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The Influence of the Carbide-Forming Metallic Additives (W, Mo, Cr, Ti) on the Microstructure and Thermal Conductivity of Copper–Diamond Composites

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Abstract: In this study, carbide-forming metallic additives (W, Mo, Cr, Ti) were introduced into the copper matrix to improve the wettability of diamond particles in the copper–diamond composites. The samples were prepared by Spark Plasma Sintering (SPS) and Hot Pressing (HP) at 920 °C. The phase composition, microstructure and thermal conductivity of the samples were investigated. The influence of the carbide-forming additive concentration, the sintering method as well as the nature of the metal introduced into the copper matrix on the thermal conductivity of copper–diamond composites was determined. Titanium ensured a more significant wettability improvement at the copper–diamond interface. This is due to its higher solubility in copper in comparison with other metals (W, Mo, Cr) and the possibility of its diffusion through the copper matrix to the diamond surface resulting in the formation of a closer contact at the copper–diamond interface.

Keywords: diamond; copper; thermal conductivity; microstructure; scanning electron microscopy

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1. Introduction

The rapid development of microelectronics and the industry requires new efficient heat sink materials to increase the performance of devices without increasing their size. The standard materials commonly used as heat sinks (copper, thermal conductivity 400 W m^{-1} K^{-1}, and aluminum, thermal conductivity 250 W m^{-1} K^{-1}) may no longer be efficient. Materials with higher thermal conductivities and lower coefficients of thermal expansion are sought. A promising candidate for high-performance heat sink elements is synthetic diamond, which has a higher thermal conductivity compared with copper [1,2] and is less expensive than natural diamond. Determining factors governing the distribution of solid-phase transformation products is a key problem pertaining to the development of the synthesis methods of composite materials. The solution of this problem allows obtaining composites with controllable morphological characteristics of the components and improved properties. The high hardness and thermal conductivity of diamond, as well as its chemical inertness, allow us to use it as a component of materials for abrasive processing, cutting tools, heat dissipation materials and as inert substrates. However, the crystals of synthetic diamond micropowders cannot be consolidated into bulk objects. This makes it impossible to produce heat sink plates or other products directly from the micropowders. The development of metal–diamond composites with high thermal conductivity requires solving a number of scientific problems, the main one being the elucidation of the mechanisms of phase, structural and morphological transformations at the metal–diamond interface. Those transformations determine the wettability of diamond by the metal during the formation of a composite material. In this connection, in order to fabricate metal–diamond composites with high thermal conductivity, it is necessary to solve the problem of low wettability of diamond particles by the metal in order to minimize the thermal resistance at the metal–diamond interface and to prevent the formation of voids, which cause significant deterioration of the properties of the composites. To increase the metal-matrix adhesion to the diamond surface, two main approaches are used: preliminary modification of the diamond surface (formation of thin coatings) and addition of an alloying element directly into the metal matrix.

Recent studies have been devoted to the preparation of copper–diamond and aluminum–diamond composites with high thermal conductivity [3–7]. Copper has a higher thermal conductivity than aluminum and does not form carbides, which can create an additional barrier to heat transfer. Unfortunately, copper has a poor wettability towards the diamond surface, which causes the pore formation at the copper–diamond interface and reduced heat transfer. For this reason, the thermal conductivity of copper–diamond composites can be lower than that of pure copper [8–10].

To overcome this problem, several approaches have been used: the preliminary modification of the diamond surface prior to sintering [11–13], the direct modification of the copper matrix with carbide-forming metals to react in situ [14–18], and the optimization of the synthesis parameters of the composites [7,19]. In [11], the effect of Ti- and W-containing coatings of different thicknesses (50, 100 and 150 nm) on the surface of diamond obtained by magnetron sputtering on mechanical properties (bending strength) and thermal conductivity of copper–diamond composites was described. This study shows that the strengthening mechanisms depend largely on the metal, from which the coating is formed. Thus, when Ti is used as a coating, the bending strength of the material gradually increases with increasing coating thickness but the thermal conductivity first increases and then decreases. In contrast, when W is used as a coating, the bending strength is lower than in the case of a Ti coating of the same thickness. In [12], the use of Ti coatings (thickness 50 nm) on the diamond surface is discussed. Copper–diamond composites were obtained at different temperatures (800 °C and 1050 °C) by hot forging of cold-pressed powder pre-forms. It was found that, at 800 °C, the roughened coating surface promotes better adhesion to the copper matrix. In [13], the use of Ti-coated diamonds with coating thicknesses from 65 nm to 850 nm produced by magnetron sputtering was described. The thermal conductivity of the copper–diamond composites in that case nonlinearly depended on the coating thickness. First, the thermal conductivity increased but then decreased with the coating thickness. In [14], the effect of the concentration of the chromium additive on the thermal and mechanical properties of copper–diamond composites was investigated. The composites were obtained by field-assisted sintering. The thermal conductivity of the composites reached a maximum at a chromium concentration of 2 wt.% (339.2 W m^{-1} K^{-1}) and, with a further increase in the chromium content, the thermal conductivity decreased. The authors relate this effect to the fact that initially a coating consisting of Cr_3C_2 is formed on the surface of the diamond particles, which promotes their wetting by the copper matrix. The introduction of higher chromium contents causes a reduction in the thermal conductivity of the matrix and the composite as a whole. In [17], a significant increase in the thermal conductivity was observed, when zirconium was added to the copper matrix (930 W m^{-1} K^{-1}). The samples were obtained by a gas pressure infiltration route. The zirconium concentration in the samples was between 0 and 1 wt.% Zr. The authors also explained an increased thermal conductivity by the formation of a ZrC layer on the surface of diamond particles. The authors of [20] reported a thermal conductivity of 688 W m^{-1} K^{-1} for a composite containing 0.3 wt.% B added to the copper matrix (the composites were obtained by the high-pressure high-temperature method). Close thermal conductivity values were obtained by adding 0.4 wt.% Cr and 1 wt.% Ti. The use of elements that form carbides (Ti, Si, Cr, Zr) to modify the copper matrix was described in [20–23].

