Microstructure and properties of (Ti, Al) N coatings on WC-Co cemented carbide

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Abstract. (Ti, Al)N films were grown on WC-Co cemented carbides by R.F. reactive sputtering using Ti/Al composite target. The crystalline structure, morphology and composition of (Ti, Al)N coatings were investigated by X-ray diffraction (XRD), optical microscope and X-ray energy dispersive spectroscope (EDS), respectively. The mechanical properties of (Ti, Al)N coatings with the variable Al content were investigated by applying nanoindentation. With the increase of the Al content, the crystal structure of (Ti, Al)N films changed from fcc to hexagonal structure. When the ratio of Ti to Al in (Ti, Al)N coatings was approximately 4:1, and the N content was 40.67 %, the nano-hardness of (Ti, Al)N coating was highly up to 28 GPa. By adjusting the Al content, the lowest value of friction coefficients was 0.1397. Keywords: (Ti, Al)N; coating; nano-hardness; friction coefficient

1. Introduction

Ceramic hard coatings are commonly applied as protective materials on tools and mechanical components to enhance their performances in combination with extension of lifetime and decrease of wear. Transition metal nitride coatings are commonly used as protective coatings because of their high hardness, wear resistance, and chemical stability [1–7]. Among these materials, binary nitrides such as TiN are the most widely studied [8]. TiN films have wide ranging applications from erosion-resistant coatings for cutting tools [9,10] to diffusion barriers used in the construction of semiconductors devices [11,12]. One disadvantage of TiN in some applications is that it oxidizes easily in air at above 500°C. Recently, ternary nitride(Ti, Al)N was developed to provide better performance over TiN since the addition of Al in the form of solid solution increased hardness, decreased coefficient of friction and improved the oxidation resistance of the coating and cutting performance [13,14,15].

The purpose of this paper is to investigate the phase structure, morphology, composition, and the mechanical properties of the (Ti, Al)N films prepared by R.F. reactive sputtering, using composite
targets, as a function of the ratio Ti to Al of the targets.

2. Experiment

WC-Co cemented carbide was used as the substrate whose surface was polished with SiC micro powder and diamond grinding cream. Then the substrate was ultrasonically cleaned in acetone, ethanol and deionized water in turn for two minutes per step. Finally, the substrates were dried with the high pure nitrogen.

(Ti, Al)N films were prepared by R.F. reactive sputtering using a series of Ti/Al composite targets (diameter of 118 mm, thickness of 5 mm and purity of 99.99%). The ratio of Ti to Al of the targets are 10:0, 9:1, 8:2, 7:3, 6:4 and 5:5, which were marked T1,T2,T3,T4,T5,T6, respectively.

| Material | (Ti, Al)N |
|----------|-----------|
| Target   | Ti/Al     |
| Substrate| WC-Co cemented |
| Substrate temperature | 200°C |
| Power    | 350W      |
| Gas contents | Ar:N₂=1:2 |
| Sputtering pressure | 0.6Pa |
| Deposition time   | 180min   |
| Base pressure     | 5.0×10⁻³Pa |

Prior to the deposition, the chamber evacuated to a base pressure of 5×10⁻³Pa, substrate heated to 200°C, then high purity argon was introduced into the chamber so that the pressure could be 0.4 Pa to clean the target and the chamber for 20 minutes by argon plasma. After cleaning, high purity argon (99.999%) and nitrogen (99.999%) gases were introduced. The (Ti, Al)N film was deposited for 180 minutes at a working pressure of 0.6Pa and the power of 350W. The deposition parameters are listed in Table 1. The crystalline structure, morphology and composition of (Ti, Al)N coatings were investigated by X-ray diffraction (XRD), optical microscope and X-ray energy dispersive spectrooscope (EDS) using Cu Kα radiation at a condition of 40 kV and 100 mA. The nano-hardness and Young's modulus of the samples were determined by nanoindentor.

