

## Research Article

# Properties of TiC Coating by Pulsed DC PACVD

Mahboobeh Azadi,<sup>1</sup> Alireza Sabour Rouhaghdam,<sup>1</sup> and Shahrokh Ahangarani<sup>2</sup>

<sup>1</sup> Surface Engineering Laboratory, Materials Engineering Department, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

<sup>2</sup> Advanced Materials and Renewable Energies Department, Iranian Research Organization for Science and Technology, P.O. Box 15815-3538, Tehran, Iran

Correspondence should be addressed to Alireza Sabour Rouhaghdam; sabour01@modares.ac.ir

Received 25 March 2013; Revised 27 September 2013; Accepted 30 September 2013

Academic Editor: Juan J. De Damborenea

Copyright © 2013 Mahboobeh Azadi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the PACVD technique, temperature and gas flow rate are two important parameters affecting the coating characteristics. Effect of these parameters on mechanical behaviors of TiC coating that was deposited on hot work tool steel (H13) was investigated in this paper. We analyzed TiC coating composition and structure with grazing incidence X-ray diffraction (GIXRD) and Fourier transformation infrared spectroscopy (FTIR). The mechanical properties of the coatings, such as microhardness, wear resistance, and surface roughness, were studied with Knoop hardness indentation, pin on disk wear tests, and atomic force microscopy, respectively. When the deposition temperature decreased from 490°C to 450°C and the CH<sub>4</sub> to TiCl<sub>4</sub> flow rate ratio was also increased from 1.5 to 6, TiC coating color changed from dark gray to silver. The best mechanical properties such as a high hardness (27 GPa), wear resistance, and low surface roughness were related to the coating that was deposited at 450°C.

## 1. Introduction

Hard coatings such as titanium carbide (TiC) and titanium nitrocarbide (TiCN) have been used in various industries such as microelectronics and aerospace due to the unique properties such as high hardness and Young's modulus, low friction coefficient, proper resistance to corrosion and wear, good electrical and thermal conductivity, and high melting temperature [1–3]. Thin and hard coatings can be deposited by different methods such as physical vapor and thermal chemical vapor techniques. In the first method due to the low temperature, the coatings adhesion strength decreases and in the second method, due to low deposition rate, the cost waste and the time waste occur [4]. Thus, plasma assisted chemical vapor deposition (PACVD) can be a proper technique for depositing thin coatings on different substrates, due to possibility to achieve the same properties in lower temperatures and higher deposition rate. Controlling the composition and the thickness of coatings by adjusting plasma parameters is easy. Additionally, rotating of the complex sample is not necessary [4–6]. Thus, PACVD is used to deposit various coatings for casting and extruding mold even with irregular

geometry and complexity [7]. In TiC coating deposition via PACVD technique, the temperature, plasma power, duty cycle, and CH<sub>4</sub> and TiCl<sub>4</sub> flux rates are the fundamental parameters, because the amount of excess carbon is a very effective factor on the coating properties. It was shown by Stock et al., in 1998, that increasing the level of excess carbon can decrease coating hardness [4, 8, 9]. It is noteworthy that different researches have studied the ratio of TiCl<sub>4</sub> to CH<sub>4</sub> flux from 3 to 10 and until now there is a lack of published information on the fewer ratios. In this study, TiC coating was deposited by PECVD on the tool steel using CH<sub>4</sub> as the reactive gas and the flux ratio of CH<sub>4</sub> to TiCl<sub>4</sub> was changed from 1.5 to 6 and the deposition temperature was increased from 450°C to 490°C to deposit coating with thickness of 2–3 micrometers and then identify the coating characteristics. The composition analysis of coating was done by grazing incidence X-ray diffraction (GIXRD) and Fourier transformation infrared spectroscopy (FTIR). Microhardness, wear hardness, surface roughness, and topography were measured with Knoop hardness indentation, pin on disk wear test, and atomic force microscopy.

TABLE 1: Chemical composition of substrate.

