Formation of the internal structure of copper particles during their ball milling followed by spheroidization

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Abstract. The paper presents the results of a study of the influence of high-energy effects on surface morphology and the formation of the internal structure of copper particles. It is shown that the ball milling of copper powder in a planetary mill leads to the formation of layered agglomerates consisting of many deformed ultrafine particles. It is noted that defects in the form of microcracks and micropores are observed in the volume of the agglomerated particle. Their subsequent treatment in a plasma jet leads to the formation of spherical particles. It is established that during the interaction of the molten material of a particle with distributed gas inclusions throughout the particle’s volume during plasma treatment, local copper oxidation occurs. Copper oxide inclusions of predominantly rounded shape are formed, ranging in size from tens of nanometers to 7 microns, uniformly distributed over the particle volume.

1. Introduction

Metal, composite, and ceramic powders are widely used in thermal spraying and cold spraying technologies, additive technologies, powder metallurgy, etc. The size, shape, and internal structure of the initial powder particles effect on the physical, mechanical, and chemical properties of the resulting coatings. For example, in [1] it was shown that the porosity of detonation coatings when replacing the initial sprayed particles of non-spherical alumina with spherical particles decreases by half, and when using spherical hollow particles it decreases by an order of magnitude. In this case, the deposition efficiency increases and amounts to 23, 40, and 51%, respectively. Also, the maximum microhardness of the coatings is obtained by spraying a spherical hollow powder.

A preliminary high-energy effect on the initial particles, for example, during the mechanical processing of powders in planetary ball mills, leads to a change in particle size and shape depending on the physical properties and chemical composition of the material. During ball milling, agglomerated particles are formed, characterized by a layered structure, the presence in its volume of closed microcracks and micropores; surface cleaning occurs due to the destruction of oxide films and adsorbed layers, etc. [2].

Usually, as a raw material for production of spherical powder particles during plasma treatment, a powder of non-equiaxed shape is used [3, 4]. Treatment of particles in a plasma jet is accompanied by heating of the material to high temperatures, sufficient for its melting and synthesis reactions, resulting in the possibility of obtaining spherical metal-ceramic, including hollow particles [5]. In [6], a method for producing dense spherical titanium particles of decamicon size by plasma treatment of...
agglomerated ultrafine particles having high open porosity is shown. The addition of 10 wt. %
titanium nitride nanoparticles to the initial powder leads to the formation of particles with distributed
gas inclusions throughout the volume. In this paper, we study the influence of the conditions of
mechanical processing of copper powder and its subsequent plasma spheroidization on the particle
size distribution, surface morphology, internal structure, and phase composition of the resulting
particles.

2. Experimental procedure
Copper powder PMS-1 was used in this work (figure 1 (a)). The volume distribution of particles was
determined on particle size analyzer (0.04 – 2000 μm) LS 13 320 (Beckman Coulter). Particle
morphology was determined using Evo MA15 electron microscope (Carl Zeiss). The classification of
powder particles by size was carried out on a vibration table using a set of analytical sieves. The ball
milling of the powders was carried out in Activator-2SL planetary mill, which has two cylinders with
volume of 250 ml each with inner radius of 42.5 mm, the mass of loaded balls is 160 g for each
cylinder, the acceleration of grinding bodies is 117 g, the mass of the processed material loaded is
30 g. Steel balls with diameter of 5 mm were used as grinding bodies. Material processing was carried
out in an air atmosphere.

Spheroidization of the powder was carried out using a plasma torch with an interelectrode insert
with a power of up to 50 kW. A single-sided injection of the treated powder was used immediately
before the exit section of the plasma torch nozzle. The main plasma-forming gas was a mixture of
argon and helium supplied at rate of 0.4 gs⁻¹ and 0.2 gs⁻¹, respectively. Argon with flow rate of 0.05 gs⁻¹
was used as a transporting gas for introducing the copper powder into the plasma jet from the powder
feeder. The processing was carried out with the following values of the operating parameters: the
feeder rate of 3.5 kgh⁻¹, the arc current of 200 A, the voltage of 160 V, the secondary gas flow
supplied to protect the anode (argon) of 0.15 gs⁻¹.

