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L. Jaworska<sup>1</sup>, Prof., Ph. D., D. Sc.; P. Klimczyk<sup>1</sup>, Ph. D.; P. Putyra<sup>1</sup>, Ph. D.; M. Rozmus<sup>1</sup>, Ph. D.;  
M. Bucko<sup>2</sup>, Prof., Ph.D., D. Sc., J. Morgiel<sup>3</sup>, Prof., Ph.D., D. Sc., L. Stobierski<sup>2</sup>, Prof., Ph. D, D. Sc.

<sup>1</sup>*Institute of Advanced Manufacturing Technology, Krakow, Poland*

<sup>2</sup>*Department of Advanced Ceramics, University of Science and Technology, Krakow, Poland*

<sup>3</sup>*Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Krakow, Poland*

## DIAMOND-MAX CERAMICS BONDING PHASE COMPOSITES – PHASES AND MICROSTRUCTURE ANALYSIS

*The possibility for improving the thermal stability of polycrystalline materials based on diamond (PCD) is to reduce the content of cobalt. Diamond compacts without cobalt phases with  $Ti_3SiC_2$  i  $Cr_2AlC$  prepared using the method of self-propagating high-temperature synthesis (SHS). The resulting compacts with 20 wt. % of the above phases were exposed to high pressure and temperature in order to further consolidate the structure by sintering. Sintering was performed at  $8\pm 0.2$  GPa and  $1950\pm 50$  °C. Phase composition and microstructural study of the original compacts and the composites made by X-ray diffraction (XRD) and scanning electron microscopy (SEM).*

**Key words:** sintering, composite material, diamond, binding phase, phase composition, microstructure.

### Introduction

Commercially available polycrystalline diamond compacts (PCD), consisting of a polycrystalline diamond-cobalt layer on a WC-Co substrate are used in a drilling and machining applications. Cobalt phase presence in diamonds layer has strong influence on the thermal resistance decreasing. Thermal stability of a PCD material can be defined as the resistance to graphitization in an inert atmosphere, at elevated temperatures.

One of the possibilities to increase the thermal resistance of PCD materials is to reduce of the cobalt content. Another is the diamond compacts manufacturing with non-cobalt bonding phase. They have been referred to as thermally stable polycrystalline diamond composite TSP sometimes as TSDC. TSP is produced by using silicon carbide binder or leaching the cobalt component from the surface layers of PCD. Diamond-silicon carbide composites find a wide use in industry application.

The most popular method of obtaining this composite is infiltration of diamond with Si and consequent reaction of Si with the carbon from diamond. During the sintering process silicon forms SiC carbide. The SiC formation is connected with volume increase, which could result in blocking of pore channels what has influence on materials porosity and roughness of the tools surface [1]. The earliest known product in this type of material was De Beer's (now Element Six) Syndax 3. This material is characterized the thermal stability up to 1200 °C, high value of the fracture toughness but lower strength and wear resistance than PCD with cobalt. Residual silicon was observed in these samples, it can be concluded that the reactive bonding-sintering process did not proceed to completion [2]. Cuttability of tool materials it is very important property, especially for diamond because diamond it is non-electrical conductive. For diamond with cobalt bonding phase the electro-discharge method of cutting is widely using. The traditional mechanical methods of cutting are not efficient.

Another is the preparing of material with non-metallic bonding phase without negative influences on diamond graphitization and with compatibility of the thermal expansion coefficient to the diamond coefficient. Therefore, a new material characterized by at least as good wetting of diamond but producing synthesis reaction products both less brittle and chemically stable at even higher temperatures than those containing cobalt would be of interest. 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. There is some new information about application minerals bonding phases for example  $CaCO_3$  [3].