C	Si	Cr	Mo	V	Mn	Ni	Cu	Fe
0.45	0.69	5.72	1.14	2.23	0.27	0.15	0.24	Balance

TABLE 2: Different parameters in plasma nitriding process.

Temp. (°C)	Pressure (mbar)	Time (min)	Hydrogen (sccm)	Nitrogen (sccm)	Argon (sccm)
470	2	60	1600	500	500

TABLE 3: Different parameters in coating process (with duty cycle = 33%, voltage = 600 V, total pressure = 6 mbar, flux argon = 0.5 NL/min, and flux hydrogen = 1.6 NL/min).

Sample number	Time (min)	Titanium chloride (sccm)	Methane (NL/min)	Temp. (°C)	CH <sub>4</sub> /TiCl <sub>4</sub>
1	80	50	80	490	1.6
2	80	50	100	470	2
3	80	50	120–300	450	2.4–6
4	80	50	100	450	2
5	80	50	120–300	470	2.4–6

## 2. Material and Methods

The present H-13 samples with composition listed in Table 1 were heat treated in order to increase the hardness. Then samples were prepared by grinding up to 2000 grit and cleaned with an alkali solution in ultrasonic bath in temperature of 100°C for 10 minutes. In order to increase adhesion of the coating to the substrate and increase the load bearing of coatings, a plasma nitriding operation with the parameters listed in Table 2 was performed. In plasma nitriding process, the flow ratio of hydrogen to nitrogen was fixed to about 3 in order to prevent white layer formation [10, 11].

The TiC coatings were deposited in a PACVD reactor using a TiCl<sub>4</sub>-CH<sub>4</sub>-H<sub>2</sub>-Ar gas mixture. The plasma was triggered by a DC pulsed power supply. The total pressure in the reaction chamber was 6 mbar. The fixed flow rates of argon, hydrogen, and titanium chloride were 500, 1600, and 50 sccm, respectively. Duty cycle for all specimens was 33% and a negative bias voltage was fixed at 600 V during the process in a chamber with height and the diameter of 70 cm × 50 cm. The substrate temperature was controlled by an auxiliary heating system in addition to the intrinsic sputtering effect. Other experimental conditions are listed in Table 3. In this paper, grazing-angle X-ray diffraction with test specifications ( $\alpha = 2^\circ$  and radiation 1.5418 Å; Cu K $\alpha$ ) was used. To identify the types of created bonds, the Fourier transformation infrared spectroscopy (FTIR) was also used. In order to determine the hardness of the samples in each situation, we perform first Knoop indentation for loads ranging from 0.25 to 0.5 N and at least five indentations for each load. The microhardness of the coatings was measured on hot work tool steel substrates. Wear test was also carried out by using a WC—6% Co ball of 6 mm diameter at a linear speed of 0.1 m/s in 1000 meters distance with applied load of 10 N at room temperature (25°C) when trace diameter was 45 mm. In order to study the topology of the surface of samples, atomic force microscope (AFM) was used.

## 3. Results and Discussion

In this paper, the temperature and the ratio of effective gas flux have been studied as two important factors. Other parameters such as voltage, duty cycle, and gas flux of nitrogen, argon, TiCl<sub>4</sub>, and coating thickness were kept fixed. The GIXRD test results for samples are shown in Figure 1.

When the ratio amount of CH<sub>4</sub> to TiCl<sub>4</sub> was lower than a critical value (about 2), despite the presence of TiCl<sub>4</sub> in the reactor and high temperature and instead of TiC deposition, a black layer consisting of iron carbide was formed. The peaks that were generated in this test in degrees of 43.9 and 51.34 were related to austenitic iron carbide phase and the rest of the peak was corresponding to the substrate. But the standard TiC peaks were at 36.9, 42.6, 62, 74.48, and 78.18 degrees. When the flux ratio of CH<sub>4</sub> to TiCl<sub>4</sub> changed from 2 to 6, the sample showed different colors from gray-copper to gray-silver. As CH<sub>4</sub>/TiCl<sub>4</sub> ratio increases to 9, the color becomes gray-black, this was reported by Archer [12]. Thus, color of the samples was related to solubility of carbon in the space network of titanium. From the GIXRD test results, these diffraction patterns show the orientation in the direction of crystalline planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2). The (2 0 0) plane was revealed to be the preferred structure and this plane is thermodynamically stable relative to the (2 2 0) and (1 1 1) planes. The temperature had no effect to change the preferred crystalline plane.

