

Diamond composite with Ti_2SnC and Zr_2SnC phases

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Materials

ABSTRACT

Purpose: Obtaining diamond compacts with a ceramic bonding phase for improving properties of this group of materials. One of the possibilities to improve the properties of PCD materials is the lowering of cobalt bonding phase content which is used in commercial materials.

Design/methodology/approach: The new bonding phases were prepared using the self-propagating high temperature method of synthesis (SHS). The MAX compounds Zr_2SnC and Ti_2SnC were produced from stoichiometric mixtures of powders. Diamond powders mixtures with participation of 10 mass% of the SHS product were prepared. Diamond composites were obtained using the high pressure - high temperature sintering method. Microstructure investigations were performed using the electron scanning microscope. Phase compositions of the SHS products and diamond compacts were analyzed by x-ray diffraction.

Findings: The X-ray phase analyses indicate that the bonding material prepared by means of the SHS method has a multiphase composition. As a result of reaction between carbon and elements of the bonding phase new carbon phases appear in the diamond compacts. Studies of the microstructures of the diamond composites show good consolidation without microcracks. There is good penetration of the bonding phase between diamond crystallites.

Practical implications: Due to the ceramic bonding phase diamond composites should have better thermal resistance than the diamond with the cobalt bonding phase. The diamond with MAX phases could be used in "dry cutting" processes without harmful lubricants.

Originality/value: MAX bonding phases with tin content for diamond compacts constitute an original value.

Keywords: Tool materials; Diamond composites; MAX bonding phases; HP-HT sintering

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1. Introduction

New cutting tool materials enable the increase of the cutting speed [1]. Most of the studies are concentrated on structured hard coatings. Coated tools can generate high wear resistance on the surface with high toughness in the substrate material. Properly applied coatings increase the surface hardness of cutting tools at high cutting temperatures, thus minimizing abrasive wear [2].

Deposition of nitrides coatings onto high-speed steel matrix composites, cemented carbides, cermet, Si_3N_4 and Al_2O_3 oxides tool ceramics substrate causes the increase of wear resistance and multiply tool life [2,3]. For ceramic cutting tools without coatings there are new directions and developments. The first group consists of FGM (Functionally Graded Materials), especially cermets and carbides [4-6]. The second group consists of materials obtained from nanopowders or with participation of nanopowders [7,8]. The last group comprises materials for high

temperature applications, for hard machining, dry cutting and high speed cutting, as well as high temperature resistance materials [9,10].

The application of diamond cutting tools increases in metalworking because of development of high speed cutting and new "hard to cut" materials. For cutting tool application large single diamond and polycrystals are used.

Synthetic diamond single crystals and polycrystals may be made by chemical vapour deposition or high temperature and high pressure synthesis (HP-HT) with cobalt or silicon constituents. The polycrystalline forms of diamond made by chemical vapour deposition are synthesized from carbon-rich gas and the diamond film is about 0.5 mm in thickness. CVD diamonds have extreme abrasion resistance but in comparison to HP-HT PCD moderate toughness [11]. The microstructure and mechanical properties of polycrystalline diamond, synthesized at high pressure and high temperature, are strongly influenced by the type of applied bonding material phase. There are basically three processes taking place during cold compaction of diamond powder: particle rearrangement, crushing of diamond particles and filling of voids by crushed particles [12]. During the high pressure sintering, the diamond grains start to deform in the zones of contact with each other and graphitization of the diamond surface, which are not in contact with another diamond surface [13]. The most popular commercial PCDs are two-layer materials with the cobalt bonding phase. Utilization of binder materials for the sintering of diamond compacts has three-fold benefits: decreasing of sintering temperatures and pressure, cleaning diamond particle surfaces of graphite and electrodischarge cuttability for tool manufacturing [14]. Due to the presence of cobalt in sintering conditions, the cobalt binder becomes liquid and starts infiltrating into diamond compact. The pores in the diamond compact are filled completely. Cobalt guarantees good distribution of stresses in the sintering diamond powders and prevents the graphitization process.

