

Thermal Stability and Coefficient of Friction of the Diamond Composites with the Titanium Compound Bonding Phase

S. Cygan, L. Jaworska, P. Putyra, W. Ratuszek, J. Cyboron, and P. Klimczyk

(Submitted November 28, 2016; in revised form March 22, 2017; published online May 10, 2017)

In this paper, processes occurring during heat treatment of the diamond-Ti compound composites without Co addition were investigated and compared with commercial PCD. Three types of materials were prepared. The first material was sintered using the mixture containing diamond and 10 mass% of TiC, the second material was prepared using diamond powder and 10 mass% of Ti-Si-C, and the third composite was sintered using the addition of 10 mass% of TiB₂. During the research, it was proved that TiO₂ formation contributes to material swelling and WO₃ (W is present from the milling process) causes a significant increase in coefficient of friction. TiC and Ti-Si-C bonded materials are very susceptible to this process of oxidation; their hardness drops absolutely after wear test at 600 °C. The diamond composite with TiB₂ is the most resistant to oxidation from investigated materials.

Keywords coefficient of friction, composite, oxidation, PCD, titanium compound

1. Introduction

Mechanical properties of the PCD (polycrystalline diamond) such as high hardness and wear resistance make its use as a cutting material very viable when abrasion plays an important role in the machining process (Ref 1). Production of the PCD tool usually is realized by processing diamond particles under HP-HT conditions with the presence of catalyst material. Such approach allows for bonding between diamond particles to form a matrix. Commonly, the metal-solvent catalyst (e.g., cobalt, nickel, iron) that promotes intergrowth of diamond particles is used. Currently, most popular in commercial use is the diamond with Co bonding phase, but cobalt catalytic properties lower the temperature, at which diamond to graphite transition occurs at atmospheric pressure. For the Co-based PCDs, thermal instability becomes an issue in the temperatures above 700 °C, where heat generated during the high-speed cutting processes can significantly exceed that temperature (Ref 1, 2). Diamond cutting tools oxidation and graphitization temperature drastically diminishes the potential use of those materials. It is possible to reduce thermal instability of diamond composites by minimalizing or completely removing Co content. In this work, the approach involved the use of three ceramic bonding phases such as TiC, Ti₃SiC₂ and TiB₂. Titanium carbide and titanium diboride, which are known to have superior physical properties such as a high melting point and high hardness, can be successfully sintered with diamond at HP-HT conditions (Ref 3-6). Ti₃SiC₂ is an

ceramic with both excellent metal and ceramic properties such as low density, high melting point, good electrical and thermal conductivities, antioxidation and thermal shock resistance (Ref 7). Plastic properties of Ti₃SiC₂ make it a very good candidate for diamond bonding, due to that attempts were made to sinter it not only in HP-HT (Ref 6) conditions but for example also with the SPS (spark plasma sintering) technique (Ref 8). In this work, these titanium compounds were used as a bonding phase for diamond powder sintering and tested for their behavior under the influence of high temperature in air atmosphere. Additionally, high-temperature tribological tests were carried at temperatures up to 800 °C, which show how changes occurring within the material as a result of heating influence the coefficient of friction. These studies give insight into behavior of the material at friction conditions without expensive cutting tests.

2. Experimental

As a base powders for the mixtures preparation, diamond (3-6 μm MDA, Element Six), titanium carbide (H.C. Starck, 1-1.5 μm), Ti-Si-C (produced by SHS—self-propagating high-temperature synthesis method, 2-4 μm, phase composition shown in Fig. 1) and titanium boride (American Elements, < 100 nm) were used.

Mixtures containing diamond and 10 wt.% TiC, 10 wt.% Ti-Si-C or 10 wt.% TiB₂ were prepared using Pulverisette six-planetary mill (Fritch). The milling time at 200 rpm was equal to 1 h (divided into six cycles, where after every cycle a change of rotation direction occurred). After the milling process, mixtures were dried and sieved through 1-mm mesh.

Sintering processes were carried out using the Bridgman-type high-pressure-high-temperature (HP-HT) apparatus. Mixtures were prepressed at 100 MPa into disks 15 mm in diameter and 5 mm high. Green bodies were then put in the graphite heater which subsequently was inserted into remaining ceramic elements of the HP-HT gasket assembly; identical procedure was closely described in Ref 9. Sintering was carried out within

S. Cygan, L. Jaworska, P. Putyra, W. Ratuszek, J. Cyboron, and P. Klimczyk, The Institute of Advanced Manufacturing Technology, Wroclawska 37a str., 30-011 Krakow, Poland. Contact e-mail: slawomir.cygan@ios.krakow.pl.

