

## Comparison of Different Metal Matrix Systems for Diamond Tools Fabricated by New Current Induced Short-Time Sintering Processes

W. Tillmann<sup>1,a</sup>, C. Kronholz<sup>1,b</sup>, M. Ferreira<sup>1,c</sup>, A. Knotz<sup>2</sup>, W. Theisen<sup>3</sup>, P. Schütte<sup>3</sup>, J. Schmidt<sup>4</sup>

<sup>1</sup>Institute of Materials Engineering, TU-Dortmund, University of Technology  
Leonhard-Euler-Str. 2, 44227 Dortmund, Germany

<sup>a</sup>wolfgang.tillmann@udo.edu, <sup>b</sup>christian.kronholz@udo.edu, <sup>c</sup>manuel.ferreira@udo.edu

<sup>2</sup>Büdiam Diamantwerkzeuge R. und N. Büttner GmbH

<sup>3</sup>Chair of Materials Engineering, Ruhr-Universität Bochum

<sup>4</sup>Fraunhofer Institute for Manufacturing and Advanced Materials (IFAM)

The new current induced sintering techniques like Spark Plasma Sintering (SPS) and Spark Plasma Consolidation (SPC) offer the possibility to fabricate diamond tools for the machining of mineral materials and concrete within a process time of several minutes down to a few milliseconds. First efforts in the fast sintering process of steel-copper diamond composites showed a very good compactibility of the powders.

In this paper the sintering behavior (SPS and SPC) of new alternative metal matrix components in combination with coated diamonds shall be analyzed. In this case it is the intention to vary the grain size of the metal powder to increase the sintering activity. To achieve the formation of a chemical bonding between diamond and metal within shorter process times, the usage of a carbide-forming metal coating on the diamonds, especially in combination with a non-reactive metal matrix should be enforced.

### Introduction

Diamond tools are mainly used for the cutting and grinding of stone and concrete. The circular saws, frame saws and drill bits consist of small diamond impregnated metal matrix segments, whose embedded diamonds are responsible for the cutting process. A well adjusted hardness of the metal matrix compared to the machined mineral material leads to a

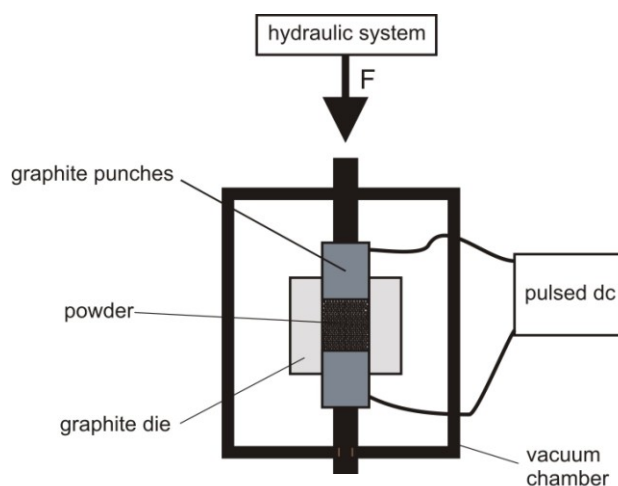


Fig. 1: SPS pressing tools

self sharpening process of the diamonds which guarantees good wear behavior [1].

Another important aspect regarding the wear resistance of these tools is the interface area between diamonds and metal matrix. The existence of a chemical reaction zone consisting of carbides or solid solutions has an advantageous influence at the diamond bonding. In this case Sung and Tai describe the reaction behavior of carbon with important transition metals. Generally the reactivity of metals against carbon depends on the number of electron vacancies in d-orbitals. Metals with a low number of vacancies (copper, zinc) are almost inert against carbon. In contrast metals with many free d-orbitals (titanium, chromium) show a tendency to form carbides or are carbon solvents [2].

