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Microstructure and mechanical property of TiSiN nanocomposite film with inserted CrAlN nanomultilayers

Wei Li [a,b,*], Ping Liu [a], Jia Meng [b], Ke Zhang [a], Fengcang Ma [a], Xinkuan Liu [a], Xiaohong Chen [a], Daihua He [a]

[a] School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[b] Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, PR China

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ABSTRACT

A series of TiSiN films inserted by CrAlN nanomultilayers with different thicknesses was prepared by reactive magnetron sputtering. The influences of CrAlN layer thickness on the microstructure and hardness of films were investigated by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and nano-indentation techniques. The insertion of CrAlN nanomultilayers destructs the nanocomposite structure of TiSiN film, leading to the decrease of hardness. As the CrAlN layer thickness increases to 2.5 nm, CrAlN layers are inclined to grow epitaxially with TiSiN layers in order to lower the interfacial energy. As a result, the TiSiN film can be further strengthened with the maximal hardness of 53.9 GPa. As the CrAlN layer thickness further increases to 3.0 nm, the epitaxial growth structure between TiSiN and CrAlN layers is broken, resulting in the deterioration of hardness.

1. Introduction

Nowadays, nanocomposite thin films successfully promote hardness, oxidation resistance, wear behavior, and other properties relevant for protective coatings [1–3]. Such films are composed of nanocrystallites (≤10 nm) of transition metal nitrides, carbides, or borides encapsulated by a covalent interfacial layer (e.g., Si_3N_4, BN, CN_x, or diamond like C). Among these films, the pseudobinary TiSiN is a representative film due to strong surface segregation of the constituent phases (TiN and SiN_x have essentially no solid solubility). Li et al. firstly synthesized Si-containing nanocrystalline TiN by plasma-assisted chemical vapor deposition (PACVD) and high hardness of about 60 GPa was reported [4]. Later, S. Veprek and his coworkers performed intensive studies on TiSiN nanocomposite films [5–7] and reported a super high hardness of 80–105 GPa was achieved in this film system in 2000 [8]. Despite this result were challenged by many researchers [9,10], it is undoubted that TiSiN nanocomposite film has attracted much attention from the scientific community.

Despite that the hardening mechanism and synthesis technique of TiSiN nanocomposite film have been widely investigated by many researchers [11–14], the influences of nanoscale-layered insertions on microstructure and mechanical property of TiSiN nanocomposite film have been rarely reported from the existing literatures. Recently, our research group tried to insert TiN nanomultilayers into TiSiN nanocomposite film [15]. However, the hardness exceeding TiSiN film was not successfully achieved. In the past few years, CrAlN films have gained much attention as a wear-resistant hard coating due to superior toughness, higher corrosion and oxidation resistance, better tribological properties with both lower friction coefficient and wear rate. As CrAlN film has been presented with superior properties over TiN film, it can be expected that, TiSiN nanocomposite film can be further strengthened with CrAlN nanoscale-layered insertions. To this end, CrAlN nanomultilayers with different thicknesses are designed to insert into TiSiN nanocomposite film by means of reactive magnetron sputtering technique. The influence of CrAlN nanolayered insertions on the microstructural evolution and hardness of TiSiN nanocomposite film will be systematically investigated.

2. Experimental

The TiSiN nanocomposite films inserted by CrAlN nanolayers were fabricated on the silicon substrates by reactive magnetron sputtering system, which could be schematically illustrated in Fig. 1. The TiSiN films were deposited from a TiSi compound target (Ti at.%:Si at.% = 84%:16%) by RF mode and the power was set at 350 W. The CrAlN nanomultilayers were deposited from a CrAl alloy target (Cr at.%:Al at.% = 50%:50%) by DC mode and the power was set at 150 W. Both TiSi and CrAl targets were 75 mm in diameter. The base pressure was pumped down to 5.0×10^{-4} Pa before deposition. The Ar and N_2 flow rates were 38 and 5 sccm respectively. The working pressure was 0.4 Pa and substrate was heated up to at 300 °C during deposition.

* Corresponding author at: School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, PR China.
E-mail address: liwei176@usst.edu.cn (W. Li).

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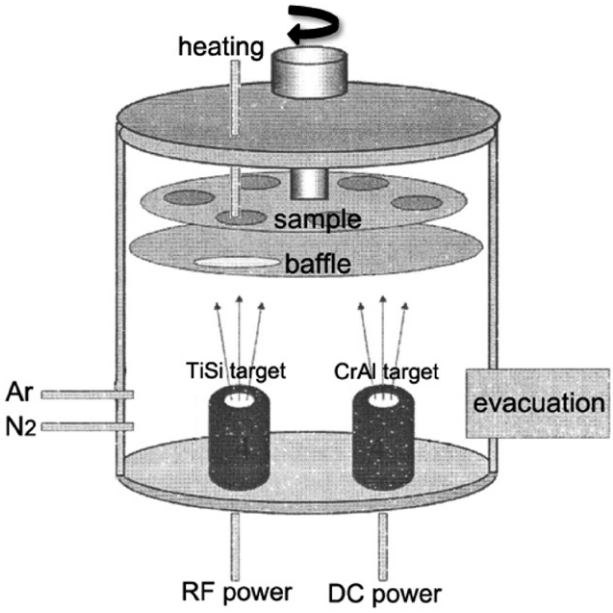

Fig. 1. Schematic figure of magnetron sputtering deposition system.