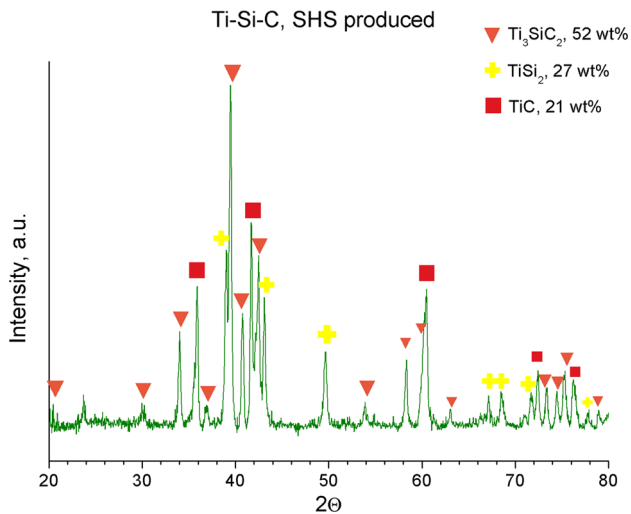


Fig. 1 X-ray phase composition of Ti-Si-C powder produced by SHS technique

the temperature ranging from 1600 °C up to 2200 °C. For all sintering processes, pressure was at 7.8 ± 0.2 GPa and sintering duration was 40 s. After sintering, the samples were grinded on a cast iron plate with diamond slurry. On thus-prepared specimens, density and Young's modulus were measured. Density was designated using hydrostatic method. For the Young's modulus measurements, ultrasonic method was utilized and the samples with the highest values of Young's modulus were designated for further investigations.

The microstructure investigations were performed using the scanning electron microscope (JEOL JSM-6460LV).

Dilatometric research was carried out using the high-temperature dilatometer Netzsch 402 E on samples cut with electrodischarge machining technique into bricks with dimensions $4 \times 4 \times 12$ mm. Heating rate was equal to 5 °C/min., and tests were carried out in air up to 1200 °C.

Phase compositions were analyzed in air using x-ray diffractometer (Empyrean, by PANalytical), with the copper radiation ($\lambda_{Cu K\alpha} = 1.5418 \text{ \AA}$), 40 kV voltage and 30 mA current. The diffractometer is equipped with high-temperature chamber (Anton Paar HTK 2000N). The measurement procedure consisted of 16 steps. Every step consisted of heating with rate of 20 °C/min, 10 min of temperature stabilization and ~ 48 min of measurement. Up to 600 °C measurements were taken every 200 °C and from 600 to 1200 °C every 50 °C.

Friction behavior was studied with the use of ball-on-disk method with the CETR UMT-2MT universal mechanical tester (prod. USA). Alumina ball, 3.2 mm in diameter, was used due to its chemical inertness. Rotation speed was 0.1 m/s, test radius was at 4 mm, and each test lasted 30 min. Tests were carried out at RT, 200, 400, 600, 700 and 800 °C, and heating rate was at ~ 13 °C/min (after reaching the desired temperature, there was a 15-min delay before start of the test for temperature stabilization). After each test, hardness of samples was measured at 9.8-N load at room temperature with a Vickers apparatus.

3. Results and Discussion

XRD analysis of powder mixtures has shown that in all investigated materials there is a strong presence of tungsten

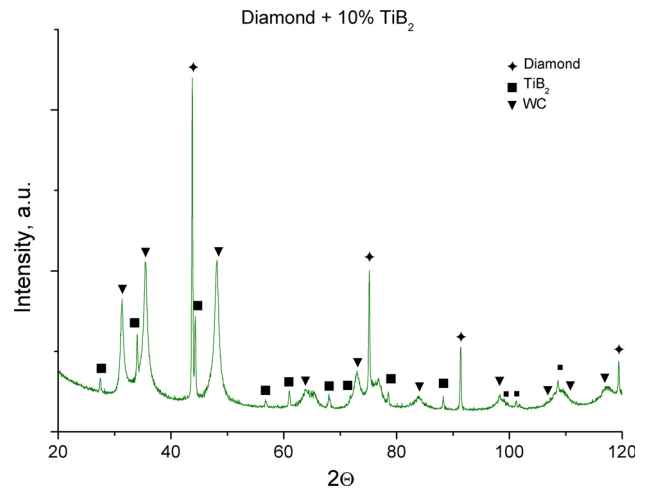


Fig. 2 XRD analysis of the diamond with addition of 10 wt.% of TiB₂ powder mixture

