REVIEW OF PHYSICAL VAPOUR DEPOSITION (PVD) TECHNIQUES FOR HARD COATING

A. Mubarak¹ E. Hamzah¹* M. R. M. Toff²

¹Department of Materials Engineering Faculty of Mechanical Engineering Universiti Teknologi Malaysia 81310 Skudai, Johor, MALAYSIA

²Advanced Materials Research Center (AMREC) SIRIM Berhad, Malaysia

ABSTRACT

This paper is a review on the status of hard coating of various physical vapour deposition (PVD) techniques and compare their properties. The use of hard and wear resistant PVD coatings on cutting tools is now widespread in global manufacturing for reducing production cost and improving productivity, all of which are essential if industry is to remain economically competitive. The review includes the drawbacks of cathodic arc evaporation (CAE) and conventional magnetron sputtering processes and in this context their improvements. PVD techniques based on sputtering and cathodic arc methods are widely used to deposit hard coating for various cutting tools and many others. From the study, it was concluded that the CAE and radio frequency (RF) magnetron sputtering are the most widely used techniques and appropriate methods for thin film coating. Each technique has its own limitations and process parameters vary with the selection of PVD techniques. These techniques were further modified where uniform and dense coatings with improved adhesion can be achieved without the emission of macrodroplets from plasma streams.

Keywords: Hard coating, cathodic arc, magnetron sputtering, deposition parameters

1.0 INTRODUCTION

The basic PVD processes fall into two general categories: sputtering and evaporation. The application of PVD techniques ranges over a wide variety of applications from decorative, to high temperature superconducting films. The thickness of the deposits can vary from angstroms to millimeters. Very high deposition rates ($25\mu m/sec$) have been achieved with the advent of electron beam heated sources. A very large number of inorganic materials—metals, alloys,

¹ *Corresponding author: Tel.: +607 5534562; Fax: +607 5566159, E-mail: <u>esah@fkm.utm.my</u>

compounds, and mixtures—as well as some organic materials can be deposited using PVD technologies.

Traditionally, the term hard coatings refer to the property of high hardness in the mechanical sense with good tribological properties. With the development of modern technology in the areas of optical, optoelectronic and related defense applications, the definition of the term hard coatings can be extended. Thus, a system, which operates satisfactorily, in a given environment, can be said to be hard with respect to that environment [1].

In recent years studies of PVD hard coating with some modified deposition techniques for cutting tools have attracted a lot of research interest because of their wide range of applications both in industry and in research. The flexibility of coating processes especially of the PVD method well supported by the superior and controllable properties of modern coatings are responsible for the almost exclusive worldwide application of coated tools. The superior machining performance of advanced surface coated mechanical parts is determined by an ability to maintain high hardness and resistance to oxidation at elevated temperatures [2]. Over the years tool lifetime has dramatically improved due to the development of hard nitride coatings such as titanium nitride (TiN), titanium aluminum nitride (TiAlN), titanium carbide (TiC) and etc.

2.0 PHYSICAL VAPOUR DEPOSITION (PVD)

In physical vapor deposition (PVD) processes, the coating is deposited in vacuum by condensation from a flux of neutral or ionized atoms of metals. Several PVD techniques are available for deposition of hard coatings. Among them, cathodic arc vapor (plasma or arc ion plating) deposition [3-18], magnetron sputtering (or sputter ion plating) [19-32], and combined magnetron and arc processes [33-39] are the most widely used techniques to deposit various hard coatings. These PVD processes differ with respect to the type of evaporation of the metallic components and the plasma conditions employed during the deposition process. The transition of the metallic component (to be deposited) from a solid to a vapor phase (in which metal atoms are ionized in different ways) may be performed by heating of an evaporation source (as in cathodic arc) or by sputtering of a target (as in magnetron sputtering). Cathodic arc and magnetron sputtering techniques allow evaporation of metals with different melting points such as Ti and Al from a Ti–Al alloy cathode/target. The PVD arc evaporation process employs higher energy input than the PVD sputtering process.