It is important to note that the additive metals differ in their solubility in copper. Aluminum, titanium and silicon have a high solubility in copper [7], which allows them to diffuse to the boundary between the matrix with the diamond and form coatings. This leads to the improvement of thermal and mechanical properties of the composites. However, with an excess of additives in the matrix, the opposite effect occurs: the total thermal conductivity of the composite may be reduced because of a reduction in the thermal conductivity of the matrix. Metals such as tantalum, molybdenum and tungsten, although forming carbides, are not soluble in copper, so in this case coatings on diamond can be formed upon a direct contact of these metals with diamond.

Various methods have been described for the preparation of composites: pulse plasma sintering (PPS) [24], Spark Plasma Sintering (SPS) [25,26] and Hot Pressing (HP) [26,27]. As different concentrations of metals (additives) in the copper matrix were used in different publications, it is difficult to compare the effectiveness of metals at improving the thermal conductivity of the composites.

In this paper, the effect of additives (soluble (Ti) and insoluble (Cr, Mo and W) in copper) introduced into the copper matrix on the thermal conductivity of copper–diamond composites obtained by the SPS and HP methods was studied.

2. Materials and Methods

Powders of synthetic diamonds (MBD10, China, particle size 100 μm) and copper (PMS-1, Russia, average particle size 40 μm) were used as raw materials. Ti (PTM-1, Russia), Cr (PH1M, Russia), Mo (MFP, Russia), W (Russia) were used as additives to modify the copper matrix.

The powder mixtures containing 0.15, 0.35, 0.7 and 2 vol.% of the additive (W, Mo, Cr, Ti) were thoroughly blended in a mortar. The diamond concentration in all samples was 50 vol.%. To produce copper–diamond composites in the bulk state, the SPS and HP methods were used. SPS experiments were carried out on a Labox 1575 facility (SINTER LAND Inc., Nagaoka, Japan) at 920 °C with holding times of 3 min and 10 min. A custom-built set-up (The Institute of Automation and Electrometry SB RAS, Novosibirsk, Russia) was utilized to conduct HP experiments. HP was conducted at 920 °C with a holding time of 15 min. The temperature during both SPS and HP experiments was measured using a pyrometer focused on the die wall at its mid-plane. The difference between the two synthesis methods is that, in the SPS, the sample is heated by electric current directly passing through the graphite die and the sample, whereas in the HP, the sample and the die are heated by radiation from the external heating elements.

A uniaxial pressure of 40 MPa was consistently applied to the samples. The consolidation of composites during HP was performed in argon at a pressure of 0.1 MPa, while the SPS experiments were carried out under the forevacuum conditions (at a residual pressure of 10 Pa). The heating rate in both methods was 50 $^{\circ}C\ min^{-1}$. To protect the inner walls of the die and the flat ends of the punches, a layer of graphite foil was used.

Examinations of the microstructure of the copper–diamond composites by scanning electron microscopy were conducted using a Hitachi TM-1000 Tabletop Microscope (Japan). Each composite sample was fractured and the fracture surface was examined. The X-ray diffraction (XRD) technique was used to investigate the phase composition of the samples. The XRD patterns were acquired using a D8 ADVANCE X-ray diffractometer (Bruker AXS, Germany). The step size was 0.02° 2θ for all samples. The XRD patterns were recorded from the flat surface of the sintered samples. Additional analyses were carried out for samples with 2 vol.% titanium. A piece of sample was mechanically ground in a mortar to extract the diamond particles from the compacts. The obtained diamond particles were placed on a single-crystal Si-cuvette to record a XRD pattern of these particles. The Rietveld refinement technique implemented in the TOPAS 4.2 software (Bruker AXS, Germany) was used to determine the parameters of the copper crystalline structure.