Silicon is the second binder for PCD materials. During the sintering process, silicon also becomes liquid and there is infiltration of Si into diamond and the SiC carbide is formed. The SiC formation is associated with the increase in volume, which could result in blocking of pore channels, which would affect the material porosity and roughness of the tool surface [15, 10]. This material is not used for metalworking application. Cobalt containing PCD is chemically stable only up to 900-1100K. During machining processes temperature may rise even higher, so intensive cooling is carried out using a huge amount of harmful for people and environment cooling lubricants. Therefore, a new bonding phase for diamond compacts, thermodynamically and chemically stable at even higher temperatures than those containing cobalt, would be interesting.

The aim of previous studies was 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 [16]. Ternary compounds (MAX phases) $M_{n+1}AX_n$, $n = 1-3$, (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 $M_{n+1}AX_n$ "nanolaminates" might make an interesting bonding phase alternative. It is stable up to 1670-1720 K [17]. Generally, $M_{n+1}AX_n$ 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 and high temperatures. The latter properties enable MAX phases to fill most voids between compacted diamonds. The ductile behaviour of the MAX phase helps most of the larger voids between diamond grains be filled, ensuring thermodynamic conditions for maintaining the presence of diamond, i.e. limiting major graphite presence in the final composite. During the sintering process very often there is MAX decomposition and carbides, silicides forming. In the sintering process the significant influence is exerted by the temperature of MAX decomposition. The best results for diamond sintering were obtained for the phases with lower temperature decomposition than temperature of sintering. These are the reactive sintering processes in which graphite was consumable to a carbide form [10,16]. The main factor lowering the hardness of diamond with a binder is the presence of graphite. This indicates a graphitization process during sintering and the presence of tensile stresses in the sintering mixture, depending on plastic properties of the bonding phase. For the studies Ti_2SnC and Zr_2SnC were selected. These are not good characterized MAX phases. Density of Ti_2SnC is 6.36 g/cm^3 , hexagonal $P6_3/mmc$ layered structure lattice parameters are 3.163, 13.679 Å, the dilatometric thermal expansion coefficient is $10 \times 10^{-6} \text{ K}^{-1}$ [18]. The investigation of thermal stability of Ti_2SnC demonstrates that material decomposes to TiC and Sn in vacuum atmosphere at 1520 K. Density of Zr_2SnC is 7.16 g/cm^3 , hexagonal $P6_3/mmc$ layered structure lattice parameters are 3.3576, 14.57 Å, the dilatometric thermal expansion coefficient is $8.3 \times 10^{-6} \text{ K}^{-1}$ [17,18]. Tin is not easily oxidized in air and has lubricant properties which are important for material machining applications. In this paper the influence of the MAX phases with tin presence on diamond compacts phase composition, especially graphite participation for diamond composites were studied.

2. Experimental procedure

MAX bonding phases were obtained by the Self Propagating High temperature Synthesis (SHS) method. The MAX compounds Zr_2SnC and Ti_2SnC were produced from stoichiometric mixtures of powders. The purity and grain size of element powders are shown in Table 1.

Table 1.
Powder characteristics

Element/Producer	Purity, %	Average Grain size, μm
Titanium/ AEE, USA	99.7	44
Tin/ Aldrich	99.8	44
Hafnium/AEE, USA	99.5	44
Zirconium/AEE, USA	99.7	297

The homogeneity of these mixtures were ascertained through extensive mixing of their components for 12 hours in a vibratory rotary mill with Teflon balls suspended in anhydrous isopropyl alcohol. Drying was carried out during mixing. Next, powders were formed into discs by pressing in the steel matrix and synthesized using SHS technique. The reaction was started at

1415°C using the graphite crucible with the graphite foils lining in an argon-filled chamber. After ignition, i.e. rising part of material to high temperature, the front of reaction propagated across the reaction crucible resulting in full transformation of the loaded material. The products of SHS reaction were crushed in the Abbich mortar to powder with grain size to 0.5mm and next they were milled in a rotary-vibratory mill with WC grinding media in anhydrous isopropyl alcohol to finer powers. The grain size distribution and average size of particles were measured using the Shimadzu apparatus. Densities of powders and compacts were measured using AccuPyc 1340 the helium pycnometer, Micrometrics Inc.