In the case of arc evaporation, a small limited cathodic area is evaporated with a very high-energy arc that quickly moves over a spot on the metal surface to be evaporated. The plasma generated consists of highly ionized metal vapor [40]. In the case of sputtering, atoms are ejected mechanically from a target by the impact of ions or energetic neutral atoms. A schematic diagram of RF magnetron sputtering can be seen in Figure 1.

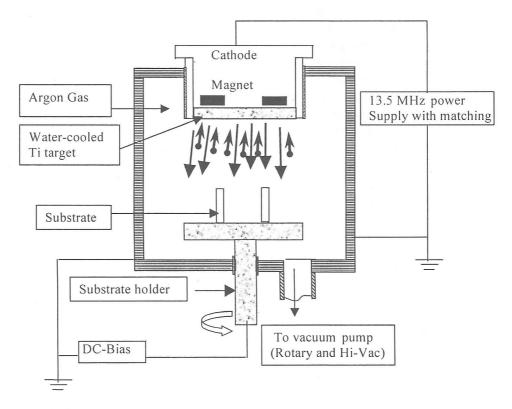


Figure 1: Schematic diagram of radio frequency planar magnetron [45]

Table 1 gives an overview of the typical parameters and the quantity of ionized target atoms of some PVD processes. As may be noted from Table 1, the cathodic arc process generates the highest quantity of ionized target atoms, 50–100%, followed by anodic arc ion plating in the range of 5-40%. The quantity of ionized atoms is rather low for magnetron sputtering. The significance of metal ionization rates can be described as follows: The energy during the deposition of coating depends on the atomic masses of the participating ionized atoms, which in turn controls momentum transfer. The total atomic mass of participating ions is highest in the case of the cathodic arc deposition process due to the ability to evaporate large percentage of metallic ions from cathodes (highest ionization rate). This leads to high deposition energy, and a dense coating. In addition, the ion plating effectiveness (defined as the potential to coat the substrate surface in micro scale) of the cathodic arc deposition technique is higher than that of conventional magnetron sputter techniques. Cathodic arc deposited coatings also exhibit a higher level of adhesion to the substrate due to the effect of ion bombardment or ion etching. During bombardment, high-energy metal ions generated from the cathode bombard the substrate surface kept at a high negative bias of 500-2000 V.

Table 1: Typical parameters and quantity of target/cathode ions/atoms of different PVD processes [40]

Parameters	Processes			
	Magnetron sputtering	Anodic arc ion plating	Electron beam ion plating	Cathodic arc ion plating
Evaporation tool	Sputter effect	Electron beam	Electron beam	Thermal arc
Phase transformation	Solid-vapor	Solid-vapor	Liquid-vapor	Solid-vapor
Geometry of target/cathode	Flexible	Limited	Limited	Flexible
Quantity of ionized target atoms (%)	1- 5	5- 40	<1	50-100
Additional ionization	Aimed	Unusual	Aimed	Not necessary
Inert gases necessary	Yes	No	Variable	No
Reactive deposition possible	Yes	Yes	Yes	Yes

In addition to cleaning and heating the substrate, energetic metal ions during ion bombardment knock off some metal atoms from within the substrate or may penetrate the substrate lattice to angstrom levels. This leads to defects and roughness on the substrate at an atomic level, and the atomic level of roughness is believed to be responsible for the improved adhesion of the coating.

Target poisoning and very low ionization rates are the two drawbacks of conventional magnetron sputtering process. The deposition rate of magnetron sputtered hard coatings decreases with increase of N_2 partial pressure [25, 33]. This reduction is caused by an increasing coverage of target by absorbed nitrogen or even nitridation of the target. This is called target poisoning. Conventional sputtering techniques were modified to improve ionization rates. High ionization magnetron sputtering techniques [19, 20, and 29] allow deposition of hard coating at a much higher ionization rate than conventional sputtering techniques. In RF plasma assisted magnetron sputtering, the plasma density in front of the target is greatly enhanced leading to a ten-fold increase in metal ionization rate [29]. Sputtered coatings generally have a columnar structure and a smooth coating surface without the presence of macro particles, a typical problem of arc evaporation.