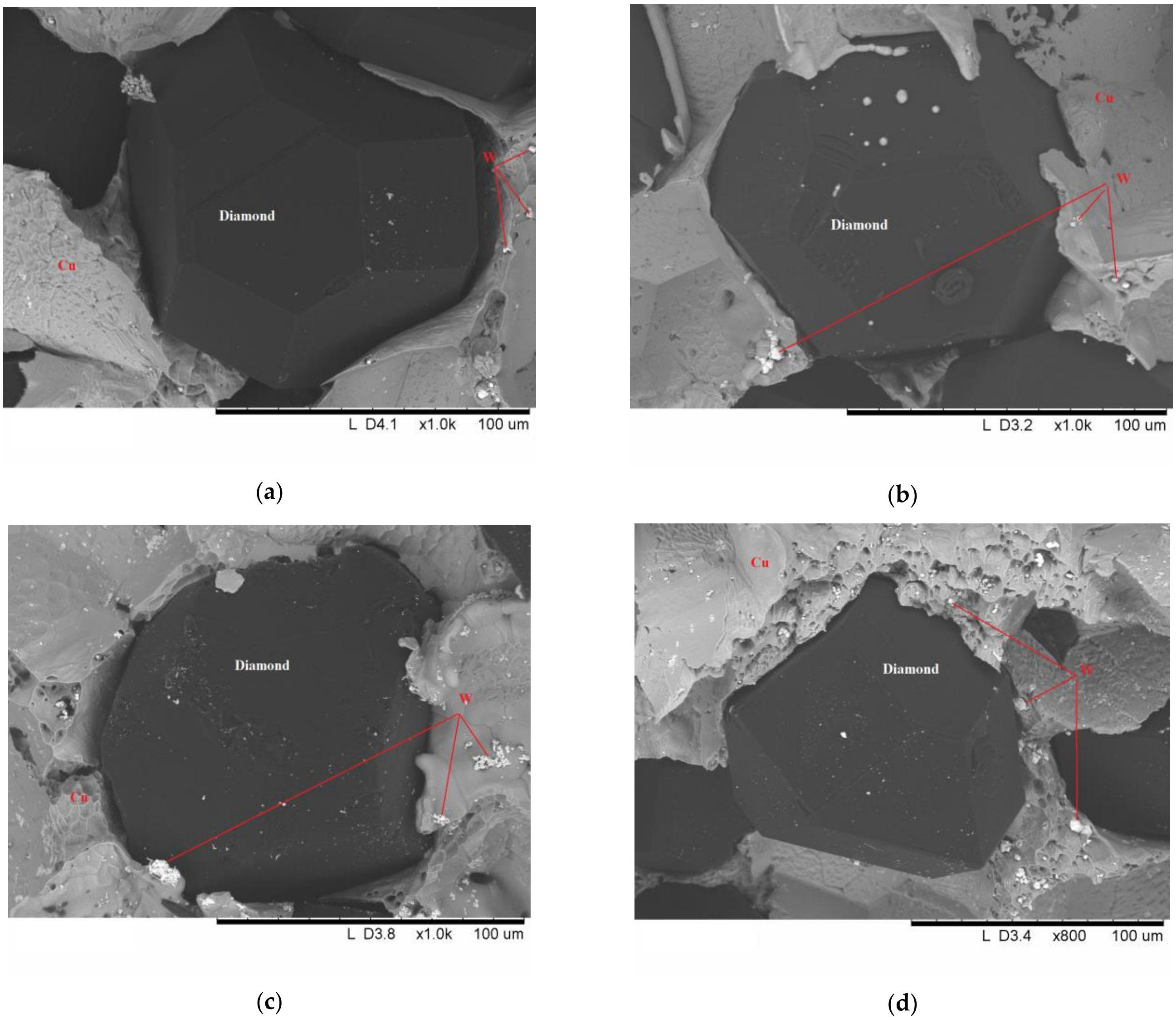
The laser flash method was used to measure the thermal diffusivity (a) of the copper–diamond composites, using an LFA-427 setup (Netzsch, Germany). An average value for the temperature diffusivity coefficient was obtained by five measurements. The thermal conductivity (λ) of the composites was then calculated as follows:

$$\lambda = a\ \rho\ \mathrm{Cp},$$

In this equation, a represents the thermal diffusivity, ρ represents density, and Cp represents the specific heat capacity of the composite. The specific heat capacity of the composite was estimated using the rule of mixtures, employing the values of pure copper (0.38 J g^{-1} K^{-1}) and diamond (0.5 J g^{-1} K^{-1}).

3. Results and Discussion

Figure 1 shows the microstructure of copper–diamond composites with different concentrations of tungsten obtained by HP. It can be seen that pores are present at the copper–diamond interface. The thermal conductivity of these composite is lower than that of pure copper (Table 1) but higher than that of copper–diamond composites obtained using unmodified copper (150 W m^{-1} K^{-1}) [28].



(**a**)

(**b**)

(**c**)

(**d**)

Figure 1. Microstructure of the copper–diamond HP-ed composites with a W-modified copper matrix: 0.15 vol.% (**a**), 0.35 vol.% (**b**), 0.7 vol.% (**c**) и 2 vol.% (**d**). Black areas are diamond, gray areas are copper and white areas are tungsten.

Table 1. Sintering conditions, relative density and thermal conductivity of the copper–diamond composites.

Sample Number	Sintering Method	Additive	Concentrations of the Additive, Cu and Diamond, Vol.%			Sintering Time, min	Relative Density, %	Thermal Conductivity, W m^{-1} K^{-1}
			Additive	Cu	Diamond			
1	HP	W	0.15	49.85	50	15	90 ± 1	188 ± 9
2	HP	W	0.35	49.65	50	15	91 ± 1	192 ± 10
3	HP	W	0.7	49.3	50	15	88 ± 1	203 ± 10
4	HP	W	2	48	50	15	90 ± 1	172 ± 9
5	SPS	W	0.7	49.3	50	3	80 ± 1	170 ± 9
6	SPS	W	0.7	49.3	50	10	86 ± 1	190 ± 10
7	SPS	Mo	0.7	49.3	50	10	91 ± 1	194 ± 10
8	SPS	Cr	0.7	49.3	50	10	89 ± 1	385 ± 19
9	SPS	Ti	0.7	49.3	50	10	86 ± 1	420 ± 21
10	HP	Ti	0.7	49.3	50	15	89 ± 1	178 ± 9
11	SPS	Ti	0.35	49.65	50	10	82 ± 1	362 ± 18
12	SPS	Ti	2	48	50	10	82 ± 1	67 ± 3
13	HP	Ti	0.35	49.65	50	15	90 ± 1	265 ± 13
14	HP	Ti	2	48	50	15	77 ± 1	63 ± 3

The XRD patterns of the sintered composites are shown in Figure 2. No carbide phases were detected in the samples, only peaks corresponding to copper, diamond and tungsten phases are present.