The configuration of TiSiN films inserted by CrAlN nanomultilayers was designed with fixed interval distance of CrAlN layer (also called "TiSiN layer thickness") and with variable CrAlN nanolayer thickness. The thickness of TiSiN and CrAlN layers was both controlled by the switch time of alternate shutters which were modulated by a programmable logic control. The TiSiN layers were unchangeably deposited for 20 s to keep a fixed thickness. According to the deposition time and deposition rate (about 0.4 nm/s) derived from the monolithic TiSiN film, the TiSiN layer thickness deposited at this condition are fixed at 8 nm. In order to obtain the different CrAlN nanolayer thicknesses, the CrAlN layers were deposited for 2 s, 3 s, 4 s, 5 s and 6 s, respectively. The overall deposition time of TiSiN film inserted by CrAlN nanomultilayers was nearly 3 h with the number for TiSiN/CrAlN bilayer of 200. TiSiN monolithic film was also fabricated for comparison. The thickness of all films was about 2 μm.

The microstructures of TiSiN films inserted CrAlN nanolayers were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance with Cu K_a radiation and field emission high-resolution transmission electron microscopy (HRTEM) using a Philips CM200-FEG. The preparation procedures of cross-section specimen for TEM observation are as follows. The films with substrate were cut into two pieces and adhered face to face, which were subsequently cut at the joint position to make a slice. The slices were thinned by mechanical polishing followed by argon ion milling. The composition was characterized by an energy dispersive spectroscopy (EDS) accessory equipped in a Philips Quanta FEG450 scanning electron microscopy (SEM). The hardness and elastic modulus were measured by a MTS G200 nanoindenter by using the Oliver and Pharr method [16]. The measurements were performed by using a Berkovich diamond tip with a load of 5 mN. The indentation depth was less than 1/10th of the film thickness to minimize the effect of substrate on the measurements. Each hardness or elastic modulus value was an average of at least 16 measurements.

3. Results and discussion

Fig. 2 shows the typical cross-sectional TEM images of TiSiN film inserted by CrAlN nanomultilayers with depositing time for each CrAlN layer of 5 s. From the low-magnification image of Fig. 2(a), it can be seen that the film presents the columnar crystal growth, with the thickness of about 2 μm. It is clear from the magnified Fig. 2(b) that, due to the insertion of CrAlN nanomultilayers, TiSiN and CrAlN form the multilayered structure.

Fig. 3 shows the XRD patterns of monolithic TiSiN film and TiSiN films inserted by CrAlN nanomultilayers with different thicknesses. It is worth noting that the Si content in monolithic TiSiN film has characterized by EDS, which is about 8.4 at.% and consistent with the content in TiSi target. It can be seen from the Fig. 3(a) that the monolithic TiSiN film and TiSiN films inserted by CrAlN nanomultilayers with the depositing time less than 5 s are only composed of TiN phase with (200) preferred orientation. According to the deposition time and deposition rate of CrAlN (about 0.5 nm/s) derived from the monolithic CrAlN film, the thicknesses of CrAlN nanolayers deposited for 2 s, 3 s, 4 s, 5 s and 6 s at this condition are 1.0 nm, 1.5 nm, 2.0 nm, 2.5 nm and 3.0 nm, respectively, which have been indexed in the corresponding XRD patterns and will be verified by the following HRTEM observations. When the CrAlN layer thickness increases to 3.0 nm, the (200) CrN diffraction peak emerges in the XRD patterns besides TiN diffraction peaks, as the fitted results of diffraction peaks further show in Fig. 3(b).

It can also be seen that the monolithic TiSiN film presents comparatively higher diffraction peak intensity, that is, crystallinity of film. With the insertion of CrAlN layers with thickness ranged from 1.0 nm to 1.5 nm, the diffraction peak intensity of TiSiN film decreases, indicated crystallinity deteriorates. While the CrAlN layer thickness increases to 2.0 nm or 2.5 nm, crystallinity of the film improves. As the CrAlN layer

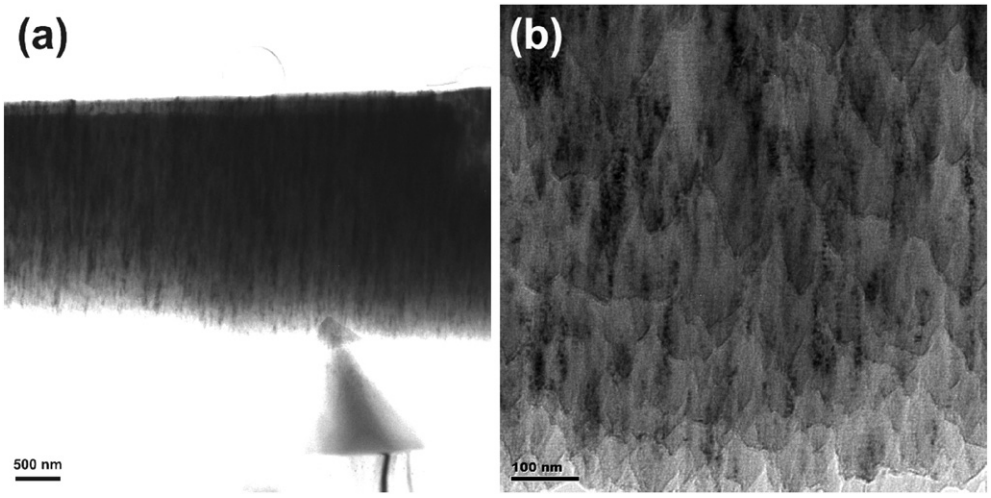

Fig. 2. Cross-sectional TEM images of TiSiN film inserted by CrAlN nanomultilayers with one-layer depositing duration of 5 s: (a) low-magnification and (b) high-magnification.