The result test of FTIR is shown in Figure 2. In this pattern, three peaks were seen in degrees of 1044, 554, and 444 cm<sup>-1</sup> that were related to TiC phase. The peaks that are related to C–C and C–H and C–N bonds have a peak in the range of 1500–3000 cm<sup>-1</sup>. These peaks were not seen in our pattern and microhardness changes just depended on the deposition temperature. The peak in the frequency range of 2900–3500 cm<sup>-1</sup> which is related to oxygen, hydrogen, and nitrogen bonds [13] was also not observed in our test. When the flux ratio of CH<sub>4</sub>/TiCl<sub>4</sub> was kept about 2.4–6, due to

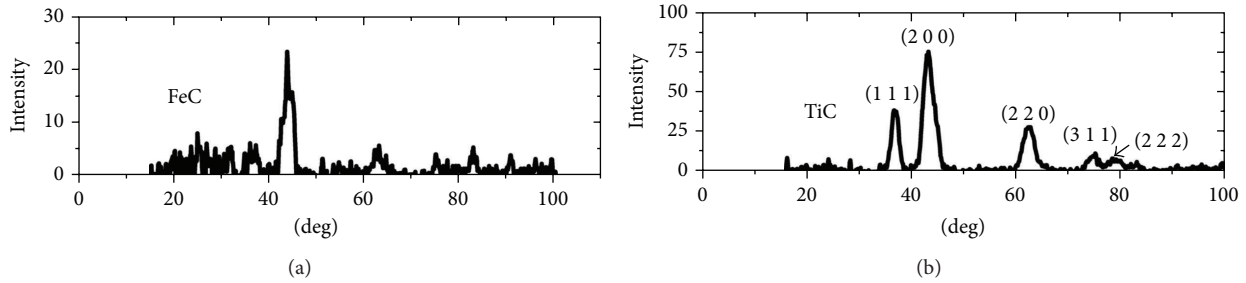


FIGURE 1: GIXRD test result for samples.

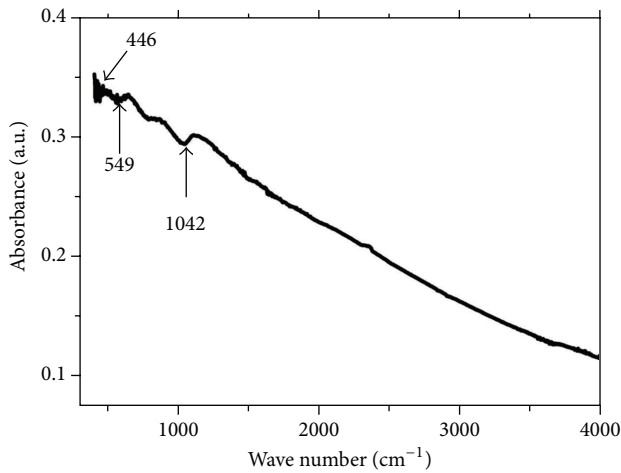


FIGURE 2: Reflective FTIR test result for sample 3.

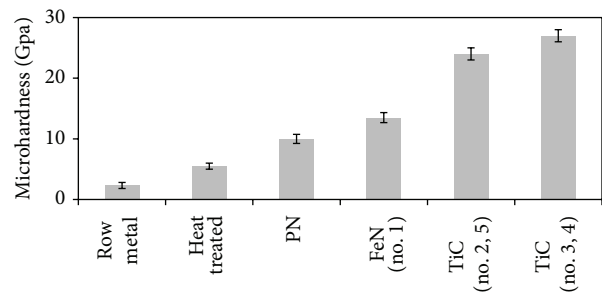


FIGURE 3: Microhardness result test.

the bond energy in reflection spectroscopy [14], TiC coatings had cubic structure with a formula that can be  $Ti_{14}C_{13}$ . Therefore, the ratio of C to Ti atom was approximately 1 to 1.

