

Characterization of TiCN and TiCN/ZrN coatings for cutting tool application

Ping Chuan Siow^a, Jaharah A. Ghani^{a,*}, Mariyam Jameelah Ghazali^a, Talib Ria Jaafar^b,
Mohamad Asri Selamat^b, Che Hassan Che Haron^a

^aDepartment of Mechanical and Materials Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

^bAdvanced Materials Research Centre, SIRIM Berhad, Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park, 09000 Kulim, Kedah, Malaysia

Received 2 July 2012; received in revised form 4 July 2012; accepted 18 July 2012

Available online 24 July 2012

Abstract

Coating a cutting tool improves wear resistance and prolongs tool life. Coating performance strongly depends on the mechanical and chemical properties of the coating material. In a machining process, the type of selected coating depends on the cutting condition because of the properties of the applied coating material. In addition, many factors, such as coating thickness, composition ratio, sequences of layers in multilayer coatings, and the deposition method influence the performance of a coating. In this study, the mechanical properties of TiCN and TiCN/ZrN were investigated using a ball on disk test. The substrate material made from a carbide-based cutting tool was also developed in-house. The analysis performed shows that the performances of TiCN and TiCN/ZrN coatings were found to be comparable to that of the commercial TiN-coated carbide-based cutting tool. Both the in-house and commercial coated inserts had significantly lower coefficient of friction than uncoated inserts, and the friction coefficient of TiCN coatings was constantly slightly lower than that of TiN coatings. Moreover, the coefficient of friction of the in-house developed TiCN was slightly lower than that of commercial TiN coating. However, the coefficient of friction of the in-house developed uncoated carbide inserts was slightly higher than that of commercial uncoated carbide inserts.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Ball on disk; Carbide tool; TiCN; TiCN/ZrN

1. Introduction

Tool wear affects the operation of the machining process and subsequently the quality of products. Thus, cutting tools must be very hard, tough, and wear resistant. The objectives above led to the development of specially tailored hardmetals over the past few decades to overcome the problems encountered in different machining processes and conditions. The term hardmetal is used for describing alloys produced from metallic hard materials (primarily carbides) and tough binder metals [1]. The range of applications and consumption of hardmetals continuously

grows, driven by tight competition and high-performance standards sought in the market and industry. Improved mechanical properties, such as hardness and toughness, enable hardmetals to compete in applications previously dominated by other tool materials, such as polycrystalline diamond (PCD). Vital requirements for hardmetal cutting tools include cost effectiveness, profitability, and tool performance, which allow cutting tools to have longer tool life, high-dimension accuracy, high-quality machined surface, and high productivity at low costs [2].

Cemented tungsten carbide is a class of hardmetal composite material that serves a tremendous practical importance and is used extensively in applications that demand high wear resistance, such as metal cutting tools, drilling and mining equipment, and metal-forming dies [3]. The excellent wear resistance exhibited by the hardmetal of cemented tungsten carbide is due to the unique

*Corresponding author. Tel.: +60 38 92 16505; fax: +60 38 92 59659.

E-mail addresses: pcsiow@eng.ukm.my (P.C. Siow),
jaharah@eng.ukm.my (J. A. Ghani),
mariyam@eng.ukm.my (M.J. Ghazali), talibria@sirim.my (T.R. Jaafar),
masri@sirim.my (M.A. Selamat), chase@eng.ukm.my (C.H. Che Haron).

combination of high density, high hardness, and moderate levels of fracture toughness of the hardmetal [3–5].

The simplest composition of cemented tungsten carbide hardmetal consists of a hard phase material, namely, the tungsten carbide (WC), and a metal acting as a binder. Cobalt (Co) is widely used as a binder metal because of its good wetting behavior, favorable solubility for WC, and good mechanical properties. Thus, WC–Co is the most common and most popular hardmetal combination, and it is also known as a straight grade hardmetal. The hard phase of WC in cemented tungsten carbide WC–Co provides the qualities of hardness and resistance, whereas the matrix phase of cobalt (Co) provides strength and toughness. The matrix phase is also referred to as the binder phase [3,6].

