Materials Research. 2015; 18(3): 441-447
DOI: http://dx.doi.org/10.1590/1516-1439.265014

Study of the TiC Coating on Powder Metallurgy Diamonds Tool's Performance

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Received: January 21, 2014; Revised: March 28, 2015

Some diamond tools use iron in their composition, and it is known that iron is a strong catalyst for the graphitization of diamonds. This graphitization occurs mainly during the processing of composite materials - conventional sintering or hot pressing, and during cutting operations. This work studies the effect of TiC coating on diamond, on structure, microstructure and mechanical properties of the processed composites. Samples were prepared by mixing powders of Fe (40 μm) and diamond (425 μm), and subsequent hot pressing at 35MPa/900 °C, during 3 minutes. Microstructural aspects were observed by SEM, and iron diffusion on diamond was studied by EDS. Structural analyses were performed by X-ray diffraction and Raman spectroscopy. Compressive tests were carried out, as well as the wear resistance of the diamond composites. The importance of employing coated diamonds was stablished. It was observed that iron did not activated the graphitization of diamond crystals.

Keywords: *graphitization, hot pressing, coated diamond, powder metallurgy, cutting tools*

1. Introduction

Usually, diamond tools are produced by conventional sintering or hot pressing (powder metallurgy), and contain segments (diamond composites) which are responsible for the cutting action[1-3]. These tools comprise the diamond saws, discs, drill bits and diamond wires[4,5]. The performance of diamond cutting tools produced by the powder metallurgy techniques is connected to two main steps that occur through the reaction in the diamond-matrix interface. A chemical reaction is usually required between the diamond surface and bonding matrix, producing adhesion through chemical bonding, as well as by mechanical anchorage. The existence of this chemical reaction depends on the composition of the metal powder, its particle size and distribution, oxidation and/or reducing gases, temperature and duration of the sintering process[6]. The reactions that may take place during the processing of diamond composites can be quite detrimental to the cutting performance of these tools, which are oxidation and diamond graphitization[7].

Currently, there is great interest in studying the oxidation of diamonds for developing their application in electronic devices[8]. Due to the wide variety of working conditions in the industry, including the ability to work in high temperatures, diamond oxidation at high temperatures is usually observed, what is detrimental to its applications[9]. The diamond oxidation promotes changes in various properties such as chemical reactivity and electrical conductivity. It is well known that the reaction on sp3 hybridized carbon with oxygen forms the gaseous products CO and CO_2. The temperature and amount of oxygen that covers the diamond surface are the most influential factors for oxidation[10]. For temperatures between 700 °C and 1500°C, and 0% oxygen, it was found that the main effect was the change in the nature of chemical bonds of sp3 to sp2, characterized by phase change (graphitization)[9]. For temperatures around 700 °C and low oxygen concentration (below 20%), diamond is firstly converted to sp2 amorphous carbon. However, the carbon oxidation occurs, resulting in gaseous products CO and CO_2. Temperatures around 500 °C, and high oxygen concentration (above 50%), diamond is mainly converted to amorphous carbon sp3. As result, the carbon oxidation leads to the formation of gaseous products, CO and CO_2[10].

The graphitization is a critical matter for the use of synthetic diamonds in the industry, since the properties of their products differs greatly from diamond, compromising its use[11]. Some studies on this topic indicate the performance reduction of some diamond cutting tools for the stone industry, which are related to diamond graphitization[4,6-8].

According to Uspenskaya and collaborators[2], their experiments showed that an increase in temperature leads to graphitization in shorter times. Total transformation of diamond into graphite at a temperature of about 1900 °C was reported[13].

Zeren and Karagöz[14] found graphite on the diamonds' surfaces, when the latter were heated to temperatures above 1700 °C. It was concluded that this phenomenon was independent of the surrounding gas pressure.

As mentioned, diamond graphitization is a negative phenomenon for the performance of diamond cutting tools produced by powder metallurgy, especially when using iron as bonding matrix. The main problem is that Fe is a strong catalyst of the reverse transformation of diamond into graphite - graphitization[15-18], and during sintering (conventional or, more usually hot pressing) this phenomenon occurs, so that the tool experiences reduction in its performance and

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lifetime. It was found that Fe reacts with carbon atoms of diamond surfaces, forming Fe_3C – cementite, and diffuses into the diamond cubic lattice, which expands to a hexagonal one – graphitic structure, promoting partial or total degradation of some diamond crystals[8].

In this sense, this work investigates the thermal damage of diamonds in the presence of iron. It is also studied the effect of TiC coatings on diamond in the processed composites, mainly in comparison with uncoated diamond crystals.

