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Microstructure and mechanical properties of (Ti,Al)(O,N) films synthesized by reactive sputtering

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Abstract

A series of (Ti,Al)(O,N) films were synthesized in a gaseous mixture of Ar, N_2 and O_2 by the reactive magnetron sputtering method using a Ti–Al mosaic target. Energy dispersive spectroscopy, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, atomic force microscopy and nanoindentation were employed to investigate films' chemical composition, microstructure and mechanical properties. The results show that oxygen content in the films increases with the rising O_2 partial pressure and nitrogen content decreases correspondingly; on the other hand, the atom ratio, (Ti+Al)/(O+N) keeps close to a stoichiometric constant of 1. (Ti,Al)(O,N) films present the same NaCl structure as the (Ti,Al)N film and columnar crystals with a (200) texture. Meanwhile, hardness and elastic modulus of (Ti,Al)(O,N) films maintain 35 GPa and 370~420 GPa, respectively, as high as those of the (Ti,Al)N film.

Keywords: (Ti,Al)(O,N) film; Reactive sputtering; Microstructure; Mechanical property

1. Introduction

High hardness and good oxidation resistance are two important properties used to evaluate a successful cutting tool coating. Hard ceramic films, represented by TiN, have been extensively applied as cutting tool coatings and accomplished great achievements [1]. On the basis of the TiN film, it is probable to further improve its properties by alloying other metals, such as aluminum [2,3], chromium [4], zirconium [5] and niobium [6] to form multi-component compound films. Among this kind of films, the (Ti,Al)N film is characterized by its high hardness (about 35 GPa) and good oxidation resistance under high temperature (800 °C), remarkably higher than those of the TiN film (22 GPa and 600°C). Such outstanding properties ensure it one of the most commonly used cutting tool films nowadays. Meanwhile some investigations claim that hardness enhancement can also be attained in films prepared by introducing nonmetals such as carbon [7] or boron [8] into the TiN film. But improvement of oxidation resistance was not accomplished in these films; Some of them even show a drop of oxidation resistance property, e.g., Ti(C,N) (400 °C) [2]. When cutting tools are used in high-speed cutting or dry machining, their tips will reach a temperature as high as 1000 °C. None of films at present can stand so high a temperature. Therefore how to further improve superhard films' oxidation resistance is still one of the most important problems left to be resolved. If the introduction of oxygen atoms will not weaken the base material, (Ti,Al)(O,N) film prepared by adding oxygen atoms into the (Ti,Al)N film might be a good choice because the formation of oxides can inhibit further oxidization [2,9].

In this paper, a series of (Ti,Al)(O,N) films different in oxygen content were synthesized and the influences of oxygen partial pressure on films' chemical composition, microstructure and mechanical property are also studied.

2. Experimental procedure

Films were deposited in an ANELVA SPC-350 magnetron sputtering system. The Ti–Al mosaic target was made up of a titanium target (99.99%) and 12 aluminum bars (99.99%). 12 holes with a same diameter of 6mm were drilled at high sputtering rate area of the target and then aluminum bars are

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inserted in these holes. The Ti–Al target was placed on the radio frequency (rf) cathode. Polished high-speed steel substrates were ultrasonically cleaned in acetone and alcohol before being mounted on the substrate holder in the chamber. After the base pressure arrived at 3.0×10^{-4} Pa, Ar, N_2 and O_2 were introduced into the chamber through three separate gas manifolds. In the mixture gas, Ar and N_2 partial pressures were kept at 2.0×10^{-1} Pa and 2.0×10^{-2} Pa, respectively. Different O_2 partial pressure (from 0 to 0.8×10^{-2} Pa) were selected and thus a series of (Ti, Al)(O,N) films different in oxygen content were deposited without deliberate heating applied to the substrates. To each sample, the sputtering power was kept at 200 W and the deposition time 1.5 h during deposition.

Chemical composition of these films was determined by energy dispersive X-ray spectroscopy (EDS) using an EDAX DX-4 energy dispersive analyzer. Their phase formation was characterized by X-ray diffraction (XRD) in a Rigaku Dmax-rC diffractometer with Cu Kα radiation. A JEM-200CX transmission electron microscope (TEM), a LEO-1530 VP scanning electron microscope (SEM) and a Multimode Nanoscope IIIa atomic force microscope (AFM) were employed to observe the microstructure and surface topography. The hardness and elastic modulus of films were measured on a Fischerscope HV100 nanoindenter.

3. Experimental results and discussion

EDS analysis results are listed in Table 1, which indicates that oxygen content in films increases gradually and nitrogen content decreases correspondingly with an increasing O_2 partial pressure. But the ratio, (Ti+Al)/(O+N) keeps close to a stoichiometric constant of 1. In addition, titanium content in the films stays almost unchanged but aluminum content increases slightly after the addition of oxygen atoms. As a result, the atomic ratio of Ti to Al gradually inclines to 1.