The properties of cemented tungsten carbide hardmetal primarily depend on the Co content and the grain sizes of WC. The different properties of the cemented tungsten carbide hardmetal can be obtained through variations in composition to suit various applications. However, amount of Co is usually less than 15% [3,6]. Finer grained hardmetals preserve their hardness better at high temperatures compared to coarser grained alloys. However, finer grade materials are extremely sensitive to processing and are more prone to carbide grain growth during consolidation [7,8]. Besides WC, titanium carbide (TiC), tantalum carbide (TaC), and niobium carbide (NbC) are also used for metal cutting tool applications [1,9]. The range of hardmetals and their applications are summarized in Table 1.

The performances of carbide cutting tools are limited if the tools are applied incorrectly, and the constraints lie within the properties of the tools. Thus, a thin layer of wear-resistant material is deposited onto the surfaces of carbide cutting tools to improve the surface properties, wear resistance, and tool life of the cutting tools. The coated carbide cutting tool was developed around the

1970s [10]. Wear resistance, friction coefficient, and hardness of cutting tools are strongly dependent on the surface properties of the cutting tools. Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are the most commonly used methods for producing coating layers on carbide substrates.

Ti-based hard coatings are common hard ceramic thin layers deposited onto carbide cutting tools. Titanium nitride (TiN) is a popular gold color coating applied on high-speed steel and carbide cutting tools [11,12]. TiN possesses some very useful properties, such as high hardness, high strength, low coefficient of friction, high chemical stability, excellent resistance to BUE formation, and high adhesivity on carbide substrates. Thus, TiN coating improves wear resistance and prolongs tool life of high-speed steel and carbide cutting tools, particularly at high cutting speeds and feed rates [12–14]. However, TiN has poor adhesivity on metals because of surface contaminants and residual tension at the coating–substrate interface [15]. Moreover, TiN does not provide a barrier to diffusion wear when cutting tools turn against stainless steel despite the material acting as a heat barrier [16]. TiN is a first-generation hard coating for carbide tools that uses the PVD method [17].

The inclusion of carbon atoms in the TiN lattice substantially increases film hardness and lowers the friction coefficient. Titanium carbonitride (TiCN) has high chemical stability and superior mechanical properties, such as low friction coefficient, high hardness (HV 2500–3000), high toughness, high melting point (3050 °C), high electrical conductivity, and excellent wear resistance [13,18,19]. Several researchers [19,20] reported that TiCN is a solid solution for FCC TiN and FCC TiC, which take on the excellent characteristics of both TiC and TiN. Thus, TiCN has better anti-wear capabilities and higher hardness than TiN and TiC [13–15,19,21,22], allowing it to replace conventional TiN in cutting tools and cold forming

Table 1
Range of hard materials and their applications [2,9].

Hard materials	Grain size (μm)	Binder content (wt%)	Range of applications
WC–Co	Ultrafine: 0.2–0.5	2–4	Wood machining and wear parts
		6–9	Microdrills and micromills for PCBs; indexable inserts for metal cutting
		10–16	Shaft tools; paper cutting knives
	Submicrometer: 0.5–0.8	4–16	Indexable inserts for metal cutting; shaft tools
	Fine: 0.8–1.3	4–25	Indexable inserts for metal cutting; chipless shaping; wear parts
	Medium: 1.3–2.5	4–25	Heavy duty machining; chipless metal forming
	Coarse: 2.5–6.0	4–25	Mining tools
	Extra coarse: > 6.0	4–20	Chipless metal forming
WC–Ni, (Cr), (Co)	0.5–2	4–20	Chemical engineering; components for corrosive environments; non-magnetic structural parts
WC–(Ti, Ta, Nb)C–Co	0.5–2	4–15	Indexable inserts for steel cutting
Cermets (Ti, Ta, Nb, W, Mo)(C, N)/(Co, Ni)	0.5–2	4–15	Indexable inserts for steel cutting

applications [20]. The blue-gray TiCN coating improves wear resistance, especially in cutting carbon alloy steels and cast irons [14].