When the amount of carbon exceeds the equilibrium composition and all space network titanium gets occupied with carbon atoms, extra carbon atom will be deposited as a separate phase usually at the grain boundaries. When this excess carbon creates graphite phase, the microhardness of TiC coating will decrease but when it forms diamond or diamond-like carbon (DLC) phase, the hardness will be increased [15]. As excess carbon is bound as C–C or C–H [9], the proper selection of ratio of effective gases prevented excess carbon to be precipitated as a separate phase in this paper. Due to the phase diagram, when the amount of carbon in the titanium network is 32–48.8%, TiC phase is formed as NaCl crystal structure. Also, in a paper in 1998 [9] was mentioned that when the flux ratio of  $TiCl_4/CH_4$  is more than 15, excess carbon will be precipitated in a separated phase. While the ratio of  $CH_4$  to  $TiCl_4$  gas flux is kept in proper level (more than 2 and less than 15), TiC phase with high hardness of 27 GPa will be deposited, and microhardness changes just depended on the deposition temperature. Microhardness test results are reported in Figure 3. The microhardness of sample 1 was 13.5 GPa and the microhardness of other samples was about 24–27 GPa. Samples 3 and 4 showed more

microhardness than the samples 2 and 5 (about 11%), due to the lower deposition temperature. When the deposition temperature was 450°C, the grain growth was minimized and the size of coating grain was decreased and as a result the microhardness increased.

Notably, according to the papers that were published by other researchers [4, 12], the minimum temperature of TiC formation had been reported at 470°C in which a continuous layer and an adhesive coating to the substrate were created. But on the contrary in this paper, the optimum TiC layer was coated at temperature of 450°C and this result can reduce the cost of coating process and the substrates will not need to bear high temperatures. Also due to these results, the flux ratio of  $CH_4$  to  $TiCl_4$  in the formation of TiC coating was more important than the temperature.

The micromechanical tribological mechanisms describe the stress and strain formation at an asperity-to-asperity level, the crack generation, and propagation, material liberation, and particle formation [16]. Landcaster proposed a simpler empirical wear formula as specific wear rate. It shows the resistance to abrasive wear as follows:

$$k = \frac{V}{S \cdot F} \quad (1)$$

In this formula,  $V$  is wear volume,  $S$  is wear distance, and  $F$  is applied force. This wear coefficient  $k$ , with units of  $m^3 \cdot N^{-1} \cdot m^{-1}$ , has proven to be more useful for the comparison of the wear behavior of different materials than Archard's equation [17, 18]. From the wear test result in Table 4, the wear rate of TiC was not dependent on the temperature in the range of 450°C to 470°C.

TABLE 4: AFM and wear result test.

Sample number	Min. downhill (nm)	Max. downhill (nm)	Average roughness (nm)	Specific wear rate ( $\text{m}^3/\text{Nm}$ ) $\cdot 10^{-13}$
1	$-46 \pm 10$	$59 \pm 10$	$24 \pm 3$	10.1
2,5	$-47 \pm 10$	$58 \pm 10$	$20 \pm 3$	3.70
3,4	$-43 \pm 10$	$43 \pm 10$	$15 \pm 3$	3.25