Diamond grinding segments are generally fabricated powder metallurgically. The conventional production cycle consists of a preforming step at high pressure with a adjacent freestanding sintering under vacuum or the hot pressing where compaction and sintering is

combined in one step. These production ways have one common disadvantage indeed. The sintering time ranges from 1-2 hours up to a maximum of 4-8 hours in case of vacuum sintering [3, 4]. For this reason a cooperation of universities and industrial participations are developing new current induced sintering techniques which are much faster. The first technique in this field is called Spark Plasma Sintering (SPS). The SPS facility consists of a vacuum chamber, where the graphite pressing tools are located, and a hydraulic pressing system for the compaction of the metal powders. In principle the process works within two combined steps similar to the hot pressing. Primarily, the diamond-metal powder is compacted by the pressing tools and following while pressing into shape it is heated up to sintering temperature. The heating process is a fundamentally different mechanism compared to hot pressing. An electrical pulsed dc current of several thousand amperes is sent directly through the metal powder with a pulse duration up to 255 milliseconds. This special technique leads to small plasma discharges and sparks between the powder particles, which results in heating rates up to 800 K/min [5, 6].

One novel approach in this research project is to enhance the first successful efforts in fabricating diamond segments with the new fast sintering technique which is called Spark Plasma Consolidation (SPC) or Electro Discharge Sintering (EDS). The development of this current supported compaction process was first published in 1976 from Clyens, Al-Hassani and Johnson. During many years the process was further developed in line with better sintering facilities. So until now it is possible to consolidate aluminium, WC-Co, high speed steel as well as titanium powders within a few milliseconds. The SPC pressing tools are composed of a non-conductive silicon carbide forming die and two high conducting copper punches. The consolidation process itself begins with the hydraulic compaction of the metal powder at high pressures. While pressing a capacitor discharge of several hundred thousand amperes is sent through the powder which is densified within a few milliseconds (Fig. 2). Due to the short time the sintering processes do not base on diffusion and grain growth. In contrast grain growth and diffusion are inhibited and it is assumed that as a result of small plasma discharges the surface of the metal particles becomes partially melted [7, 8, 9].

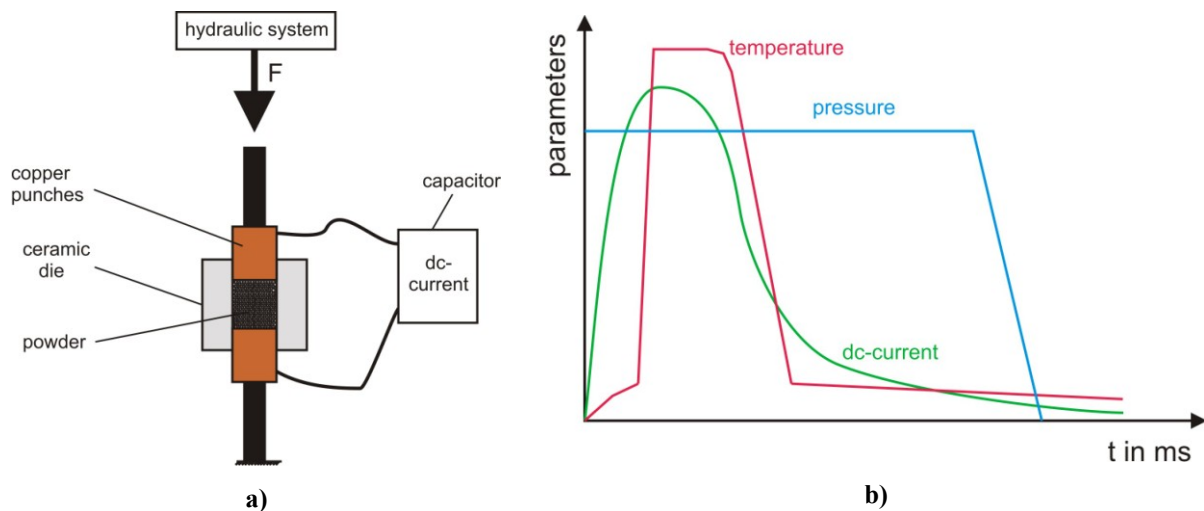


Fig. 2: Spark Plasma Consolidation; a) pressing tools, b) principal process

The first attempts in the fabrication of diamond tools with these new short-time sintering techniques showed generally a good compactibility of the metal-diamond composites. The following work shall now illustrate the carbide forming properties and graphitization of different metal-diamond composites which are fabricated by the new short-time sintering processes.

## Experimental work

For the characterization of interface reactions like carbide formation or graphitization in short-time sintering processes, four diamond-metal powder mixtures were used. First of all the metal binder shall be varied, using a high reactive iron-copper compound and on the other

side an inert pure bronze matrix. Two types of diamonds are embedded in each metal-matrix system. Usual uncoated 40/50 mesh diamonds and diamonds of same type with a titanium layer (Table 1) were used.