Narasimhan et al. [13] found that TiN coating had larger crystallite sizes and better adhesion property than TiCN, but TiCN had higher microhardness than TiN. The smaller grain sizes of TiCN produce a smoother and slightly more surface lubricity than TiN, and thus, the friction coefficient of TiCN is constantly lower than that of TiN, and TiCN coating can significantly reduce the cutting force more than TiN coating. TiCN-coated cutting tools have better wear resistance and longer tool life than TiN-coated cutting tool in turning AISI 4340 steel. However, TiCN becomes coarser with increasing nitrogen content. The wear resistance of TiN- and TiCN-coated carbide tools can be further improved by combining TiN and TiCN to become a multilayer TiN/TiCN [13]. The deposition of a very thin interlayer is an effective solution for improving the adhesivity of the coating on the substrate [23–25].

Wear resistance, hardness, and coefficient of friction of a coated cutting tool is strongly dependent on the surface properties of the coating layer [13,20]. Narasimhan et al. [13] improved the surface properties of TiCN coating, such as hardness, wear resistance, and surface smoothness, by providing a carbon-rich top layer. Similarly, several researchers discovered that depositing TiCN coating as the surface layer on a Ti-base multilayer coating can significantly improve wear resistance because of the lower friction coefficient of TiCN compared with those of TiN and TiAlN [22,26].

The current study compares the mechanical properties of the in-house developed TiCN/ZrN- and TiCN-coated tungsten carbide inserts with commercially available TiCN- and TiN-coated tungsten carbide inserts.

2. Methodology

Buffalo Tungsten Inc., New York, supplied all the WC and Co elemental powders used in this study. The particle sizes of WC were less than 1.0 μm , whereas the particle sizes of Co were less than 1.5 μm . The WC and Co powders were weighed to obtain the compositions of 94% WC and 6% Co, respectively. 60 mL of heptane and 1 g of paraffin wax powder were also added into the mixture. Heptane was added to minimize any possibility of oxidation prior to sintering and waxing to reduce the friction between the green compact and die wall, preventing the adherence of green compact on the die wall [9,27]. The mixtures were blended in a tubular mixer with 10 mm tungsten carbide balls at 50 rpm for 3 h. The weight ratio of ball to powder was maintained at 3:1. After wet mixing, the green mixture was dried at 55 $^{\circ}\text{C}$, which was a temperature slightly above the boiling point of the solvent, for 2 h. The dried green mixture was granulated and sieved before pressing it into the desired shape.

Green compacts were prepared via uniaxial compaction at a pressure of 20 US tons/in.² (275 MPa). The specimen

had dimensions of 16 mm \times 16 mm \times 4 mm with green densities of about 70–75% of theoretical density. Then, the green compacts underwent cold isostatic pressing (CIP) to improve their densities, and pressure was exerted uniformly in all directions at 30,000 psi (200 MPa). The CIPed green compacts were then sintered for 1 h at 1450 $^{\circ}\text{C}$ under a nitrogen-based atmosphere (95% N_2 + 5% H_2) at flow rate 1 l/h. Fig. 1 shows the sintering cycle. The heating rate was 5 $^{\circ}\text{C}/\text{min}$ to 450 $^{\circ}\text{C}$ and 10 $^{\circ}\text{C}/\text{min}$ for the remaining sintering cycles before cooling the furnace to room temperature at 7 $^{\circ}\text{C}/\text{min}$. Holding steps (450, 1320, and 1450 $^{\circ}\text{C}$) were introduced to minimize the pores and gases generated during the sintering process. The first holding at 450 $^{\circ}\text{C}$ for 10 min was performed to remove all oxides and residue gases [28]. Further holding at 1320 $^{\circ}\text{C}$ for 10 min promoted uniform melting and homogenous distribution of Co, improving the properties of the sintered composite. Several researchers reported that a heating schedule with holding steps (450, 1320, and 1450 $^{\circ}\text{C}$) produced higher density and hardness of sintered composites compared to direct heating (450–1450 $^{\circ}\text{C}$) without any steps [8,9]. The densities of the sintered samples were validated through Archimedes method by using an electronic densimeter MD 300S specific gravity meter.