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. Ternary compounds (MAX phases)  $Mn + 1AX_n$ ,  $n = 1-3$ , where M – an rare 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  $MN+1AX_N$  «nanolaminates» might make an interesting bonding phase alternative. It is stable up to 1400–1450 °C [4], has a

hexagonal P63/mmc layered structure and combines the high stiffness of ceramic materials with some ductility characteristic for metals. Cr<sub>2</sub>AlC, one of the M<sub>2</sub>AX 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) × 10<sup>6</sup> Ω<sup>-1</sup> m<sup>-1</sup>) and thermal conductivity (17.5–22.5 W/(m·K)), excellent oxidation resistance at 800–1300 °C and corrosion resistance against molten Na<sub>2</sub>SO<sub>4</sub> at 900–1000 °C [4].

Generally, Mn+1AX<sub>n</sub> 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 or cBN crystallites [5, 6]. It is possible to replace the ductile cobalt bonding phase. Ti<sub>3</sub>SiC<sub>2</sub> or Cr<sub>2</sub>AlC materials fill the voids between diamond particles and because their ductile properties preserve 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.

#### Experimental

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

#### 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, Kawina)	99.50	Submicrometer

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

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 0.5 mm, 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 m<sup>2</sup>/g.

Mixtures were prepared containing 80 mass % diamond (3–6 μm MDA, Element Six), 20 mass % Ti<sub>3</sub>SiC<sub>2</sub>.

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

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<sub>Kα1</sub> radiation. Microstructure investigations were performed using transmission (Tecnai FEG 200 kV) microscope. The resulting mixture was formed into discs (∅ = 15 mm, h = 5 mm) by pressing in a steel matrix under pressure of 200 MPa. Before sintering, powders were baked at 600 °C 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 toroid high pressure apparatus.

#### Results and discussion

X-ray analysis of the Ti-Si-C SHS product shows the presence of 47.1 vol. % Ti<sub>3</sub>SiC<sub>2</sub>, TiSi<sub>2</sub>, 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. %  $\text{Cr}_2\text{AlC}$  and 14.8 vol. %  $\text{Cr}_7\text{C}_3$ .