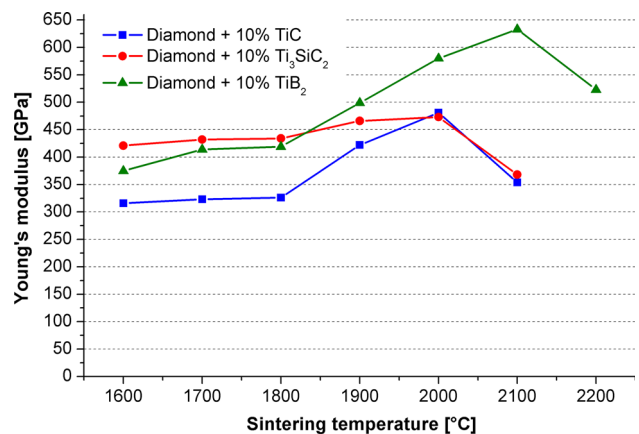


Fig. 3 Young's modulus dependence on sintering temperature for investigated diamond composites

carbide (WC) contamination. This addition is present from the milling process, due to the use of WC millers and vessel. Figure 2 shows a phase composition of diamond with 10 wt.% titanium diboride powder mixture; the peaks corresponding to WC are substantial.

Despite the presence of WC in powder mixtures, research was continued due to the wide use of similar mixing/milling techniques in PCD industry (Ref 10); furthermore, in commercially available PCD tools a participation of tungsten carbide was detected (Ref 11).

As it can be seen in Fig. 3, the highest values of Young's modulus for mixtures of diamond with 10 wt.% TiC and 10 wt.% of Ti-Si-C were obtained after sintering at 2000 ± 50 °C; for diamond with 10 wt.% TiB₂ the peak value of Young's modulus was reached after sintering at 2100 ± 50 °C. Thus, sintered samples were designated for further investigations. As shown in Fig. 3, Young's modulus for all investigated materials increases with the increase of sintering temperature. This is due to the improvement of bonding between diamond grains and diamond with bonding phase. The decrease in Young's modulus after reaching its maximum is due to the graphitization process of diamond.

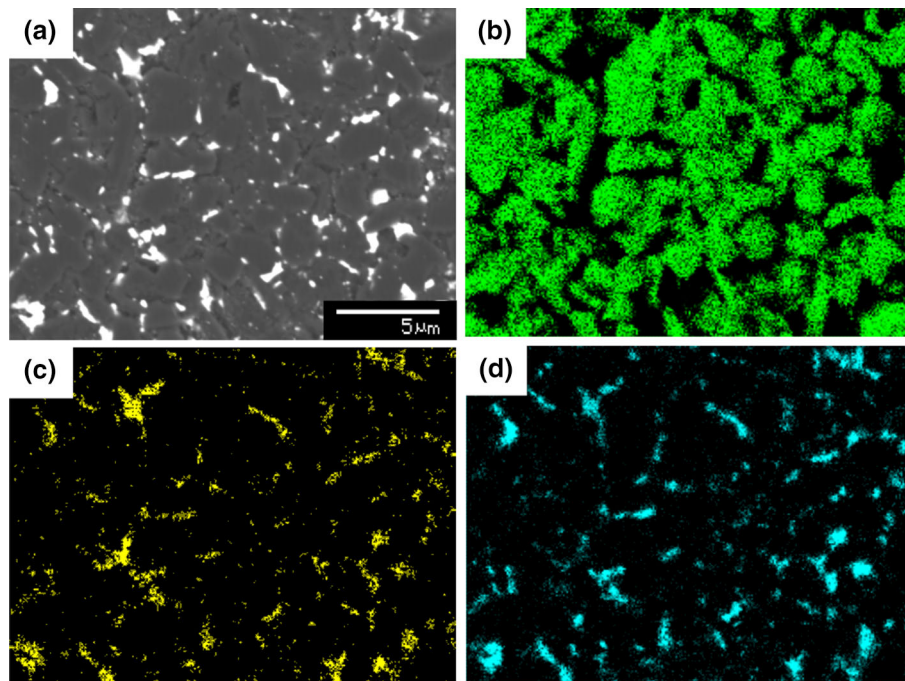


Fig. 4 SEM microstructure of the sample with 10 wt.% TiB₂ (a), EDS mapping analysis of C dispersion (b), Ti dispersion (c) and W dispersion (d)