The sintered samples were ground (Fig. 2) according to SPUN 120308, and ultrasonic cleaning in isopropanol was performed for 15 min to remove any dirt before sending the samples for coating deposition under cathodic arc physical vapor deposition (CAPVD) for 2 h. The deposition parameters are summarized in Table 2. The growth rate of the coating was approximately 0.75 $\mu\text{m}/\text{h}$, and 0.1 μm thickness of the ZrN interlayer was deposited onto some inserts prior to TiCN coating to improve the adhesivity of TiCN on the substrate before becoming a TiCN/ZrN coating. CH_4 was not used in the deposition of ZrN. After coating deposition, a Bruker-D8 X-ray diffractor (XRD) was used to examine the compositions of the coatings. The source was Cu $\text{K}\alpha$, with wavelength 0.15406 nm.

After performing the processes mentioned above, three types of inserts, namely, uncoated cemented tungsten

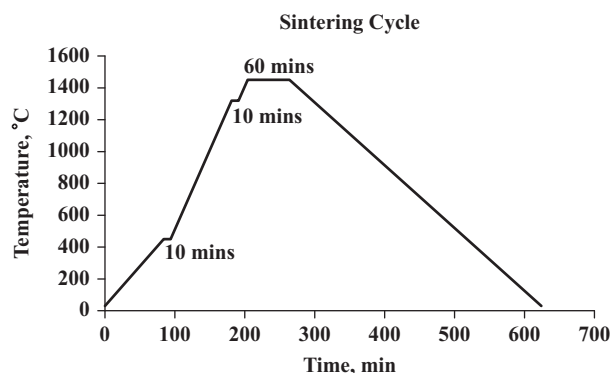


Fig. 1. Sintering cycle of WC-6Co.

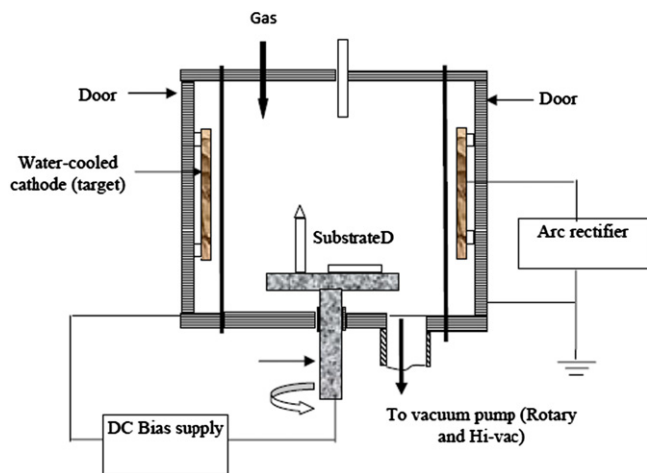


Fig. 2. Schematic diagram of CAPVD.

Table 2

Deposition parameters under CAPVD.

Temperature	300 °C
Current	100 A
Ion bombarding	5 min
N ₂ flow rate	250 sccm
CH ₄ flow rate	< 10 sccm

carbide inserts (IH1), TiCN/ZrN-coated carbide inserts (IH2), and TiCN-coated carbide inserts (IH3), were developed in-house. The mechanical properties of the in-house developed inserts, such as microhardness, surface roughness, and coefficient of friction, were determined and compared with the mechanical properties of commercially available uncoated WC inserts (C1), TiN-coated carbide inserts (C2), and TiCN-coated carbide inserts (C3), which were supplied by Sumitomo Electric.

