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Carbon reactivity of binder metals in diamond–metal composites – characterization by scanning electron microscopy and X-ray diffraction

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ABSTRACT

Diamond tooling is a successfully used technique in machining of very hard materials such as minerals and concrete. The type and strength of bonding between the diamond grains, that are mainly responsible for the machining process (e.g. cutting or grinding), and the metallic binder phase is directly linked to the tools quality. Therefore it is of interest to investigate the carbon reactivity of commonly used binder materials.
This paper reports about the investigation of the interfacial area between diamonds and one-component metallic binder matrices. As matrix material pure chromium, cobalt, copper, iron, and nickel was used. After the sintering process the diamonds were extracted from the metallic matrix and analyzed by scanning electron microscopy and X-ray diffraction. The morphology of the diamond surface was investigated and a phase analysis was done. These experimental studies support the hypothesis that the carbon reactivity of transition metals is linked to their d-orbital electron configuration.

1. Introduction

Diamond tools in application of drill bits, wire saws or circular saws are widely established for the machining of hard mineral materials such as natural stone and concrete. Due to the extreme hardness and brittleness of these materials diamond containing machining tools on the basis of metal matrix composites (MMC) are able to fulfill the high demands of the machining process [1]. Hence the grinding process is mainly done by the embedded diamonds. On the materials side the wear resistance is highly influenced by the hardness of the metal binder and the bonding strength of the diamonds within. The formation of an interfacial area between diamonds and surrounding metal matrix depends on the sintering parameters (temperature and time) and on the carbon reactivity of the metal matrix components.

In the diamond tool industry two main fabrication procedures are well established and commonly used. Both the vacuum sintering and the hot pressing are techniques for the mass fabrication of diamond grinding segments. The main difference between these two sintering processes is that vacuum sintering requires the preparation of near-net shape greenbodies by cold pressing, too. Therefore this production route consists of two successive steps: the cold pressing and the sintering. Sintering can be performed in a vacuum furnace or in a conveyor furnace enabling a continuous throughput [2,3]. In contrast, the hot pressing technique combines the mechanical densification and the heating process of the diamond-metal powder in one single step. Therefore the total fabrication process of hot pressing (from the powder to the sintered end product) is significantly faster compared to the one of vacuum sintering. A further advantage of hotpressing is that due to the simultaneous pressing and heating the porosity is much lower [4]. As the sintering parameters, particularly time and temperature, have a great influence on the reactions between the diamond surface and the metal matrix the negative thermally induced degradation of diamond into graphite, which occurs during vacuum sintering, can be inhibited by the hot pressing procedure that requires less duration time and lower temperature [4,5]. Finally, the second main influence on the diamond-metal interaction is based upon the carbon reactivity of the metal matrix components. Sung and Tai [6] published that the carbon reactivity of transition metals in the 4th period of the periodic table depends on its electron configuration. Metals which have fully assigned 3d-orbitals (Cu, Zn) are inert to carbon. In contrast elements that have many electron vacancies in the 3d-orbital (Cr, Ti) are good carbide formers. Elements which have two-thirds filled d-orbitals (Fe, Co) show a catalytic effect on diamonds and therefore support the graphitization process.

Previous X-ray diffraction (XRD) and scanning electron microscopy (SEM) investigations on diamond-metal composites revealed three

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characteristics at the interfacial layer between diamond and metal during the sintering process [5,7,8]:

1. **Carbide formation**: By the chemical reaction a strong bonding between carbon and metal is realized. We expect that by increasing strength of bonding also the tools quality increases.
2. **Diamond degradation and graphite formation**: The degradation of diamonds that occurs in combination with the formation of graphite at the diamonds surface is expected to decrease the tool quality in two ways. First the diamond itself gets damaged and second the bonding between diamond and metal matrix is enervated by the graphite layer on the diamonds surface.
3. **Inert behavior**: No chemical reactions or diffusion processes occur. The diamond surface is almost unaffected and no reaction product such as graphite is formed during the sintering process. The diamonds are only mechanically bonded within the metal matrix

In former studies diamond-cobalt composites were also investigated by Molinari [9] and Tillmann [10] using XRD (X-ray diffraction) and TEM (transmission electron microscopy). In contrast to Molinari whose XRD-analysis revealed the formation of Co-C solid solutions and graphite in hot-pressed segments, focused ion beam assisted TEM-investigation by Tillmann et. al on prepared grinding-segments showed the existence of graphite only [10].

Nowadays the usage of cobalt alternatives is enforced in the diamond tool industry. Therefore the impact of various metal powders like iron or stainless steel as matrix components in sintered composite materials increases. As a result, also the importance of alloying elements as chromium or nickel rises necessitating a good understanding of the chemical reactions between these alloying elements and carbon during the sintering process.