3. Results and discussion

3.1. Structure and surface morphology

X-ray diffraction investigations of coatings deposited onto cemented carbides using various targets are shown in Fig.1. Figure 1 shows that the (Ti, Al)N film was deposited with the TiN face-centered cubic (fcc) structure and AlN hexagonal structure. (111) plane is the close-packed plane of TiN with fcc structure. Growth along the close-packed plane has the lowest surface energy. So fcc structure was the main phase of the (Ti, Al)N film using T1 target. The introduction of the Al changes the crystal planes and also causes lattice distortion that induces distortion energy changing the preferred
orientation. With the increase of the Al content, (111) orientation of (Ti, Al)N films is gradually weakened, while the (200) orientation have been enhanced [16, 17]. Hexagonal structure (002) appears using T3 target. With the Al content increasing, the (002) diffraction intensity was gradually increased, and (Ti, Al)N film structure changed from fcc to hexagonal structure, consistent with Ikeda and Satoh findings [18].

![Fig 1. XRD patterns of the (Ti, Al) N films deposited with different targets](image)

The orientation of the deposited film is the result of the interfacial energy, the strain energy and the surface dominant factors affect energy. When the Al content of target is low, fcc (111) plane of preferential growth and the film orientation at this time is dominated by the interfacial energy between the film and the substrate. (111) plane parallels to the substrates surface to reduce surface energy of the film. The higher the Al content is, the more serious the fcc phase lattice distortion is and the higher strain energy that produces. When the strain energy reaches a certain value, the lattice structure will shift to reduce the strain energy. Hexagonal phase appears to correspond to the transition point by using T4 target.

The morphology of the film has been observed by Metallurgical Microscope. Figure 2 presents the surface topography of the sample. There is no obvious defect on relatively flat surface of film from Figure A. The adhesion between the film and the substrate at the part edge of the sample is not good from Figure B which possibly is caused by defects and stress of the boundary.

### 3.2. Element composition

Elements concentration (at. %) in (Ti, Al)N coatings as a function of the Al content of Ti/Al target taken by using EDS analysis is shown in Fig.3. The Al content increased slightly from 0 to 48 at. %; the Ti content decreased from 53 to 18 at. %; the N content gradually decreased from 47 to 33 at. %. The Al to Ti atom ratio in (Ti, Al)N films quickly increased from 0 to 2.7 with using T1 to T6 target. The Al content of the target increased from 0 to 50 at. %; meanwhile, the Ti content of the targets decreased from 100 to 50 at. %. Therefore the Al content of the (Ti, Al)N films gradually
increased, otherwise the Ti content slowly decreased. While the proportion of Al and Ti of (Ti, Al)N film was not the same with the target. The Al content of (Ti, Al)N film was much higher than one of the target; on the contrary, the Ti was lower. According to the usual sputtering theory, the sputtering coefficient of Al is greater than Ti at the same condition. When the energy of the argon ions was 500eV, the sputtering coefficient ratio of the Al to Ti is 2.01 [19].

In reactive sputtering, since the partial pressure of the reactive gas varied, it made the respective components of the composite target forming compounds. The formation heat of TiN (~305.6 kJ/mol) is lower than that of AlN (-241 kJ/mol) [20]. The N ions bombarded easily Ti on target surface with the low formation heat to form a thin nitride layer. Usually metallic state sputtering is greater than the non-metallic state sputtering. Therefore, in low reactive nitrogen, Ti and Al atoms sputtering from targets reacting with nitrogen generated (Ti, Al)N film. Another part cannot participate in the reaction existed in the form of metal amorphous of the (Ti, Al)N film.

3.3. Mechanical properties
The nano-hardness and Young’s modulus of the (Ti, Al)N coatings deposited onto the WC-Co cemented substrates with different targets are shown in Fig. 4. The mechanical properties of (Ti, Al)N films were analyzed by Nanoindentation which is a very powerful technique [21-26]. In order to minimize the substrate effects, the maximum indentation force was limited to 5000μN so that the
indentation depth was less than 10% of the film thickness. Three indentations at different places on the samples surface were performed and the values averaged were assigned as the nano-hardness and Young's modulus of the (Ti, Al)N films.

