Obtaining of tungsten nanopowders by high energy ball milling

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Abstract. The objective of the work is identifying the modes of ball milling of the W16,5 and PWT grade tungsten that ensure obtaining nanosized powders. Milling was performed with the AGO-2U planetary-centrifugal mill for 5, 15, 60, and 120 min at the carrier rotation frequencies of 400, 800, and 1000 rpm. After milling, the shape and size of tungsten powder particles was studied by scanning electron microscopy. The effect of work hardening and aggregation on milling of the powders has been demonstrated. As a result of ball milling, nanoparticles of tungsten sized from 25 nm have been obtained. It has been found that the minimum size of particles is achieved at the carrier rotation frequency of 800 rpm and milling duration of not less than 60 min.

1. Introduction
Powdered tungsten is used as a component of metallic binders in diamond abrasive tools. In work [1] it is demonstrated that tungsten improves adhesive activity of the Sn-Cu-Co-W binder to diamond. Adding micropowder of tungsten to the Sn-Cu-Co binder helps reduce shrinkage stress and prevents cracking during sintering of shaped diamond tools [2].

An efficient method of enhancing the mechanical properties of metallic binders is the introduction of nanosized particles into their composition. Under the Orowan mechanism, the presence of distributed finely dispersed particles in the material leads to its hardening [3-7]. In liquid-phase sintering, the finely dispersed high-melting particles play the part of crystallization centers, which ensures the formation of a fine-grained structure contributing to improvement of mechanical properties of the material [8].

Nanopowders of tungsten produced by the methods of electric exploding wire, reduction or by the carbonyl method are expensive and have a short storage life due to their tendency to oxidation. For these reasons, the development of cheaper and more technological methods of obtaining tungsten nanopowders are of special interest. Tungsten is a hard and brittle metal. Annealed tungsten of high purity features hardness of 225-300 HV, ultimate tensile strength of 800-1200 MPa, and the close to zero maximum elongation [9]. These properties of tungsten allow obtaining powders by crushing the source material [10-12].

The duration of the ball milling of tungsten to obtain nanopowders can reach 30-60 hours [12]. In this regard, the reduction of milling time is of great practical interest. The tungsten refinement is obviously affected by both the state of the starting material and the ball milling mode.

The objective of this work is to identify the modes of ball milling of the W16,5 and PWT grades tungsten that ensure obtaining nanosized powders.
2. Materials and methods
Milling was performed on powders of tungsten of the W16,5 and PWT grades. The W16,5 special tungsten powder containing not less than 99.9% of W has been obtained by reducing the tungsten oxide by hydrogen (technical specifications TU 48-19-417-8). The PWT technical tungsten powder containing not less than 99.69% of W has been obtained by reducing the ammonium paratungstate (technical specifications TU 48-19-72-92). Before milling, the powders had an equiaxial shape, their sizes are shown in table 1.

The processes of obtaining nanosized tungsten powder were studied using the AGO-2U planetary-centrifugal mill (figure 1).

![Figure 1. Appearance and arrangement of the AGO-2U planetary centrifugal mill: (1) drum; (2) carrier; (3) working chambers.](image)

The mill features a planetary mechanism with two working chambers and the adjustable carrier rotation speed [13]. Under the effect of centrifugal forces, the working chambers are pressed to the guide rails of the mill drum and start revolving about their axes owing to friction contact with the guide rails. Thus, the chambers perform planetary movement being engaged in two rotation types. During this, intensive water cooling of the working chambers is provided by water supplied to the mill drum. The material was milled under the effect of the milling media by multiple repeated impact and abrasion cycles in the centrifugal field [14]. As the milling media, steel balls of the 5 mm diameter were used. The ratio of working chambers filling with the balls was 40%. Milling was conducted for 5, 15, 60, and 120 minutes at the carrier rotation frequencies of 400, 800, and 1000 rpm.

After milling, the shapes and sizes of tungsten powder particles were studied by scanning electron microscopy (SEM JEOL JSM-7500F).
3. Results and discussion

Figure 2 shows the tungsten powder particles before and after milling. Before milling, the particles have the polygonal shape with clearly traced faces. After milling for 60 minutes at the 800 rpm carrier rotation frequency, the bulk of the particles have the equiaxial shape, their surface is rough, and no edges and flat faces are observed on the particles. A small quantity of particles have the fragmented shape. As the duration of milling is increased, the quantity of fragmented particles goes down. After milling, there are only minor differences in the size of particles of the W16.5 and the PWT powders (see table 1).

![Figure 2. SEM images of tungsten powders: (a) W16.5, before milling, ×1000; (b) W16.5, after milling, ×30000; (c) PWT, before milling, ×1000; (d) PWT, after milling, ×10000.](image)

| Powders | Sizes of particles, μm |
|---------|------------------------|
|         | Before milling         | After milling        |
| W16.5   | 10 - 30                | 0.025-0.8             |
| PWT     | 1-8                    | 0.027-0.9             |

A significant part of the milled powders stuck together into loose aggregates sized 1 to 80 μm. In these aggregates, particles retain their shape and each particle can be distinguished. The formation of
aggregates is due to the increased surface energy of the milled particles. As such particles aggregate, the quantity of uncompensated interatomic bonds decreases, and so does the free energy. The formation of aggregates is undesirable. If there are aggregates, the distribution of tungsten particles in the Sn-Cu-Co-W powder material will be uneven, and, consequently, hardening of the material can be achieved only in part.

According to the adopted classification, particles sized 1 to 100 nm belong to nanoparticles [6]. It can be seen from table 2, that particles the sizes of which fall within the nano range have been obtained with the milling duration of 60-120 min. The minimum size of powders making 25 nm has been obtained at the 800 rpm carrier rotation frequency and the 60-120 min milling duration.

| Carrier rotation frequency, rpm | Duration of milling, min |
|---------------------------------|--------------------------|
|                                 | 5 | 15 | 60 | 120 |
| 400                             | 160 | 132 | 90 | 83 |
| 800                             | 137 | 116 | 25 | 25 |
| 1000                            | 128 | 85 | 90 | 102 |

The shapes and sizes of the resulting powders point to the fact that under ball milling, the following processes occur: splitting of large particles; rolling of fragments which gain a rounded shape by that; welding small particles together and the formation of aggregates. Alongside this, the material is exposed to work hardening, which hinders further milling. In work [15], measurement of microhardness of both milled and non-milled tungsten in the Sn-Cu-Co-W materials sintered at a temperature lower than the tungsten re-crystallization one. For non-milled tungsten, hardness is 467–525 HV, while it is 823–1162 HV for milled tungsten, which gives evidence about work hardening during milling.

It is seen from table 2 that raising the duration of milling from 60 to 120 min yields almost no reduction in particle sizes. Apparently, this is explained by work hardening of the particles. The increase of rotation frequency results in greater centrifugal forces and the kinetic energy of the milling media. As a result, the milling processes described above are intensified, including welding leading to larger particle sizes. Due to this, increasing the carrier rotation frequency from 800 to 1000 rpm gives no positive effect.

4. Conclusion
The research conducted has shown that for obtaining nanosized powders of the W16,5 and PWT grades tungsten, it is expedient to mill tungsten in the AGO-2U ball mill at the carrier rotation frequency of 800 rpm for at least 60 min milling duration. The said mode ensures obtaining nanoparticles sized from 25 nm. The milling process is affected by work hardening and aggregation of the powders. Further studies of tungsten milling modes have to be conducted for reducing aggregation of the powders.

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