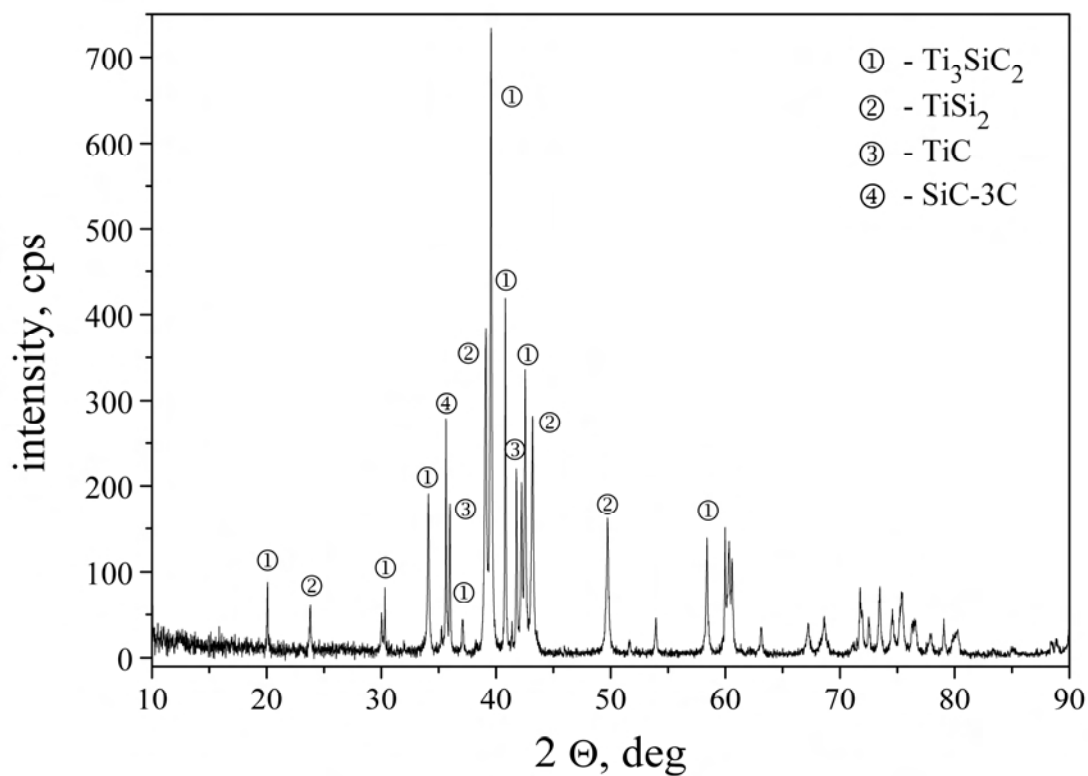


Fig. 1. X-ray pattern of SHS product for the Ti-Si-C system

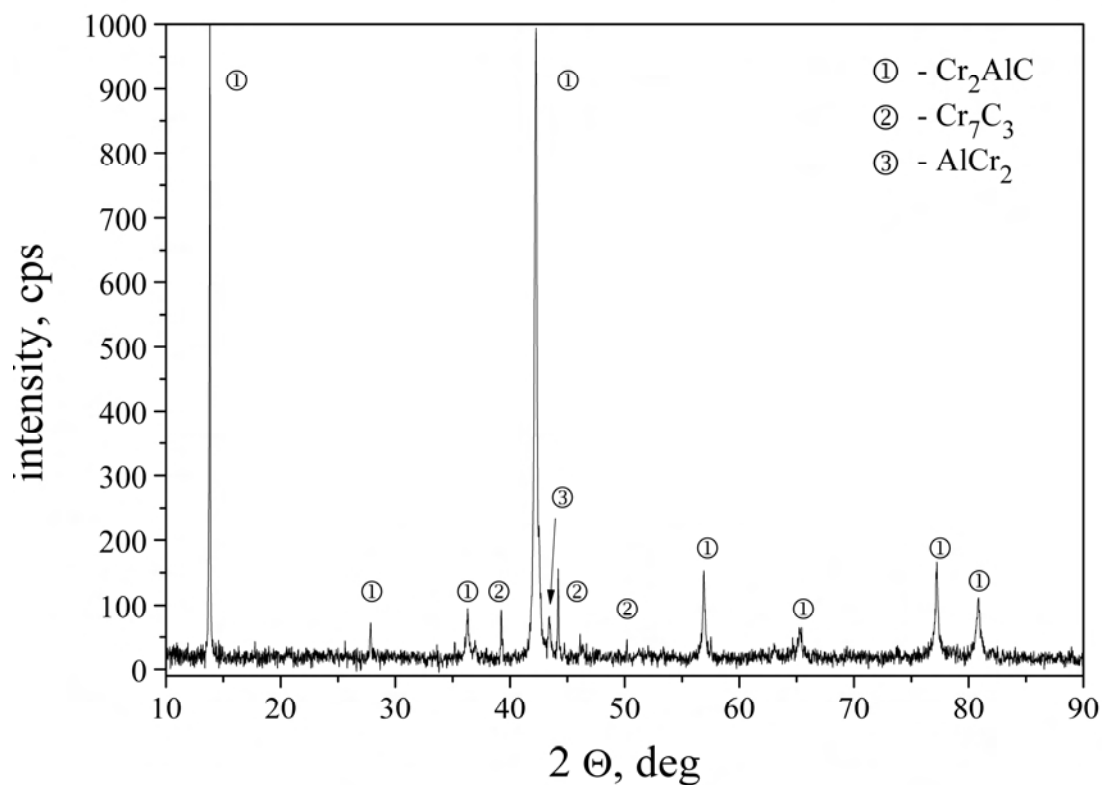