**Table 1: Materials**

<b>Sample</b>	<b>Metal-matrix</b>	<b>Diamonds</b>
<b>4D</b>	60% carbonyl iron + 40% copper	40/50 mesh
<b>4DTi</b>	60% carbonyl iron + 40% copper	40/50 mesh Ti-coated
<b>6D</b>	bronze (85/15)	40/50 mesh
<b>6DTi</b>	bronze (85/15)	40/50 mesh Ti-coated

As reference the materials shown in Table 1 were sintered with conventional techniques. 4D and 4DTi were sintered under vacuum in a “PVA TePla AG” furnace at a suitable temperature for liquid phase sintering. 6D and 6DTi were densified in a hot pressing facility (Table 2).

Two specimen which were compacted by Spark Plasma Sintering (SPS) were chosen for investigation. The SPS machine in that case was a “HP D 250” from “FCT Systeme GmbH” which is operated by the “Fraunhofer Institute for Manufacturing and Advanced Materials (IFAM)” in Dresden (Table 3). At last samples are fabricated by the new Spark Plasma Consolidation process (SPC) or Electro Discharge Sintering (EDS). This prototype facility constructed by “Frey GmbH and M. Schlemmer GmbH” is located at the “Chair of Materials Engineering” at the “Ruhr-Universität Bochum” (Table 4).

**Table 2: Vacuum sintering and hot pressing parameters**

<b>Sample</b>	<b>Process-route</b>	<b>Temperature [°C]</b>
<b>4D-B</b>	Vacuum sintering	Up to 1200
<b>4DTi-B</b>	Vacuum sintering	Up to 1200
<b>6D-B</b>	Hot pressing	Up to 800
<b>6DTi-B</b>	Hot pressing	Up to 800

**Table 3: SPS process parameters**

<b>Sample</b>	<b>Pressure [MPa]</b>	<b>Temperature [°C]</b>	<b>Dwell time [min]</b>
<b>4D-SPS</b>	50	500	1
<b>4DTi-SPS</b>	50	750	1
<b>6D-SPS</b>	50	500	1
<b>6DTi-SPS</b>	50	500	1

**Table 4: SPC process parameters**

<b>Sample</b>	<b>Pressure [MPa]</b>	<b>1<sup>st</sup> impulse [%]</b>	<b>2<sup>nd</sup> impulse [%]</b>
<b>4D-SPC</b>	235	30	50
<b>4DTi-SPC</b>	235	30	50
<b>6D-SPC</b>	235	50	---
<b>6DTi-SPC</b>	235	50	---

## Results

In the following chapter embedded diamonds in fabricated diamond grinding segments shall be analyzed regarding eventually occurring graphitization and reactions. In this case it is made an attempt to verify the degradation and conversion of diamonds in different reactive metal matrix compounds as well as in alternative new short time sintering processes like Spark Plasma Sintering and Spark Plasma Consolidation.

### Conventional sintering

The SEM-pictures (Fig. 3) of vacuum sintered diamond tools consisting of a high amount of iron in the metal matrix component, show a massive degradation of the embedded diamonds. It can be assumed that the presence of iron, which is directly contacting the diamond surface, has a catalytic effect on the crystalline structure of diamond carbon. This leads to a visible deformation of the diamond in the metal matrix. Additionally titanium coated diamonds in such a reactive metal matrix show indeed a lesser damaging. Probably a carbide forming process of the titanium coating has a protective influence on this diamonds. If a transformation of diamond to graphite takes place, this shall be investigated in the following.

