PROPERTIES OF (Ti, Al)N FILM PREPARED BY PVD CATHODIC ARC

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Abstract

(Ti, Al)N film is a type of metal alloy film which can be prepared by cathodic arc physical vapor deposition using a compound target or 2 single-metal targets. It is a hard thin film which significantly increases tool lifetime. In this work, 2 types of Ti-Al compound targets (low and high sintering temperature targets) were used. Cold tool steel (SKD11) was used as a substrate for the film coating. The deposition bias voltage, bias arc current, and deposition time were set at 100V, 70A, and 90 min, respectively. The N_2 gas pressure was varied from 1, 1.5, and 2 Pa. After coating, the film was characterized for phase structure, thickness, adhesion, and hardness. It was found that all the coated films showed the same phase structure of $Ti_{0.5}Al_{0.5}N$ and $TiN_{0.5}$. However, the films deposited from a high temperature target perform with higher adhesion strength than that of the films deposited from a low temperature target.

Keywords: TiAlN film, PVD, phase structure, mechanical properties

Introduction

PVD hard coating technology is commonly applied to various kinds of steel cutting, tool forming, molds and dies, etc. It has been an essential task in developing various advanced surface modified materials for many engineering applications. Among PVD coating technologies, cathodic arc plasma deposition is a well-developed process which provides a higher deposition rate and good mechanical properties of film. There are various new coating materials that have been produced by the PVD method such as (Ti, Al)N (Kimura *et al.*, 1999; Ohnuma *et al.*, 2004; Hsu *et al.*, 2008), (Ti, Zr)N (Randhawa *et al.*, 1988), and (Ti, Si)N (Wo *et al.*, 2010). (Ti, Al)N film performs with high hardness and a resistance to oxidation at high temperature. Several works have reported the effects of the processes' parameters on the properties of (Ti, Al)N film. It was reported that the

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$Ti_{1-x}Al_xN$ films' hardness could be increased to 3200 HV by adding the aluminum content up to 0.6, but the hardness decreased abruptly when the aluminum content is higher (Kimura *et al*., 1999). Some other works reported the effects of targets on the microstructures and adhesion properties of synthesized films which had been coated by using different types of Ti-Al targets (Kimura *et al*., 2004; Larpkiattaworn *et al*., 2009). Moreover, the dependence of the N_2 gas pressure on the surface roughness of (Ti, Al)N films was also studied (Chenga *et al*., 2000; Bujak *et al*., 2004; Chokwatvikul *et al*., 2010). The lower N_2 gas pressure resulted in high surface roughness which is due to the large number of macroparticles on the film surface. In this study, 2 types of Ti-Al sintered alloy were used as cathode targets at various pressures of N_2 reactive gas to produce (Ti, Al)N films, and then the mechanical properties and morphology of the films were characterized.

Materials and Methods

The commercial SKD11 (1.40-1.60%C, ≤0.40%Si, ≤0.60%Mn, 0.030%P, 0.030%S, 11.0-13.0%Cr, 0.80-1.20%Mo, and 0.20-0.50%V) (Japanese Standards Association, 2002) with an approximate hardness of 60 HRC was used as a coating substrate. The substrate was prepared in the size of 32 mm in diameter and 5 mm in thickness, and then it was mirror-polished and cleaned in an ultrasonic bath filled with trichloroethylene. Two types of sintered Ti-Al alloy (at low and high sintering temperatures) with a Ti:Al atomic ratio of 1:1 which were made by the Thailand Institute of Scientific and Technological Research were used as coating targets.

Coating was processed in PVD machines (NS-1, Nanoshield PVD Hard Coating, Samutprakarn, Thailand). Samples were loaded into the vacuum chamber and after evacuation, when the pressure had dropped down to the high vacuum range, the samples were cleaned with an Ar glow discharge. Then the samples were cleaned further with titanium plasma from NanoShield metal plasma sources, and the interface layer was deposited with the same metal plasma sources for better adhesion. The TiAlN coating was synthesized by using the substrate bias voltage and arc current at 100V and 70 A, respectively. The N_2 gas pressure in the coating chamber was varied at 1, 1.5, and 2 Pa, while the coating time was fixed at 90 min for each N_2 pressure.

