Sintering of diamond composites with SHS-prepared bonding phases

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Properties

ABSTRACT

Purpose: The aim of this study was to investigate materials with reduced cobalt content as well as diamond compacts with non-cobalt bounding phase.

Design/methodology/approach: Phases Ti_3SiC_2 and Cr_3AlC obtained using the self-propagating High-Temperature Synthesis (SHS) technique were used as a PCD (polycrystalline diamond) bonding phases. Diamond composites with 10-20 mass% of SHS bonding phase were prepared by using a Bridgmann-type High Pressure - High Temperature (HP-HT) apparatus. Sintering of the composites were carried out at $1950\pm50°C$ and 8 ± 0.2 GPa. Phase compositions of MAX powders and compacts were tested using X-ray diffraction. Microstructure investigations were performed using scanning (JEOL) and transmission (Tecnai FEG 200kV) microscopes and high spation resolution EDS mapping.

Findings: During the sintering processes, bonding phase decomposition processes occur in the material. Mainly carbides and silicides are formed. Diamond phase materials are characterized by multi-phase composition.

Research limitations/implications: Future research in the field of reduced cobalt content composites and cobalt replaced by bonding phase with Cr_2AlC should focus on reduction of the graphite which affects on lower composite hardness. Such materials require an improvement in stress deposition.

Originality/value: Due to the low thermal stability of the cobalt as a bonding phase in PCD there is a need to reduce its volume in the composite. Application of the newest non-cobalt bonding phases (Ti_3SiC_2 and Cr_3AlC) obtained by SHS sythesis.

Keywords: SHS synthesis; HP-HT sintering; Composites, Microstructure-final; Diamond, Cutting tools

1. Introduction

Commercial polycrystalline diamond compacts (PCD) are used in drilling and other machining applications. Their thermal stability (TS), defined as resistance to temperature-induced graphitization in an inert atmosphere, is significantly compromised by compacting with a cobalt binding phase. One of the possibilities to maintain an acceptable thermal resistance in

PCDs is to keep the cobalt content as low as possible. The microstructure and mechanical properties of polycrystalline diamond (PCD) synthesized at high pressure and high temperature are strongly influenced by a type of applied binding material phase. The most popular commercial PCDs are two-layer materials with a cobalt phase. Cobalt provides good wetting of diamond crystallites. This property allows the production of compacts characterized by a low amount (below 10 wt.%) of bonding phase, resulting in their high hardness. But when the compact is cooled from sintering temperature to room temperature, very high radial compressive stresses are induced in the diamond layer, while much lower radial tensile stresses are induced in the cemented tungsten carbide substrate [1]. However, the high brittleness of these binding materials results in the poor toughness of such PCDs, undermining their practical applications. In addition, cobalt-containing PCDs are chemically stable only up to 900°C, while working temperatures may rise even higher. Today, these materials are the most popular PCDs. A second popular method of obtaining diamond composite with a high TS is its infiltration with silicon, forming SiC, rather than allowing graphite to form. However, SiC formation is associated with an increase in volume, blocking PCD porosity during compacting and adversely affecting the porosity and roughness of the tool surface [2]. PCDs with a silicon bonding phase may be used only in drilling applications. In such a situation, the development of new bonding phases is very much needed.

Ternary compounds (MAX phases) $Mn + {}_1AX_n$, n = 1-3, (where M is an early transition metal, A - an element of the A group such as IIIA or IVA, X - carbon or nitrogen) have been studied since the 1960s. Ti_3SiC_2 based on $M_N + {}_1AX_N$ "nanolaminates" might make an interesting bonding phase alternative. It is stable up to 1400-1450°C [2], has a hexagonal P63/mmc layered structure and combines the high stiffness of ceramic materials with some ductility characteristic for metals. Cr_2AlC, one of the M_2AX phases (also known as the 211 phase), has relatively low hardness (3.5-5.5 GPa), high elastic modulus (278-288 GPa), good mechanical performance at room temperature (flexural strength of 378-494 MPa and compressive strength of 625-1159 MPa), good electrical (1.4-$2.3 \times 106\ \Omega^{-1}\,m^{-1}$) and thermal conductivity (17.5-22.5 W/m K), excellent oxidation resistance at 800-1300° and corrosion resistance against molten Na_2SO_4 at 900-1000°C [3,4].