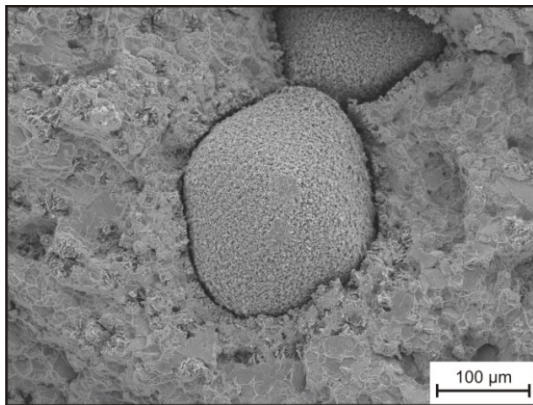


Fig. 3a: Embedded diamond in 4D

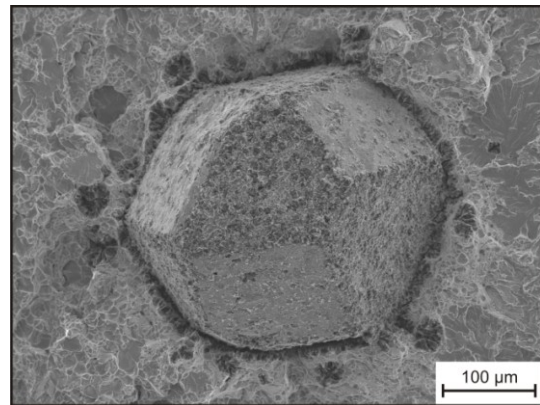
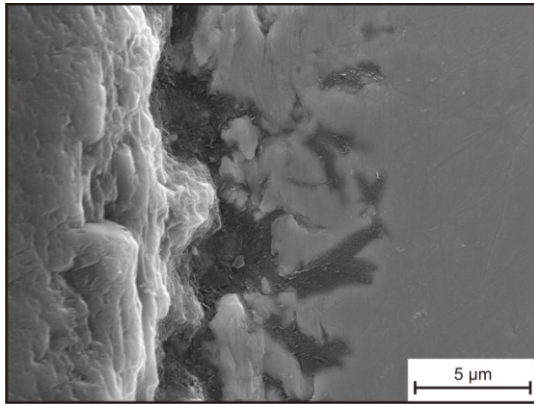


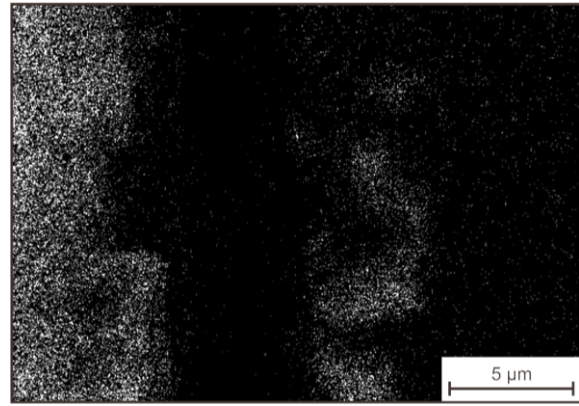
Fig. 3b: Embedded diamond in 4DTi

Generally, the transformation of diamond to graphite in the presence of metals is a catalytic process. For this reason diamond carbon is partially solved to a certain amount in the iron matrix at higher temperature during the vacuum sintering. While cooling down the diamond segment, this dissolved carbon can either stay in the crystalline structure of the iron or is segregated as graphite or carbides and can be found also in higher distance from the diamond surface (Fig. 3). Another part of the converted carbon stays on the diamond surface and forms a sharp-edged structure. For a more explicit determination of these structures which have formed during the sintering process the deformed diamonds were extracted electrochemical in hydrochloric acid and analyzed in a “D8 Series 2 X-ray Diffractometer” with an iron x-ray tube operated at 30 kV. The scan type was 2 theta/theta locked with a step size of 0,05° and a time per step of 30 s. The analysis resulted in one single peak of high intensity which can be split in three characteristic reflexes (Fig. 4). Each of these reflexes defines a different graphite modification. So the adherences on the diamond surface consist of graphite, graphite-H and especially Cliftonite. Cliftonite is a polycrystalline aggregate of graphite with a spherulitic structure and has been found in iron containing meteorites [10].