3. Results and discussion
During ball milling, dispersion of the initial copper particles first occurs, which leads to an increase of
their specific surface area. Then, due to the high surface activity, ultrafine particles form agglomerates
having a layered structure [7-11]. During the interaction of the grinding body with the particle, kinetic
ergy has losses on plastic deformation of the particle with the release of a large amount of heat, up
to 95% [12]. It was shown in [13] that the temperature in the contact can reach the melting
temperature of materials. An increase in the machining time leads to an increase in the temperature of
the entire system up to a temperature close to the melting temperature of the material processed.
Particles under such conditions become plastic and begin to form agglomerates; granulation is
observed by the rolling method (figure 1 (b)). Figure 2 shows the particle size distribution depending
on the time of mechanical processing of the initial powder in the form of curves that characterize the
change in the average particle size and the main range \(d_{10} - d_{90}\).

![Figure 1](image.png)

**Figure 1.** Morphology of copper particles: (a) initial and (b) ball milled for 180 s.
Figure 2. Volume size distribution of the initial and ball milled copper particles.

X-ray phase analysis of the ball milled powder showed the presence of peaks corresponding to the phase of only copper with a lattice parameter of 3.615 Å.

Particles ball milled during 180 seconds of fraction 90 – 300 µm was used as the initial powder for plasma treatment (figure 1 (b)). As a result of treatment of the copper powder in a plasma jet, spherical particles are obtained, the morphology of which is shown in figure 3. The average particle size $d_{\text{mean}} = 24$ µm, $d_{10} = 6$, and $d_{90} = 46$ µm. The obtained sizes indicate the disintegration of particles in the plasma jet during processing.

Figure 3. SEM micrographs of a general view of a spheroidized copper powder.

The initial powders consist of agglomerated particles, which are characterized by internal porosity due to the formation of a variety of randomly packed copper particles during ball milling. Their treatment in a plasma jet leads to the formation of either dense spherical particles or hollow microspheres and microspheres with distributed gas inclusions (figure 4). The realization of this or that process depends on the size of the agglomerates, their porosity, the intensity of the interphase heat exchange “agglomerated particle – plasma flow”, and the time of their stay in the plasma jet [14]. As a rule, hollow spheres cannot be obtained for metal powders. This is due to the high thermal conductivity of metals, in contrast to ceramics, since to obtain hollow spheres a large temperature gradient is required over the cross section of the treated particle. Preliminary mechanical processing of the powder allows one to obtain closed porosity, which affects the final structure of the material.
Figure 4. A cross-section of spheroidized copper particles: (a) dense microspheres; (b, c) microspheres with distributed gas inclusions; (d) hollow microsphere.

The interaction of the molten material of the particle with localized gas volumes leads to its oxidation. Figure 4 shows the distribution of finely dispersed particles of copper oxide over the volume of the treated particle with inclusions ranging from tens of nanometers to several micrometers. X-ray phase analysis of the spheroidized powder showed the presence of peaks corresponding to the phase of copper and not more than 7 at. % of copper oxide Cu₂O.

4. Conclusion
It is shown in the work that an increase in the ball milling time leads to an increase in the mass fraction of particles larger than 90 µm in the machined material and an increase in the temperature of the entire system. Heated particles become ductile, which leads to a granulation process by the rolling method. The internal structure of the ball milled particles has a layered structure with microcracks and closed micropores. Treatment of agglomerated particles in a plasma jet allows one to obtain spheroidized particles. The internal structure of spheroidized particles contains distributed gas pores along with finely dispersed inclusions of copper oxide (with a content of not more than 7 at. %) ranging in size from tens of nanometers to several micrometers formed during plasma treatment. This preliminary ball milling of the powder allows one to produce hollow metal spheres.

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