2. Methodology

Materials used were water atomized 99.8% pure iron (Fe) powder from Merk, with mean particle size 40μm. The diamond from Element Six, granulometry 40/50 mesh (average size of the cube-octahedral crystals is 425μm). It was used two batches: uncoated diamonds, TiC coated diamond. All composites were produced using Powder Metallurgy techniques.

Fe-diamonds mixtures were performed in industrial mixer – Pyramid – for 30 minutes. The diamond content added to the Fe powder was 4% weight, which corresponds to concentration 50, widely used in some usual impregnated diamond tools. The diamond composites were produced by hot pressing. This step was performed in accordance with industrial parameters: 35MPa/900 °C/3 minutes, at room atmosphere.

XRD and Raman spectroscopy techniques were employed to observe possible graphitization of diamond crystals. In this sense, after sintering, diamond crystals were released from the Fe matrix using pure hydrofluoric. TiC coatings were also removed in this chemical treatment. XRD was performed in accordance with the parameters: 2θ: 20-60º, step ($\Delta\Theta$): 0,01º and step time (t): 0,5 second. It was used a Shimadzu diffactometer, operated with Cu kα radiation and Ni filter. Raman spectroscopy was used to identify different carbonaceous phases associated with different hybridization states of carbon, and possibly different degrees of crystallization to observe if there was diamond graphitization after sintering – the used equipment was a micro-Raman spectrometer constructed at the Physics department of the Universidade Federal do Rio Grande do Sul – UFRGS.

Mechanical properties of interest were also measured, using compression and wear tests for the Fe-diamonds composites. Compressive strength tests were performed to determine the rupture stress, yield strength and modulus of elasticity for the diamond composites. It was conducted in a universal mechanical testing machine INSTRON, model 5582 - 100 kN capacity, using a speed of 1 mm/min.

Microstructural analyses were performed by scanning electron microscopy (SEM), aiming to observe diamond crystals distribution in the matrix and fracture surface observations – for samples submmited to compression tests. The diamond crystals adhesion in the matrix was also studied by the observation of of the interfaces. Observations on the diamond coating and thermal damage were also performed. It was also used fluorescence spectrometer of X-ray energy dispersive (EDS) to perform qualitative analyses of elements in selected points of the matrix and diamonds.

All composites were submitted to wear test in a physical simulator fabricated by CONTENCO Ltda company, where the samples were mounted vertically in a fixture against a granite disc, with disc rotation 20 rpm, for cummulative periods of 2, 6, 12 and 20 minutes. These tests were conducted to evaluate the bonding matrix-diamond adhesion and abrasion resistance.

3. Results and Discussion

3.1. XRD analyses

Figures 1-3 show XRD patterns of diamonds under four different conditions: as received (prior to hot pressing), and the last three etched to release diamond from the Fe matrix and for the TiC coating removal to detect whether some kind of graphitization there occured.

Uncoated diamonds, in the conditions - as received and hot pressed - showed XRD patterns as illustrated in Figures 1 and 2. It can be noted that there is no evidence of residual phases present, only carbon in the diamond phase was observed. The peaks observed are in agreement with the works[15,16].

Figure 3 reffers to the diamond originally covered by TiC. It shows a lower intensity of the diamond peak. Diamond is the only material identified. However, a noise can be observed throughout the scan, but without significant effect. This

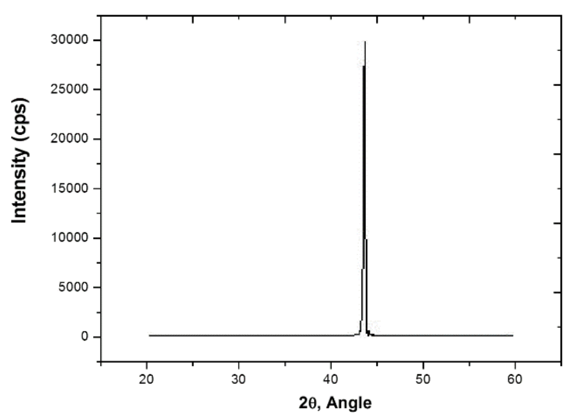

Figure 1. XRD pattern. Diamond crystals as received from the manufacturer.

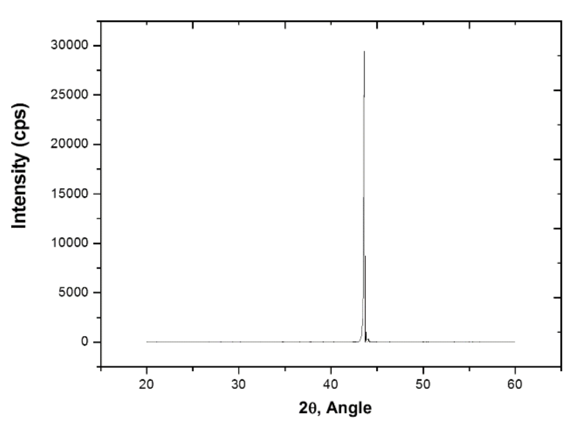

Figure 2. XRD pattern. Uncoated diamond crystals (hot pressed).

result can be attributed to impurities in the sample. Thus, in general, XRD did not found graphitization evidence, but the resolution of this technique is about 3%. Therefore, it is necessary to carry out further characterization for the observation of graphitization evidence.