The main disadvantage of the cathodic arc process is the formation of macro particles. Macro particles (or macro droplets) are the result of droplet formation during arc evaporation of low melting point materials (e.g. aluminum in the case of (Ti,Al)N coating). It is also believed that very fast evaporation during the cathodic arc process produces excess atoms that are not completely ionized before they arrive at the substrate surface. These excess neutral atoms may coalesce to form macro particles during the flight [3]. Attempts were made to alleviate this problem. The arc was improved by using 'distributed discharge over hot cathode' [41] and 'enhanced arc' [42, 43] principles. Coll et al.'s [8] approach of

distributing the arc discharge on a thermally insulated cathode (hot cathode) led to a significant reduction of macro droplets. In another approach, Coll et al. [8] refined the plasma stream by an electromagnetic field and eliminated macro particles. Wang et al. [9] used a straight duct particle filter to reduce macro particle ejection from the cathode source and to enhance plasma intensity in front of the cathode surface. The Filtered Arc Deposition (FAD) system based on the 'enhanced arc' principle is suitable to deposit high quality electrical and optical coatings [44].

A trend has been to combine the advantages of sputtering and cathodic arc techniques. The Arc Bond Sputter (referred to as ABS) PVD technique was developed by combining the features of steered cathodic arc and unbalanced magnetron processes [33, 36-39]. This technique yields coatings with high levels of adhesion, dense structure, and provides a smooth macro particle free surface. In the ABS technique, the cathodes can be evaporated either by the arc method or the sputtering method. In some cases, the arc mode was used only to metal ion etch or bombard the substrate prior to actual coating deposition by unbalanced magnetron sputtering [34-36]. A schematic diagram of Random Arc Evaporation Technique can be seen in Figure 2.

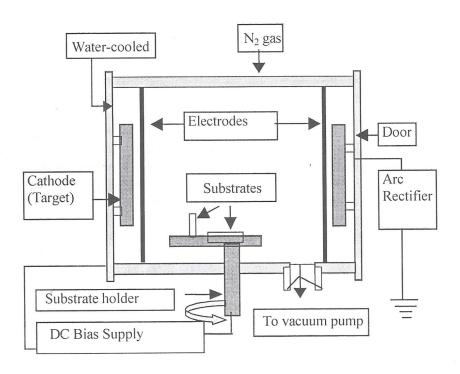


Figure 2: A schematic diagram of the Cathodic Arc Evaporation (CAE) PVD Technique [46, 47].

A hybrid arc-magnetron process (where magnetron sputtering of a pure aluminum cathode was coupled with cathodic arc evaporation of a TiAl alloy cathode) resulted in a (Ti,Al)N coating with a low number of macro particles and excellent

adhesion [39]. Donohue et al. [33] suggested that deposition of highly reactive elements, such as Group IVa elements, by steered arc mode, and of less reactive elements, by unbalanced magnetron sputtering mode. The approach by Donohue et al. [33] minimized poisoning of targets by reactive gases, especially when the reactivity of the elements differ widely.

The property requirements for coating vary widely from application to application. The target/cathode ratio, coating micro hardness and microstructure of the coatings are among the most important properties that determine the wearing resistance of hard coating for cutting tools. A rating of the properties for various PVD coating techniques is difficult because they depend on coating system, deposition processes and parameters. However, the target composition, substrate temperature, bias voltage, gas flow and ion bombardment rates are most important parameters in case of CAE process. Whereas magnetron Power, ion current density, substrate bias, gas pressure, target composition and substrate temperature were found to be most influential parameters in the case of magnetron sputter deposition. These parameters directly affect the mechanical, tribological, structural and thermo-oxidation properties of coating. The choice of base material also plays an important role for actual industrial application. Various industrial tools and dies were used to deposit various coatings such as TiN, TiCN, TiC, (Ti,Al)N and etc. Cemented carbides, cermets and high speed steels are the most common tool materials used in industries for various types of machining operations, namely drilling, metal cutting, milling and turning.

3.0 CONCLUSIONS

In this paper, deposition of hard coatings using different PVD techniques has been reviewed which include a summary of target/cathode materials and various synthesis techniques. Pure metal cathodes/targets or alloy cathodes/target made either by casting or by powder metallurgy were used in PVD processes. Deposition parameters were different for cathodic arc deposition method and for magnetron sputtering. From the above study, It was noted that ABS Technique for PVD hard coating is the best technique but at the same time the most expensive one. A systematic study on the influence of deposition parameters on the morphology of the arc deposited coatings needs to be carried out. Such an investigation can be used to develop a correlation between the arc deposited coating morphology and its properties. By the previous research, it is concluded that the process parameters in PVD hard coating played an important role to optimize the properties for specific application.