Fig 2. X-ray pattern of SHS product for the Cr-Al-C system

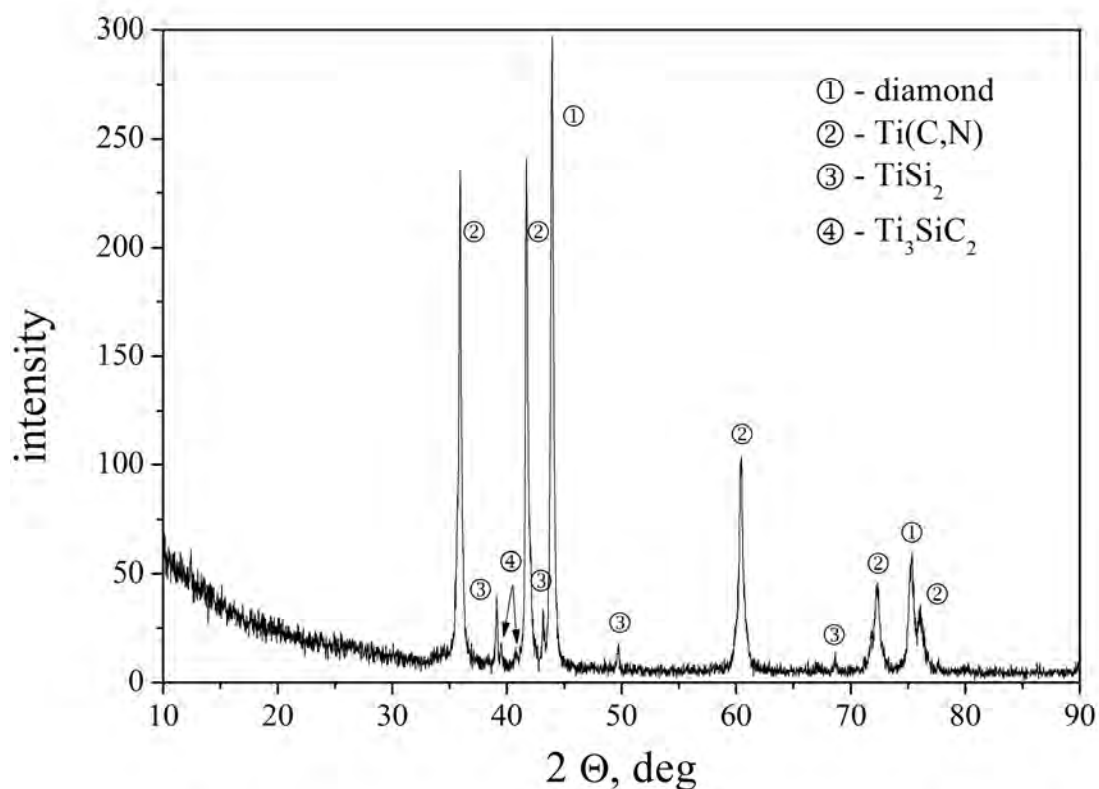


Fig. 3. X-ray pattern of diamond composite with the bonding phase from the Ti-Si-C system