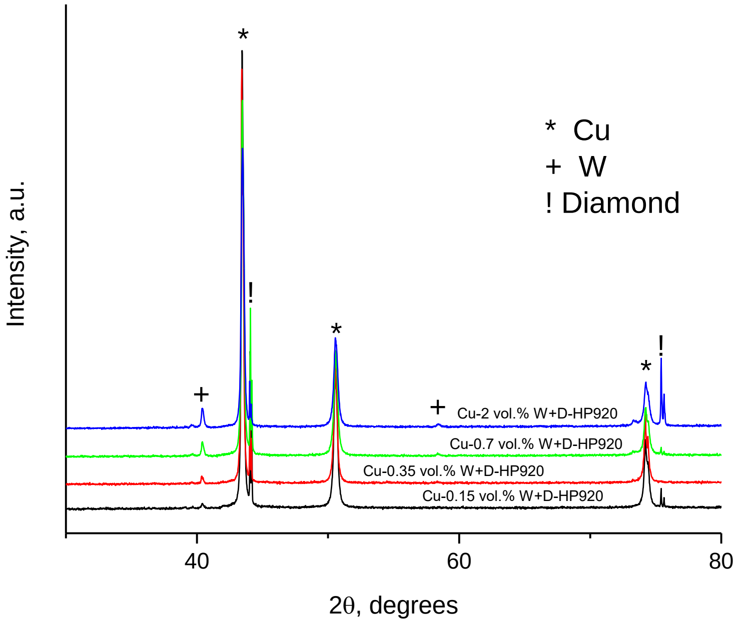


Figure 2. XRD patterns of the composites with a W-modified copper matrix.

In the W-modified matrix series, composites obtained with the addition of 0.7 vol.% of W demonstrate the highest thermal conductivity (Table 1). The thermal conductivity of the composites first increases, reaching a maximum at 0.7 vol.%, and then decreases. This effect can be explained by the fact that, at first, the addition of tungsten to the matrix contributes to increasing the wettability of diamonds by the modified copper matrix. As the thermal conductivity of tungsten is much lower than that of copper, a further increase in the tungsten concentration leads to a decrease in the thermal conductivity of the composites.

Since the composite with 0.7 vol.% W has the highest thermal conductivity in the W-modified matrix series, additional experiments were carried out to obtain composites with the same composition using another sintering method, SPS. When the holding time during SPS was only 3 min, the thermal conductivity of the composite was lower than that of the composite obtained by HP (Table 1). Therefore, the holding time was increased to 10 min, which resulted in an increase in the thermal conductivity of the composite, so that it became close to that of the composite obtained by HP with 15 min sintering time (203 and 190 W m^{-1} K^{-1}, respectively).

In order to investigate the influence of the nature of the metal additive on the thermal conductivity of the composites, experiments were carried out using 0.7 vol.% of Mo, Cr and Ti additives. The XRD patterns of the sintered samples are shown in Figure 3. For samples with the W and Mo additives, there are peaks corresponding to metals, but for the samples with the Cr and Ti additives, only copper and diamond peaks are present in the XRD patterns. As Cr and Ti possess lower atomic numbers, their concentration in the composites may be too small for the detection by the XRD phase analysis.

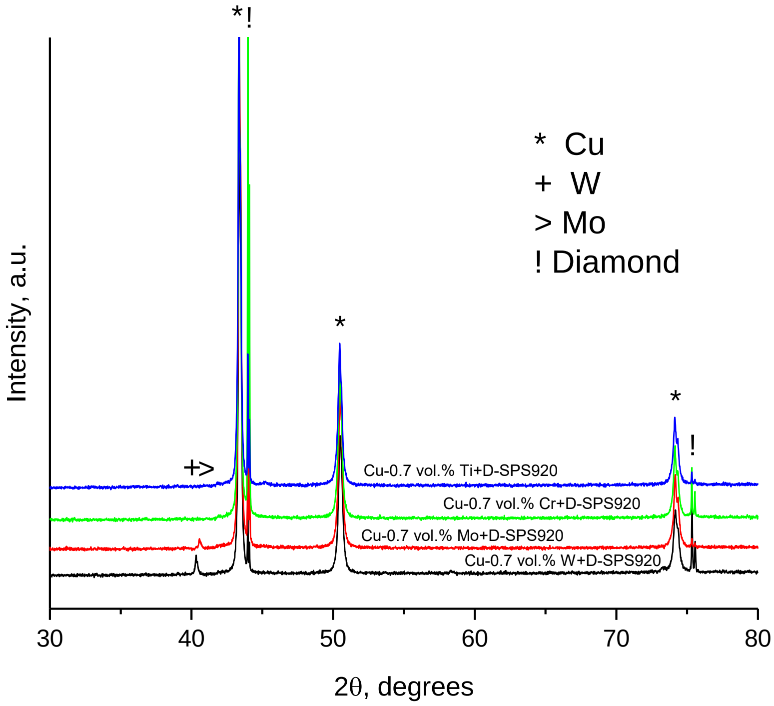
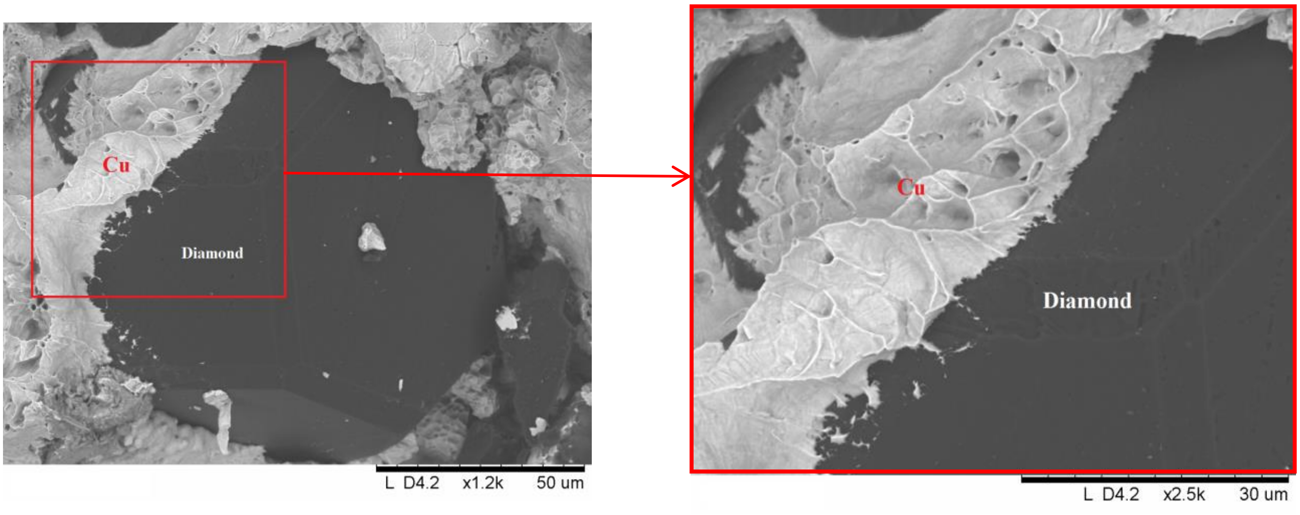


