Effect of tungsten nanoparticles on sintering of the Sn-Cu-Co-W powder material

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Abstract. The effect of tungsten nanoparticles on the kinetics of sintering of the Sn-Cu-Co-W powder material used as a binder in diamond tools was studied. The W16,5 grade tungsten powder was mechanically activated in the AGO-2U planetary centrifugal mill for 60 minutes at the carrier rotation frequencies of 800 RPM. The mixture of tungsten, tin, copper, and cobalt powders was compacted by static pressing in press dies and then sintered in vacuum at the temperature of 820°C. The morphology and sizes of powder particles, as well as the structure of the sintered samples, were studied by the methods of scanning electronic microscopy. It has been demonstrated that tungsten nanoparticles have a noticeable effect on the process of dissolution-reprecipitation of cobalt in liquid-phase sintering.

1. Introduction
Numerous studies to improve the properties of diamond and metal composite materials and diamond tools have been conducted by the present day. Enhancing the properties of the said materials further by designing chemical composition of binders has only limited opportunities to offer. So, a promising method for improvement of the properties of diamond and metal composite materials is modification of binders using nanoparticles [1-5].

The additive of tungsten micro-powder in Sn-Cu-Co metal binders is known to affect their properties in an ambivalent manner [6]. With regard to this, tungsten is a carbide-forming metal which is adhesion-active to diamond; it features the high hardness of 350-400 HB, too. However, under certain conditions, the additive of tungsten can prevent the binder from sintering, which leads to increasing porosity while also reducing hardness and strength. As for the effect of tungsten nanoparticles on sintering of Sn-Cu-Co-W alloys, this is only studied scarcely. So, the objective of this work is to investigate the effect of tungsten nanoparticles on sintering of Sn-Cu-Co-W alloys used as binders in diamond tools.

2. Materials and methods
For preparation of the samples, commercially pure powders of tin, copper, cobalt, and tungsten were used. The powder particles were equiaxial and had the following sizes: tin – 17–30 µm, copper – 45–70 µm, and cobalt – 1–2 µm. Tungsten powder having the 19–24 µm particles was ground in the AGO-2U planetary-centrifugal mill at the rotation frequency of 800 RPM for 1 hour.

Next, mixtures were prepared from the described powders, the ground tungsten powder, and the non-ground one, with the following proportion of the components, % (wt.): 20 Sn, 43 Cu, 30 Co, 7 W. The
20 g weighted powdered samples were subjected to single-action compacting in an all-steel mould at the 12 t/cm² press power. The obtained samples were sintered in vacuum at the temperature of 820°C for 20 minutes.

The structure of sintered alloys and distribution of elements within them were studied by the scanning electron microscopy and X-ray microanalysis methods using JSM-7500F (by Jeol) and EVO HD 15 (by Zeiss) digital microscopes. Microhardness \((HV_{0.01})\) of the structural constituents was measured with the DuraScan80 (by EmcoTest) hardness meter by indentation of a tetrahedral diamond pyramid under the load of 10 g. Hardness of the alloys was measured according to the Rockwell method (scale B) using the TK-2M hardness meter. The sintered samples were weighed with the Adventurer AR2140 (by OHAUS) assay balance to find out their density as the ratio of weight to volume.

3. Results and discussion

After milling, the size of tungsten particles ranged from 20 µm to 25 nm. The shape of the particles was mainly equiaxial, yet a certain quantity of the particles gained the splintery shape (figure 1a). A part of the ground powder stuck together into agglomerates having the cross dimension from 1 to 80 µm.

![Figure 1. Nanoparticles of tungsten: (a) in the ground powder, ×30000; (b) in the sintered material, ×50000.](image)

With the above proportion of its components, the Sn-Cu-Co-W powder materials are sintered with the formation of a liquid phase. Structure formation of Sn-Cu-Co-W materials containing non-ground tungsten was discussed in works [6-8]. At the sintering temperature of 820°C, the powders of tin and copper get melted, cobalt gets recrystallized via the liquid phase, and the material shrinks, too. During the subsequent cooling down, the copper and tin liquid phase containing some dissolved cobalt is crystallized.

In figure 1b, tungsten nanoparticles with the cross-section of around 100 nm can be seen, nested in the sintered Sn-Cu-Co-W material. As compared to microparticles, nanoparticles are known to have a lower melting temperature, higher chemical activity, and higher solubility in the liquid phase. Nevertheless, after sintering of Sn-Cu-Co-W materials, nanoparticles are preserved in their structure. Tungsten nanoparticles can be found both in the copper and tin phase and within the particles of cobalt. Thus, they did not get dissolved either in the liquid phase or in cobalt during sintering.