Diamond powders of 3-6 μm (MDA, Element Six) were mechanically mixed with 10 wt.% of the MAX Zr_2SnC and Ti_2SnC bonding phase. The resulting mixture was formed into discs ($\phi = 15 \text{ mm}$, $h = 5 \text{ mm}$) by pressing in a steel matrix under pressure of 200 MPa. Samples were heated using an assembly provided with an internal graphite heater. Compacts were sintered at pressure of $8.0 \pm 0.2 \text{ GPa}$ and temperature $1800 \pm 50^\circ\text{C}$ in the high pressure Bridgman type apparatus. Phase composition of the SHS powders and sintered bodies were identified by X-ray diffraction analysis, based on the ICDD database. XRD measurements were taken using an X'Pert Pro system (Panalytical) with monochromatic $\text{Cu K}\alpha 1$ radiation. Microstructure investigations were performed using electron scanning microscope Jeol JSM-6440LV with EDS Oxford spectrometer.

3. Description of the author's achieved results

The microstructure of X-ray analysis of the powders for Zr-Sn-C system is presented in Fig. 1.

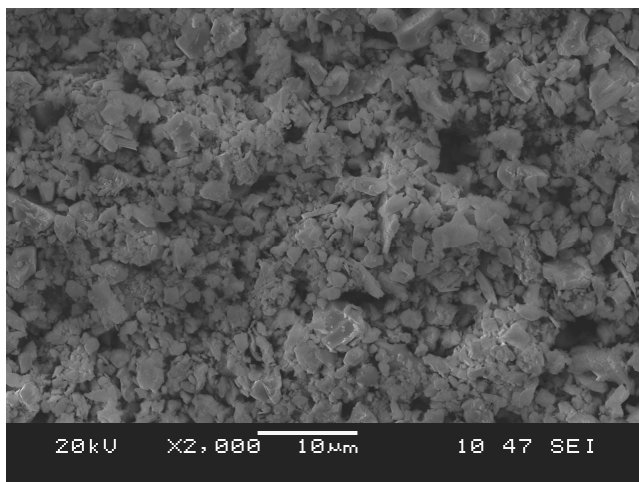


Fig. 1. Microstructure of the powder for the Zr-Sn-C system

Zr-Sn-C SHS product shows the presence of 82.8% Zr_2SnC , 5.7% $\text{Zr}_5\text{Sn}_3\text{C}$, 5.7% $\alpha \text{ ZrC}$, 2.5% Sn, 3.0% $\beta \text{ ZrC}$.

XRD patterns are shown in Fig. 2.

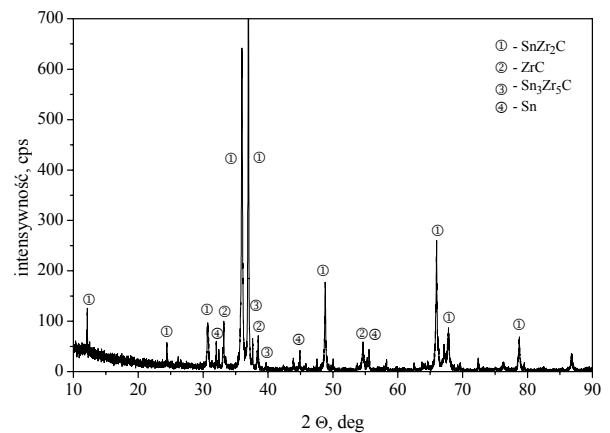


Fig. 2. X-ray pattern of SHS product for the Zr-Sn-C system

The pycnometric density of powder is 6.55 g/cm^3 . Average size of particles, for this powder is $3.88 \mu\text{m}$.

The microstructure of X-ray analysis of the powders for Ti-Sn-C system is presented in Fig. 3.