Figure 3. XRD patterns of the composites with 0.7 vol.% Me (Me = W, Mo, Cr, Ti)-modified copper matrix.

As seen in Table 1, the composite with 0.7 vol.% Ti has the highest thermal conductivity (420 W m^{-1} K^{-1}). The detailed microstructure of this composite is presented in Figure 4. It can be seen that the copper-based matrix wets the diamond surface well. As Ti has a higher solubility in Cu (~5 at.% at 920 °C and ~3 at.% at 1000 °C) in comparison with W, Mo and Cr, solid solutions form during sintering of the mixtures, which improves the wettability of diamond by the matrix (the titanium concentration in the sample is less than 5 at.%).



(**a**)

(**b**)

Figure 4. Microstructure of the copper–diamond composite obtained by SPS with titanium Ti additive 0.7 vol.%: lower magnification ×1200 (**a**) and higher magnification ×2500 (**b**). Black areas are diamond, gray areas are copper.

We believe that, during sintering, a metal soluble in copper (Ti) can diffuse through the copper matrix to the interface with diamond to form carbides, whereas in the case of copper-insoluble metals (W, Mo, Cr), carbides can be formed only if a direct contact of these metal particles diamond is established. The carbides are formed according to reactions:

$$\mathrm{W} + \mathrm{C_D} \rightarrow \mathrm{WC} \tag{1}$$

$$2\mathrm{W} + \mathrm{C_D} \rightarrow \mathrm{W_2C} \tag{2}$$

$$\mathrm{Mo} + \mathrm{C_D} \rightarrow \mathrm{MoC} \tag{3}$$

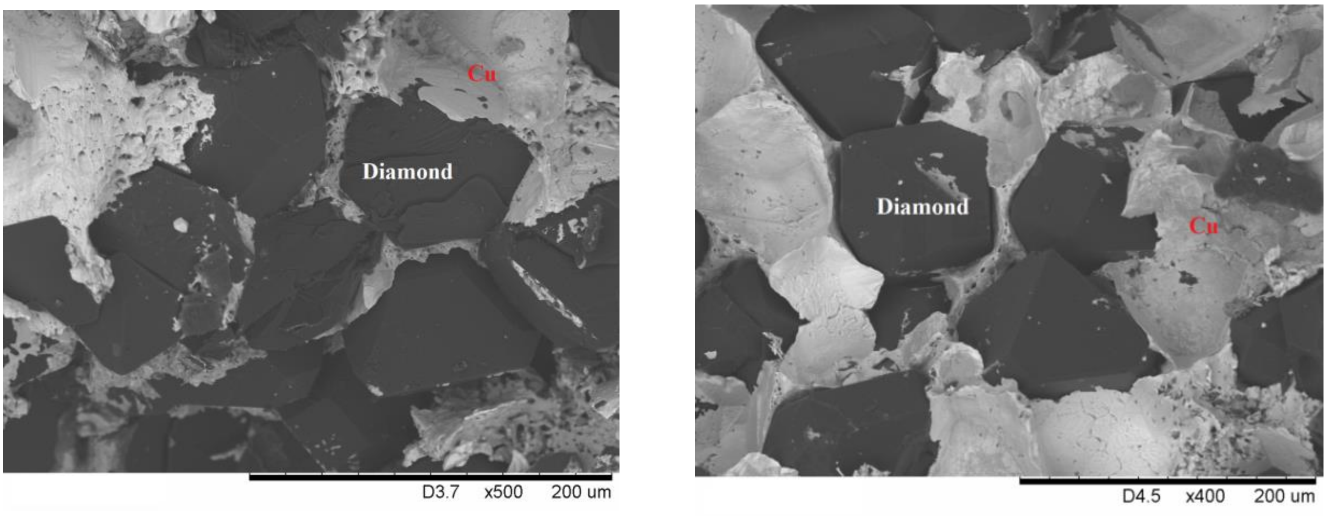
$$2\mathrm{Mo} + \mathrm{C_D} \rightarrow \mathrm{Mo_2C} \tag{4}$$

$$3\mathrm{Cr} + 2\mathrm{C_D} \rightarrow \mathrm{Cr_3C_2} \tag{5}$$

$$\mathrm{Ti} + \mathrm{C_D} \rightarrow \mathrm{TiC} \tag{6}$$

The Gibbs free energy of these reactions at 920 °C was calculated using FACT online calculator (http://www.crct.polymtl.ca/FACT/) and are given below (per 1 mol of atoms): $\Delta_{r1}G^\circ$ = –21 kJ, $\Delta_{r2}G^\circ = -11$ kJ, $\Delta_{r3}G^\circ = -19$ kJ, $\Delta_{r4}G^\circ = -22$ kJ, $\Delta_{r5}G^\circ = -20$ kJ, $\Delta_{r6}G^\circ = -87$ kJ. It can be seen that the formation of all carbides is thermodynamically possible, and TiC is the most stable compound among the studied carbides. Its formation is favored during sintering. So, not only the solubility of the carbide-forming metal in copper, but also the thermodynamic characteristics of the carbidization reactions can play an important role in the structural evolution of the mixture during sintering.