ACKNOWLEDGEMENT

The Govt. of Malaysia under the award Letter No JPA (L) KD333487 (MTCP) has financed this work and the Ministry of Science, Technology and Innovation of Malaysia supports the IRPA funding Project No: 03-02-06-0067 SR0006/06-02.

REFERENCES

- 1. Bunshah, R.F. and Deshpandey, C.V., (1989), "Hard Coatings", *Vacuum*, 30, p. 955.
- 2. Tonshoff, K., Mohlfeld, A., Leyendecker, T., Fuß, H.G., Erkens, G., Wenke, R., Cselle, T. and Schwenck, M., (1997), "Wear mechanisms of (Ti_{1-x}Al_x)N coatings in dry drilling", *Surf. Coat. Technol.*, 94/95, pp. 603-609.
- 3. Lin, K.L., Hwang, M.Y. and Wu, C.D., (1996), "The deposition and wear properties of cathodic arc plasma deposition TiAIN deposits", *Mater. Chem. Phys.* 46, pp. 77–83.
- 4. Mubarak, A., Hamzah, E., Toff, M.R.M. and Hashim, A.H., (2005), "The effect of Nitrogen gas flow rate on the properties of TiN-coated HSS using Cathodic Arc Evaporation PVD Technique", *Surface Review and Letters*, 12, pp. 631-643.
- 5. Han, J.G., Nam, K.H. and Choi, I.S., (1998), "The shear impact wear behavior of Ti compound coatings", *Wear*, 214, pp. 91–97.
- 6. James, R.D., Paisley, D.L., Gruss, K.L., Parthasarthi, S., Tittmann, B.R., Horie, Y. and Davis, R.F., (1996), *Mater. Res. Soc. Symp. Proc.*, 410, pp. 377–382.
- 7. Wang, Y., (1997), "A study of PVD coatings and die materials for extended die-casting die life", *Surf. Coat. Technol.*, 94–95, pp. 60–63.
- 8. Coll, B.F., Fontana, R., Gates, A. and Sathrum, P., (1991) "(Ti---Al)N advanced films prepared by arc process", *Mater. Sci. Eng. A*, 140, pp 816–824.
- 9. Wang, D.-Y., Chang, C.-L., Wong, K.-W., Li, Y.-W. and Ho, W.-Y., (1999), "Improvement of the interfacial integrity of (Ti,Al)N hard coatings deposited on high speed steel cutting tools", *Surf. Coat. Technol.*, 120–121, pp. 388–394.
- 10. Kimura, A., Hasegawa, H., Yamada, K. and Suzuki, T., (2000), "Metastable Ti_{1-x}Al_xN films with different Al content", *J. Mater. Sci. Lett.*, 19, pp. 601–602.
- 11. Suzuki, T., Huang, D. and Ikuhara, Y., (1998), "Microstructures and grain boundaries of (Ti,Al)N films", *Surf. Coat. Technol.*, 107, pp. 41–47.
- 12. Ikeda, T. and Satoh, H, (1991), "Phase formation and characterization of hard coatings in the Ti---Al---N system prepared by the cathodic arc ion plating method", *Thin Solid Films*, 195, pp. 99-110.
- 13. Tanak, Y., Gür, T.M., Kelly, M., Ikeda, T. and Sato, H. (1992), "Properties of (Ti_{1-x}Al_x)N coatings for cutting tools prepared by the cathodic arc ion plating method", *J. Vac. Sci. Technol. A*, 10, pp.1749-1756.
- 14. Roos, J.R., Celis, J.P., Vancoille, E., Veltrop, H., Boelens, S., Jungblut, F., Ebberink, J. and Homberg, H., (1990), "Interrelationship between processing, coatingproperties and functional properties of steered arc physically vapour deposited (Ti,AI)N and (Ti,Nb)N coatings", *Thin Solid Films*, 193–194, pp. 547–556.
- 15. Celis, J.P., Roos, J.R., Vancoille, E., Boelens, S., Ebberink, J., Gühring, G., (1993), *Metal Finishing*, pp. 19–22.