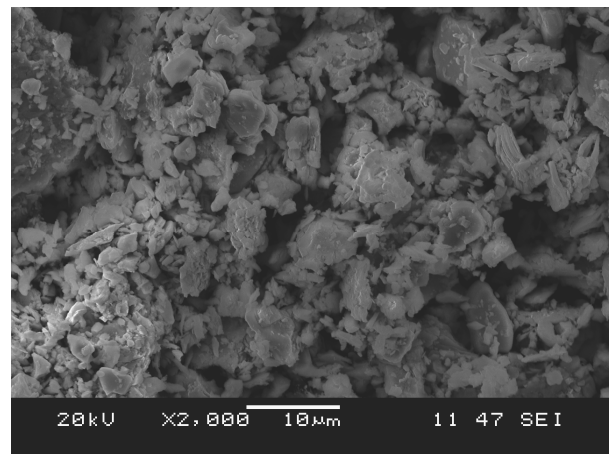


Fig. 3. Microstructure of the powder for the Ti-Sn-C system

Ti-Sn-C SHS product shows the presence of 78.6% Ti_2SnC , 10.9% Sn, 10.5% TiC , 2.5% Sn, SHS is characterized by the presence of the mixtures of phases from the system. One of the phases is the main and overwhelming like Zr_2SnC for Zr-Sn-C and Ti_2SnC for Ti-Sn-C system. The synthesis only one phase is for the SHS method practically impossible, it strongly depends on process parameters.

XRD patterns are shown in Fig. 4.

The pycnometric density of powder is 6.01 g/cm^3 . Average size of particles, for this powder is $5.14 \mu\text{m}$.

The phase composition diamond compacts with 10 mass% of MAX bonding phase are presented in the Figs. 5 and 6.

X-ray diffraction of the compact with the bonding phase from Zr-Sn-C system shows the presence of 87.7% diamond, 4.7% graphite, 3.9% ZrC (1:1), 1.4% Sn and 2% monoclinic ZrO_2 and 0.3% tetragonal ZrO_2 . Oxygen appears from atmosphere during the sintering process.

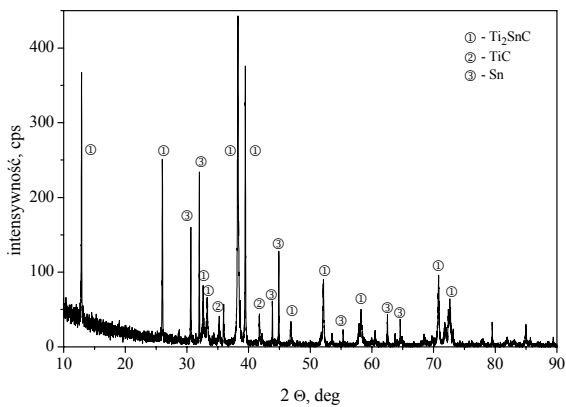


Fig. 4. X-ray pattern of SHS product for the Ti-Sn-C system

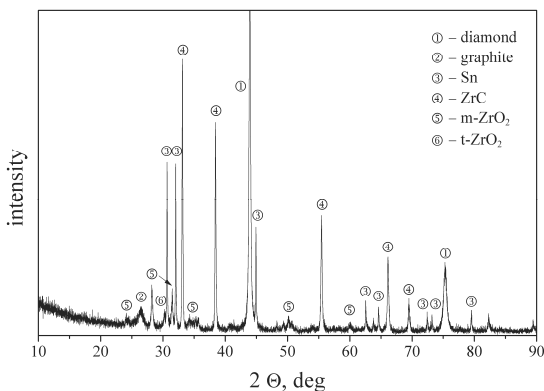


Fig. 5. X-ray pattern of diamond compact with the bonding phase from the Zr-Sn-C system

X-ray diffraction of the compact with the bonding phase from Ti-Sn-C system shows the presence of 80 % diamond, 8.7% graphite, 2.4% TiC, 2.9% Sn and 6.0% perovskite (MeTiO_3). Oxygen for the first system appears from atmosphere during the sintering process, Fig. 6.