For comparison, an additional experiment was carried out to sinter a composite with the same composition by HP. However, the thermal conductivity of the obtained composite (178 W $\mathrm{m^{-1}}$ $\mathrm{K^{-1}}$) was significantly lower than that of the composite obtained by SPS (420 W $\mathrm{m^{-1}}$ $\mathrm{K^{-1}}$). It is important to note that, although the relative densities of these composites are close, the thermal conductivity of the SPS-ed composite is much higher. The microstructure of these composites is shown in Figure 5. It appears possible that the SPS conditions of consolidation can promote a homogeneous distribution of Ti in the copper matrix, which can facilitate uniform wetting of diamonds by the copper matrix. For example, in the study of the formation of Mo-containing coatings on diamond [29], it was found that, under the SPS conditions, a more homogeneous coating was deposited on the surface of diamond particles than under the HP conditions. This can be influenced both by the passage of electric current and by the atmosphere (vacuum in the SPS and argon in the HP).



(**a**) (**b**)

Figure 5. Microstructure of copper–diamond composite obtained with titanium Ti additive 0.7 vol.% by SPS (**a**) and HP (**b**). Black areas are diamond, gray areas are copper.

When the concentration of titanium was 0.35 vol.%, the thermal conductivity was 265 W m^{-1} K^{-1} for the HP composite and 362 W m^{-1} K^{-1} for the SPS composite. When the Ti concentration was increased up to 2 vol.%, the thermal conductivity of the composites sharply decreased (Figure 6). The SEM data show that, at this concentration of titanium, a coating is formed on the surface of the diamond particles, which probably leads to a decrease in the thermal conductivity of these composites (Figure 7).

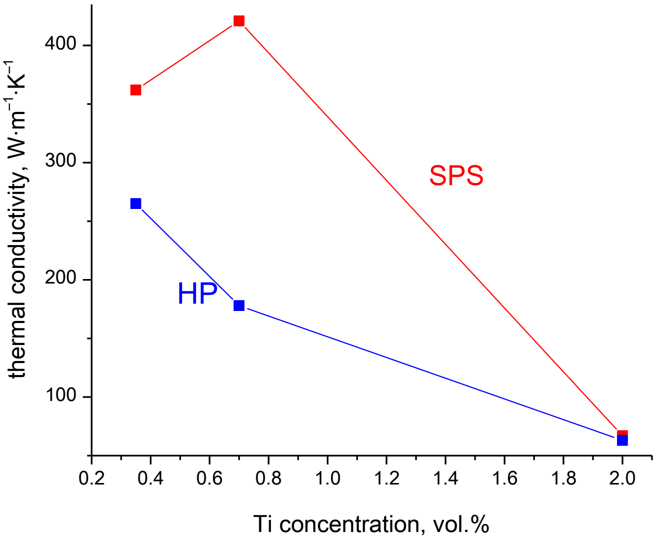
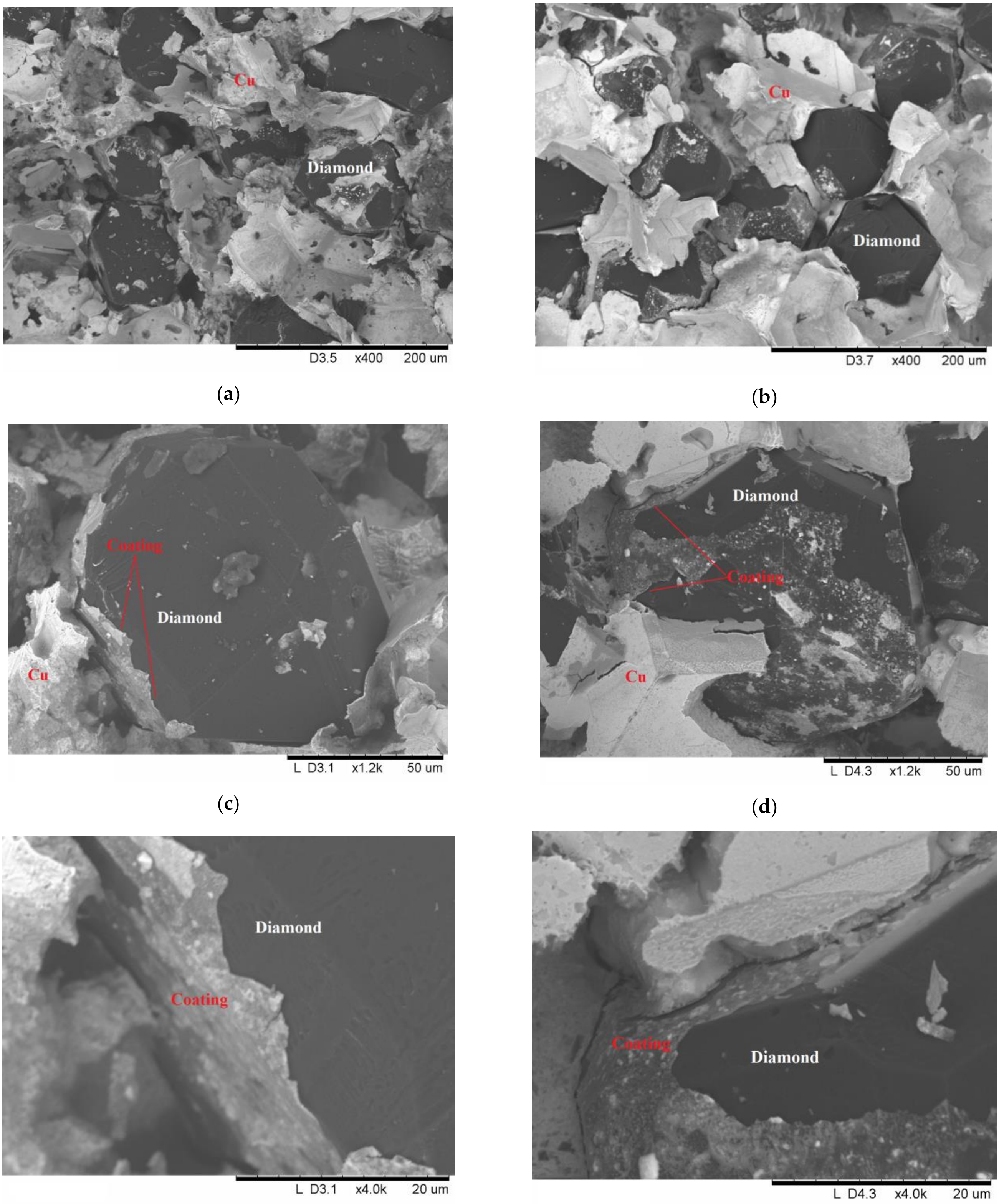


