

## Application of the liquid anode method to obtain spherical particles in plasma spraying of gold, silver, and copper

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A method for producing spherical particles with a diameter less than  $150\mu\text{m}$  by spraying metals with high thermal conductivity (gold, silver, copper) on a liquid anode is described. The elemental composition of the obtained spherical particles is determined.

**Keywords:** liquid anode, spherical particles, discharge in liquid.

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The liquid anode method for producing spherical particles by plasma spraying of metals is of interest due to its simplicity and lower energy consumption in comparison, e.g., with the liquid cathode method [1] or the use of a pulse generator in water [2]. The fabrication of spherical particles by sputtering metal cathodes with a low thermal conductivity (titanium, iron, stainless steel) on a liquid anode was discussed in our study [3], but we failed to produce spherical particles by the liquid anode method with the use of metals with a high thermal conductivity coefficient, such as copper. This lack of success was probably attributable to the fact that the temperature of cathode heating in a discharge was insufficiently high to satisfy the conditions for effective influence of surface tension forces on the formation of spherical particles during the phase transition of molten metal into a solid. The aim of the present study is to obtain spherical particles with a diameter greater than  $10\mu\text{m}$  and less than  $150\mu\text{m}$  by spraying metals with a high thermal conductivity coefficient (copper, silver, gold) using the liquid anode method. Spherical particles of this size range find application in additive manufacturing [4]. The production of spherical gold, silver, and copper particles with the use of different methods was discussed by other research groups in [5–10], [11–15], and [16–21], respectively.

The schematic diagram of the experimental setup implementing the liquid anode method is shown in Fig. 1. Single-phase alternating voltage was rectified by an MDS100-1800V diode bridge and a K41I-7 smoothing capacitor. The cathode was a copper conductor (taken from the core of electrical copper wire), a fine silver wire, or a fine gold wire.

The liquid anode was a water-salt solution with a temperature of  $80\text{--}90^\circ\text{C}$ . Its electrical conductivity was adjusted by adding sodium chloride (table salt). The liquid anode temperature was monitored with a TL-2 thermometer. The electrical conductivity of the solution was measured with an Ekspert-002 conductometer at room temperature of the solution (approximately  $20^\circ\text{C}$ ). Upon the application of voltage, the solid metal cathode was sputtered, and the

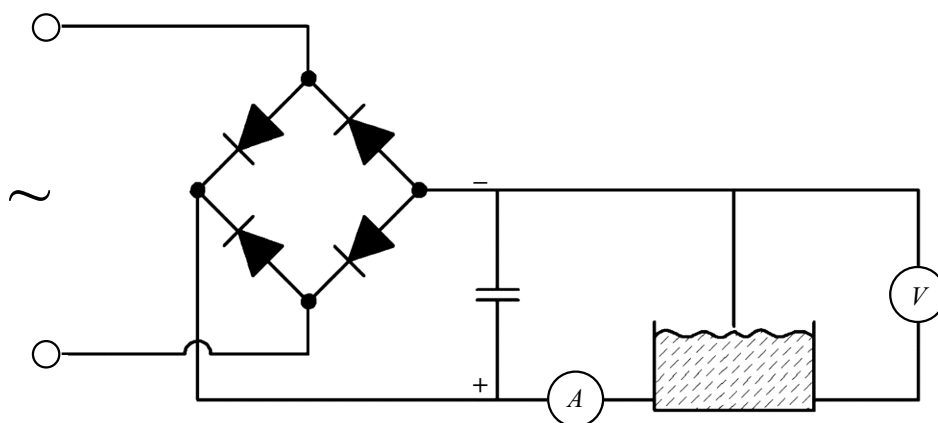
resulting spherical particles ended up in the anode solution and were deposited on the filter substrate. Following the experiment, the substrate was removed, rinsed with tap water, and dried at a temperature of approximately  $50^\circ\text{C}$ .

The electrical parameters of a discharge occurring when the cathode was brought into contact with the liquid anode were recorded with a YB4835HVA digital voltmeter-ammeter. The discharge was initiated in air by bringing the metal cathode and the liquid anode into contact. The voltage across the discharge gap was  $270\text{--}320\text{ V}$ . The current varied from 1 to 5 A depending on the area of cathode–anode contact.

