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Self-assembling WC interfacial layer on diamond grains via gas-phase transport mechanism during sintering of metal matrix composite

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ABSTRACT

Diamond wire saws are widely used in machining of high strength reinforced concrete and steel structures. In such operation conditions, the tools wear down rather quickly, which has significant technical and economic implications. Currently, there are three main ways to improve a quality of diamond cutting tools: increasing (1) strength of a binder (metal matrix), (2) diamond grain grade and (3) adhesion strength between diamond and a binder. In this work, an effective approach involving simultaneous improvement of (1) and (3) during diamond composite material sintering is reported. The mechanism of spontaneous formation of WC layer on a diamond surface during sintering with metal matrix composite in the presence of WC nanopowder as a reinforcing additive is studied. The layer is formed via gas-phase transport mechanism leading to chemisorption of volatile tungsten oxide WO_3 onto a diamond surface followed by WO_3 reduction and carbide formation. The simultaneous enhancement of mechanical properties of the binder and formation of protective WC interfacial layer on diamonds provide a synergistic effect, which results in increased productivity and cutting speed of diamond tools.

1. Introduction

Diamond cutting tools with metal binders (saw blades, core drills and wire saws) are widely used to machine the most difficult-to-cut materials, such as reinforced concrete, stone and ceramics. Diamond wire saws are commonly used for machining and disassembling of high strength reinforced concrete and metallic structures, such as gas and oil transporting pipelines, ships, bridges, atomic power plants etc. [1,2]. In such applications, especially in steel cutting, diamond tools suffer from severe wear, which leads to premature failure of these expensive devices. This is a major and long-standing problem, the ultimate solution to which is yet to be offered [3].

Working layer of a tool contains diamond grains embedded in a metal matrix (binder). The role of the matrix is to retain the diamond grains until they are completely worn out [4]. The grain retention strength depends on the strengths of the matrix material and its interface with diamond, which is affected by chemical interactions between the two phases [5].

The iron triad metals (Ni, Co, Fe) are usually added to the matrices to increase their mechanical properties. However, these metals have a negative effect on diamond retention, as they catalyze the diamond (sp^3)–graphite (sp^2) phase transition at elevated temperatures [6–11]. As a result, a low-strength graphite layer is formed on the diamond surface when a tool is manufactured and/or used, which causes diamonds to prematurely chip off the metal matrix.

Adhesion-active metal matrices and coated diamond powders are employed to increase binder adhesion to diamond grains. Metallic cementation is used to provide strong chemical bonds between a diamond grain and a binder and to enhance their strength, which has a negative effect on diamond quality [12]. Protective metal coatings also might be deposited onto diamond powders by CVD [4] and PVD techniques [13]. The drawbacks of the former method include toxicity and explosion risk of used gas mixture components as well as low adhesion of the produced coatings. In PVD, a powder has to reach the pseudo boiling point for the coating to be deposited onto all diamond facets, which is a rather challenging task.

Diamonds coated with various refractory compounds (WC, TiN, TiC, Si_3N_4, SiC) are used to manufacture cutting tools [14,15]. Also, such intermediate layers are used for increasing adhesion of diamond coatings to different substrates, e.g. steel and cemented carbides [16–18]. The layers form an interfacial diffusion barrier, which prevents chemical interaction between the metal/ceramic phase and the diamond responsible for its catalytic graphitization.

Diamond-containing composite materials with copper-based binders are characterized by a unique combination of mechanical and thermophysical properties; however, it is difficult to attain high adhesion without additional coating of diamond grains. Protective coatings based on niobium, boron, chromium, nickel and titanium are known [19–22]. Thus, the problem of enhancing adhesion of diamonds to the

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metal binder is solved by an additional coating step, which complicates the manufacturing process and increases costs.

Another efficient method to enhance the mechanical properties of various binders is to add a controlled amount of nano additives (e.g., WC, ZrO_2, Al_2O_3, and carbon nanotubes), which allows improving performance of diamond tools considerably [23–29]. A significant increase in performance of tools with tungsten carbide alloyed binder was reported [27,28]. Enhanced wear resistance was caused by the simultaneous increase in hardness and strength of binder, reduced friction coefficient and increased diamond retention. It was determined that solid-state sintering using Fe-based binder with WC nanoparticles reduces graphitization of diamonds [29]. There are two reasons for that: (1) the WC nanoparticles decrease a contact area between a diamond and the metal catalyst in the binder and (2) they catalyze the grain-boundary graphite diffusion from the diamond surface into the binder. Nevertheless, the questions whether these are the only factors leading to reduced graphitization and what role is played by impurities, such as oxygen presented in the nano powder, remain open.

In this work, spontaneous formation of tungsten-carbide surface layer on single-crystal diamonds during sintering with Cu-Fe-Co-Ni binder in the presence of alloying WC nanopowder additive is reported and investigated. Up-to-date, the interlayer formation on diamond grains via chemical reaction with carbide forming elements (Cr, Ti, V, B) has been known only for solid state processes [30–32]. The present paper discusses the formation of WC interlayer via gas-phase transport mechanism.