Figure 6. Dependence of thermal conductivity of the composites on the titanium concentration.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 7. Microstructure of the composites with 2 vol.% Ti additive obtained by HP (**a**,**c**,**e**) and SPS (**b**,**d**,**f**), different magnifications. Dark areas are diamond, and light areas are copper.

The XRD patterns of composites with the Ti titanium-modified copper matrix are shown in Figure 8. No peaks other than those corresponding to copper and diamond were detected, even at a titanium concentration of 2 vol.%. It can be seen that the copper peaks shift towards smaller 2θ angles as the concentration of titanium in the samples increases. This shift indicates an increase in the lattice parameter of copper due to the incorporation of titanium into its crystal structure (Table 2).

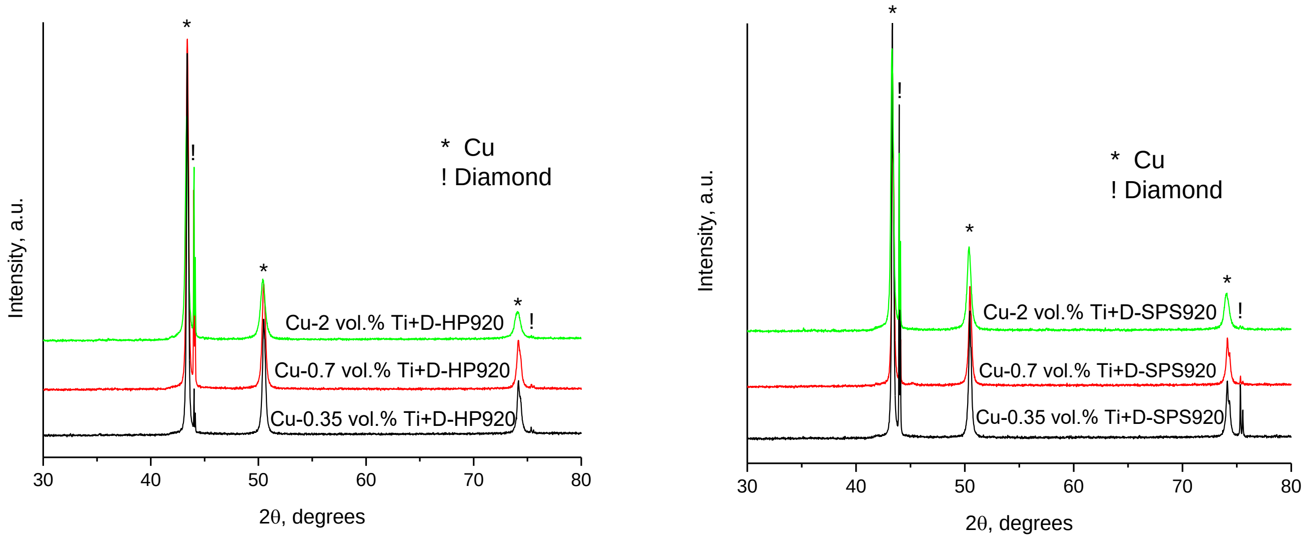


Figure 8. XRD patterns of composites with a Ti-modified copper matrix.

Table 2. Titanium concentration, the sintering method and the lattice parameter of Cu in the composites.