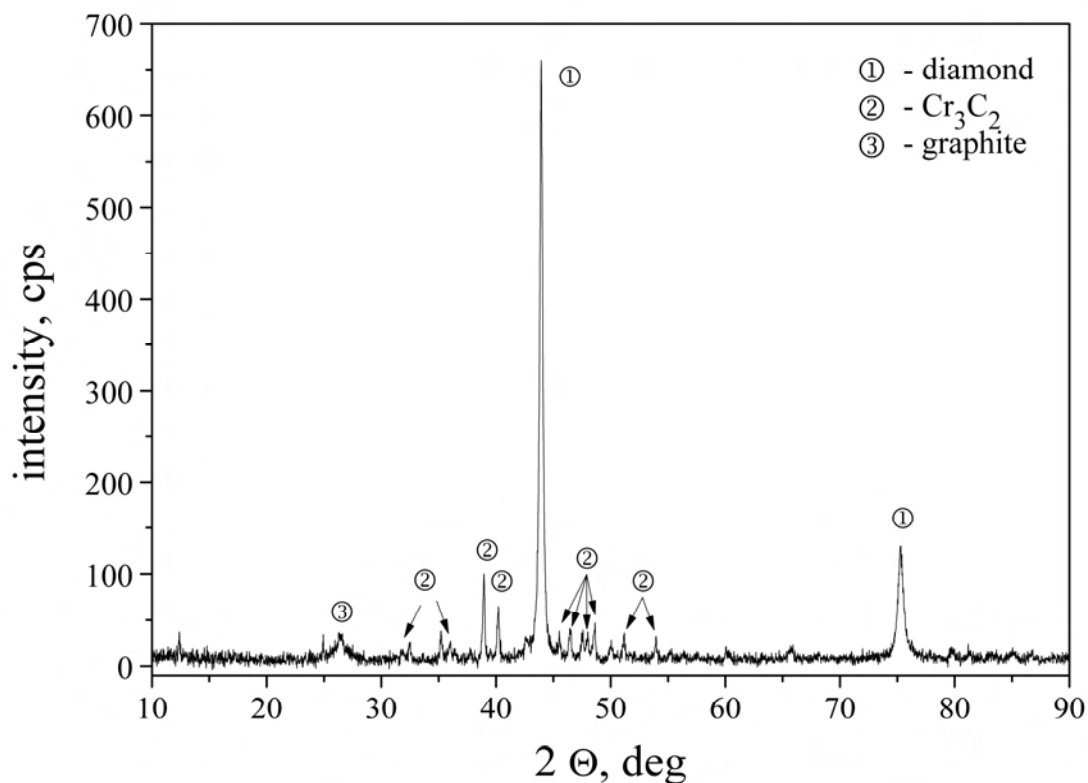


Fig. 4. X-ray pattern of diamond composite with the bonding phase from the Cr-Al-C system

X-Ray analysis and TEM microscopy confirmed the fine crystalline character of the binding material. Fig. 1 shows that the bonding has a multi-phase character, containing SiC, TiC and possibly TiSi<sub>2</sub> crystallites. The presence of a ductile Ti<sub>3</sub>SiC<sub>2</sub> 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<sub>3</sub>SiC<sub>2</sub> is a low-temperature phase stable below 1400–1450 °C. Above these temperatures, decomposition of Ti<sub>3</sub>SiC<sub>2</sub> occurs and phase reactions take place with the carbon from the diamond (fig. 3). The ductile behavior of the Ti<sub>3</sub>SiC<sub>2</sub> 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.