Fig. 1 displays the XRD patterns of (Ti,Al)(O,N) films. After oxygen atoms were introduced into the (Ti,Al)N film, (Ti,Al)(O,N) films remain the NaCl structure, the same as the (Ti,Al)N film. But they present a strong (200) preferred orientation of texture.

In Fig. 2, the AFM image of the (Ti,Al)(O,N) film reveals that its growing surface is compact and characterized with a cellular-like growing pattern. Its roughness fluctuates in a range of about 15 nm.

As shown in Fig. 3, the SEM image demonstrates clearly that refined and concentrated columnar crystals grow perpendicularly to the (Ti,Al)(O,N) film's surface. These crystals penetrate almost the whole 2.6 ìm range of the film.

Fig. 4 illustrates the TEM images and selected area electron diffraction pattern (SAED) of the (Ti,Al)(O,N) film. Images indicate

Table 1
Composition of (Ti,Al)(O,N) films

No.	1#	2#	3#	4#
P_{O_2} (10^{-2} Pa)	0	0.2	0.5	0.8
O (at.%)	0	7.5	20.2	23.6
N (at.%)	53.1	44.3	32.3	27.1
Ti (at.%)	27.3	29.4	26.6	26.0
Al (at.%)	19.6	18.8	20.9	23.3
(Ti+Al):(O+N)	0.88	0.93	0.91	0.97

$P_{Ar}=2.0\times10^{-1}$ Pa; $P_{N_2}=2.0\times10^{-2}$ Pa.

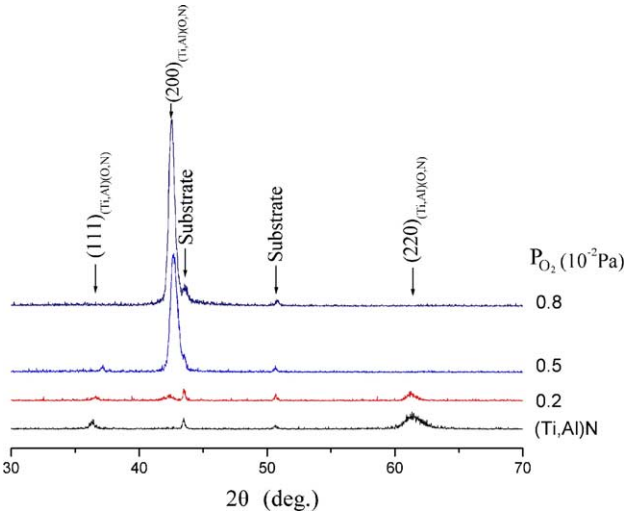

Fig. 1. XRD patterns of (Ti,Al)(O,N) films.

that a fine and dense crystal structure with the grain size of about 10 nm forms in the film; the SAED pattern is indexed as a NaCl structure according to the occurring diffraction rings, which approves that the (Ti,Al)(O,N) film remains in the same structure as the (Ti,Al)N film, matching the XRD analysis results.

As the composition and microstructure analysis results discussed above, it can be concluded that the multi-component (Ti,Al)(O,N) films maintain the same NaCl structure as the (Ti,Al)N film when oxygen atoms are introduced to replace part of nitrogen atoms. Refined and concentrated columnar crystals grow along a (200) preferred orientation in these films.

In order to get the reliable values of (Ti,Al)(O,N) films' mechanical properties, a two-step penetration method [10] was used. The first step is to employ a load large enough, e.g., 50 mN as used in this experiment, to attain curves of loading hardness, HU (universal hardness [11]) vs. penetration load. Fig. 5 illustrates such curves, in which platforms with high hardness values can be found to each sample. The width of each platform varies a little, indicating that the addition of oxygen atoms does not remarkably change films' deposition rate. If the penetration load is selected in the range of the platforms' width, from 4 mN to about 25 mN, the deformation area under the indenter tip is within the films and does not spread

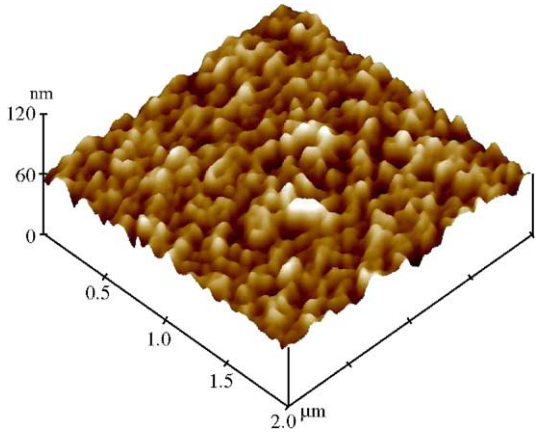

Fig. 2. AFM image of the (Ti,Al)(O,N) film's surface topography (sample 4#).