3.2. Raman spectroscopy

The study of the Raman spectra aim to identify the presence of sp2 carbon derived from diamond graphitization. For this reason, different samples of diamond was selected: diamond crystals in the as received condition (prior to hot pressing); uncoated diamond - sintered with iron by hot pressing and chemically treated to release diamonds from the Fe matrix, and TiC coated diamond - sintered with Fe by hot pressing and chemically treated to release diamonds from the Fe matrix, and to remove the TiC coating. 100 crystals per type of diamond were used.

In Figures 4 to 6, all spectra reveal peaks corresponding to diamond, with wavenumber near 1338 cm^{-1}, which is in agreement with work of reference[16]. In comparison to the as received diamond, all the others spectra revealed distortions in the background, probably due to thermal stresses, and due to the TiC coating and Fe traces. Despite of such traces, it was not found any sign of graphitization, which is manifested by its characteristic peak with wavenumber by 1580 cm^{-1}. A single change can be observed around the wavenumber equivalent to 650 cm^{-1}, and it is not regarded to graphite, as also observed in the work of Zhao et al.[17]. Up to now, this peak was not defined in the literature. Thus it may be noted that diamonds are of high quality, without any kind of graphitization.

3.3. Compression tests

The compressive strength is very important for cutting elements, since their type of work is mostly compressive. It is a function of the bonding matrix to absorb and resist the loads imposed during cutting operations, especially concerning elastic loads, since a permanent deformation can cause loss of the unique properties of the tool, leading to formation of "gap" between diamond and metal matrix - fatigue, compromising the cutting tool performance[18]. Figures 7 and 8 show results of rupture stress (σ_r), yield strength (σ_y) and elastic modulus (E) for the diamond composites – it was used sets of 5 samples of each composite. It is worth saying that no literature data were found in this subject for similar composite.

The rupture stress and elastic modulus did not vary significantly for the composites. Nevertheless, TiC coated diamond composites presented slightly higher level in rupture stress and yield strength. This indicates that TiC coating is more effective regarding the observed properties. A slight

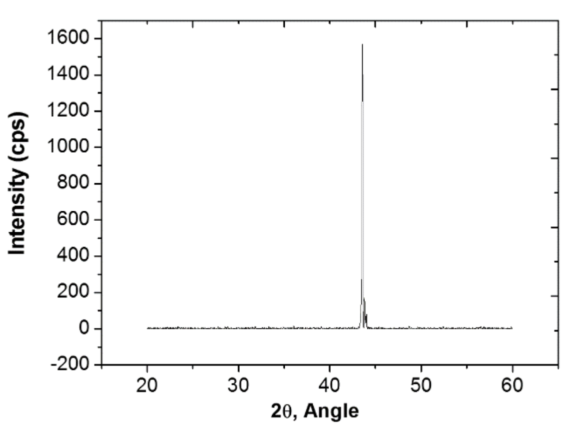

Figure 3. XRD pattern. TiC coated diamond crystals (hot pressed).

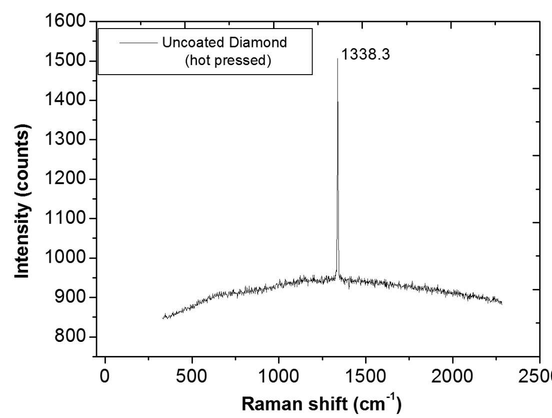

Figure 5. Raman spectroscopy of uncoated diamond, after hot pressing and chemical etching.