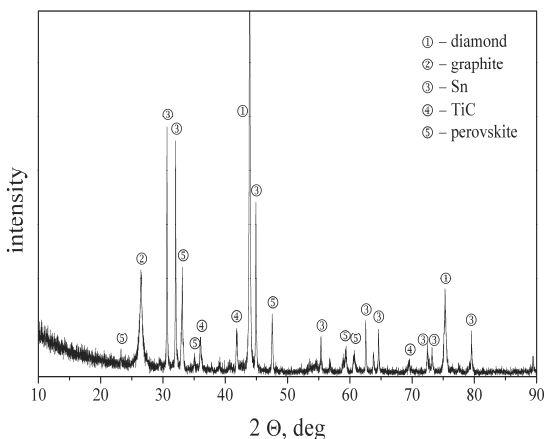


Fig. 6. X-ray pattern of diamond compact with the bonding phase from the Ti-Sn-C system

In the composites with the studied carbides binding material, due to the sintering in solid state, the tendency to the graphitization process is observed. More graphite appears in the material with the bonding phase for Ti-Sn-C in which perovskite is formed.

In Fig. 7, the microstructure of diamond compact with the 10 mass% of the bonding phase from the Zr-Sn-C system is presented.

Studies of the microstructures of the diamond composites presented in Fig. 7 show good consolidation without microcracks. There is good penetration of the bonding phase between diamond crystallites. Fig.7a shows large areas of the bonding phase which have a distinctly various microstructure, Fig. 7 c, d.

The microstructure for diamond with 10 mass% of the bonding phase for Ti-Sn-C system, presented in Fig. 8, is very similar to the previously described material.

The results of some physical, mechanical and wear properties of diamond compacts are presented in detail in Table 2.

Table 2.

Densities and Young modulus of diamond composites with 10 mass% of the bonding phase, SHS products from Zr-Sn-C and Ti-Sn-C systems

Type of the bonding phase (system)	Apparent Density (g/cm^3)	Young modulus (GPa)
Zr-Sn-C	3.77	523
Ti-Sn-C	3.51	520

Despite the fact that in the materials there are tin and graphite materials, they are characterized by a high value of Young modulus. Tin and graphite could influence tribological properties of composites, especially wear resistance.

4. Conclusions

- The SHS produced MAX compounds have high chemical activity at high pressure and high temperature, at which these PCD compacts are prepared.
- The performed investigations indicate that mixing of diamond powder with MAX compounds allow producing composites characterized by good bonding of filler material and diamond crystallites.
- The X-ray phase analyses indicate that the bonding material prepared by the SHS method has a multiphase composition. As a result of the reaction between carbon and elements of the bonding phase a new carbon phases appear in the material.
- For the both studied composites tin and graphite is detected.

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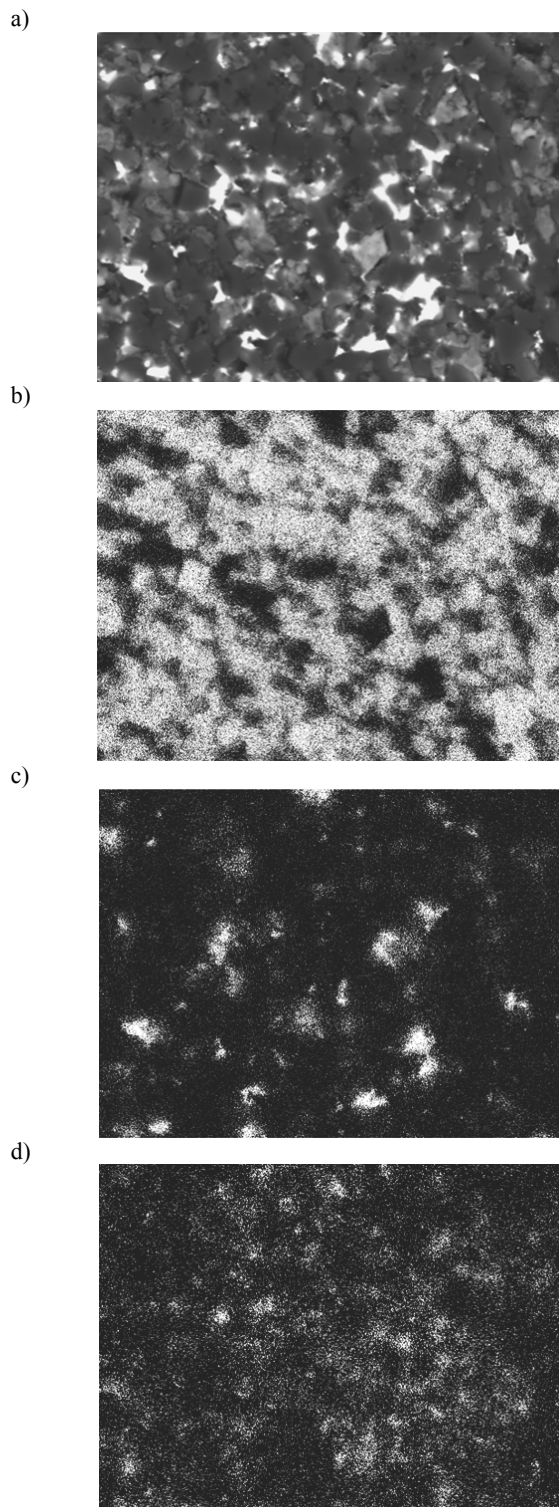


