The use of ultrasound to produce metallic powder in the plasma discharge electrolyte

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Abstract. In this work, a new process of plasma-electrolyte sputtering under the action of ultrasonic vibration is proposed, which makes it possible to obtain a finely dispersed metal powder with an average particle diameter of about 100 μm. The process involves irradiation with a high-power continuous laser on a consumable metal substrate vibrating at an ultrasonic frequency. The burning of a gas discharge around the vibrating electrode causes the surface to melt and small droplets are ejected. Preliminary results of spraying stainless steel 12X18H9T with a discharge power of 800 W and an ultrasonic vibration frequency of 20 kHz are presented. Vibration displacement does not significantly affect average particle size and size distribution according to capillary wave spray theory. The microstructure of the larger atomized particles exhibits a fine dendritic structure on the surface and shrinkage porosity at the center of the particles, indicating multiple surface nucleation for solidification.

1. Introduction
With the development of technologies for the additive production of metals, there is a steady growth in demand for high-quality metal powder [1]. Additive manufacturing (AM) metal technologies are increasingly being used for rapid prototyping and serial production in various industries. The demand for metal powder is predicted to grow rapidly in the coming years due to the emergence of new applications such as additive manufacturing, also cause the established powder metallurgy (P/M) market and plasma/thermal spraying technology. Highly productive and inexpensive production of metal powder with consistent quality and properties for the desired application is a key challenge in powder production. For the production of metal powders, traditional methods of powder preparation are widely used, such as chemical, mechanical, electrolytic and spray (gas, water/oil, vacuum, centrifugal atomization and ultrasonic capillary wave atomization) [2]. Among these methods, spraying is one of the most versatile methods for producing metal powder with a wide particle distribution range and high productivity for several metal materials, including several steels, aluminum alloys, titanium alloys and superalloys.

While the average particle size and particle size distribution of the powder can be controlled by varying the spraying parameters, spraying processes require a lot of energy to supply high pressure water (water atomization) or expensive inert gases (gas atomization), resulting in very low total energy. (efficiency ~ 3-4%) [3]. The use of water spray is often limited because water reacts with highly reactive metals (titanium and superalloys) and leads to the formation of an undesirable surface
oxide layer on the powder particles [1]. In addition, conventional spraying processes that require large volumes of powder are not well suited for small batch production of special alloy powder for research and development.

Methods for the production of metal powder have also been investigated, such as centrifugal and ultrasonic spraying based on displacement of molten material / molten film, especially for low-melting materials [4]. In centrifugal atomization, a stream of molten material is distributed over a rotating surface and centrifugal forces cause the melt to be ejected in the form of droplets. On the other hand, during ultrasonic spraying, capillary waves and / or cavitation forces destroy the liquid metal film on the surface of the vibrating surface, causing the ejection of small drops [5]. The size of the sprayed particles depends on the thermophysical properties of the liquid metal and the parameters of ultrasonic vibrations. Ultrasonic atomization produces a narrower particle size distribution and spherical particles. Due to the high cooling rates, the particles obtained with these technologies also exhibit very good compositional uniformity and microstructure. In one of the earliest studies of ultrasonic sputtering of metal melts, Lierke and Griesshammer reported particle sizes of 43 \( \mu \)m and 39 \( \mu \)m for Sn and Pb melts, respectively, at an ultrasonic frequency of 20 kHz [6].

The next stage in the development of the SLM process is the creation of technologies for the production of micro and nanopowders, devoid of the above disadvantages. One of the solutions is the use of a gas discharge with liquid electrodes using ultrasonic emitters [7,8,9], this method is simple and does not require expensive equipment. Therefore, in this work, the goal was to investigate the plasma-electrolyte process of sputtering steel using ultrasonic emitters.

2. Main part
A known method of dispersing a metal anode under the influence of a discharge plasma with an electrolytic cathode. The cylindrical anode is located vertically above the surface of the electrolyte - the cathode. The formation of a metal powder begins when the discharge current reaches a certain value. This current value is linearly dependent on the anode diameter. Therefore, the main universal parameter that determines the process of metal powder formation is the current density at the anode. Based on this information, the installation was modernized, the functional diagram of which is shown in Figure 1. It consists of an electrical supply system - 1, an electrolytic bath - 2, an electrode system - 3, an oscilloscope - 4, an additional resistance - 5, a voltmeter - 6, an ammeter - 7, thermocouples - 8. Using the electrode system, the distance between the anode and the electrolyte solution was controlled. Oscilloscope 4 was used to control the shape of the applied voltage and current, and the voltage and discharge current were measured with a voltmeter and ammeter.