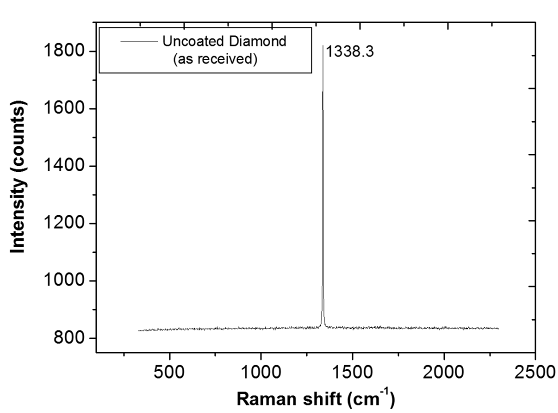

Figure 4. Raman spectroscopy of diamond crystals as received from the manufacturer.

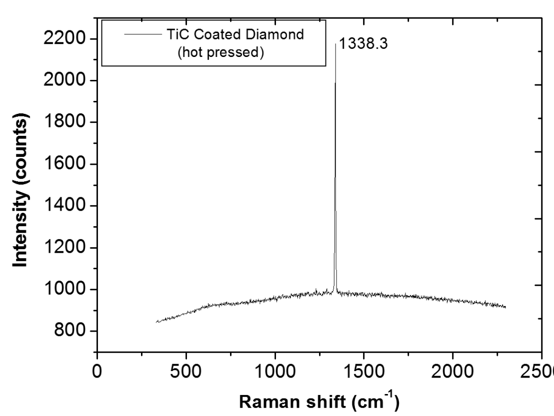

Figure 6. Raman spectroscopy of TiC coated diamond, after hot pressing and chemical etching.

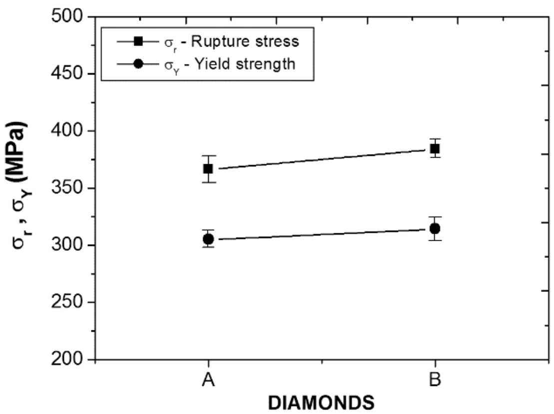

Figure 7. Rupture stress (σ_r) and yield strength (σ_y) of diamond composites. A: uncoated diamonds composites and B: TiC coated diamonds composites.

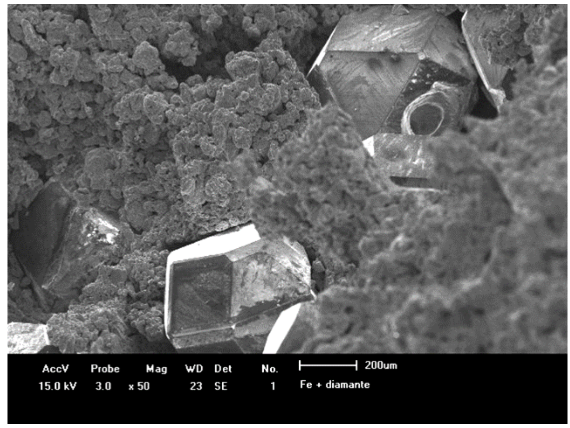

Figure 9. Micrograph of uncoated Fe-diamond composite after compression test.

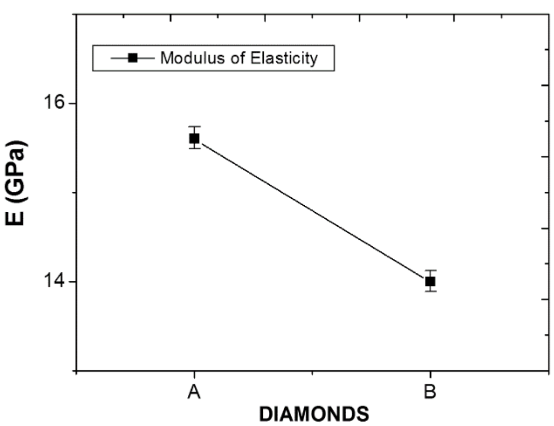

Figure 8. Modulus of Elasticity of diamond composites. A: uncoated diamonds composites and B: TiC coated diamonds composites.

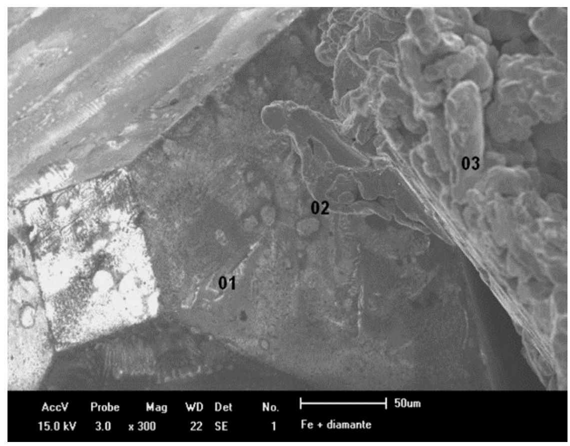

Figure 10. Micrograph of Fe-uncoated diamond composite after compression test. Points 1 to 3 are regarded to EDS analyses.