After deposition, the films were characterized by using an X-ray diffractometer (XRD: D8, Bruker Corp., Billerica, Mass, USA) with the Cu target Kα radiation at 40 kV, 30 mA, the low incident angle of 1^o, and the scanning angular (2θ) ranging from 30^o to 90^o at the rate of 2^o/min, to identify the films' phase structure. The Calotest (CSM Instruments SA, Peseux, Switzerland) method was used to determine the films' thicknesses. Coating adhesion was initially evaluated by the Rockwell C indentation test (VDI-3198 German industrial standard–Verein Deutscher Ingenieure, (2008)) with a load of 150 kg, while the indentation damage was examined under an optical microscope (Olympus Corporation, Tokyo, Japan and LOMO, St. Petersburg, Russia). The surface roughness of the films was measured using a surface roughness analyzer (Diavite DH-7, Hahn & Kolb Werkzeuge GmbH, Stuttgart, Germany). Field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6340F, JEOL Ltd., Tokyo, Japan) was utilized to observe surface morphologies of the films. The hardness and adhesion strength of the films were measured further with a nano-indentation tester (NHT: Berkovich, CSM Instruments SA, Perseux, Switzerland) and a Revetest Scratch Tester (RST:CSM Instruments SA), respectively. Scratches were observed under an optical microscope to determine the critical load (Lc)

Results and Discussion

The 2 sintered Ti-Al targets (at low and high sintering temperatures) were identified for the phase components before the coating process. Figure 1 shows the XRD patterns of the low and high temperature sintered targets. The XRD spectra of the low temperature target consist of Ti, Al, Ti_3Al, and TiAl, while the spectra of the high temperature target consist of TiAl as the major peak and Ti as the small peak. The films produced from both targets were measured for the thickness and surface roughness as shown in Figure 2. The films' thicknesses are approximately in the range of 2.3-3.5 µm which included the top and Ti/TiN interlayer (Figure 3); the interlayer is very thin, around 0.4 µm for all samples. It was found that a films' thicknesses and roughnesses are independent on the target for N_2 pressure 1 and 1.5 Pa, but are dependent on the target at 2 Pa N_2. A film's surface prepared at N_2 pressure 1.5 Pa is smoother than the surfaces of those films prepared at the other pressures for both targets.

All coatings show an adhesion strength at HF1 which is the best adhesion according to German industrial standard VDI-3198. The film hardness of most samples is around 36-41 GPa. The samples coated from the low temperature target at 1.5 Pa N_2 have the highest hardness around 47.8 GPa which is known as superhard hardness (exceeding 40 GPa) as shown in the results in Figure 4. In contrast, the good scratch resistance with low friction is obtained on the films coated from the high temperature target at 1.5 Pa N_2 (Table 1).

In order to explain these different properties of the films, the films' structure and