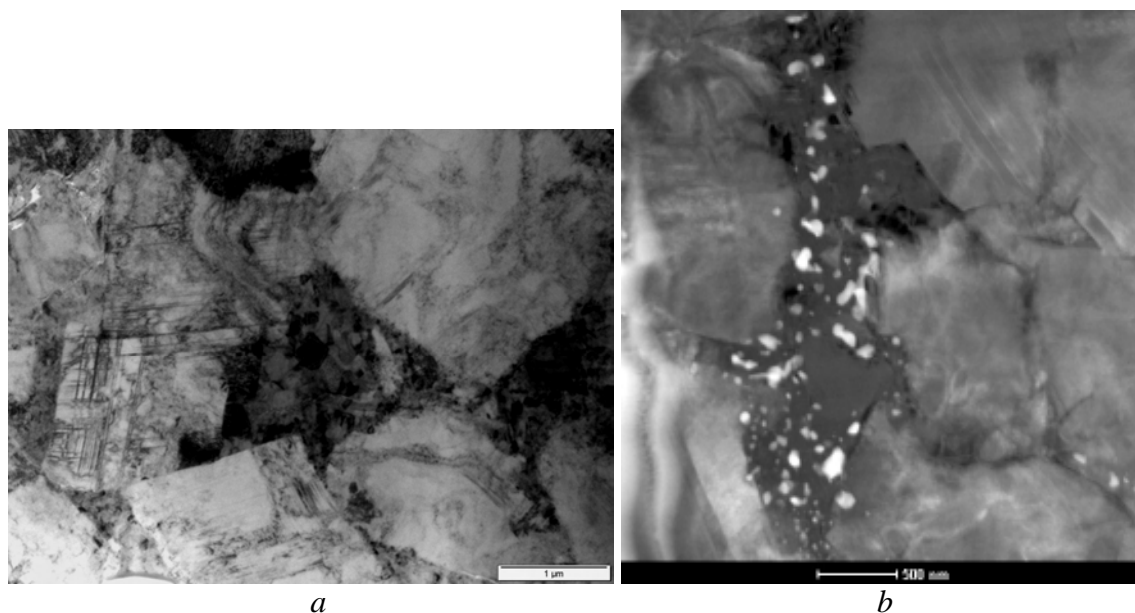


Fig. 5. TEM image of: a – diamond-20 mass % Ti<sub>3</sub>SiC<sub>2</sub> composite; b – diamond-20 mass % Cr<sub>2</sub>AlC composite (area of the bonding phase). The diamond crystallites are characterized by their light contrast

Cr<sub>2</sub>AlC is a more thermally stable material than Ti<sub>3</sub>SiC<sub>2</sub>. This has an influence on the graphitization process for a diamond-Cr<sub>2</sub>AlC composite. Such materials are characterized by residual porosity, dark places along diamond-bonding phase border (fig.5, b). The Cr<sub>2</sub>AlC phase is insufficient to fill most of the larger voids between diamond grains but there is a graphite presence in the final composite (fig. 4). The amount of graphite in this composite, calculated from the X-ray diffraction, is 6.1%. For both systems, the SHS products are multi-composite compounds. Bonding phases for both composite are composed of fine crystallites.

### Conclusions

1. The ductile behaviour of the Ti<sub>3</sub>SiC<sub>2</sub> 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. During the sintering process there is Ti<sub>3</sub>SiC<sub>2</sub> decomposition and carbides, silicides forming.
2. 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. For this composite there is residual porosity in the composite.
3. On the sintering process result the significant influence has the temperature of MAX decomposition.

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Одна з можливостей підвищення термостійкості полікристалічних матеріалів на основі алмазу (PCD) полягає в зменшенні вмісту в них кобальту. Алмазні компакти без кобальту з фазами  $Ti_3SiC_2$  і  $Cr_2AlC$  отримували з використанням методу само поширюваного високотемпературного синтезу (SHS). Отримані компакти з 20 мас. % зазначених фаз піддавали дії високого тиску і температури з метою подальшої консолідації структури шляхом спікання. Процес спікання здійснювали при  $8 \pm 0,2$  ГПа і  $1950 \pm 50$  °С. Фазовий склад і мікроструктурні дослідження вихідних компактів і отриманих композитів виконані методами рентгенівської дифрактометрії (XRD) і скануючої електронної мікроскопії (SEM).

**Ключові слова:** спікання, композиційний матеріал, алмаз, зв'язувальна фаза, фазовий склад, мікроструктура.

Одна из возможностей повышения термостойкости поликристаллических материалов на основе алмаза (PCD) заключается в снижении содержания в них кобальта. Алмазные компакты без кобальта с фазами  $Ti_3SiC_2$  и  $Cr_2AlC$  получали с использованием метода самораспространяющегося высокотемпературного синтеза (SHS). Полученные компакты с 20 % по мас. указанных фаз подвергали воздействию высокого давления и температуры с целью дальнейшей консолидации структуры путем спекания. Процесс спекания осуществляли при  $8 \pm 0,2$  ГПа и  $1950 \pm 50$  °С. Фазовый состав и микроструктурные исследования исходных компактов и полученных композитов выполнены методами рентгеновской дифрактометрии (XRD) и сканирующей электронной микроскопии (SEM).

**Ключевые слова:** спекание, композиционный материал, алмаз, связующая фаза, фазовый состав, микроструктура.

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