Generally, $M_n + {}_1AX_n$ phases possess high stiffness; are machinable; exhibit good damage tolerance, excellent thermal shock resistance, good corrosion resistance, good thermal and electrical conductivity, good oxidation and/or corrosion resistance, and excellent mechanical performance both at room temperature and high temperatures. The latter properties enable MAX phases to fill most voids between compacted diamond crystallites [5]. It is possible to replace the ductile cobalt bonding phase. Ti_3SiC_2 material fills the voids between diamond particles and preserves the isostatic conditions in sintered diamond [5]. Removal of voids is crucial, as otherwise the diamond particle is only locally bound with the binder or second diamond, keeping the diamond in a compressive force state, i.e. preserving diamond stability. The simultaneous presence of multiple voids leads to a tensile force state on the diamond surface, leading to its local graphitization. The aim of this study is to analyze the possibility of the application of SHS-synthesized powders from Ti-Si-C and Cr-Al-C systems as a binding phase for PCDs. In order still better to fill in the voids, the microcrystalline Ti3SiC2 was mixed with nanocrystalline TiCN. This paper presents the results of phase composition, microstructure and hardness studies of the high-temperature sintering of microcrystalline diamond with Ti_3SiC_2-nanocrystalline TiCN powders (related to diamond-Ti_3SiC_2 composite) and of diamond compacts with a Cr_2AlC bonding phase.

2. Experimental

2.1. Preparation of bonding phases by SHS

The SHS bonding phases were produced from stoichiometric mixtures of powders. Purity and grain size of the element powders are shown in Table 1.

The homogeneity of these mixtures was ascertained through extensive mixing of their components for 12 hours in a rotary-vibratory mill with Teflon balls, suspended in anhydrous isopropyl alcohol. Drying was carried out during mixing. Next, the powders were formed into discs by pressing in a steel matrix, and synthesized using the SHS technique. The reaction was begun at up to 1500°C, using a graphite crucible with a graphite foil lining in an argon-filled chamber. After ignition by raising part of material to high temperature, the front of reaction is propagated across the crucible, resulting in full transformation of the loaded material. The products of the SHS reaction were crushed in an Abbich mortar to a powder with grain size up to 0.5mm, and then milled in a rotary-vibratory mill with WC grinding media, in anhydrous isopropyl alcohol, to a powder with a specific surface area up to 10 m²/g.

Table 1.
Powder characteristics

Element	Purity (%)	Grain size (μm)
Silicon*	99.80	0-60
Titanium (Goodfellow)	99.50	<45
Graphite (Aldrich)	99.99	<45
Chromium (AEE)	99.95	<45
Aluminium (NPA, Skawina)	99.50	submicrometer

*Obtained by milling of silicon waste chips produced by ZA Tarnow, Poland.

2.2. Ultra High Pressure-High Temperature sintering

Mixtures were prepared containing 70 mass% diamond (3-6μm MDA, Element Six), 15 mass% Ti_3SiC_2 and 5 mass% nanometric TiCN50:50 (SHS, Neomat Co) powders and, as a reference binder, 70 wt.% diamond, 30 wt.% Ti3SiC2.

Diamond powders of 3-6 μm (MDA, Element Six) mechanically mixed with 10, 20 and 30 mass% of bonding phase powders from the Cr-Al-C system were also obtained.

The resulting mixture was formed into discs (ϕ =15 mm, h=5 mm) by pressing in a steel matrix under pressure of 200 MPa. Before sintering, powders were baked at 600ºC for 30 min under pressure 0.8 Pa. Samples were heated using an assembly equipped with an internal graphite heater. Compacts were sintered at pressure 8.0±0.2 GPa and temperature 1920±50°C in a Bridgman-type ultra high pressure apparatus.

2.3. Characterization

Particle size of the bonding phase powders was measured using a Shimadzu SA-PB3 centrifugal particle size analyzer. Density was measured using the hydrostatic method.

Phase composition of the SHS powders and sintered bodies was identified by X-ray diffraction analysis, based on the ICDD database. XRD measurements were taken using an X′Pert Pro system (Panalytical) with monochromatic Cu Kα1 radiation. Microstructure investigations were performed using scanning (JEOL JSM-6460LV with EDS and WDS spectrometers) and transmission (Tecnai FEG 200 kV) microscopes. Samples for microanalysis and Vickers hardness measurement were prepared through lapping on a cast iron plate with diamond paste. Hardness was measured with a Vickers apparatus at 9.8 N load.

3. Results and discussion

3.1. SHS powders

X-ray analysis of the Ti-Si-C SHS product shows the presence of 47.1 vol% Ti_3SiC_2, $TiSi_2$, TiC and SiC XRD patterns are shown in Fig. 1.