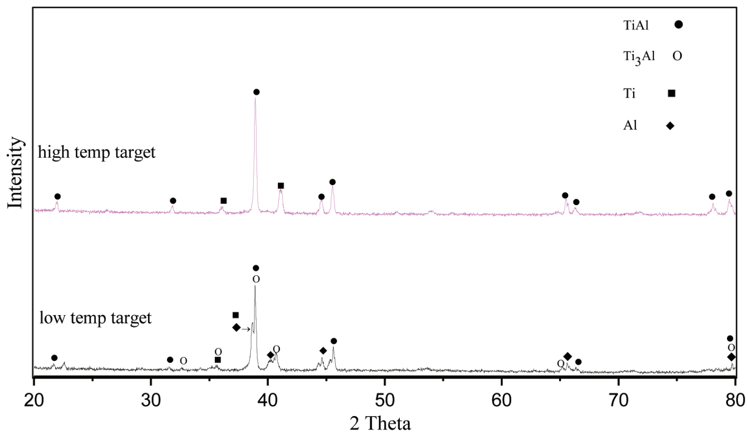

Figure 1. XRD patterns of Ti-Al targets

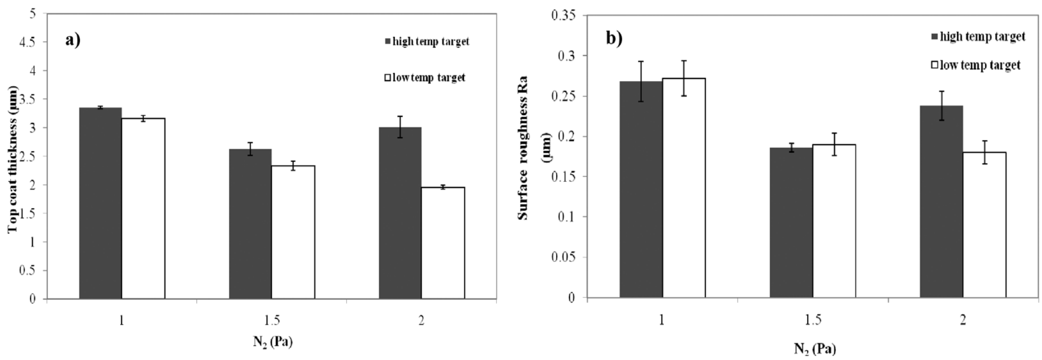

Figure 2. The film thickness (a) and surface roughness (b) of samples coated by PVD using different targets and N_2 pressure.

surface morphology were investigated. Figure 5. shows the XRD patterns of films deposited on an SKD11 substrate coated using low and high temperature targets at a different N_2 pressure. These XRD peaks identify the same diffraction pattern of phases $Ti_{0.5}Al_{0.5}N$ and $TiN_{0.5}$ for all films. This can be explained by the phase structure of the films being independent on the phase components of the Ti-Al target [7] and the reactive N_2 pressure of 1-2 Pa.

The FE-SEM images in Figure 6 show macroparticles and voids dispersed over the coated surface for all samples. However, the size and density of the macroparticles and voids are dependent on the target and N_2 pressure. The films deposited using N_2 pressure 1.5 Pa have a smaller size and less density of macroparticles and voids than those films deposited at other pressures from both targets. This can be explained by the optimum nitrogen pressure for depositing good films being at 1.5 Pa. A too low N_2 pressure causes high collision energy of the nitrogen atoms and metal ions resulting in more macroparticles being formed on the surface (Bujak *et al.*, 2004). At a high N_2 concentration, nitrogen atoms may diffuse and form nitrogen gas as voids in the films. Furthermore, when comparing the macroparticles of the films prepared from the low and high temperature targets at 1.5 Pa N_2 pressure, the macroparticles on the films prepared from the low temperature target present a smaller size of particles resulting, therefore, in the highest hardness but with less density of particles on the films

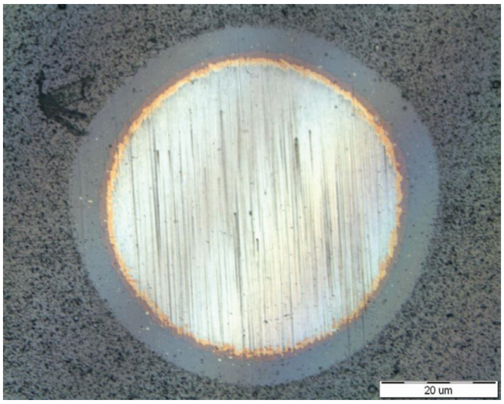

Figure 3. Optical micrographs of film thickness from calotest sample

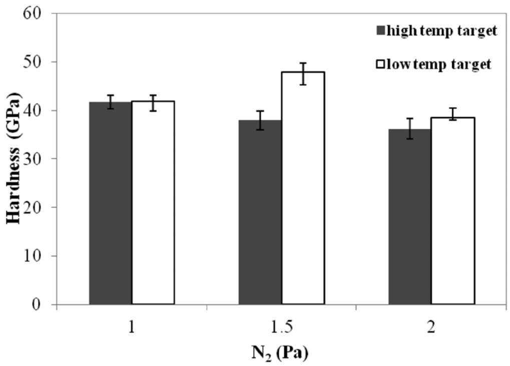

Figure 4. Nanoindentation hardness of the films coated by PVD using different targets and N_2 pressure