2. Method

A mixture of a Co-Fe-Cu alloy and Ni powders at a 70:30 weight ratio was used as a metal binder (N). The mixture was prepared using 50% Cu–25% Fe–25% Co alloy powder (wt%) (Eurotungstene, France) with a grain size of 2–12 μm and PNK-UT3 carbonyl nickel powder (Kola MMC, Russia) with a grain size of 2–15 μm. The impurities content in these powders was less than 1%. Diamond powder of SDB 1085 grade (Element Six) with fraction size of 40/50 and 35/40 meshes and nanodispersed tungsten carbide powder produced by PECVD method (Institute of Metallurgy and Materials Science, Russian Academy of Sciences) with a specific surface area of 6.5 $m^2\,g^{-1}$, an average grain size of 70 nm, and a total oxygen content of 0.89% were used. The WC nanoparticles were added to the mixture using MPP-1 planetary ball mill and mixed for 3 min. To determine the mechanical properties, diamond-free segments were manufactured by a hot pressing in nitrogen atmosphere using DSP-475 sintering press (Dr. Fritsch, Germany), whereas the diamond-containing samples were produced using a DSP-515SA setup under vacuum with residual pressure of 1 Pa. The samples were exposed to the maximum pressure of 350 kg cm^{-2} at a temperature of 850°C for 3 min. Subsequent annealing of the hot-pressed samples and sintering of those containing diamonds were carried out in a VSl-16-22-U vacuum furnace (OOO Vak ETO, Russia) at 850°C and residual pressure of $1 \cdot 10^{-3}$ Pa for 5, 15 and 30 min.

The interfacial layer structure was studied by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The XPS spectra were recorded using a PHI 5500 ESCA instrument (Physical Electronics, USA). To record the XPS spectra, the diamonds were removed from the sintered binder and fixed on adhesive conductive tape. The analysis was performed on the crystals removed from the binder and etched by Ar^+ ions to remove adsorbed impurities. Monochromatic AlKα radiation ($h\nu = 1486.6$ eV) was used for high-resolution spectra and standard MgKα radiation ($h\nu = 1253.6$ eV) was used to obtain a survey spectrum. SEM and EDS analyses were carried out on fractured surfaces of sintered samples using a Hitachi S-3400N instrument (Japan) equipped with a Thermo Scientific Ultra Dry energy dispersive spectrometer.

To study the effect of nanodispersed WC particles addition on mechanical properties of the binder, we measured hardness and bending strength of the hot pressed samples. The hardness was measured using a 600 MRD Rockwell hardness tester (Wolpert Wilson, Germany) at a load of 980 N, with results presented as mean average values of 10 measurements. The three-point bending tests were carried out using LF-100 universal testing machine (Walter + Bai AG, Switzerland). Mechanical properties were determined for five various samples, and the results of measurements were processed statistically. The relief of diamond facets was studied by a Wyko NT1100 optical profiler (Veeco, USA).

Two experimental batches of wire saws with N and N + 5.1 wt% WC binder were produced and tested to evaluate the effect of WC addition on tool performance. Both types of wire saws contained monocrystalline diamond powders (Element Six, Luxembourg) of 40/45 mesh. Total concentration of diamonds in working layer was 20 wt%. All wire saws had a length of 10 m with 40 diamond beads per 1 m.

The tests of wire saws were carried out using a Hilti D-LP32 hydraulic wall cutting machine. The linear velocity of wires was kept at 15 m/s. To prevent overheating and damage of the tool and diamonds in the working layer, the water was fed to a contact area at a flow rate of 10 l/min. The cutting force was controlled by the supplied power of the cutting machine, which was maintained at 15 kW. An ingot of ASTM A414 Grade A steel with yield strength of 470 MPa and tensile strength of 550 MPa was used as a testpiece. The tests were conducted until the full fading of the cutting performance and the time of each test was recorded by chronometer with accuracy of ±1 s. After testing, the wire saw was dismantled from the machine and tool life was counted as a total area of cut, the cutting speed was calculated as total area of cut to cutting time ratio, and a number of diamond beads were taken out to study their surface by means of SEM. Five saws were tested in each batch (with N and N + 5.1 wt% WC binders) to determine the values of the mean average and the standard deviation of the characteristics of cutting performance.

3. Results and discussion

3.1. Mechanical properties of the binder

Introduction of a dispersed alloying nano-additive to a metal matrix composite (MMC) binder may have both positive and negative effects on its mechanical properties, which determines the operation performance of a diamond tool. We studied the effect of nanodispersed WC powder on mechanical properties of MMC manufactured by a hot pressing. The results presented in Table 1 shows that the addition of up to 5.1 wt% WC led to increase in hardness and bending strength of the MMC via disperse strengthening mechanism.

At tungsten carbide concentrations higher than 5.1%, the mechanical properties were decreased because of an increase in residual porosity from 5% (all samples except N + 6.8%) to 7% (for N + 6.8% sample). Porosity increase was attributed to the fact that WC nanoparticles inhibit sintering of metal grains. Hence, we selected the MMC with 5.1% WC, which was characterized by the optimal combination of properties, for our further research.

3.2. Structure and composition of interfacial layer

Special attention was given to studying the surfaces of diamond grains that contacted with the original binder and that containing

Table 1
Effect of WC addition on mechanical properties of the matrix material.

Composition	Hardness, HRB	Three-point bending stress, MPa
N	95 ± 1	1080 ± 30
N + 1.7% WC	98 ± 1	1080 ± 60
N + 3.4% WC	99 ± 1	1120 ± 20
N + 5.1% WC	99 ± 1	1180 ± 20
N + 6.8% WC	96 ± 1	1100 ± 50