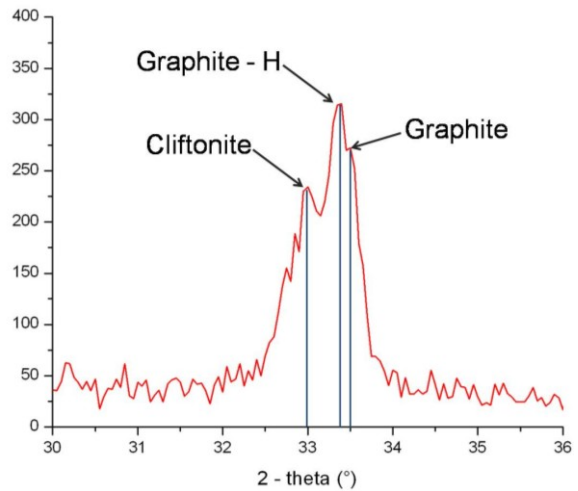
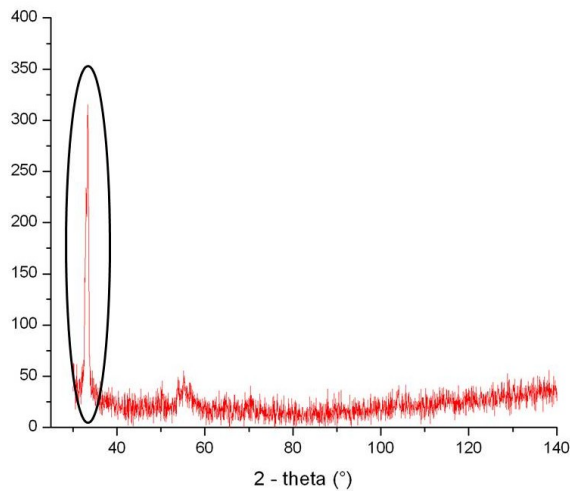




**Fig. 4a: Diamond-metal interface of 4D**

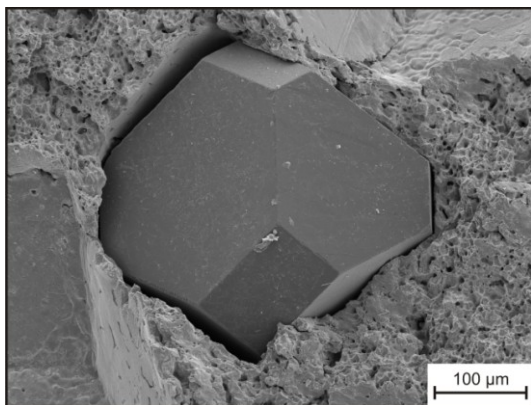


**Fig. 4b: Carbon EDX-Mapping of the interface**

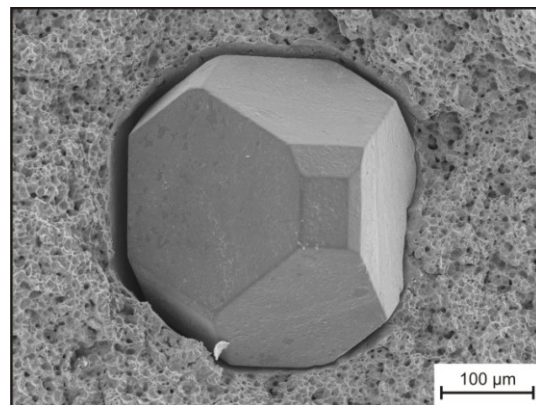


**Fig. 5: X-ray diffractograms of extracted diamonds of sample 4D**

In contrast to the iron containing metal matrix (4D) shown above the samples 6D and 6DTi based on a pure bronze matrix have a totally different behavior. Overall carbon shows no solubility in copper and tin. For this reason the bronze matrix in both specimens is almost inert against the diamonds and there is no visible indication of degradation of the diamond surface. Taking a closer look at the metal-diamond interface in those samples, the bonding of the diamonds to the metallic binder is not as good as in the sample 4DTi.



**Fig. 6a: Embedded diamond in 6D**



**Fig. 6b: Embedded diamond in 6DTi**

## Spark Plasma Sintering

The first results with spark plasma sintered diamond segments based on a iron-copper matrix show an almost unchanged diamond surface. Only the SEM-picture of a cross section indicates a weak catalytic attack on the diamond carbon. The Spark Plasma Sintering

process is similar to the hot pressing, with the essential difference that the heating rates are much faster and dwell times at sintering temperature are very short.