Table 1. Friction coefficient and scratch load of the films coated by PVD using different targets and N_2 pressure

Target	N_2	Friction coefficient	Scratch load First - Lc 1 (N)	Scratch load Full - Lc 2 (N)
low-temp Sintered target	1	μ = 0.20	16.84±13.69	> 150
	1.5	μ = 0.23	8.80±1.77	> 150
	2	μ = 0.20	14.20±1.76	128.43±3.95
high-temp Sintered target	1	μ = 0.20	9.81±0.68	124.17±2.92
	1.5	μ = 0.10	72.85±10.55	> 150
	2	μ = 0.10	15.92±0.06	113.77±10.65

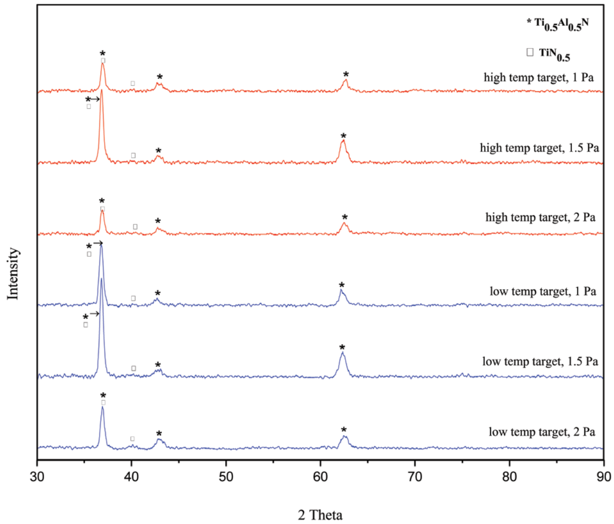

Figure 5. XRD patterns of films coated by PVD using low and high temperature targets at different N_2 pressure

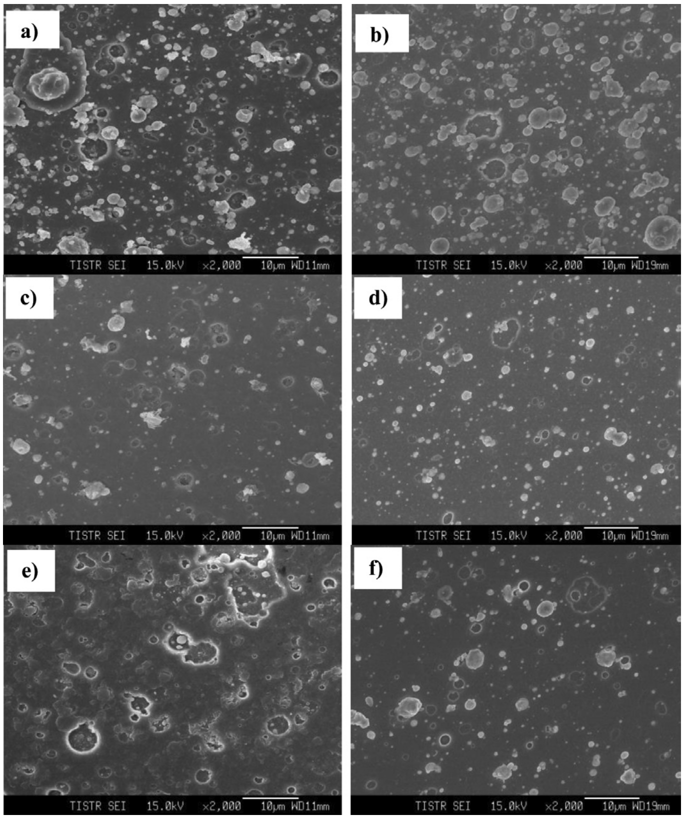

Figure 6. FE-SEM image of coated surface deposited using (a) high temperature target; N_2 = 1 Pa (b) low temperature target; N_2 = 1 Pa (c) high temperature target; N_2 = 1.5 Pa (d) low temperature target; N_2 = 1.5 Pa (e) high temperature target; N_2 = 2 Pa (f) low temperature target; N_2 = 2 Pa

prepared from the high temperature target, which causes lower friction and better scratch resistance.

