crystalline coatings, the amorphous coatings and the nanocomposite coatings [5]. Reactive magnetron sputtering is well-known technique to deposit these coatings. Main advantages of these techniques are ease to control coating microstructures, composition by varying deposition parameters and suitability of industrial application. On the basis of hardness, coatings are divided into three groups: (1) hard coatings with hardness $H < 40$ GPa; (2) superhard coatings with hardness (H) between 40 and 80 GPa; and (3) ultrahard coatings with hardness $H > 80$ GPa [6]. At present, two groups of hard and superhard, two-phase nanocomposite coatings are known:

1. *nc*-MeN/amorphous phase (e.g. *a*-Si_3N_4, *a*-BN, etc.)
2. *nc*-MeN/metal phase (e.g. Ti, Ni, Cr, Mn, etc.)

The hardness (H) of the both groups films, i.e. nanocomposites of the type *nc*-MeN/*a*-nitride and *nc*-MeN/metal, can be continuously varied from low values of approximately 10 GPa to high values reaching up to 70 and 55 GPa, respectively.

Veprek reported that there are two mechanisms that cause the increase of hardness in hard and superhard nanocomposite coatings [7]. The first mechanism is hardness improvement by energetic ion bombardment. This phenomenon is complex due to synergistic effect concerning a decrease of crystallite size, increases the density of grain boundaries, development of Frenkel pairs and other point defects and built-in biaxial compressive stress. The second mechanism for the hardness enhancement by the formation of stable nanocomposite structure

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due to self-organization upon spinodal phase segregation. This model is based on a strong thermodynamically influence, and diffusion rate controlled (spinodal) phase segregation that leads to the development of a stable nanostructure by self-organization. The dislocation activity is absent in the case of superhard, thermally high stable nanocomposites. These materials consist of a few nanometre small crystallites of a hard transition metal nitride (or carbide, boride) attach together by about one monolayer of non-metallic, covalent nitride such as Si_3N_4, BN (or in the case of carbides by extra carbon, CN_x, and others). The effects mentioned above may hinder the dislocation activity depending on the crystallite size in the material. These coatings, when correctly prepared, shows a good combination of mechanical properties, such as a high hardness, high elastic recovery, elastic strain, and high tensile strength.

A substantial number of nanocomposite coatings have been studied. Among them, nanocomposite coatings of (Ti,Si)N have been studied extensively due to its high hardness and elastic modulus, improved wear resistance and high oxidation resistance [8]. The prominent hardness of the nanocomposite (Ti,Si)N coatings and enhanced thermal stability of TiAlN coatings led to the exploration of (Ti,Al,Si)N nanocomposite coatings. Carvalho et al. reported that with increasing Si content, grain size decreases and nanocomposite system has lower residual stress [9]. Barshilia et al. deposited nc-TiAlN/a-Si_3N_4 coating changing Si content and achieve maximum hardness 43 GPa at approximately 11 at% silicon contribution [8]. Kang et al. deposited TiAlSiN nanocomposite coating with varying Si content. At 9 at% silicon contain, coating shows maximum hardness (40.9 GPa) [10]. She-quan et al. reported the addition of Al and Si in TiN coating decreases of grain size and increasing of hardness [11]. Chen et al. reported the effect of Al content on mechanical and structural property of nc-TiAlN/a-Si_3N_4 coating. The increased Al content decreases grain size and increases hardness [12]. Farkas et al. prepared nc-TiAlN/a-Si_3N_4 coating changing nitrogen flow. Nanocomposite structure change with nitrogen flow [13]. Ravi et al. reported the effect of substrate roughness. Adhesion and wear volume decreases with increasing surface roughness resulting brittle nc-TiAlN/a-Si_3N_4 nanocomposite coating [14].

Controlling the microstructure evolution in the multi-element coating system have a significant effect on nanocrystalline growth. In this study nc-TiAlN/a-Si_3N_4 coating were deposited by using reactive magnetron sputtering. The coating has been deposited at different Si_3N_4 target power. With increasing Si_3N_4 power, change in the structural and mechanical property is investigated using GIXRD, Raman, EDS, FESEM, stylus profiler and nanoindentation. The various mechanical properties like hardness, elastic modulus, elastic recovery, and resistance to plastic deformation of films are discussed particularly.