The carbon affinity of nickel was already investigated by Nagakura [11]. It was discovered that a treatment of thin nickel films with CO gas at a temperature of 350 °C within 4–6 h led to the formation of Ni_3C. Heating experiments indicated a thermal instability of Ni_3C, the nickel carbide began to decompose at 433 °C. After 2 min at 433 °C Ni_3C was completely converted to nickel and graphite. Hence all of these carburization experiments were performed with a gaseous carbon source. The transferability and analogies of these results for the case of a solid carbon source (diamond) have to be considered carefully.

2. Experimental

2.1. Vacuum sintering and diamond extraction

In order to analyze the interfacial interactions between diamond and metal matrix compositions during the sintering process single component metal powders were premixed with 5 vol-% synthetic diamonds (SDB1055 – 40/50 mesh) and 10 vol-% "Licowax" pressing additive. The use of metal powders, such as chromium or nickel, which are rather unconventional for industrial purposes, can be motivated with the fact that these elements are alloy components in currently utilized steel powders for diamond tools. All investigated sample systems are listed in Table 1.

After mixing the diamond metal–powder mixtures were compacted in a 25 × 5 × 5 mm^3 cold pressing mould at 45–55 kN. Subsequently, the obtained greenbodies were dewaxed in a "GERO" furnace at 500 °C for 2 h. Finally the dewaxed specimen were sintered in a "TORVAC" vacuum furnace. The sintering parameters are listed in Table 2. After the sintering process some diamond grains were mechanically extracted from the diamond–metal composites so that XRD-analysis and SEM investigations on single diamonds could be carried out. Furthermore nickel (Ni/Dchem) and chromium (Cr/Dchem) samples have been extracted chemically in sulfuric acid to clear up a possible influence of strong acids on the diamond's interfacial area. (Table 2).

Table 1
Materials used.

	Metal powder (grain size)
Cr/D	Chromium (44 μm)
Ni/D	Nickel (5 μm)
Fe/D	Iron (<75 μm)
Co/D	Cobalt (1–3 μm)
Cu/D	Copper (<37 μm)

Table 2
Sintering parameters and extraction methods.

	Heating rate	Max. Temperature	Sintering time	Extraction method
Cr/D	10 K/s	1150 °C	4 h	Mechanical
Cr/Dchem	"	"	"	Chemical
Ni/D	10 K/s	1100 °C	3 h	Mechanical
Ni/Dchem	"	"	"	Chemical
Fe/D	10 K/s	1100 °C	3 h	Mechanical
Co/D	10 K/s	1050 °C	3 h	Mechanical
Cu/D	10 K/s	815 °C	3 h	Mechanical

2.2. X-ray diffraction experiments

XRD experiments using synchrotron radiation were performed at beamline I15 at the Diamond Light Source in Didcot, Oxfordshire, UK. One single diamond was fixed on top of a capillary using two-component glue. A PerkinElmer Digital Flat Panel detector with 2048 × 2048 pixels (200 × 200 μm^2) was used to measure a wide range of the scattering pattern. The alignment of the diamond grain was done with a microscope. The wavelength of the incoming beam was $\lambda = 0.3378$ Å (photonenergy E = 36.7 keV), the beam-size was 20 × 20 μm^2. The XRD reference data that was used to determine the crystal phases present in the samples were calculated using the POWDRIX V2 software [12].

2.3. SEM investigations

SEM studies were performed in order to investigate the surface morphology of diamonds extracted from sintered diamond metal composites. 6–10 diamonds of each sample system were coated with a thin layer of gold. This coating was necessary to enhance good image quality of the electric non conducting diamonds. The high resolution photographs with various magnifications were made using a field emission SEM (Jeol JXA840, JSM 35).

3. Results

3.1. XRD analysis

3.1.1. Carbide formation

Fig. 1 shows the XRD patterns of diamonds extracted from a pure chromium matrix and calculated reference data of chromium carbide and oxide (Cr_2O_3) phases. Comparing the experimental with the reference data reveals that chromium forms stabile carbide structures (Cr_3C_2, Cr_7C_3) during the sintering process. This result confirms that chromium is a good carbide former. As chromium has a high number of electron vacancies in its 3d-orbital this result is in agreement to Sung et al. [6].

In contrast to the chromium sample no carbide phases could be identified within the sample systems consisting of iron, cobalt, nickel and copper matrix.

3.1.2. Graphite formation

In Fig. 2 the XRD patterns of all investigated sample systems are plotted. In addition also a calculated graphite reference pattern is