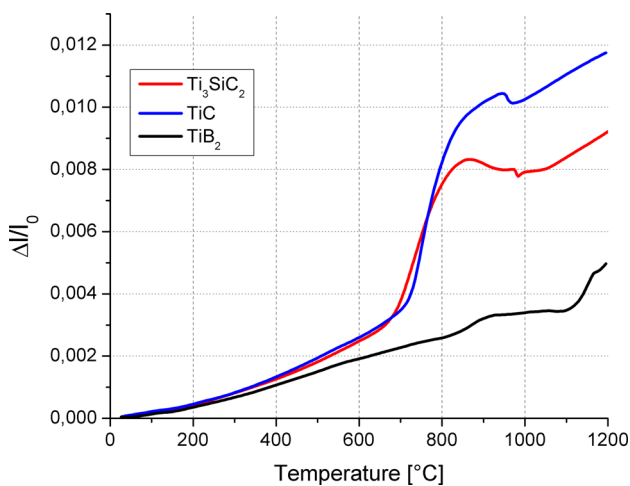


Fig. 5 Dilatometric research of investigated diamond composites

The densities of selected samples were at 3.7, 3.7 and 3.9 g/cm³ for TiC, Ti-Si-C and TiB₂ bonded materials, respectively.

As shown in Fig. 4, which shows SEM microstructure of the sample with 10 wt.% TiB₂ and EDS mapping analysis of C, Ti and W, milling/mixing with the use of planetary mill results in very homogenous samples. TiB₂ particles are evenly dispersed around diamond grains.

Dilatometric research (Fig. 5) shows that there is much more dynamic elongation of the material with the increase of temperature above 650 °C for materials with TiC and Ti₃SiC₂, whereas for diamond with TiB₂ material elongation is almost linear up to 1100 °C. The cause of this behavior is thoroughly explained by the means of high-temperature XRD analysis.

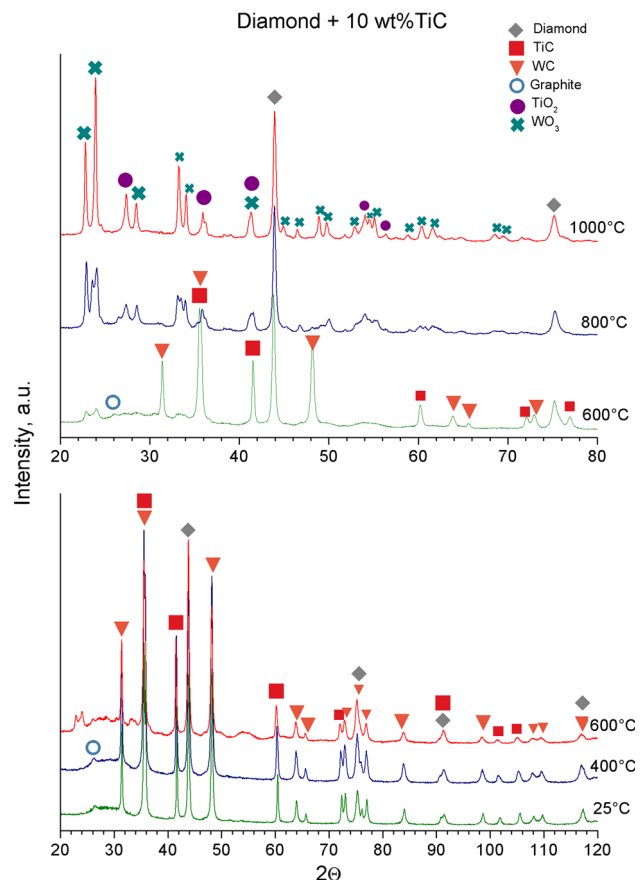


Fig. 6 XRD results for the sintered sample of diamond with 10 wt.% TiC in air atmosphere

Figure 6 shows results of the XRD analysis at selected temperatures within the range from room temperature up to 1000 °C for sintered sample with the 10 wt.% TiC addition.