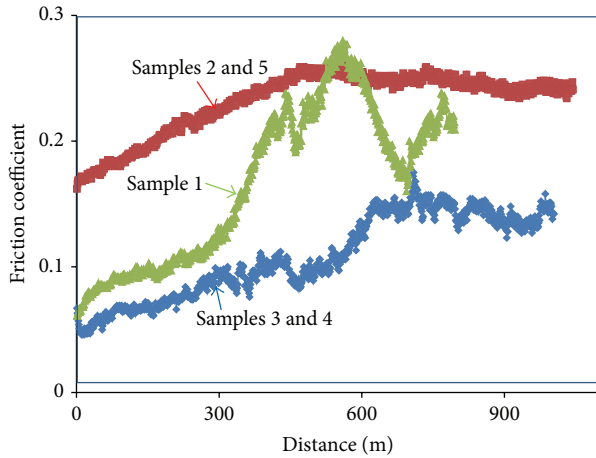


FIGURE 4: Friction coefficient versus wear time diagram of sample.

Changes in the coefficient of friction of the TiC coating determined during wear measurements are shown in Figure 4. For TiC coatings that were deposited in lower temperature, during the run-in 600 meter, the coefficient of friction was lower than 0.1 and then it increased to 0.15. Once this value was reached, the coefficient of friction became constant for the remaining distance. This result was in accordance with other papers independent from the method of deposition [8, 19]. When the deposition temperature increased to  $470^\circ\text{C}$ , coefficient of friction also increased and reached 0.2-0.3. For FeN coating, coefficient of friction was increased. It reached to 0.27 and then decreased to a value below of 0.15. This drop was due to the separation of coating from the substrate surface. Thus, the changes in deposition for  $20^\circ\text{C}$  caused variation of friction coefficient of about 50%. But the variation of the flux ratio could not lead to a change in the friction coefficient for TiC coating as reported by Jarms et al. [9]. During the running-in, owing to the interaction between the tip and the roughness of surface coatings, the friction coefficient ( $\mu$ ) rises. In the initial stage, the friction coefficient is controlled by the film roughness and the build-up of a transfer layer (tribolayer), and in the second stage, the friction and the wear are controlled by the nature of the tribolayer [20].

The micrographs of wear path for the samples are shown in Figure 5. The wear mechanism of samples was different from each other. The FeN coating was easily separated from the surface by the pin. The wear track for this coated sample was empty of debris and the wear edges were smooth. As TiC coating had a higher hardness than the iron carbide coating, the abrasive wear mechanism could be cutting.

The total wear observed in the ceramic can be divided into two main broad categories such as (a) mechanically activated wear which includes abrasion, adhesion, plastic deformation, and fracture and (b) chemically activated wear also called tribochemical wear which includes diffusion or dissolution wear [21]. At higher speeds (to produce higher temperature), under dry or semidry conditions, chemical wear becomes the predominant mode of wear [22]. Thus, the speed of the mechanical mechanism is the dominant mode of wear for all coated samples.

The mechanical wear process is also divided into three stages for single layer of coating of TiC: crack nucleation, crack propagation along a given direction under applied force, and forming of wear debris and damages on the rubbing surface. The image for TiC coating (Figure 5) shows that the wear track was full of debris. Debris was observed to pile up along the outer edges of the wear track. They were small near the wear edges but the debris size increased when we were far from the wear edges and near the center. The wear areas were separated by broken lines from other areas. When the deposition temperature was increased to  $470^\circ\text{C}$ , the debris size in wear track was increased and gathered in holes, but abrasion boundary was separated by curved lines. Due to the increasing debris size in wear track and formation of holes in TiC coated sample with higher deposition temperature, the wear rate increased.

Three-dimensional surface topography of the samples is shown in Figure 6 and their surface roughness is summarized in Table 4. The surface roughness was about 20 nm for samples 2 and 5. But the surface roughness of samples 3 and 4 with lower temperature was lower and was about 15 nm. In other papers, the amount of TiC coating surface roughness was reported less than 10 nm, this may be related to the higher temperature ( $500^\circ\text{C}$ ) with different mechanism [5, 23]. The effect of temperature on the grain growth was very severe. In this paper, the AFM images values showed that a lower deposition temperature decreased the surface roughness, due to the grain growth when the deposition temperature increased. The surface roughness was also independent of flux ratio of important gas when this ratio is proper to deposit TiC coating. Higher coefficient of friction was seen for TiC coatings with high deposition temperature and this result was related to the lower surface roughness.