X-ray analysis of the second SHS product from the Cr-Al-C system (Fig. 2) shows the presence of 85.2 vol% Cr_2AlC and 14.8 vol% Cr_7C_3.

For both systems, the SHS products are multi-composite compounds.

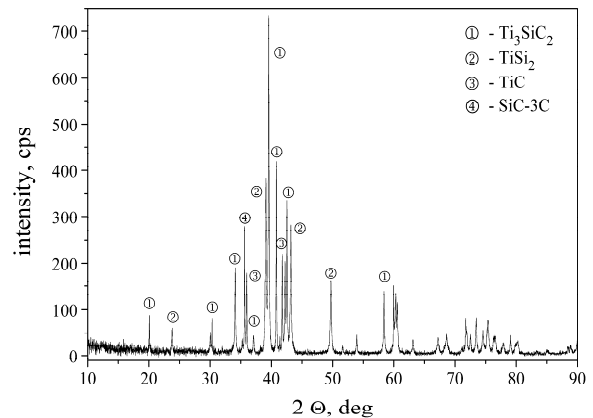The TiCN50:50 used was a commercial SHS product.

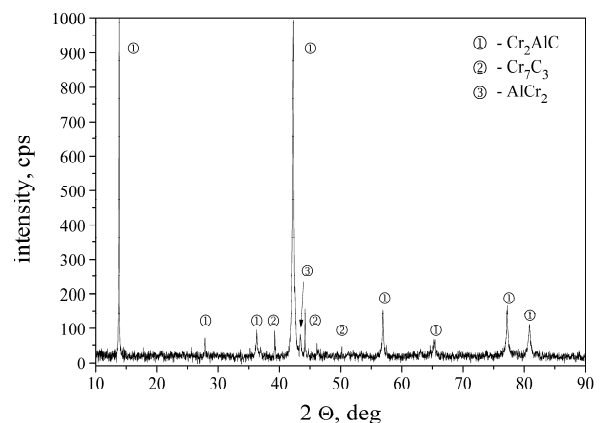Fig. 1. X-ray pattern of SHS product for the Ti-Si-C system

Fig. 2. X-ray pattern of SHS product for the Cr-Al-C system

Density and grain size of the SHS powders are shown in Table 2.

Table 2.
Density and grain size of the SHS powders

SHS system	Density (g/cm³)	Median diameter of powder particles (μm)
Ti-Si-C	4.93	4.93
Cr-Al-C	4.52	6.72
TiCN50:50 (Neomat Co., Latvia)	-	40±5 nm

3.2. PCD with Ti3SiC2 bonding phase

The reference compacts with 30 mass% Ti_3SiC_2 (see Fig. 3) are characterized by good distribution of the binding phase in channels between the diamond crystallites. The contrast changes from light-grey to dark-grey point toward a multi-phase final binder composition. The presence of frequent but relatively small (i.e. staying well below sub-micron range) very dark areas indicates the presence of pores.
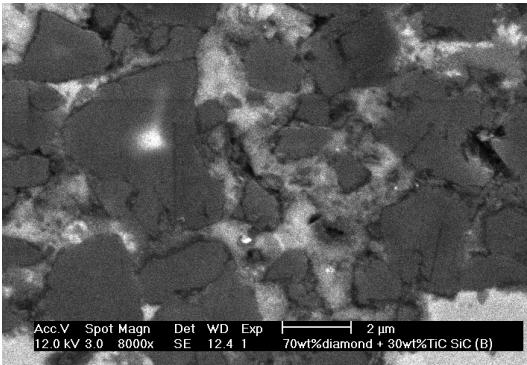

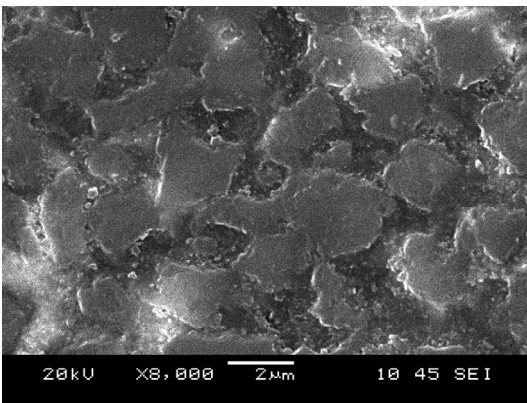Fig. 3. SEM image of diamond-30 mass% Ti_3SiC_2 composite

Fig. 4. SEM image of diamond+Ti_3SiC_2+TiCN composite

The compacts with 15 wt.% Ti_3SiC_2 and 5 wt.% TiCN present a similar good distribution of the binding phase as in the reference compact (see Fig. 4). In addition, the binder

phase shows an average contrast in SEM (SE) imaging, indicating good homogenization and an absence of voids or cracks.