Fig. 7. a) Microstructure of diamond compact with the 10 mass % of the bonding phase from the Zr-Sn-C system; and EDS mapping taken from diamond - bonding material presenting of distribution of b) carbon; c) zirconium; d) tin

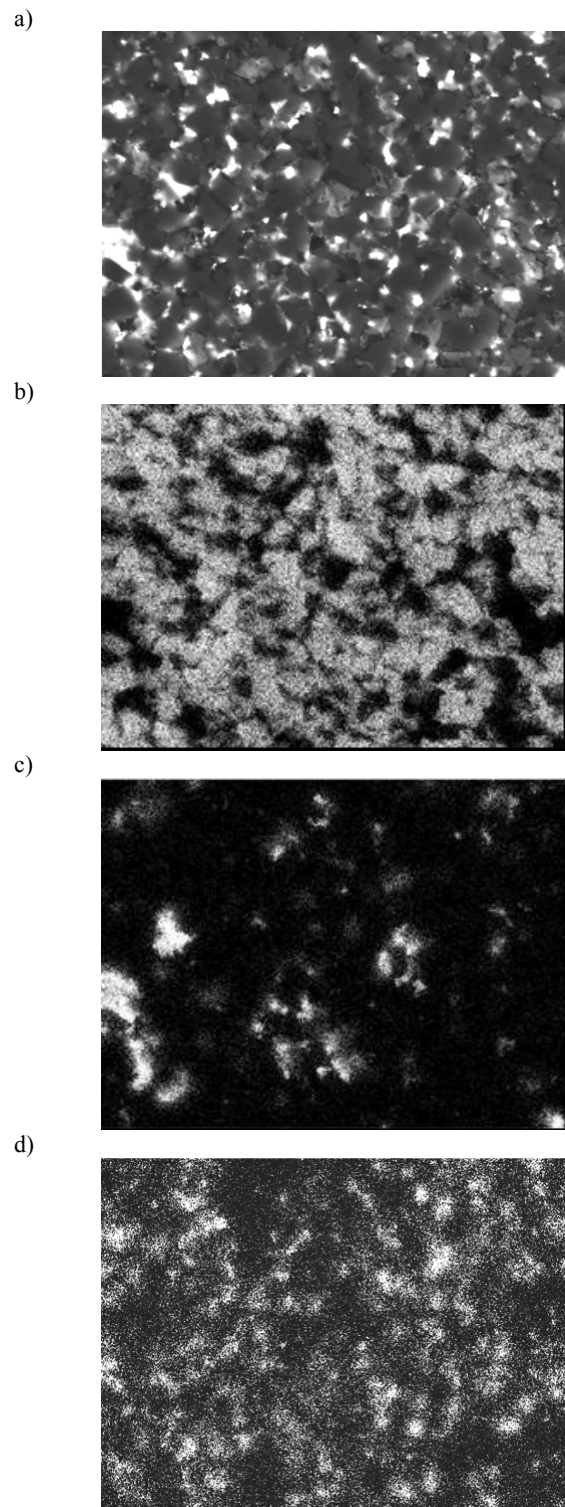


Fig. 8. a) Microstructure of diamond compact with the 10 mass % of the bonding phase from the Ti-Sn-C system; and EDS mapping taken from diamond - bonding material presenting of distribution of b) carbon; c) titanium; d) tin

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