The steel electrode on which the discharge was initiated was subjected to vibration with a frequency of 20 kHz and an ultrasound output power of 20, 30, and 40%, which corresponds to vertical (longitudinal) vibrational displacements of 20, 40, and 50 \( \mu \)m, respectively. The interaction of the low-temperature plasma of the gas discharge with the electrode surface causes the vibrating surface to melt, which leads to the ejection of droplets in the form of small particles of metal powder. The ultrasonic vibration displacements used in this study were optimized parameters resulting in effective melt displacement at a given ultrasonic frequency (20 kHz) and 800 W discharge power.
The gas discharge combustion takes place between a metal anode made of (Russian alloy-12X18H9T) AISI 321 stainless steel and an electrolytic cathode. The anode is a metal cylinder 3 mm in diameter located above the electrolyte surface at a height of 1 to 5 mm. Aqueous solutions of NaCl and Na$_2$CO$_3$ with a concentration of 0.1 - 1% by weight were used as an electrolytic cathode.

When certain values of current and voltage are reached, the process of spraying of the metal anode is observed, most of the powder enters the electrolytic cathode and crystallizes. In parallel, the process of evaporation of the liquid electrode occurs. The resulting powder was washed with deionized water and dried in an oven. The dispersion composition was determined by the sieve sieving method with a set of sieves from 10 to 300 μm. The sieving time was on average 30 minutes.

Features of physicochemical processes of plasma-electrolyte powder production are associated with the properties of plasma. This type of discharge is similar to arc and glow discharges. It should be understood that the main difference between these types of discharges is the mechanism of electron emission from the cathode.

The main parameters of the plasma-electrolytic production of steel powder are voltage, current, discharge power spent on heat generation, physical and chemical properties of the metal anode. The power supplied to the discharge is determined by the current-voltage characteristic, on the basis of which the energy contribution can be estimated.

The anode material does not have a significant effect on the plasma itself, but only affects the sputtering process, since the melting and sputtering temperature of the electrode depends on the type of material. Powder formation is observed in a narrow range of voltages and discharge currents. Namely, at low input powers, sputtering of the metal electrode is not observed, since the generated heat is spent on the evaporation of the electrolyte and the increase in the anode temperature to 300 - 700 °C. At higher input powers, we observe complete melting of the electrode and the formation of one large drop of metal at the bottom of the electrolytic chamber.

The concentration of the electrolyte has a significant effect on the discharge burning process; it was found that the electric field strength decreases with increasing concentration. Therefore, for the stability of the results, solutions with a concentration of less than 1% were used.

While the effects of surface tension tend to hold the molten pool in place, ultrasonic vibrations of the substrate tend to destabilize the molten pool. When the volume of the melt pool reaches a critical size, ultrasonic vibrations destroy the surface film and cause the melt to be ejected in the form of small droplets. The melt droplets solidify rapidly to form solid metal powders. Metal powders are very spherical in shape. High magnification SEM photomicrographs show fine dendritic structure on the particle surface and interdendritic porosity. The particle size distribution reaches a maximum at
about 100–125 μm. The average particle size was 90 ± 30 μm, 80 ± 20 μm, and 85 ± 20 μm for vibration displacements of 20, 40 and 50 μm, respectively. In general, intense ultrasonic vibrations with higher displacements resulted in finer atomized particles, possibly due to the efficient ejection of smaller droplets from the melt volumes. In ultrasonic atomization, several mechanisms, such as cavitation wave and capillary wave, cause destruction of the liquid surface film. In the cavitation-wave mechanism, vibrations of bubbles under the surface of a liquid caused by acoustic vibrations cause droplets to be ejected. Cavitation forces can also cause uneven breakage of the liquid film, ejecting larger pieces of liquid metal. It has been reported that when acoustic cavitation is the main sputtering mechanism, there is a non-uniformity in the shape and size of the sprayed droplets. On the other hand, with a capillary wave mechanism, a liquid film on an oscillating surface becomes unstable and creates surface capillary waves (ripples). The capillary wave amplitude continuously increases, and eventually the wave peaks are detached from the liquid film and ejected as droplets.

3. Conclusions
The production of (russian alloy-12X18H9T) AISI 321 stainless steel powder from a sacrificial substrate has been successfully demonstrated using a novel ultrasonic vibration laser atomization. Sputtering is a direct result of surface melting and droplet ejection under the simultaneous action of ultrasonic vibrations and low-temperature plasma on the steel substrate. The sputtered steel particles had a highly spherical shape with an average diameter of about 80–90 μm. The average diameter and particle size distribution were not significantly affected by changes in vibrational displacements, which indicates the presence of a capillary-wave sputtering mechanism. The microstructure in the cross section of the larger solidified particles showed a relatively faceless structure near the outer surface, a fine dendritic structure in the intermediate region, and shrinkage porosity at the center of the particles, indicating rapid solidification with multiple nucleation on the surface. The proposed spraying by ultrasonic vibrations offers an attractive approach to producing metal powder of the required consumable metal substrate, especially for small batch production.

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