An uncoated 6 mm AC100Cr6 steel ball was used to dry turn the samples at 10 cm/s for 1000 m under 10 N normal load, with turning radius 4 mm. Ball on disk tests were performed using a CSEM Tribometer, and mass loss of the samples after the tests was considered as the wear loss. The microhardness of the coating was determined using an Affri microhardness tester at 50g, and Micromaterials-made nano-indentator. The surface roughness of the inserts was measured using a Shimadzu SPM 9500 J2.

3. Results and discussion

XRD results show that the deposition parameters indicated in Table 2 can successfully deposit TiCN and ZrN on cemented WCs (Fig. 3). However, the TiN formation was also significant within the deposition parameters. This is due to the inadequate 'C' atoms to form Ti(C)N. Thus, the gas flow rate of CH₄, which is the source for 'C' atom, needs to increase for promoting the increment of TiCN formation rate. Nevertheless, increasing of 'C' atom may increase the formation of TiC, which is very

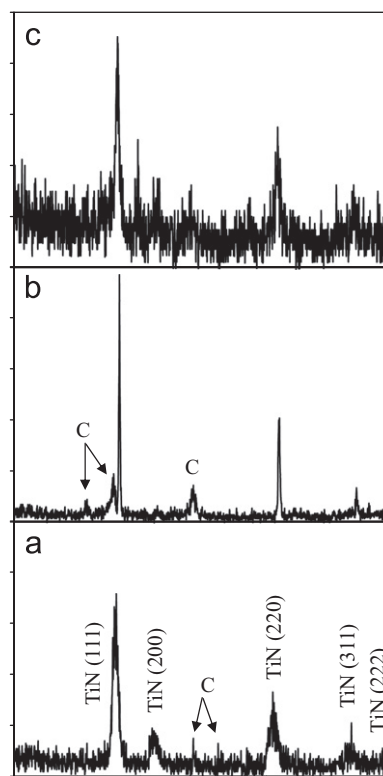
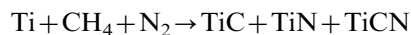


Fig. 3. XRD patterns of the (a) commercial TiCN, (b) in-house developed TiCN, and (c) in-house developed TiCN/ZrN coatings.

little and negligible within the deposition parameters described in Table 2.



The coated inserts were found to have significantly lower coefficient of friction than uncoated inserts, and the coefficient of friction of TiCN was consistently slightly lower than that of TiN. The in-house developed inserts were comparable to commercially available inserts in terms of the coefficient of friction. The friction coefficient of the in-house developed uncoated carbide inserts was slightly higher than that of the commercial uncoated carbide inserts. After PVD-coating with TiCN/ZrN and TiCN, the friction coefficient of in-house developed carbide inserts was significantly reduced. The in-house developed TiCN-coated carbide inserts had a similar friction coefficient value with commercial TiCN-coated carbide inserts. However, the in-house developed TiCN/ZrN-coated carbide inserts had slightly higher coefficient of friction than that of the in-house developed and commercial TiCN-coated carbide inserts. The commercial TiN-coated carbide inserts had the highest coefficient of friction among the coated carbide inserts (Fig. 4).