Transmission microscopy observations (see Fig. 5) confirmed the fine crystalline character of the binding material. Fig. 6 shows that the bonding has a multi-phase character, containing SiC, TiC and possibly TiCN crystallites (the high thickness of FIB cut foils results in strong absorption of light elements, preventing differentiation of the latter).
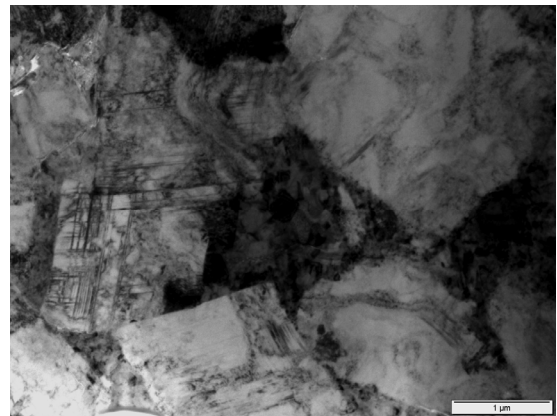

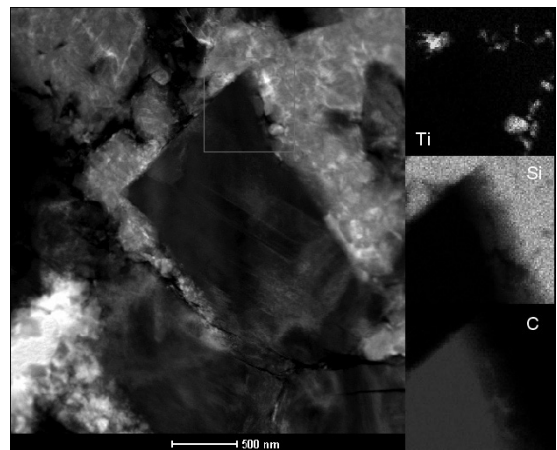Fig. 5. TEM image of diamond+Ti_3SiC_2+TiCN composite

Fig. 6. TEM image of diamond-15 mass% Ti_3SiC_2 - 5 mass% TiCN composite (TEM image of the bonding phase; Si, Ti, C element map distributions)

Table 3.
Selected physical and mechanical properties of PCD with 15 mass% Ti_3SiC_2, 5 mass% TiCN, and of PCD with 30 mass% Ti_3SiC_2

Bonding phase	Density* (g/cm³)	Hardness** HV1	Young's modulus (GPa)
30 mass.% Ti_3SiC_2	3.608	4440±290	567
25 mass% Ti_3SiC_2 5 mass% nano-TiCN	3.500	5060±300	706

* Average measurement for three samples.
** Average of five hardness measurements, $\alpha = 0.05$

The diamond crystallites are characterized by their light contrast, square shape and parallel sets of faults. The crystallites in the binder phase remaining in contact with, or at least close to, the diamond crystallites are usually in the nanometer range. The density, hardness and Young's modulus of the investigated compacts are presented in Table 3.

The presence of a ductile Ti_3SiC_2 bonding phase in the HP-HT process is especially important in the first stage of the sintering process, when the pressure is generated. The stress distribution in the sintering samples is dependent on the bonding phase distribution and plasticity. The second stage of the HP-HT process is sintering. If the sample is not under pseudo-isostatic conditions, then graphite appears. Hexagonal Ti_3SiC_2 is a low-temperature phase stable below 1400-1450°C [6]. Above these temperatures, decomposition of Ti_3SiC_2 occurs and phase reactions take place with the carbon from the diamond. The ductile behaviour of the Ti_3SiC_2 phase helps to fill most of the larger voids between diamond grains, ensuring thermodynamic conditions for maintaining the presence of diamond, i.e. limiting major graphite presence in the final composite. The addition of a nanometric TiCN phase into the Ti_3SiC_2 binding phase helps to eliminate the compacts' residual porosity and further stabilize conditions for maintaining the diamond phase. The newly developed binder, i.e. admixture of nanocrystalline TiCN into Ti_3SiC_2 helps to raise both the hardness and Young's modulus of diamond compacts by approximately 10%.