#### 4. Conclusions

The result showed that the TiC coating color was directly related to the amount of dissolved carbon in titanium crystal network. When the ratio of C atoms to Ti in TiC network was 1 to 1, coating color was silver gray and while this ratio

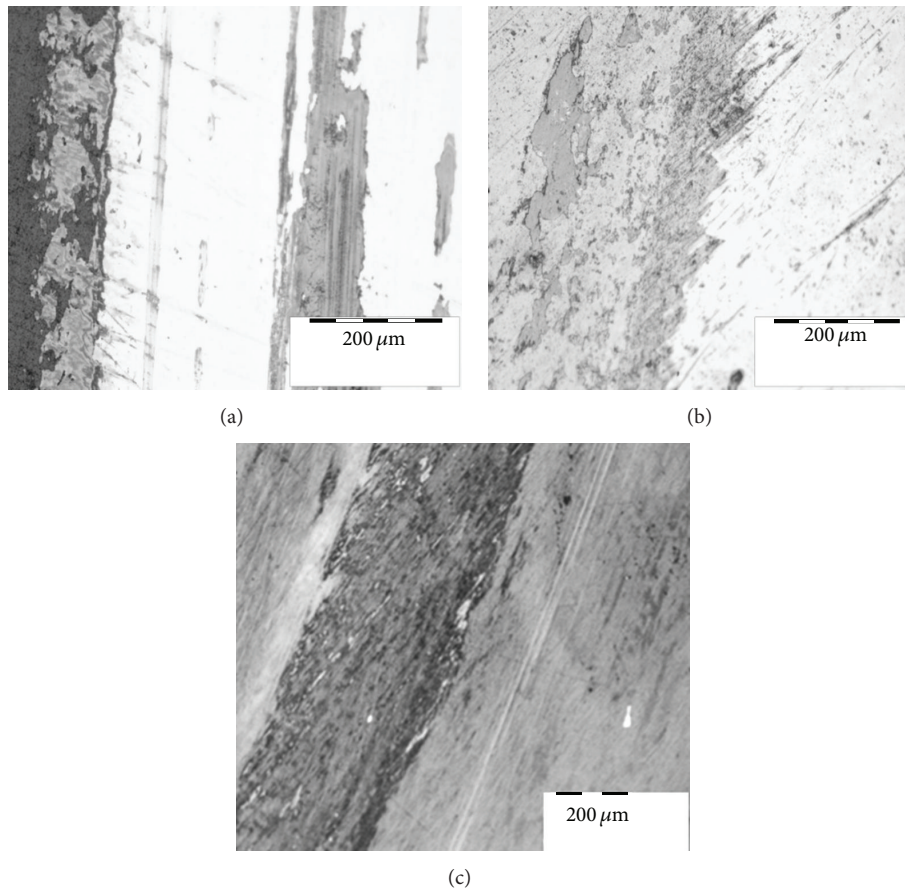


FIGURE 5: Wear path pictures of samples including (a) sample 1, (b) sample 3, and (c) sample 5.