Sintered compact with TiC bonding phase from room temperature up to 600 °C, as indicated by XRD analysis, consisted of diamond, TiC and tungsten carbide (from the milling process) and very small amount of graphite, which for these materials is below 2 wt.% (Ref 11) (graphite forms during sintering on diamond grain surfaces in void areas). From 600 °C, formation of oxides begins. The oxidation of titanium carbide for the sample with 10 wt.% TiC starts above 600 °C. This temperature is higher than for powder samples investigated in Ref 12, but lower than for bulk TiC samples, investigated in Ref 13. Although in work Ref 13 it is proved that above 600 °C TiO and Ti₂O₃ oxides should form, there were no such titanium compounds detected in the investigated materials besides TiO₂. As for the WC, the peaks corresponding to tungsten oxide are already visible at 600 °C. In work Ref 14 oxidation process of WC-Co carbides is described; this research indicates that for tungsten carbide oxide layer forms above 500 °C, but very slowly, at 600 °C the duration needed for WC to oxidize is much shorter. Figure 6 shows that all oxidation processes are fully completed up to 1000 °C, and there were no further changes in the material phase composition, and it consisted of diamond, TiO₂ and WO₃.

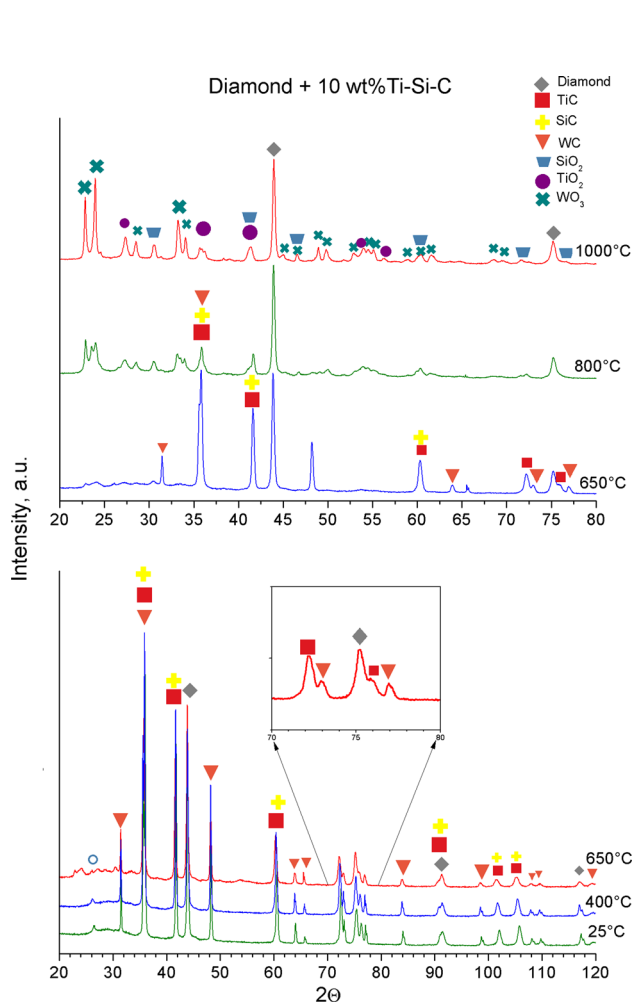


Fig. 7 XRD results for the sintered sample of diamond with 10 wt.% Ti-Si-C in air atmosphere

Figure 7 shows results of XRD analysis at selected temperatures within the range from room temperature up to 1000 °C for the sample with the addition of 10 wt.% Ti-Si-C (SHS produced) powder. Although there is a 52 wt.% participation of the Ti₃SiC₂ in raw powder (Fig. 1), it decomposed alongside TiSi₂ into TiC and SiC. This behavior is consistent with the research carried out in Ref 15, where it was described that Ti₃SiC₂ is stable at HP-HT conditions (~4 GPa) up to 1800 °C, whereas investigated sample was obtained at ~8 GPa and 2000 ± 50 °C. XRD investigations at room temperature of the diamond sample with the addition of 10 wt.% Ti-Si-C show that there are no remaining Ti₃SiC₂ and TiSi₂ phases; material consists of diamond, TiC, SiC and WC from the milling process. Despite the lack of the targeted Ti₃SiC₂ phase in the sintered sample, titanium and silicon carbides have positive impact of the PCD properties and both were investigated as potential binding material in diamond composites (Ref 16-18). During the high-temperature investigations, Ti-Si-C bonded material behaved very similarly to TiC bonded one despite the presence of the SiC, which also oxidizes in similar temperatures as TiC [SiO₂ starts to form above 600 °C (Ref 19, 20)]. In this case, also oxidation processes become apparent above 600 °C and are fully completed at 1000 °C, with no further changes in the material composition above that temperature.