The surface roughness of the commercial inserts was found to be lower than that of the in-house developed inserts. The in-house developed uncoated carbide inserts exhibited higher surface roughness and higher coefficient

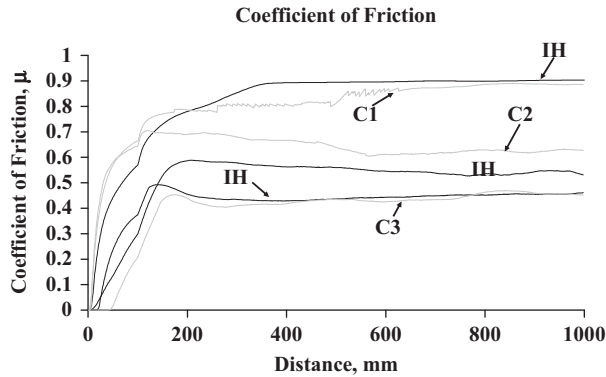


Fig. 4. Comparison of the coefficients of friction.

of friction than those of commercial uncoated carbide inserts, indicating that the higher surface roughness of uncoated inserts could marginally increase the coefficient of friction. On the other hand, the in-house developed TiCN-coated carbide inserts exhibited higher surface roughness, but they had a similar coefficient of friction value as that of the commercial TiCN-coated carbide inserts. Both the in-house developed and commercial TiCN-coated carbide inserts had higher surface roughness than that of the commercial TiN-coated carbide inserts, but they both had lower coefficient of friction, indicating that TiCN coating had better lubricity than that of TiN coating, which is in agreement with the findings of previous studies [13,18,19]. Thus, the coefficient of friction of a coating is strongly dependent on the lubricity rather than on the surface roughness of the coating material.

Hard Ti-based coating was proven to increase the surface hardness of the inserts. The surface hardness of the commercial uncoated carbide inserts increased when they were coated with thin layers of TiN and TiCN. Moreover, the surface hardness of the in-house developed uncoated carbide inserts increased when they were coated with TiCN/ZrN and TiCN. Despite the in-house developed uncoated carbide inserts exhibiting higher surface hardness compared to commercial uncoated carbide inserts, the surface hardness of in-house developed TiCN/ZrN and TiCN coatings was lower than that of commercial TiCN coating but higher than that of commercial TiN coating. The lower surface hardness of the in-house developed TiCN/ZrN and TiCN coatings may be due to the formation of TiN that reduced film hardness. The surface hardness of the in-house developed TiCN/ZrN and TiCN coatings is expected to increase with increasing of TiCN formation.

On the other hand, coating was also proven to reduce the wear loss and improve abrasive wear resistance. The wear of the cutting inserts is predominantly due to abrasive wear during the ball on disk tests. Moreover, the coated cutting inserts exhibited lower wear loss than uncoated cutting inserts. However, the wear loss throughout the experiment was not significant (0.002–0.003 g). Thus, the

Table 3

Results of the mechanical properties tests.

Tests	Inserts					
	IH1	IH2	IH3	C1	C2	C3
Coefficient of friction μ_t	0.90	0.56	0.49	0.85	0.66	0.45
Wear loss (g)	0.003	0.002	0.002	0.003	0.002	0.002
Surface roughness, R_a (nm)	80.58	89.97	99.02	56.56	51.80	60.92
Microhardness, 0.2 HV	1600	2500	2650	1400	2300	3000
Nano indentation (GPa)	16	25	26	13	20	32

influences of surface roughness and the coefficient of friction on wear loss cannot be concluded. Nevertheless, saying that coating could improve the wear resistance and reduce wear loss is also not wrong.

The results obtained from the mechanical properties tests are summarized in Table 3. Thus, the coated carbide inserts can be predicted to have longer tool life than uncoated carbide inserts. Moreover, the in-house developed TiCN/ZrN- and TiCN-coated carbide inserts had comparable tool life and performance with those of commercial TiCN-coated carbide inserts, and they may perform better than commercial TiN-coated carbide insert in real machining application.