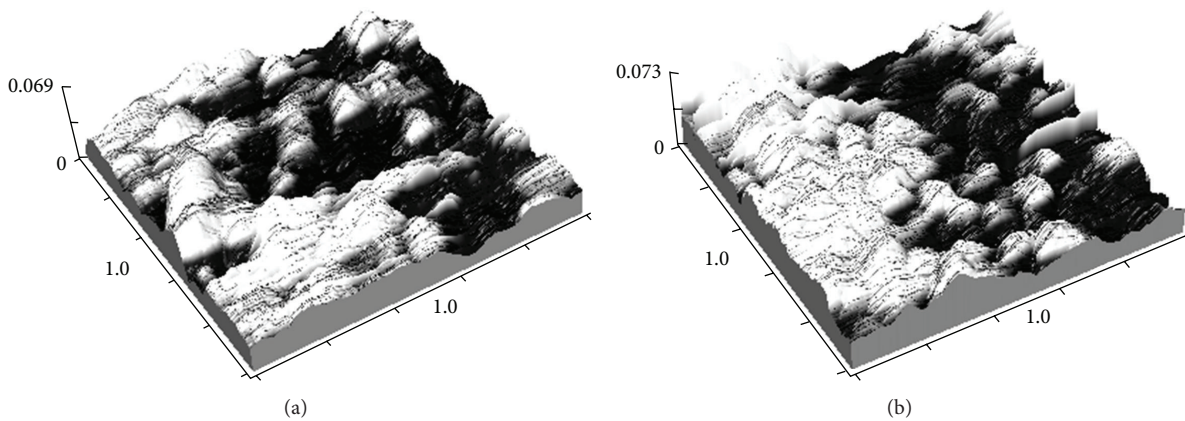


FIGURE 6: Topography of surface samples including (a) sample 3 and (b) sample 5.

increased, coating color would be dark copper-like. A very important parameter in deposition of TiC coating was the flux ratio of CH<sub>4</sub> to TiCl<sub>4</sub>. This was more effective parameter than the deposition temperature. But when TiC coating was deposited, the deposition temperature had important role in coating characteristic changes like hardness, wear, friction coefficient, and surface roughness. Thus, selecting the correct flux ratio of gases at a temperature of 450°C can create

uniform TiC. Hardness of TiC coating was dependent on the formation of excess carbon. But dissolved carbon in TiC crystal had no severe effect on the hardness variation (only about 10%). On the other hand, wear mechanism was changed abruptly when the deposition temperature changed from 450°C to 470°C. Minimum friction coefficient (about 0.18) for TiC coating with deposition temperature of 450°C was observed.