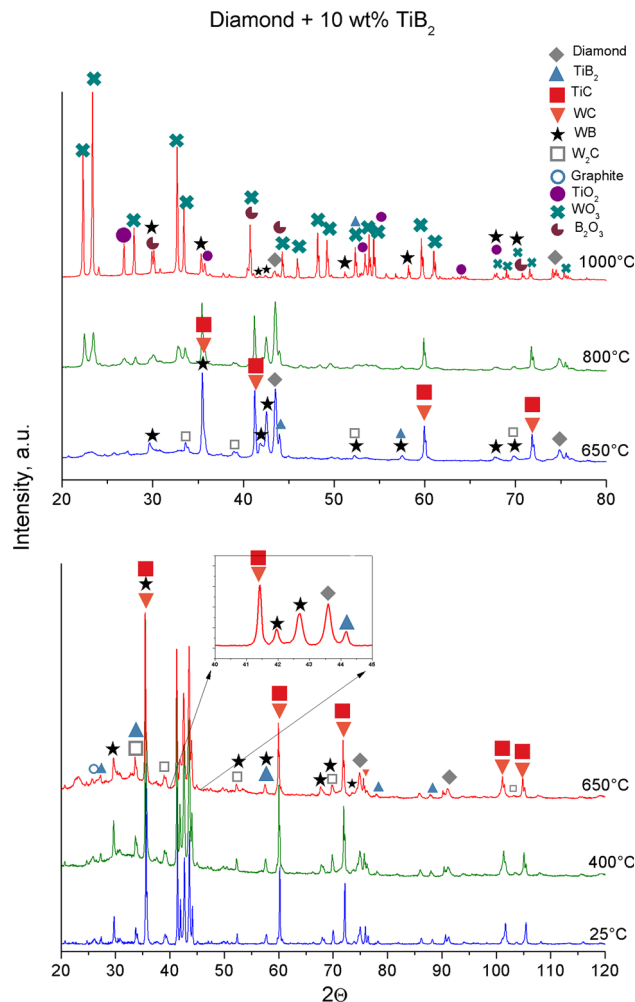


Fig. 8 XRD results for the sintered sample of diamond with 10 wt.% TiB₂ in air atmosphere

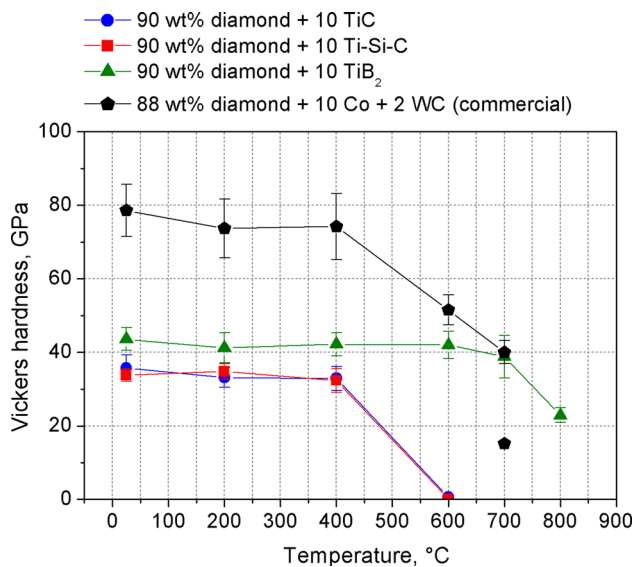


Fig. 9 Hardness of investigated diamond composites after tribological tests at elevated temperatures

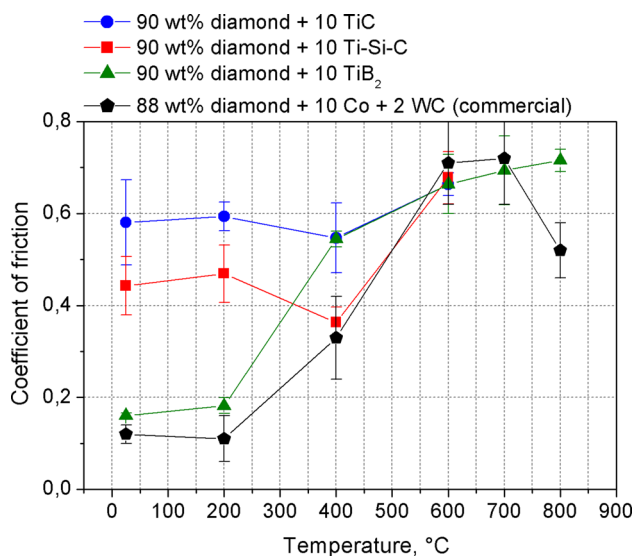


Fig. 10 Coefficient of friction of investigated diamond composites and commercial material at temperatures up to 800 °C