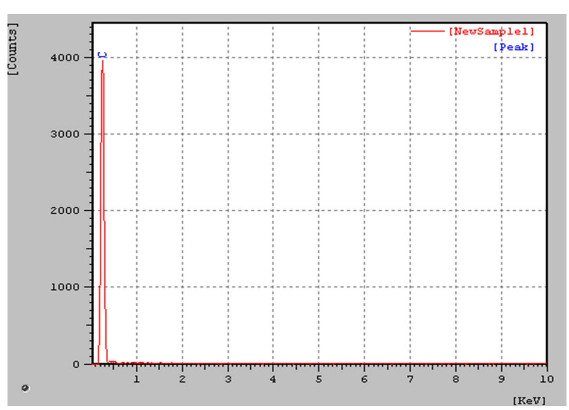

Figure 11. EDS analysis of uncoated diamond in point 01 of Figure 10.

improvement in results by the TiC coating is explained by mechanical anchorage or adhesion of diamonds crystals in Fe matrix.

3.4. Microstructural analyses

Figures 9 and 10 show the microstructures of the uncoated diamond composite. It can be observed from Figure 9 that fracture surfaces (after compression tests) exhibit weakly adhered diamonds in iron matrix. This can be explained by considering two aspects: (1) poor adhesion due to the absence of a coating on diamonds, (2) low compatibility iron/diamond, especially in the absence of the elements already established for the diamond adhesion, such as cobalt and nickel. These explanations are in agreement with works[6,19-21].

Figure 10 shows points analyzed by EDS. It can be seen in Figures 11, 12 and 13 that no reaction at the interface Fe-diamond there occured. The edges of the diamonds are well defined, the regular surfaces are indications that there was no consumption of diamond by graphitization or reaction with iron, for example, to form cementite (Fe_3C). Several cracks between matrix and diamond crystals are observed. The presence of these cracks is attributed to two factors: the first is the differential shrinkage of diamond and iron. During the heating of the composite, differences in the thermal expansion coefficients may remove diamond crystals from the Fe matrix. The most important factor is

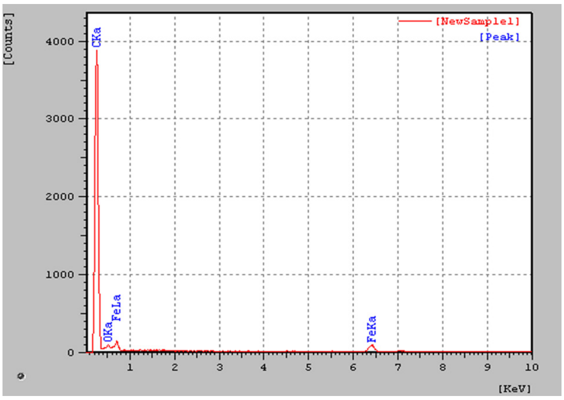

Figure 12. EDS analysis of uncoated diamond in point 02 of Figure 10.

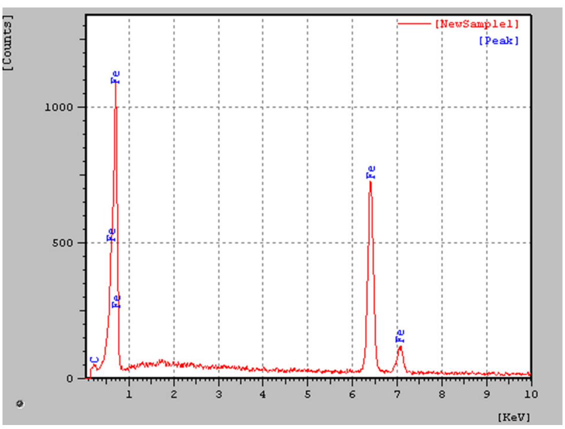

Figure 13. EDS analysis of uncoated diamond in point 03 of Figure 10.

attributed to the manner that the surface was obtained for analysis (plastic deformation by compression test). The compressive stresses deform the Fe matrix rather than the diamond crystals. Such tensions can also cause mechanical detachment of the diamond crystals.

Figures 14 and 15 show the fracture region of the TiC coated diamond composite. As observed for the other composite, cracks among the particles dispersed in the matrix can be observed in similar degree, and can be attributed to same causes discussed above, for the Figures 9 and 10.