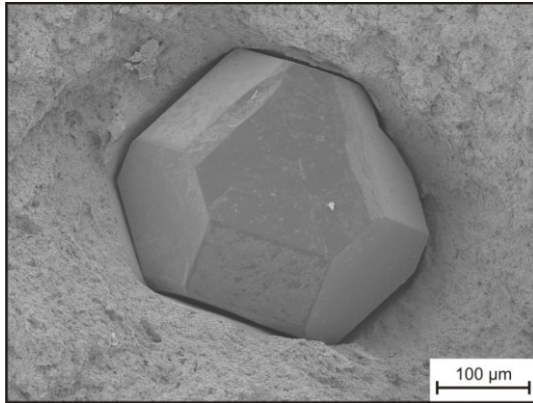


Fig. 7a: Embedded diamond in 4DTi-SPS

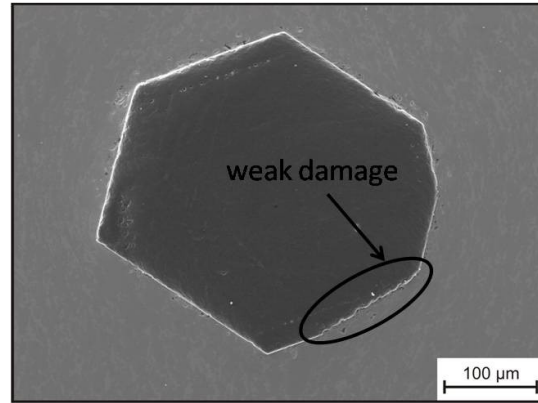


Fig. 7b: Cross section of 4DTi-SPS

It is of high interest to know if carbon diffusion during the short SPS process is possible as it is seen in vacuum sintered samples. Fig. 7a shows an almost intact diamond surface with no significant signs of destructive graphitization. BSE pictures and EDX-elemental mappings of SPS-specimen show indeed the presence of low amounts of diffused carbon in the vicinity of the diamonds (Fig 8+9).

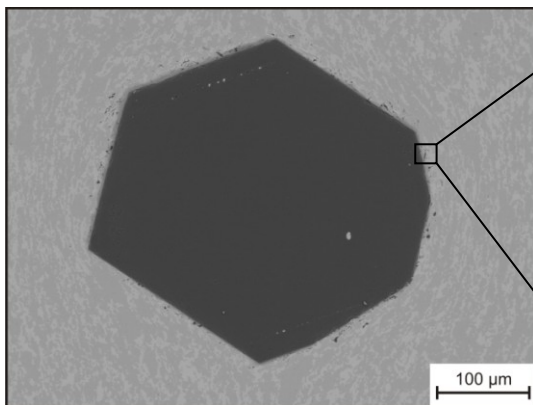


Fig. 8a: Diamond in 4DTi-SPS (BSE-mode)