XRD investigations for diamond with TiB₂ (Fig. 8) show that after sintering small amount of titanium diboride decomposed, remaining titanium and boron formed TiC and WB (with the tungsten from the milling process). Additionally in the case of this material, W₂C has formed after sintering and WC has Fm-3m space group, whereas for the sintered samples with TiC and Ti-Si-C tungsten carbide has P-6m2 space group. These differences may be due to higher sintering temperature of the TiB₂ bonded sample (2100 ± 50 °C) than the TiC or Ti-Si-C bonded ones (2000 ± 50 °C). The formation of tungsten boride is beneficial because this compound is known to be resistant to thermal shock and is a good thermal conductor with high hardness, chemical inertness and resistance to high temperatures (Ref 21). In the case of TiB₂ bonded composite, there is much lower material elongation during heating (Fig. 5), this may be due to much lower amount of TiC within the sintered

sample, and this also indicates that formation of WO₃ has much less significant influence on material swelling than formation of rutile. Although TiB₂ oxidation becomes an issue at around 600 °C (TiO₂ and B₂O₃ are products of this process), its oxidation is strongly dependant on purity (Ref 22), and it can be seen that there is no significant change in its peaks intensities in investigated material at 800 °C. At 1000 °C, the TiB₂, TiC, WC and W₂C phases are fully oxidized, but WB which formed after sintering process appears to be still present within the material.

Figure 9 and 10 show results of hardness measurements and tribological tests, respectively. TiC and Ti-Si-C bonded composites were characterized by much higher value of coefficient of friction up to 400 °C than diamond with TiB₂ and commercial material; also hardness of those materials dropped rapidly after tribological test at 600 °C. Coefficient of friction of diamond with TiB₂ bonding phase and commercial material up to 200 °C was very low (below 0.2), but above this temperature it rose to reach about 0.7 at 700 °C. Hardness of commercial material decreases with the increase of temperature (about 17 GPa at 700 °C in cobalt rich spots) to no measurable hardness at 800°, where TiB₂ bonded composite retained its properties up to 700 °C (~20 GPa at 800 °C). For all investigated materials, there is a significant rise in coefficient of friction above 600 °C. As indicated by investigations carried out, this is a result of more extensive oxidation above that temperature and material degradation linked with this process.

4. Conclusions

High-temperature XRD analysis and dilatometric research indicate that for the investigated diamond composites, TiO₂ and WO₃ oxides begin to form above 600 °C. W is present in the material from the milling process. TiC and Ti-Si-C bonded materials are very susceptible to this process of oxidation, their hardness drops absolutely after wear test at 600 °C, and coefficient of friction of these materials is above 0.4 even at room temperature.

The diamond composite with TiB₂ is more resistant to oxidation than TiC and Ti-Si-C system max phase bonded materials. This material friction behavior mirrors that of commercial PCD; moreover, it retains its hardness at higher temperatures. It is also visible that TiO₂ formation contributes to extensive material swelling and oxidation process causes a significant increase in coefficient of friction.

Acknowledgments

This study was supported by the statutory activity of the Institute of Advanced Manufacturing Technology, Krakow, DS.14-4.1.