- 16. Minevich, A.A. (1991), Proceeding of International Seminar on Tribologist-7M, Rostov, 20–24, 28–31.
- 17. Eizner, B.A., Markov, G.V. and Minevich, A.A., (1996), "Deposition stages and applications of CAE multicomponent coatings", *Surf. Coat. Technol.*, 79, pp. 178–191.
- 18. Kimura, A., Murakami, T., Yamada, K. and Suzuki, T., (2001), "Hot-pressed Ti-Al targets for synthesizing Ti_{1-x}Al_xN films by the arc ion plating method", *Thin Solid Films*, 382, pp. 101–105.
- 19. Jindal, P.C., Santhanam, A.T., Schleinkofer, U. and Shuster, A.F., (1999), "Performance of PVD TiN, TiCN, and TiAlN coated cemented carbide tools in turning", *Int. J. Refractory Metals Hard Mater.*, 17, pp. 163–170.
- 20. Prengel, H.G., Santhanam, A.T., Penich, R.M., Jindal, P.C. and Wendt, K.H., (1997), "Advanced PVD-TiAlN coatings on carbide and cermet cutting tools", *Surf. Coat. Technol.*, 94–95, pp. 597–602
- 21. Zlatanović, M., (1991), "Deposition of (Ti,Al)N coatings on plasma nitrided steel", Surf. Coat. Technol., 48, pp. 19–24.
- 22. Gredić, T. and Zlatanović, M., (1991), "Plasma deposition of (Ti,Al)N coatings at various magnetron discharge power levels", *Surf. Coat. Technol.*, 48, pp. 25–30.
- 23. Lugscheider, E., Knotek, O., Barimani, C., Leyendecker, T., Lemmer, O. and Wenke, R., (1999), "PVD hard coated reamers in lubricant-free cutting", *Surf. Coat. Technol.*, 112, pp. 146–151.
- 24. Håkansson, G., Sundgren, J.E., McIntyre, D., Greene, J.E. and Münz, W.D., (1987), "Microstructure and physical properties of polycrystalline metastable Ti_{0.5}Al_{0.5}N alloys grown by d.c. magnetron sputter deposition", *Thin Solid Films*, 153, pp. 55–65.
- 25. Jehn, H.A., Hofmann, S., Rückborn, V.E. and Münz, W.D., (1986), "Morphology and properties of sputtered (Ti,Al)N layers on high speed steel substrates as a function of deposition temperature and sputtering atmosphere", *J. Vac. Sci. Technol. A*, 4, pp. 2701–2705.
- 26. Huang, C.T. and Duh, J.G., (1995), "Deposition of (Ti,Al)N films on A2 tool steel by reactive r.f. magnetron sputtering", *Surf. Coat. Technol.*, 71, pp. 259–266.
- 27. Wahlström, U., Hutman, L., Sundgren, J.E., Petrov, I. and Gren, J.E., (1993), "Crystal growth and microstructure of polycrystalline Ti_{1-x}Al_xN alloy films deposited by ultra-high-vacuum dual-target magnetron sputtering", *Thin Solid Films*, 235, pp. 62-70.
- 28. Jindal, P.C., Quinto, D.T., Rödhammer, P. and Maierhofer, A., Metallwerk Plansee GmbH, Route, Tirol, Austria, C5, pp. 391–409.
- 29. Zhou, M., Makino, Y., Nose, M. and Nogi, K., (1999), "Phase transition and properties of Ti–Al–N thin films prepared by r.f.-plasma assisted magnetron sputtering", *Thin Solid Films*, 339, pp. 203–208.
- 30. Schäffer, E. and Kleer, G., (2000), "Mechanical behavior of (Ti,Al)N coatings exposed to elevated temperatures and an oxidative environment", *Surf. Coat. Technol.*, 133–134, pp. 215–219.

31. Wu, S.K., Lin, H.C. and Liu, P.L., (2000), "An investigation of unbalancedmagnetron sputtered TiAIN films on SKH51 high-speed steel", Surf. Coat. Technol., 124, pp. 97-103.