4. Conclusions

The following can be concluded from the study carried out:

1. The coating deposition parameters used in this experiment could successfully deposit TiCN and ZrN on cemented WC substrates. However, the gas flow rate of CH_4 should be further increased to increase the formation rate of TiCN.
2. The in-house developed uncoated, TiCN/ZrN-coated and TiCN-coated WC inserts, were comparable to commercially available uncoated TiN-coated and TiCN-coated WC inserts.
3. The coefficient of friction of the in-house developed TiCN was slightly lower than that of the commercial TiN coating, and it was comparable to that of the commercial TiCN coating.
4. Coating could significantly reduce the coefficient of friction and consequently improve the abrasive wear resistance of carbide inserts.
5. The higher surface roughness of uncoated inserts led to a higher coefficient of friction, but the coefficient of friction of a coating strongly depends on the lubricity rather than on the surface roughness of the coating.
6. Ti-based hard coating could significantly improve the surface hardness of cutting tools. The surface hardness of the in-house developed TiCN/ZrN and TiCN coatings was lower than that of commercial TiCN coating but higher than that of commercial TiN coating.

Acknowledgments

The authors would like to thank the government of Malaysia, Universiti Kebangsaan Malaysia, and Advanced Materials Research Centre, SIRIM Berhad, for their financial, manpower and facilities supports.