Figures 16-18 show EDS points from Figure 15. It can be observed in Figure 17 that elements Al and Mg are contaminants from the sample preparation. N, C, and O interstitials are present in the normal chemical composition of the iron powder. In Figure 15, point 2 is located on a surface where there was a partial release of the TiC coating. Therefore, it presents basically diamond and iron. Point 3 is located on the TiC coating. However, it is possible that the peak around 6.4 keV is related to iron, which can mean a partial reactivity between Ti and Fe – thus explaining the chemical adhesion, which improves diamonds’ retention in the tool.

From the standpoint of graphitization prevention, TiC coating was efficient as can be seen in Figure 15, and EDS spectra shown in Figures 16, 17 and 18. The TiC coated diamond composite cleary showed different behavior when

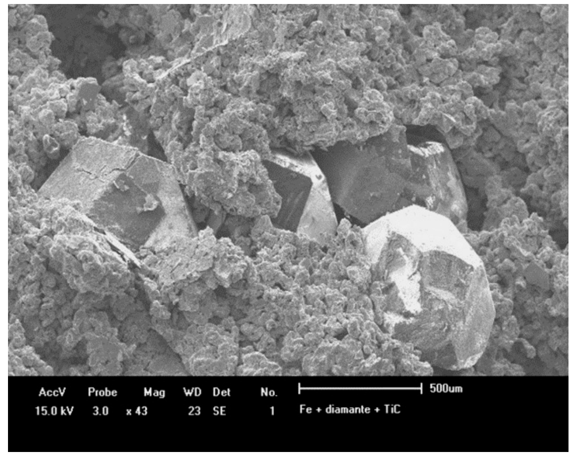

Figure 14. Micrograph of Fe-TiC coated diamond composite after compression tests.

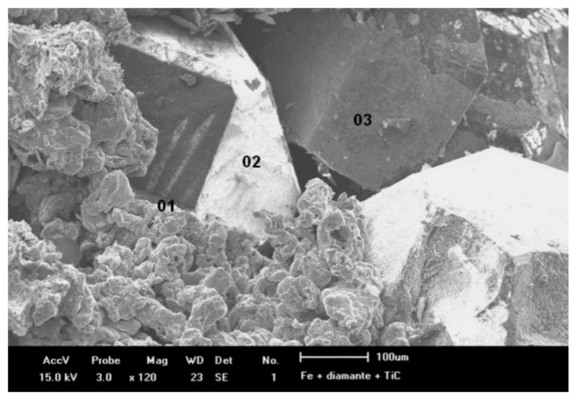

Figure 15. Micrograph of Fe-TiC coated diamond composite after compression tests. Points 1 to 3 are regarded to EDS analyses.

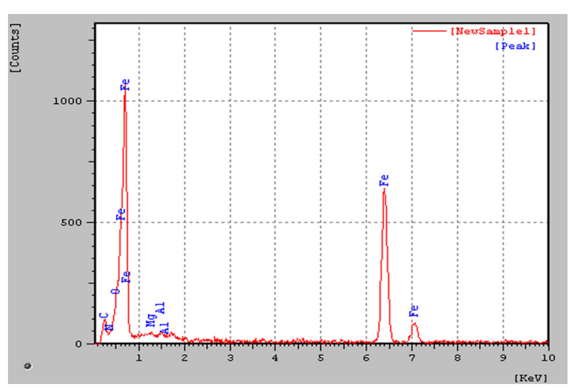

Figure 16. EDS analysis of TiC coated diamond in point 01 of Figure 15.

compared to the uncoated diamond, by analyzing the adhesion of the coating in the crystals and matrix. While uncoated diamond are poorly adhered, the TiC coating, in turn, adheres to the diamond crystals. This fact can be clearly noticed in Figures 14 and 15, where the TiC coating is well adhered on the surfaces of diamond crystals, even after the severe conditions of the compression test. The key for the coating adhesion in the matrix or diamond crystals is related to the

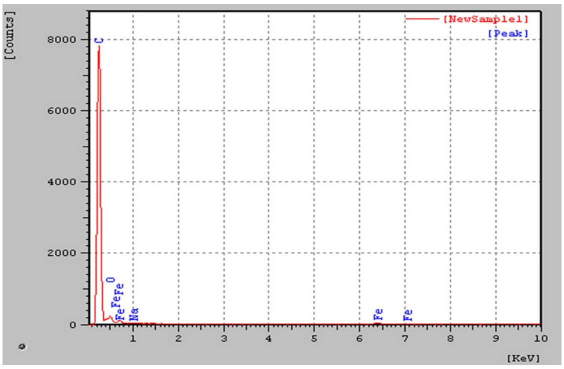

Figure 17. EDS analysis of TiC coated diamond in point 02 of Figure 15.