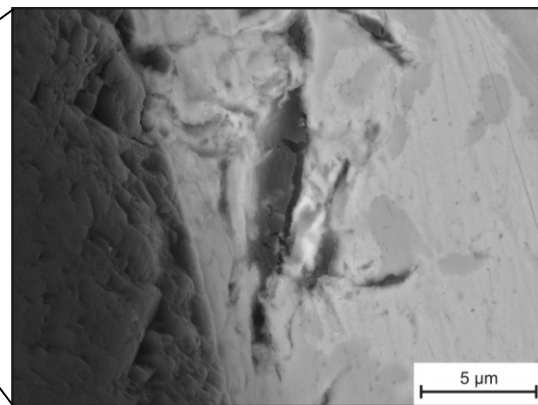


Fig. 8b: Carbon diffusion in the SPS process

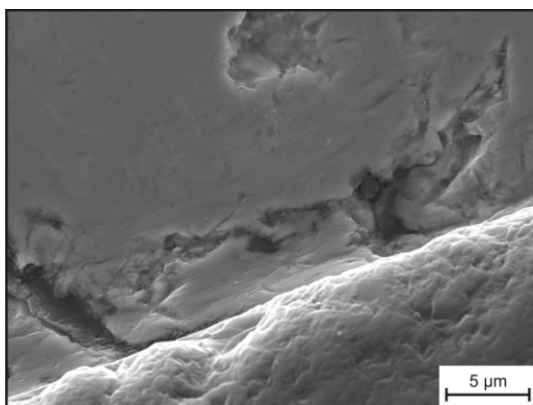


Fig. 9a: Interface between diamond and metal

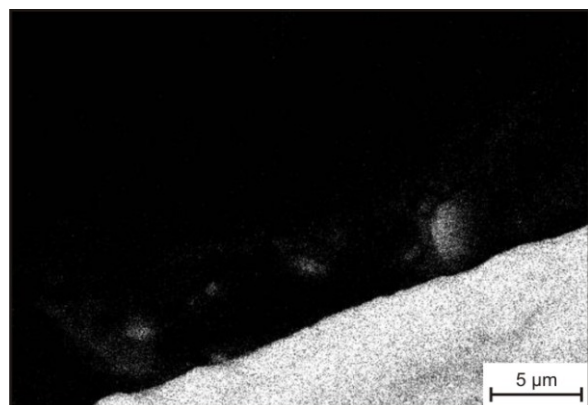


Fig. 9b: EDX-carbon-mapping

## Spark Plasma Consolidation

The first results regarding the fabrication of diamond tools with Spark Plasma Consolidation were promising. It was possible to achieve a very high density of the segments with a adjusted compaction energy. The next development step is to foster a stronger diamond-

metal bonding with titanium coated diamonds. The effects of two different metal matrix compounds with a different carbon reactivity will be illustrated in the following.

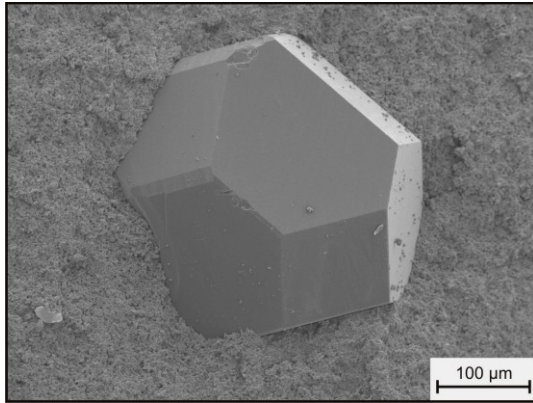


Fig. 10a: Embedded diamond in 4D-SPC

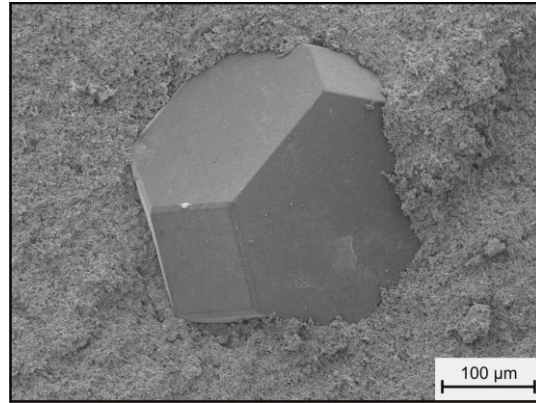


Fig. 10b: Embedded diamond in 4DTi-SPC

The most visible characteristic of iron containing diamond segments produced by Spark Plasma Consolidation is the entire absence of structural damages. Embedded diamonds reveal definitely no signs of graphitization or carbon diffusion. Even the wetting of metal particles on uncoated diamond surfaces is as good as on titanium coated diamonds (Fig. 10). In contrast to this high reactive iron component the usage of bronze in connection with a titanium interlayer shall demonstrate a better diamond-metal bonding. The direct comparison of uncoated and titanium coated diamonds sintered in a pure bronze matrix indicates the assumed behavior. The incomplete diamond-bronze connection in Fig. 11a should be observed carefully. This cavity between diamond and the metal matrix could have formed due to the metallographic preparation. But nevertheless the interface structure of specimen 6DTi-SPC (Fig. 11b) is even better and more uniform.