Sample Number	Concentrations of the Ti, Vol.%	Sintering Method	Cu Lattice Parameter, Å
1	0.35	HP	3.6172 ± 0.0014
2	0.35	SPS	3.6169 ± 0.0018
3	0.7	HP	3.6176 ± 0.0016
4	0.7	SPS	3.6181 ± 0.0012
5	2	HP	3.623 ± 0.002
6	2	SPS	3.6221 ± 0.0016

In addition, a more detailed analysis of the sample containing 2 vol.%Ti was conducted. The sample was mechanically ground in a mortar, after which the diamond particles were separated and placed on a single-crystal Si-cuvette. The obtained XRD patterns are shown in Figure 9. In the 2θrange of 10–70°, only the diamond peak is present (Figure 9a). Due to its high intensity, a 2θrange of 30–44° was analyzed separately (Figure 9b). In this case, we can see a peak corresponding to copper and two small peaks that may correspond to titanium carbide. These two peaks are broadened, which indicates the small size of crystallites. Their position is slightly shifted towards larger 2θangles, suggesting a smaller lattice parameter as compared with stoichiometric TiC. Based on the obtained data, we can assume that the coating consists of titanium carbide TiC_x. The presence of copper is probably due to the fact that some copper particles remained adhered to the surface of the diamond particles.

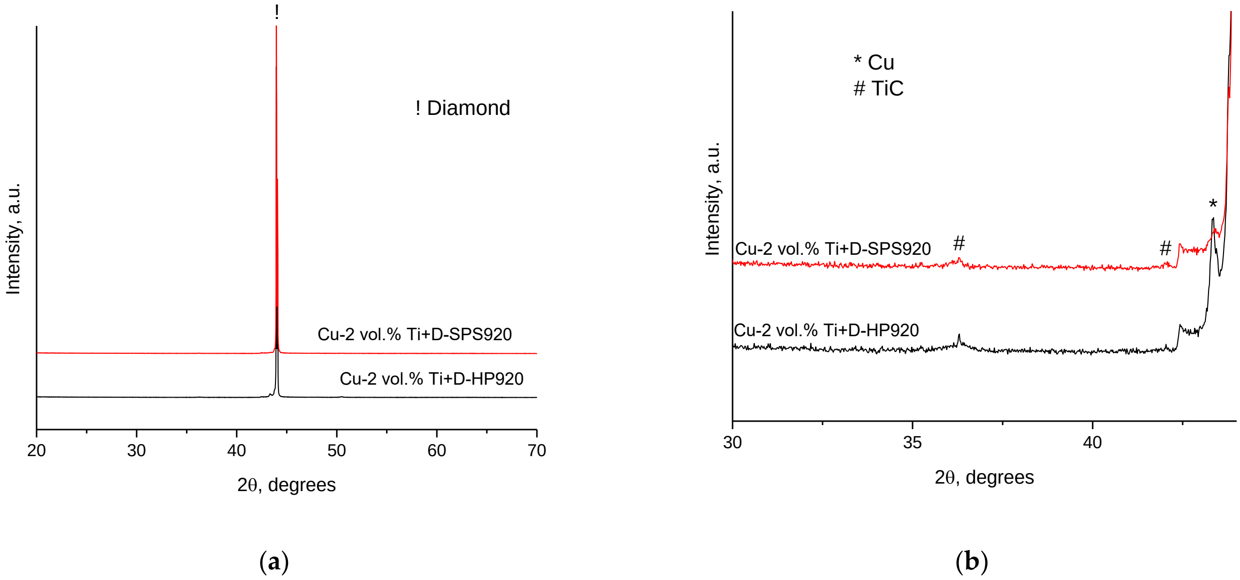


Figure 9. XRD patterns of composites with a 2 vol.% Ti-modified copper matrix, 2θ ranges from 20° to 70° (**a**) and from 30° to 44° (**b**).

Thus, when composites were sintered by SPS, the thermal conductivity of the samples first increased with increasing titanium concentration and then sharply decreased. When composites were processed by HP, there is a continuous decrease in the thermal conductivity with increasing titanium concentration (Figure 7a). The observed effect cannot be related to the features of dissolution of titanium in the copper matrix as, in both cases, the lattice parameter of copper increased with increasing titanium concentration (Table 2). It is possible that, during SPS, diffusion of titanium through the copper matrix to the diamond surface occurs faster than during HP owing to a higher real temperature of the sample (50–100° higher than the measured temperature) and local overheating/melting of the metals in the former [30]. When Ti-Cu alloys are sintered in contact with carbon materials, titanium diffuses towards the surface of the carbon particles [31,32]. The peculiarities of heating by electric current can lead to the formation of a Ti-Cu alloy with a more uniform structure and a more uniform wetting of the diamond crystals. The formation of local high-temperature regions at the inter-particle contacts, including those between particles of different metals, during SPS can cause the development of temperature gradients at the particle size scale, accelerating diffusion and alloying between the metals [33]. A direct effect of electric current on diffusion in the Cu-Ti system cannot be ruled out and requires further investigation. It is interesting to note that, when tungsten was added to modify the matrix, the thermal conductivity of the composite was higher when HP was used for consolidating the powders instead of SPS. Thus, depending on the grade of solubility of the metal in the copper matrix, different approaches may be instrumental for increasing the thermal conductivity.

4. Conclusions

Based on results of the present study, it can be concluded that a critical factor for achieving a high thermal conductivity of copper–diamond composites with a modified copper matrix is the solubility of the additive metal in copper. Since Ti has the highest solubility among the studied metals (W, Mo, Cr, Ti), Ti-containing composites possess the highest thermal conductivity. Titanium diffuses through the copper matrix to the diamond surface, which promotes better wetting of the diamond surface by the copper matrix. The composite with a titanium concentration of 0.7 vol.% obtained by the SPS has the highest thermal conductivity (420 W m^{-1} K^{-1}) in the studied series. Another important factor is the sintering method—even with the same (measured) sintering temperature and Ti concentration, the samples obtained by the SPS have higher thermal conductivity, which can be explained by the difference in the heating mechanisms and overheating of local areas of the sample due to influence of electric current passing through the sample.

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