32. Musil, J. and Hrubý, H., (2000), "Superhard nanocomposite Ti_{1-x}Al_xN films prepared by magnetron sputtering", Thin Solid Films, 365, pp. 104-109.

33. Donohue, L.A., Münz, W.D., Lewis, D.B., Cawley, J., Hurkmans, T., Trinh, T., Petrov, I. and Greene, J.E., (1997), "Large-scale fabrication of hard superlattice thin films by combined steered arc evaporation and unbalanced magnetron sputtering", Surf. Coat. Technol., 93, pp. 69-87.

34. Münz, W.D., Hurkmans, T., Keiren, G. and Trinh, T., (1993), "Comparison of TiAlN coatings grown by unbalanced magnetron and arc bond sputtering

techniques", J. Vac. Sci. Technol. A, 11, pp. 2583-2589.

35. Smith, I.J., Münz, W.D., Donohue, L.A., Petrov, I. and Greene, J.E., (1998),

Surface Eng. 14, pp. 37-41.

36. Smith, I.J., Gillibrand, D., Brooks, J.S., Münz, W.D., Harvey, S. and Goodwin, R., (1997), "Dry cutting performance of HSS twist drills coated with improved TiAlN", Surf. Coat. Technol., 90, pp.164-171.

37. Schönjahn, C., Bamford, M., Donohue, L.A., Lewis, D.B., Forder, S. and Münz, W.D., (2000), "The interface between TiAIN hard coatings and steel substrates generated by high energetic Cr+ bombardment", Surf. Coat. *Technol.*, 125, pp. 66–70.

38. Münz, W.D., Lewis, D.B., Creasey, S., Hurkmans, T., Trinh, T. and Ijzendorn, W.V., (1995), "Defects in TiN and TiAIN coatings grown by combined cathodic arc/unbalanced magnetron technology", Vacuum, 46, pp. 323-330.

39. Yoon, J.S., Han, J.G. and Hahn, J.H., (2000), J. Kor. Inst. Metals Mater. 38,

pp. 495–499.

- 40. Lugscheider, E., Barimani, C., Wolff, C., Guerreiro, S. and Doepper, G., (1996), "Comparison of the structure of PVD-thin films deposited with different deposition energies", Surf. Coat. Technol., 86-87, pp. 177-183.
- 41. Vasin, A.I., Dorodnov, A.M. and Petrosov, V.A., (1979), Sov. Phys.-Technol. Phys. 5, pp. 425–428.
- 42. Askenov, I.I., Belous, V.A., Padalka, V.G. and Khoroshikh, V.M., (1979), Sov. J. Plasma Phys. 4, pp. 425-428.
- 43. Demidenko, I.I., Lominov, N.S. and Padalka, V.G., (1976), Sov. Phys.-Technol. Phys. 21, p. 284.
- 44. Martin, P.J., Bendavid, A., Netterfield, R.P., Kinder, T.J., Jahan, F. and Smith, G., (1999), "Plasma deposition of tribological and optical thin film materials with a filtered cathodic arc source", Surf. Coat. Technol., 112, pp. 257–260.
- 45. Suffian Saad, Abdul Hakim Hashim, Mansor Abdul Hamid, M. Zakuan Abdullah and Talib Ria Jaafar, (2003), "Effect of radio-frequency sputtering power on the composition of Ti-6Al-4V thin film and its growth morphology" Advanced Technology Congress, May 20-21, Putrajaya.
- 46. Mubarak, A., Hamzah, E., Toff, M.R.M., Hashim, A.H. and Amin, M., (2005), "The Deposition and Characterization of TiN coated HSS by using Cathodic Arc Evaporation Technique", The National Seminar on Advanced Processes and Systems in Manufacturing (APSIM), 17-18 May, Universiti Kebangsaan Malaysia.

47. Mubarak, A., Hamzah, E., Toff, M.R.M. and Hashim, A.H., (2005), "Effect of ion-bombardment on the properties of TiN deposited on HSS using cathodic arc evaporation technique", *Proceedings of the International Conference on Recent Advances in Mechanical & Materials Engineering (ICRAMME)*, 30-31 May, Kuala Lumpur, Malaysia.