Open Access

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. E.M. Trent and P.K. Wright, *Metal Cutting*, 4th ed., Butterworth-Heinemann, Boston, 2000
2. J.E. Field, *The Properties of Natural and Synthetic Diamond*, Academic Press, London, 1992
3. S.M. Hong, M. Akaishi, and S. Yamaoka, High-Pressure Synthesis of Heat-Resistant Diamond Composite Using a Diamond-TiC_{0.6} Powder Mixture, *J. Am. Ceram. Soc.*, 1999, **82**(9), p 2497–2501
4. M. Szutkowska, L. Jaworska, M. Rozmus, P. Klimczyk, and M. Bucko, Diamond Composites with Nanoceramic Boride Bonding Phases, *Arch. Mater. Sci. Eng.*, 2012, **53**(2), p 85–91
5. L. Jaworska, P. Klimczyk, M. Szutkowska, P. Putyra, M. Sitarz, S. Cygan, and P. Rutkowski, Thermal Resistance of PCD Materials with Borides Bonding Phase, *J. Superhard Mater.*, 2015, **37**(3), p 155–165
6. L. Jaworska, Diamond Composites with TiC, SiC and Ti₃SiC₂ Bonding Phase, *High Press. Res.*, 2002, **22**, p 531–533
7. M.W. Barsoum and T. El-Raghy, Synthesis and Characterization of a Remarkable Ceramic: Ti₃SiC₂, *J. Am. Ceram. Soc.*, 1996, **79**(7), p 1953–1956
8. Y. Mu, J. Guo, B. Liang, and Q. Wang, Rapid Fabrication of the Ti₃SiC₂ Bonded Diamond Composite by Spark Plasma Sintering, *Int. J. Refract. Met. Hard Mater.*, 2011, **29**, p 397–400
9. P. Klimczyk, SiC-Based Composites Sintered with High Pressure Method, *Silicon Carbide—Materials, Processing and Applications in Electronic Devices*, InTech, 2011, p 309–334
10. A. Hara and S. Yazu, Diamond/Sintered Carbide Cutting Tool. Google Patents (1979)
11. L. Jaworska, M. Szutkowska, P. Klimczyk, M. Sitarz, M. Bucko, P. Rutkowski, P. Figiel, and J. Lojewska, Oxidation, Graphitization and Thermal Resistance of PCD Materials with the Various Bonding Phases of up to 800 °C, *Int. J. Refract. Met. Hard Mater.*, 2014, **45**, p 109–116
12. S. Shimada and M. Kozeki, Oxidation of TiC at Low Temperatures, *J. Mater. Sci.*, 1992, **27**(7), p 1869–1875
13. R.F. Voitovich and É.A. Pugach, High-Temperature Oxidation of Titanium Carbide, *Powder Metall. Met. Ceram.*, 1972, **11**(2), p 132–136
14. L. Chen, D. Yi, B. Wang, H. Liu, and C. Wu, Mechanism of the Early Stages of Oxidation of WC-Co Cemented Carbides, *Corros. Sci.*, 2015, **103**, p 75–87
15. J. Qin and D. He, Phase Stability of Ti₃SiC₂ at High Pressure and High Temperature, *Ceram. Int.*, 2013, **39**(8), p 9361–9367
16. S. Nauyoks, M. Wieligor, T.W. Zerda, L. Balogh, T. Ungar, and P. Stephens, Stress and Dislocations in Diamond-SiC Composites Sintered at High Pressure, High Temperature Conditions, *Compos. Part A Appl. Sci. Manuf.*, 2009, **40**(5), p 566–572
17. X. Zhou, Y. Wang, T. Li, X. Li, X. Cheng, L. Dong, Y. Yuan, J. Zang, J. Lu, Y. Yu, and X. Xu, Fabrication of Diamond-SiC-TiC Composite by a Spark Plasma Sintering-Reactive Synthesis Method, *J. Eur. Ceram. Soc.*, 2015, **35**(1), p 69–76
18. M.W. Cook and P.K. Bossom, Trends and Recent Developments in the Material Manufacture and Cutting Tool Application of Polycrystalline Diamond and Polycrystalline Cubic Boron Nitride, *Int. J. Refract. Met. Hard Mater.*, 2000, **18**(2), p 147–152
19. N. Al Nasiri, N. Patra, N. Ni, D.D. Jayaseelan, and W.E. Lee, Oxidation Behaviour of SiC/SiC Ceramic Matrix Composites in Air, *J. Eur. Ceram. Soc.*, 2016, **36**(14), p 3293–3302
20. J. Roy, S. Chandra, S. Das, and S. Maitra, Oxidation Behaviour of Silicon Carbide—A Review, *Rev. Adv. Mater. Sci.*, 2014, **38**(1), p 29–39
21. S. Yazici and B. Derin, Production of Tungsten Boride From CaWO₄ by Self-Propagating High-Temperature Synthesis Followed by HCl Leaching, *Int. J. Refract. Met. Hard Mater.*, 2011, **29**(1), p 90–95
22. V.B. Voitovich, V.A. Lavrenko, and V.M. Adejev, High-Temperature Oxidation of Titanium Diboride of Different Purity, *Oxid. Met.*, 1994, **42**(1–2), p 145–161