Conclusions

The 2 types of Ti-Al targets are composed of different phase structures; the compositions of the Ti, Al, Ti_3Al, and TiAl phases were formed in the low temperature target while only the TiAl, and Ti phases were formed in the high temperature target. However, using a target with these different phase components under the deposition condition of N_2 pressure between 1-2 Pa produces the same structure of $Ti_{0.5}Al_{0.5}N$ and $TiN_{0.5}$ films. The best property of films was produced from the films deposited at 1.5 Pa N_2 pressure by using the high temperature target. The films exhibit high hardness, low friction coefficient, and high scratch resistance.

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References

Bujak, J., Walkowicz, J., and Kusinski, J. (2004). Influence of the nitrogen pressure on the structure and properties of (Ti, Al)N coatings deposited by cathodic vacuum arc PVD process. Surf. Coat. Tech., 180–181:150–157.

Chenga, Y.H., Tay, B.K., Lau, S.P., Shi, X., and Chua, H.C. (2000). Deposition of (Ti, Al)N films by filtered cathodic vacuum arc. Thin Solid Films, 379:76–82.

Chokwatvikul, C., Surinphong, S., Busabok, C., Termsuksawadand, P., and Larpkiattaworn, S. (2010). Characterization of (Ti, Al)N thin film coated by PVD cathodic arc using TiAl target. Adv. Materials Res., 93-94:276-279.

Hsu, C-H., Lee, C-C., and Ho, W-Y. (2008). Filter effects on the wear and corrosion behaviors of arc deposited (Ti, Al)N coatings for application on cold-work tool steel. Thin Solid Films, 516: 4826–4832.

Japanese Standards Association. JIS Hand Book. (2002). Ferrous Materials and Metallurgy. Japanese Standards Association, Tokyo, Japan, 107-8440.

Kimura, A., Hasegawa, H., Yamada, K., and Suzuki, T. (1999). Effects of Al content on hardness, lattice parameter and microstructure of $Ti_{1-x}Al_xN$ films. Surf. Coat. Tech., 120-121:438-441.

Kimura, A., Murakami, T., Yamada, K., and Suzuki, T. (2004). Hot-pressed Ti-Al targets for synthesizing $Ti_{1-x}Al_x$ N films by the arc ion plating method. Thin Solid Films, 382:101-105.

Larpkiattaworn, S., lkeuchi, J., and Eamchotchawalit, C. (2009). Comparison of properties of titanium aluminum nitride film produced by using two different types of Ti-Al target. Surf. Interface Anal., 41:794-798.

Ohnuma, H., Nihira, N., Mitsuo, A., Toyoda, K., Kubota, K., and Aizawa, T. (2004). Effect of aluminum concentration on friction and wear properties of titanium aluminum nitride films. Surf. Coat. Tech., 177–178:623–626.

Randhawa, H., Johnson, P.C., and Cunningham, R.. (1988). Deposition and characterization of ternary nitrides. J. Vac. Sci. Technol., 6:2136-2139.

Verein Deutscher Ingenieure. (2008). VDI 3198. Coating (CVD, PVD) of Cold Forging Tools. Verein Deutscher Ingenieure, Dusseldorf, Germany, 8p.

Wo, P.C., Munroe, P.R., Zhou, Z.F., Li, K.Y., and Xie, Z.H. (2010). Effects of TiN sublayers on the response of TiSiN nanocomposite coatings to nanoidentation and scratching contacts. Mater. Sci. Eng. A., 527:4447–4457.