Figure 2 shows the microstructure of the sintered Sn-Cu-Co-W materials with non-ground tungsten and the ground one. The structural constituents with their respective microhardness values are given in
table 1: cobalt and tungsten particles, solid solution of tin in copper (Cu), and the Cu₃Sn intermetallic compound.

![Figure 2](image-url). The structure of the sintered Sn-Cu-Co-W material (×500) containing tungsten powder: (a) non-ground and (b) ground.

**Table 1.** Microhardness of the structural constituents of the sintered Sn-Cu-Co-W materials.

| Sintered materials | Microhardness HV₀.₀₁ of the structural constituents |
|--------------------|----------------------------------------------------|
|                    | Co                     | (Cu)                   | Cu₃Sn                  | W                     |
| With non-ground W  | 121-153                | 232-259                | 361-374                | 467-525               |
| With ground W      | 124-157                | 237-281                | 370-398                | 823-1162              |

During sintering, in the material containing non-ground tungsten, the size of cobalt particles increased from 1.6 µm up to 9-15 µm owing to dissolution of small particles of cobalt and their reprecipitation against the larger ones (figure 2 a). In the material with ground tungsten, particles of cobalt grew up to 3-10 µm (figure 2 b), which is indicative of the less pronounced dissolution-reprecipitation. The effect of finely dispersed tungsten on dissolution-reprecipitation of cobalt is explained by the following mechanism. In systems containing two solid metals and a liquid phase, the mass transfer is directed toward the metal having the largest free energy [8-9]. Apparently, high-melting nanoparticles of tungsten in the sintered Sn-Cu-Co-W material play the role of crystallization centers for cobalt. However, around the high-melting nanoparticles, nanosized grains of the solid phase are formed that are unstable in terms of energy. The tendency of the system to equilibrium entails dissolution of these grains and repeated activation of the high-melting nanoparticles. Obviously, under such conditions, the nanoparticles which are not soluble in the liquid phase prevent the mass transfer of the solid phase of the material being sintered.

In the sintered Sn-Cu-Co-W materials, there is a minor quantity of isolated closed pores. The material with non-ground tungsten has the density of 8.16 g/cm³ (porosity of 8%). Meanwhile, the material with ground tungsten has the density of 7.72 g/cm³ (porosity of 13%). Featuring the high chemical activity, finely dispersed tungsten tends to adsorb atmospheric gases and get oxidized. As the oxides are decomposed at the temperature of sintering, gases are extracted in the closed pores subsequently. The pressure of gases in the closed pores prevents them from healing, which results in higher porosity of the sintered material.
In spite of its higher porosity, the material containing nanodispersed tungsten features a higher hardness (105-107 HRB) than that with non-ground tungsten (103-104 HRB). The higher hardness of the material containing nanoparticles of tungsten is explained by dispersion hardening under the Orowan mechanism [10].

4. Conclusion
Tungsten nanoparticles featuring the high surface energy have a noticeable effect on dissolution-reprecipitation of cobalt in liquid-phase sintering of the Sn-Cu-Co-W powder material. Introduction of nanodispersed tungsten into the material slows down the growth of cobalt particles and helps obtain a fine-grained structure.

The sintered Sn-Cu-Co-W material containing nanoparticles of tungsten has the higher hardness of 105-107 HRB, which is explained by dispersion hardening under the Orowan mechanism.

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References
[1] Levashov E A, Andreev V A and Kurbatkina V V 2006 Pat. of the Russian Federation No 2286242 appl. 11.14.2005, publ. 10.27.2006
[2] Loginov P A, Sidorenko D A, Levashov E A and Andreev V A 2017 Russ. J. Non-Ferr. Met. 1 64-75
[3] Sidorenko D A, Zaitsev A A, Kirichenko A N, Levashov E A, Kurbatkina V V et al. 2013 Diamond Relat. Mater. 38 59-62
[4] Vityaz’ P A, Zhornik V I, Kovaleva S A, and Kukareko V A 2014 Russ. J. Non-Ferr. Met. 4 12–18
[5] Polushin N I, Kudinov A V, Zhuravlev V V, Stepareva N N and Maslov A L 2011 Russ. J. Non-Ferr. Met. 4 49-53
[6] Sokolov E G and Artemiev V P 2015 Russ. Russian Metallurgy 3 62-67
[7] Sokolov E G 2015 Russ. J. Non-Ferr. Met. 3, 62–67
[8] Sokolov E G, Ozolin A V and Svidstun L I 2019 JP. J. Heat Mass Transf. 16(2) 297–305
[9] Shatinskij V F, Zbozhnyaya O M and Maksimovich G G 1976 Obtaining diffusion coatings in an environment of low-melting metals (Kiev: Naukova Dumka)
[10] Kostikov V I, Agureev L E and Eremina Zh V 2014 Russ. J. Non-Ferr. Met. 1, 35–38