## References

- [1] H. Liepack, K. Bartsch, W. Brückner, and A. Leonhardt, "Mechanical behavior of PACVD TiC-amorphous carbon composite layers," *Surface and Coatings Technology*, vol. 183, no. 1, pp. 69–73, 2004.
- [2] N. Kumar, R. Krishnan, D. Dinesh Kumar, S. Dash, and A. K. Tyagi, "Tribological properties of nanostructured TiC coatings deposited on steel and silicon substrates using pulse laser deposition technique," *Tribology*, vol. 5, no. 1, pp. 1–9, 2011.
- [3] A. Shanaghi, A. R. S. Rouhaghdam, S. Ahangarani, P. K. Chu, and T. S. Farahani, "Effects of duty cycle on microstructure and corrosion behavior of TiC coatings prepared by DC pulsed plasma CVD," *Applied Surface Science*, vol. 258, no. 7, pp. 3051–3057, 2012.
- [4] D.-J. Kim, Y.-R. Cho, M.-J. Lee, J.-M. Hong, Y.-K. Kim, and K.-H. Lee, "Properties of TiN-TiC multilayer coatings using plasma-assisted chemical vapor deposition," *Surface and Coatings Technology*, vol. 116–119, pp. 906–910, 1999.
- [5] A. Shanaghi, A. Sabour Rouhaghdam, S. Ahangarani, and P. K. Chu, "Effect of plasma CVD operating temperature on nanomechanical properties of TiC nanostructured coating investigated by atomic force microscopy," *Research Bulletin*, vol. 47, pp. 2200–2206, 2012.
- [6] H. L. Wang, J. L. He, and M. H. Hon, "Sliding wear resistance of TiCN coatings on tool steel made by plasma-enhanced chemical vapour deposition," *Wear*, vol. 169, no. 2, pp. 195–200, 1993.
- [7] K. Kawata, H. Sugimura, and O. Takai, "Effects of chlorine on tribological properties of TiN films prepared by pulsed d.c. plasma-enhanced chemical vapor deposition," *Thin Solid Films*, vol. 407, no. 1-2, pp. 38–44, 2002.
- [8] T. Arai, H. Fujita, and K. Oguri, "Plasma-assisted chemical vapour deposition of TiN and TiC on steel: properties of coatings," *Thin Solid Films*, vol. 165, no. 1, pp. 139–148, 1988.
- [9] C. Jarms, H.-R. Stock, H. Berndt, K. Bartsch, A. Leonhardt, and B. Arnold, "Influence of the PACVD process parameters on the properties of titanium carbide thin films," *Surface and Coatings Technology*, vol. 98, no. 1-3, pp. 1547–1552, 1998.
- [10] S. Ma, Y. Li, and K. Xu, "The composite of nitrided steel of H13 and TiN coatings by plasma duplex treatment and the effect of pre-nitriding," *Surface and Coatings Technology*, vol. 137, no. 2-3, pp. 116–121, 2001.
- [11] R. D. Torres, P. C. Soares Jr., C. Schmitz, and C. J. M. Siqueira, "Influence of the nitriding and TiAlN/TiN coating thickness on the sliding wear behavior of duplex treated AISI H13 steel," *Surface and Coatings Technology*, vol. 205, no. 5, pp. 1381–1385, 2010.
- [12] N. J. Archer, "The plasma assisted chemical vapor deposition of TiC, TiN and, TiCN," *Thin Solid Films*, vol. 80, no. 1, pp. 221–225, 1981.
- [13] A. F. G. Tan der Meer, "FELs, nice toys or efficient tools?" *Nuclear Instruments and Method in Physics Research A*, vol. 528, pp. 8–14, 2006.
- [14] K. Oguri and T. Arai, "Friction coefficient of SiC, TiC and GeC coatings with excess carbon formed by plasma-assisted chemical vapour deposition," *Thin Solid Films*, vol. 208, no. 2, pp. 158–160, 1992.
- [15] J. A. Avila and H. E. Jaramillo, "Synthesis and characterization of aluminum titanium carbonitride TiAlCN via mechanical alloying," *Journal of Scientific and Industrial Research*, vol. 69, no. 10, pp. 773–776, 2010.
- [16] K. Holmberg, A. Matthews, and H. Ronkainen, "Coatings tribology—contact mechanisms and surface design," *Tribology International*, vol. 31, no. 1-3, pp. 107–120, 1998.
- [17] J. Lee, K. Euh, J. C. Oh, and S. Lee, "Microstructure and hardness improvement of TiC/stainless steel surface composites fabricated by high-energy electron beam irradiation," *Materials Science and Engineering A*, vol. 323, no. 1-2, pp. 251–259, 2002.
- [18] J. Pirso, M. Viljus, and S. Letunovits, "Sliding wear of TiC-NiMo cermets," *Tribology International*, vol. 37, no. 10, pp. 817–824, 2004.
- [19] J. Tang, J. S. Zabinski, and J. E. Bultman, "TiC coatings prepared by pulsed laser deposition and magnetron sputtering," *Surface and Coatings Technology*, vol. 91, no. 1-2, pp. 69–73, 1997.
- [20] D. G. Liu, J. P. Tu, C. D. Gu, R. Chen, and C. F. Hong, "Tribological and mechanical behaviors of TiN/CNx multilayer films deposited by magnetron sputtering," *Thin Solid Films*, vol. 519, no. 15, pp. 4842–4848, 2011.
- [21] A. S. Kumar, A. R. Durai, and T. Sornakumar, "Wear behaviour of alumina based ceramic cutting tools on machining steels," *Tribology International*, vol. 39, no. 3, pp. 191–197, 2006.
- [22] J. Vleugels, "Fabrication, wear, and performance of ceramic cutting tools," *Advances in Science and Technology*, vol. 45, pp. 1776–1785, 2006.
- [23] T.-H. Fang, S.-R. Jian, and D.-S. Chuu, "Nanomechanical properties of TiC, TiN and TiCN thin films using scanning probe microscopy and nanoindentation," *Applied Surface Science*, vol. 228, no. 1-4, pp. 365–372, 2004.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