2. Experimental procedures

2.1. Deposition technique

The nanocomposite films of nc-TiAlN/a-Si_3N_4 were deposited on single crystal silicon (100) substrates by using reactive DC/RF magnetron co-sputtering system (Moorfield, Model-ES60A, UK) in an argon and nitrogen atmosphere. The sputtering system consists of four magnetrons of ~50 mm diameter each. Magnetron was fixed at ~20° angle to the substrate normal. The coatings were deposited using highly pure TiAl and Si_3N_4 target having 99.99% purity. The composition ratio in TiAl target is 50:50 wt% of Ti and Al respectively. DC power supply was applied to sputter one TiAl target and RF power supply was applied to sputter one Si_3N_4 target. The substrates were cleaned by ultrasonicator using ethanol and distilled water and dried in air. In the chamber, the substrates were mounted on a rotational substrate holder that lies on TiAl target and Si_3N_4 target after the preliminary treatments, and its revolving speed was controlled 4 rpm during the deposition. The distances between the substrate material and TiAl target, Si_3N_4 target were fixed about 10 cm. The main chamber was evacuated to ~2×10^{-6} mbar using turbo molecular pump. Once the pressure was achieved, argon gas was introduced into the chamber to achieve 0.8 Pa pressure. Both the targets of TiAl and Si_3N_4 were cleaned by pre-sputtering for 5 min at 25 W DC and 24 W RF power respectively. Shutters were closed to prevent coming out target material from reaching to the substrate at the time of pre-sputtering. After nitrogen and argon were introduced into the chamber and working chamber pressure was 4.1×10^{-3} mbar while deposition. Partial pressure of nitrogen (P_{N2}) was maintained 0.12 Pa. Films were deposited at 300 °C substrate temperature and total growth time was 2 h. The film thicknesses were typically 560 nm with deposition rate 4.7 nm/min. Other experimental parameters are listed in Table 1.

Table 1
Deposition parameters for nc-TiAlN/a-Si_3N_4 film coating.

Si_3N_4 power (RF)	40 W, 50 W, 70 W, 90 W
TiAl power (DC)	200 W
Target power density (DC)	10.19 W/cm^2
Base pressure	2×10^{-6} mbar
Working pressure	4.1×10^{-3} mbar
Argon flow rate	14 sccm
Nitrogen flow rate	6 sccm
Substrate temperature	300 °C
Substrate bias	Grounded
Deposition time	2 h
Substrate rotation frequency	4 rpm

2.2. Film characterization

The GIXRD was used to study nc-TiAlN/a-Si_3N_4 crystallographic structure, using Rigaku band equipment (Cu-Kα line with a wavelength of 0.154 nm). A Leica BM 2700 m Raman spectrometer and HeNe 20 mW laser beam was used as the excitation source for Raman spectroscopy study. Details study of the microstructure was done by Zeiss Olympus FESEM. This microscope is also attached an EDS microprobe from which chemical composition of the film can be obtained. The thickness of deposited samples was determined by stylus profiler (NanoMap-500LS, AEP Technologies). The hardness and elastic modulus of the films were measured with a UMIS nano-indenter (Frishercripps, Australia). The indentation was done at 10 different places with 10 mN load and an average value was taken for final result.

3. Experimental results and discussion

3.1. XRD study

The GIXRD patterns of TiAlSiN films deposited at 200 W TiAl power along with varying Si_3N_4 power were shown in Fig. 1. Although content

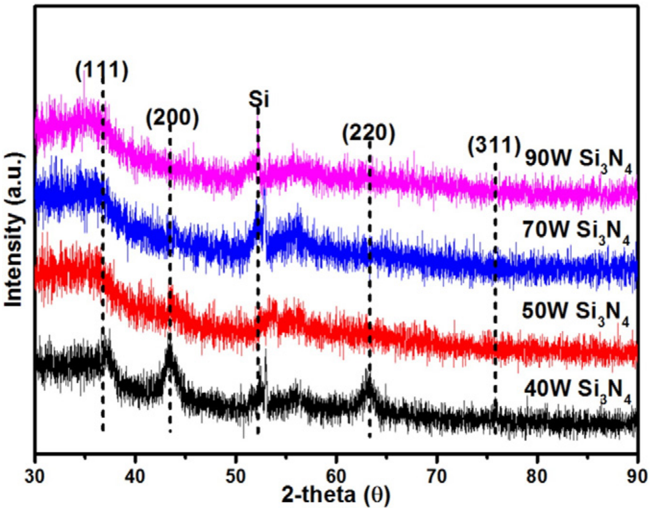

Fig. 1. GIXRD pattern of nc-TiAlN/a-Si_3N_4 at different Si_3N_4 power.