3.3. PCD with Cr2AlC bonding phase

Cr_2AlC is a more thermally stable material than Ti_3SiC_2. This has an influence on the graphitization process for a diamond-Cr_2AlC composite. Such materials are characterized by residual porosity (see Table 4). The Cr_2AlC phase is insufficient to fill most of the larger voids between diamond grains but there is a graphite presence in the final composite (see Figs. 7, 8). Graphite is formed parallel to (111) crystallographic planes of diamond, at the voids. These white particles are Cr_3C_2 and Al_4C_3 carbides in the graphite. X-ray diffraction of these carbides is presented in Fig. 8. The amount of graphite in this composite, calculated from the X-ray diffraction, is 6.1%.

The combination of such important properties as high hardness, good strength, medium fracture toughness and excellent oxidation resistance has resulted in growing interest in Cr_3C_2-based cermets. Cr_3C_2-based materials could be used in erosion-corrosion conditions at temperatures near 800°C [8]. Further

increase in temperature leads to more severe oxidation (10 times per 100°C). Aluminum carbide is a moisture-sensitive material which decomposes slowly in the presence of water or moisture. However, the Al_4C_3 is surrounded by the other diamond and graphite carbides, which preserve its high mechanical properties. The main factor lowering the hardness of diamond with a binder from the Cr-Al-C system is the presence of graphite. This indicates a graphitization process during sintering and the presence of tensile stresses in the sintering mixture.
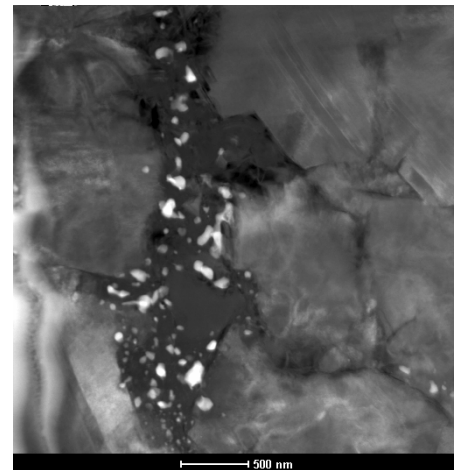

Fig. 7. TEM image of diamond-10 mass% - Cr_2AlC composite: area of the bonding phase
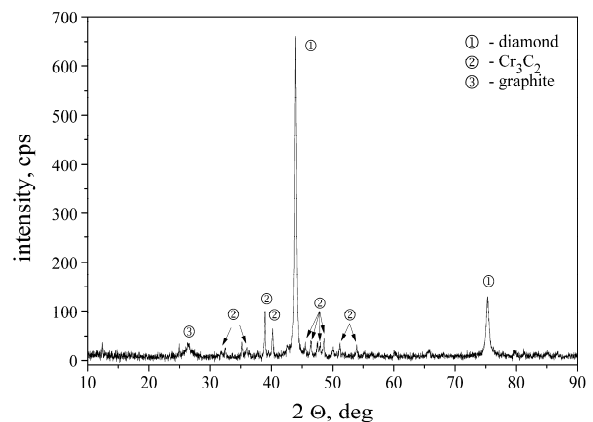

Fig. 8. X-ray diffraction of the composite with Cr_2AlC bonding phase

Table 4
Selected physical and mechanical properties of diamond composites

Mass% of bonding phase	Density (g/cm³)	Porosity (%)	Young's Modulus (GPa)	Hardness (HV1)
10	3.45	0.19	472	3440±66
20	3.64	1.13	240	2190±108
30	3.79	0.90	314	2015±80

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4. Conclusions

The final composites formed a skeleton-like diamond structure with pores filled with carbides and/or nanometrc TiCN.

The ductile behaviour of the Ti_3SiC_2 phase helped to fill most of the larger voids between diamond grains, ensuring thermodynamic conditions for maintaining the presence of diamond, i.e. limiting major graphite presence in the final composite.

The addition of a nanometric TiCN phase into the Ti_3SiC_2 binding phase helped to eliminate the compacts residual porosity and further stabilize conditions for maintaining the diamond phase.

The newly developed binder, i.e. admixture of nanocrystalline TiCN into the Ti_3SiC_2 helped to raise both the hardness and Young's modulus of the diamond compacts by approximately 10%.

For the bonding phase with Cr_2AlC, there is residual porosity of composites, and graphite is formed parallel to (111) crystallographic planes of diamond, at the voids. The presence of graphite reduces the hardness of diamond composites. Such materials require an improvement in stress deposition.

Acknowledgements

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