![Graph](image)

**Fig 4.** (a)Nano-hardness, Young’s modulus, (b) H/E of (Ti, Al)N coatings as a function of Al fraction x of Ti/Al target

The maximum value of the nano-hardness occurred at using T1 target while the modulus at using T3 target. The maximum was approximately 28 GPa and 297 GPa, respectively. They both increased, firstly. With the further increased of the Al content of the targets, the nano-hardness values decreased. The value of Young’s modulus was fluctuation, while also decreased in the whole. Vlasveld et al. [27] reported the highest nano-hardness of the (Ti, Al)N film was 34 Gpa using partially filtered arc technique. Zywitzki et al. [28] reported the highest Nano-hardness of (Ti, Al)N film was 38 Gpa deposited by reactive pulsed magnetron sputtering.

The hardness of (Ti, Al)N films strongly depends on the Al content. This may be ascribed to a solid-solution strengthening mechanism. Since the Al atomic radius ($R_{Al} = 1.43$ Å) is smaller than the Ti atomic radius ($R_{Ti} = 1.46$ Å), it is possible that the Al atom goes entirely into the fcc TiN cell, substituting part the Ti atom at a face-centered position, forming fcc (Ti, Al)N phase. With the Al content increasing of (Ti, Al)N film, the vibration of each atom in the fcc cell changes by atom force. The position of each atom vibrating inwardly offset. That eventually leads to a change of the lattice constant to reduce the energy of the system. The more the Al content is, the smaller the lattice constant is. As described above, since the introduction of the Al atoms, the crystal structure was distorted, which resulted in the increase of the hardness of the film.

The nano-hardness value of Nitrides is relative directly with the key and the atom space, but also by the influence of the valence electron density in the unit cell (VEC) [29]. The VEC value is related to the composition of the coating and the vacancy concentration [30]. With the increase of the Al content in the coating, more and more Ti ions ($Ti^{4+}$) were replaced by Al ions ($Al^{3+}$). The value of VEC tended to decrease, which caused a higher hardness value. When the Al content exceeded a certain
value, the hardness of the (Ti, Al)N coatings reduced for the crystal gradually disappearing and Al supersaturating.

The N content in (Ti, Al)N films was gradually decreased from 47% to 33%. In low nitrogen, the part Ti and Al atoms sputtering from targets cannot participate in the reaction existed in (Ti, Al)N film in the form of amorphous metal, which reduced the nano-hardness of the film. All these factors above could explain the reason of the hardness of (Ti, Al)N film changing.

![Graph showing friction coefficient of (Ti, Al)N coatings as a function of Al fraction x of Ti/Al target.](image)

Fig.5 The friction coefficient of (Ti, Al) N coatings as a function of Al fraction x of Ti/Al target

The friction coefficient of (Ti, Al)N films deposited at various targets was illustrated in Fig.6. The lowest friction coefficient was 0.2011 at using T1 target. As introduction of the Al, friction coefficient decreased quickly to 0.1463. In other words, the friction coefficient of (Ti, Al)N was much lower than that of TiN. With further increase of the Al content, friction coefficient increased again. The reason of lower friction coefficient was probably ascribed to the better surface morphology of the (Ti, Al)N films. Wu et al. [31] reported the friction coefficient of the (Ti, Al)N films ranged from 0.2 to 0.3 by using unbalanced-magnetron sputter technique.

4. Conclusion
In this paper, the (Ti, Al)N films were deposited by R.F. reactive sputtering using Ti/Al composition target. The basic characteristics of the (Ti, Al)N films deposited under different targets were investigated systematically. With the increase of the Al content of the target, the crystal structure of the films changed from fcc to hexagonal structure. The Al content had great influence on the mechanical properties of the (Ti, Al)N films, such as hardness, friction coefficient. When the ratio of Ti and Al of the (Ti, Al)N coating was approximately 4:1 and the N content was 40.67 %, the nano-hardness of the (Ti, Al)N coating was highest. By adjusting the Al content, the highest values of the nano-hardness and friction coefficient could be 28 GPa and 0.1397, respectively.

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