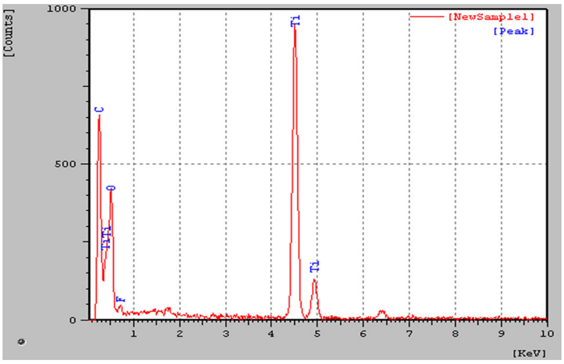

Figure 18. EDS analysis of TiC coated diamond in point 03 of Figure 15.

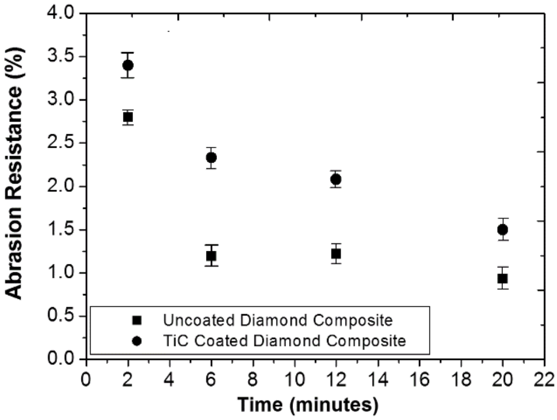

Figure 19. Abrasion Resistance (AR %) of Fe-diamond composites as a function of time. Mean values for three samples of each system.

nature of each material. So, the ceramic coating (TiC) present preferential adhesion to the diamond (also ceramic). This same conclusion was highlighted in the work of Oliveira[21], when studying the effects of this coating in diamonds and metal bonding based on Fe-Cu-Co alloys.

3.5. Wear tests

Figure 19 shows results of abrasion resistance as a function of time for all diamond composites. Sets of 3 samples of each composite were used. For 2 minutes, it is observed higher levels of abrasion resistance, which was expected, because wear occurs primarily in the metal matrix, which leads to the exposition of the diamonds' cutting faces - that begin the process of cutting stone. Thereafter, a slight decrease in abrasion resistance took place, especially in the range 6 to 12 minutes of testing. It happens because diamonds are already exposed on the matrix surface, and they're ready to start the cutting operation, thus resulting in a uniform loss of the matrix. Therefore, there is a constant wear rate. After 12 minutes, a decrease in abrasion resistance for Fe-diamond composites there occurred, again. In general, it is noted that there is a decrease in abrasion resistance as test time progresses. This is a classic behavior for diamond impregnated tool. The tool (diamond composite) tends to loose its cutting points for longer periods of testing. Therefore, there is a reduced abrasion resistance. It is stablished that the wear mechanism of diamond impregnated tools is continuous, so as the outer layers will be wearing, there are new cutting diamond layers emmerging from the composite bulk to continue the cutting process, until the end of life of the tool[18].

Analyzing the results, one can clearly observe that Fe-TiC coated diamond composite showed higher values of abrasion resistance for the four times testing, in relation to uncoated diamond composite. This can be attributed to the chemical adhesion TiC/Fe matrix (probably Fe-Ti solid solution formation during hot pressing). In addition, as the TiC coating is rough, it also improves the mechanical adhesion, in comparison to the smooth surface of uncoated diamonds. As studied previously, Figures 9 and 15 strenghten this discussion, where the TiC coated diamond (Figure 15) are more embedded in the Fe matrix than the uncoated one (Figure 9).

4. Conclusions

According to the overall characterizations, the TiC coated diamond composite presented the best results in relation to uncoated diamonds composites. In this work, it was stablished that the industrial hot pressing conditions did not generate diamond graphitization, even in the presence of iron - strong catalyzer agent for the diamond-graphite transformation.

The adhesion conditions between diamond and matrix are favorable for its application in cutting tools. The use of TiC coated diamond shows better properties, as compared to uncoated diamonds, when Fe is the metal matrix.

X-ray diffraction and Raman spectroscopy analyses indicate that graphitization did not occured. SEM and EDS results showed that there was no interaction between diamond and iron, what is a confirmation that diamonds' crystals didn't suffered thermal damage.

Acknowledgements

The authors would like to express their gratitude to the Brazilian agencies FAPERJ and CNPq. Authors are indebted to Prof. Altair Sória Pereira, from UFRGS, by performing the Raman spectroscopies.