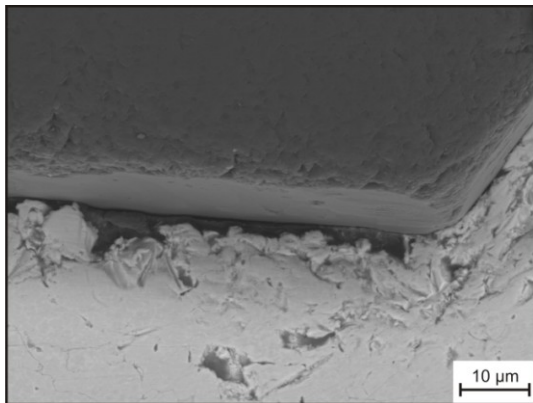


Fig. 11a: Interface area of 6D-SPC

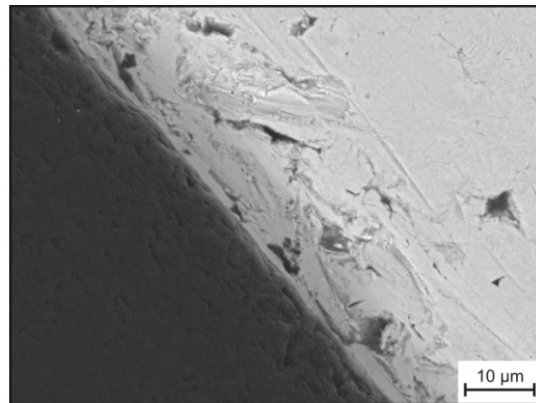


Fig. 11b: Interface area of 6DTi-SPC

## Conclusion

Generally the work in this paper revealed the major differences regarding the graphitization damages of diamonds in conventional sintered and in short-time sintered metal matrix composites. Even the influence of a thin titanium coating on the used diamonds, which were processed in the SPS-and the SPC-technique, has been pointed out. In this case the protective effect of this layer on the diamond carbon is definite and visible on SEM pictures. However, due to the moderate degradation on titanium coated diamonds (Fig. 3b) it seems that this protection depends on the used coating material as well as on the layer thickness. The experiments with Spark Plasma Sintering and Spark Plasma Consolidation showed, that the progress of graphite forming reactions can be inhibited. While the carbon diffusion in SPS-samples can be examined by means of EDX-mappings, the catalytic processes are completely inhibited during the SPC-sintering. For this reason particularly the SPC-technique



offers the possibility to use metal matrix components which have a lower amount of toxic cobalt than iron, steel or copper. The higher reactive metal compounds can be now processed with a lower damaging of the embedded diamonds and that by a reduction of the process time by using these short time sintering facilities.

On the other hand the usage of an almost inert pure bronze metal binder leads to problems with the diamond metal interfacial bonding. The attempts to enforce the formation of a stronger chemical bonding with a titanium coating on diamonds are partially successful. Indeed the examination of other diamond coatings or multilayer systems with materials which are stronger carbide formers will be the subject of further investigation and research.

## References

- [1] Denkena B., Tönshoff H. K., Friemuth T., Gierse A., Glatzel T., Hillmann-Apmann H.: Innovative Trennschleifprozesse in der Natursteinbearbeitung, Werkstatttechnik online, Jahrgang 92, H. 6, 2002, p. 290-296
- [2] Sung C. M., Tai M. F.: Reactivities of transition metals with carbon: Implications to the mechanism of diamond synthesis under high pressure, International Journal of Refractory Metals and Hard Materials, Band 15, Heft 4, 1997, p. 237-256
- [3] Werner Schatt, Klaus-Peter Wieters: Pulvermetallurgie, VDI-Verlag GmbH, Düsseldorf 1994, p.96-120
- [4] Konstanty J., Bunsch A.: Hot pressing of cobalt powders, Powder Metallurgy, Vol. 34, No. 3, 1991, p. 195-198
- [5] Schmidt J., Boehling M., Burkhardt U., Grin Y.: Preparation of titanium diboride TiB<sub>2</sub> by spark plasma sintering at slow heating rate, Science and Technology of Advanced Materials 8, 2007, p. 376-382
- [6] Handtrack D., Despang F., Sauer C., Kieback B., Reinfried N., Grin Y.: Fabrication of ultra-fine grained and dispersion-strengthened titanium materials by spark plasma sintering, Materials Science and Engineering: A, Volume 437, Issue 2, 2006, p. 423-429
- [7] Schütte P., Garcia J., Theisen W.: Electro Discharge Sintering as a process for rapid compaction in PM-Technology, Proceedings EURO PM Copenhagen Oktober 2009
- [8] Rajagopalan P.K., Desai S.V., Kalghatgi R.S., Krishnan T.S., Bose D.K.: Studies on the electric discharge compaction of metal powders, Materials Science and Engineering A280, 2000, p. 289-293
- [9] Fais A., Maizza G.: Densification of AISI M2 high speed steel by means of capacitor discharge sintering (CDS), Journal of Materials Processing Technology, Volume 202, Issues 1-3, 2008, p. 70-75
- [10] Brett R., Higgins G.T.: Cliftonite: A proposed origin, and its bearing on the origin of diamonds in meteorites, Geochimica et Cosmochimica Acta, Vol. 33, 1969, p. 1473-1484