References

- [1] M.A. Selamat, N.I.I. Mansor, N.M. Diah, T.R. Jaafar, Powder metallurgy and applications of hardmetals—the opportunities for Malaysian industries, *Journal of Industrial Technology (SIRIM)* 17 (1) (2008) 1–11.
- [2] H. Van Den Berg, Hardmetals: trends in development and application, *Powder Metallurgy* 50 (1) (2007) 7–10.
- [3] R.T. Faria Jr, M.F. Rodrigues, I.d. Andrade Esquef, H. Vargas, M. Filgueira, On the thermal characterization of a HPHT sintered WC–15% wt Co hardmetal alloy, *International Journal of Refractory Metals and Hard Materials* 23 (2) (2005) 115–118.
- [4] J. Pirso, S. Letunovits, M. Viljus, Friction and wear behaviour of cemented carbides, *Wear* 257 (3–4) (2004) 257–265.
- [5] L.J. Prakash, Application of fine grained tungsten carbide based cemented carbides, *International Journal of Refractory Metals and Hard Materials* 13 (5) (1995) 257–264.
- [6] S.A. Manaf, A.A. Rahman, N.M. Diah, M.A. Selamat, T.R. Jaafar, A study on microstructure, physical and mechanical properties of submicron WC–Co hard metals through press and cold isostatic pressing (CIP) routes, in: *Proceedings of the Malaysian Metallurgical Conference —MMC 2008, Kelab Golf Danau, Bangi (Universiti Kebangsaan Malaysia)*, 2008, p. 7.
- [7] W.D. Schubert, A. Bock, B. Lux, General aspects and limits of conventional ultrafine WC powder manufacture and hard metal production, *International Journal of Refractory Metals and Hard Materials* 13 (5) (1995) 281–296.
- [8] M.A. Selamat, S.A. Manaf, T.R. Jaafar, Microstructure, mechanical properties and cutting performance of sintered sub-micron WC–Co hardmetal powder, in: *Proceedings of the Malaysian Metallurgical Conference (MMC 2009), UniMAP, Perlis, Malaysia, 2009*, p. 4.
- [9] M.A. Selamat, S.A. Manaf, N.M. Diah, T.R. Jaafar, Powder metallurgy processing of hardmetal powder, *Solid State Science and Technology* 18 (1) (2010) 194–201.
- [10] R. Yigit, E. Celik, F. Findik, S. Koksul, Tool life performance of multilayer hard coatings produced by HTCVD for machining of nodular cast iron, *International Journal of Refractory Metals and Hard Materials* 26 (6) (2008) 514–524.
- [11] B. Navinšek, P. Panjan, I. Milošev, Industrial applications of CrN (PVD) coatings, deposited at high and low temperatures, *Surface and Coatings Technology* 97 (1–3) (1997) 182–191.
- [12] S. Kalpakjian, S.R. Schmid, *Manufacturing Processes for Engineering Materials*, 5th ed., Pearson Education, 2008.
- [13] K. Narasimhan, S.P. Boppana, D.G. Bhat, Development of a graded TiCN coating for cemented carbide cutting tools—a design approach, *Wear* 188 (1–2) (1995) 123–129.
- [14] J. Destefani, Cutting tools 101, in: *Manufacturing Engineering*, vol. 129 No. 3, Society of Manufacturing Engineers, Michigan, USA, 2002, p. 18.
- [15] Y.L. Yang, D. Zhang, H.S. Kou, C.S. Liu, Laser clad TiCN coatings on the surface of titanium, *Acta Metallurgica Sinica (English Letters)* 20 (3) (2007) 210–216.
- [16] S. Agrawal, A.K. Chakrabarti, A.B. Chattopadhyay, A study of the machining of cast austenitic stainless-steels with carbide tools, *Journal of Materials Processing Technology* 52 (2–4) (1995) 610–620.
- [17] P.C. Jindal, A.T. Santhanam, U. Schleinkofer, A.F. Shuster, Performance of PVD TiN, TiCN, and TiAlN coated cemented carbide tools in turning, *International Journal of Refractory Metals and Hard Materials* 17 (1–3) (1999) 163–170.
- [18] Y.H. Cheng, T. Browne, B. Heckerman, Influence of CH₄ fraction on the composition, structure, and internal stress of the TiCN coatings deposited by LAFAD technique, *Vacuum* 85 (1) (2010) 89–94.
- [19] Y. Yang, W. Yao, H. Zhang, Phase constituents and mechanical properties of laser in-situ synthesized TiCN/TiN composite coating on Ti–6Al–4V, *Surface and Coatings Technology* 205 (2) (2010) 620–624.
- [20] E. Bemporad, C. Pecchio, S. De Rossi, F. Carassiti, Characterization and hardness modelling of alternate TiN/TiCN multilayer cathodic arc PVD coating on tool steel, *Surface and Coatings Technology* 0 (146–147) (2001) 363–370.
- [21] E. Aslan, Experimental investigation of cutting tool performance in high speed cutting of hardened X210 Cr12 cold-work tool steel (62 HRC), *Materials and Design* 26 (1) (2005) 21–27.
- [22] C.-C. Tsao, H. Hong, Comparison of the tool life of tungsten carbides coated by multi-layer TiCN and TiAlCN for end mills using the Taguchi method, *Journal of Materials Processing Technology* 123 (1) (2002) 1–4.
- [23] T. Wang, L. Xiang, W. Shi, X. Jiang, Deposition of diamond/ β -SiC/cobalt silicide composite interlayers to improve adhesion of diamond coating on WC–Co substrates by DC-plasma assisted HFCVD, *Surface and Coatings Technology* 205 (8–9) (2011) 3027–3034.
- [24] C. Donnet, A. Erdemir, *Tribology of Diamond-like Carbon Films: Fundamentals and Applications*, Springer, 2008.
- [25] K.L. Mittal, Adhesion Aspects of Thin Films, *VSP* 1 (2001) 195–206.
- [26] J.H. Hsieh, C. Liang, C.H. Yu, W. Wu, Deposition and characterization of TiAlN and multi-layered TiN/TiAlN coatings using unbalanced magnetron sputtering, *Surface and Coatings Technology* 0 (108–109) (1998) 132–137.
- [27] N.I. Izura, M.A. Selamat, N.M. Diah, T.J. Jaafar, The evaluation of microstructure and mechanical properties of sintered sub-micron WC–Co powders, in: *Proceedings of the National Metallurgical Conference 2007, Johor Bahru, Malaysia, 2007*.
- [28] G.-H. Lee, S. Kang, Sintering of nano-sized WC–Co powders produced by a gas reduction–carburization process, *Journal of Alloys and Compounds* 419 (1–2) (2006) 281–289.