References

1. Przyklenk K. Diamond impregnated tools: uses and production. *Industrial Diamond Review*. 1993; 4:192-195.
2. Filgueira M and Pinatti DG. Production of diamond wire by Cu-15%vol.Nb in situ process. In: *Proceedings of the 15th Int. Plausee Seminar. Reutte: Plansee Holding*; 2001; p. 360-374.
3. Jakobuss M. The dynamics of diamond retention in grinding wheel systems. In: *Proceedings of the Intertech*; 2000 July, 17-21. Vancouver; 2000.
4. Webb SW. Crystal retention improves ROI and performance of diamond tools. In: *Proceedings of the Intertech*; 2000 July, 17-21. Vancover; 2000.
5. Oliveira LJ. *Processing and characterization of the system Fe-Cu-diamond for use in diamond wire beads* [Dissertation]. Rio de Janeiro: UENF; 2005.
6. Oliveira LJ, Bobrovnitchii GS and Filgueira M. Processing and Characterization of Impregnated Diamond Cutting Tools Using a Ferrous Metal Matrix. *International Journal of Refractory Metals & Hard Materials*. 2007; 25(4):328-335. http://dx.doi.org/10.1016/j.ijrmhm.2006.08.006.
7. Zeren M and Karagöz S. Defect characterization in the diamond cutting tools. *Materials Characterization*. 2006; 57(2):111-114. http://dx.doi.org/10.1016/j.matchar.2005.12.010.
8. Cabral SC. *Influence of the use coated diamonds on the properties of diamond composites obtained by powder metallurgy* [Dissertation]. Rio de Janeiro: UENF; 2009.
9. Dresselhaus MS, Dresselhaus G and Eklund PC. *Science of fullerenes and carbon nanotubes*. San Diego: Academic Press; 1995.
10. Breusov ON, Drobishev VN and Ivanchihina GE. Effect of high temperature vacuum annealing on properties of detonation synthetic diamond. In: *Proceedings of International Symposium on Physico-chemical Properties of Ultra-hard Materials*. Kiev: Academy of Science; 1987. p. 48-53.
11. Shao WZ, Ivanov VV, Zhen L, Cui YS and Wang Y. A study on graghtization of diamond in copper-diamond composite materials. *Materials Letters*. 2004; 58(1-2):146-149. http://dx.doi.org/10.1016/S0167-577X(03)00433-6.
12. Uspenskaya KC, Tormashev UN and Fedoceev DV. Oxidization and graphitization of diamond in condition of low pressure atmosphere. *Journal of Physical Chemistry*. 1982; 56:495-496. [in Russian]
13. Fedoseev DV, Buhovets VL and Vnukov SP. Graphitization of diamond at high temperatures, surfacial and thermo-physical properties of diamond. In: *Proceedings of International Symposium on Physicochemical Properties of Ultra-hard Materials*. Kiev: Academy of Science; 1985.
14. Zeren M and Karagöz S. Defect characterization in the diamond cutting tools. *Materials Characterization*. 2006; 57(2):111-114. http://dx.doi.org/10.1016/j.matchar.2005.12.010.
15. Donneta JB. 13C NMR characterization of nanodiamonds. *Comptes Rendus de l'Académie des Sciences - Series IIC - Chemistry*. 2000; 3:831-838.
16. Li HS, Qi YX, Gong JH, Wnag M and Li MS. High-pressure synthesis and characterization of thermal-stable boron-doped diamond single crystals. *International Journal of Refractory Metals & Hard Materials*. 2009; 27(3):564-570. http://dx.doi.org/10.1016/j.ijrmhm.2008.07.015.
17. Zhao JG, Li FY, Yu RC and Jin CQ. Graphitization of activated carbon under high pressures and high temperatures. *Solid State Communications*. 2009; 149(19-20):818-821.
18. Oliveira LJ. *A new wear mechanism of metal-diamonds composites obtained by powder metallurgy* [Thesis]. Rio de Janeiro: UENF; 2009.
19. Barbosa AP. *Processing by Powder Metallurgy and characterization of the Fe-Cu-Co alloys for use in diamond tools* [Dissertation]. Rio de Janeiro: UENF; 2008.
20. Barbosa AP, Bobrovnitchii GS, Skury ALD, Guimarães RS and Filgueira M. Structure, microstructure and mechanical properties of pm Fe-Cu-Co Alloys. *Materials & Design*. 2010; 31(1):522-526. http://dx.doi.org/10.1016/j.matdes.2009.07.027.
21. Oliveira HCP. *Influence of niobium additions on system iron-copper matrix to act as bonding in diamond tools* [Thesis]. Rio de Janeiro: UENF; 2010.