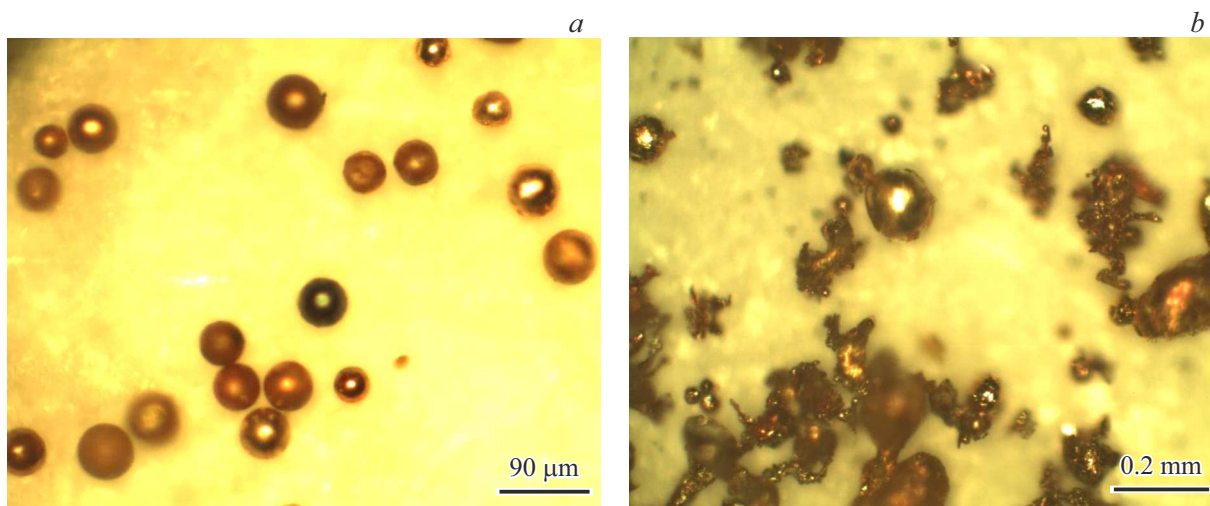
The obtained particles were photographed using an Altami MET 5 optical microscope with an Altami USB 3150R6 1/2CMOS camera. Images were processed and analyzed in Altami Studio 3.5.

Energy dispersive (elemental) analysis of the resulting spherical particles was carried out with a Tescan Vega 3 electron microscope.

Increasing the electrical conductivity of the liquid anode, we found that spherical particles of metals with a high thermal conductivity coefficient smaller than  $150\mu\text{m}$  in size may also be obtained at the same discharge voltage of  $270\text{--}320\text{ V}$  that was used to produce spherical particles of metals with a low thermal conductivity coefficient using a liquid anode with a much lower electrical conductivity [3]. The electrical conductivity of the electrolyte (a solution of tap water with table salt), which allowed us to obtain spherical particles with a diameter less than  $150\mu\text{m}$  by sputtering metals (copper, silver, gold), was measured to be  $240\text{ mS/cm}$  at room temperature. Examples of spherical particles produced from the copper cathode are shown in Fig. 2: the electrolyte conductivities are  $240\text{ mS/cm}$  (a) and less than  $31.85\text{ mS/cm}$  (b). The copper wire diameter was 2 mm in Fig. 2, a and 1 mm in Fig. 2, b. The discharge voltage was  $270\text{--}320\text{ V}$ , and the current was 1–5 A (it depended on the depth of immersion of the cathode in the liquid anode).



**Figure 1.** Schematic diagram of the setup for production of spherical particles by the liquid anode method.



**Figure 2.** Spherical (*a*) and dendritic (*b*) particles obtained in a discharge with a copper cathode at different electrical conductivities of the liquid anode solution.

**Table 1.** Elemental composition of spherical particles obtained by plasma spraying of a copper cathode (copper wire)

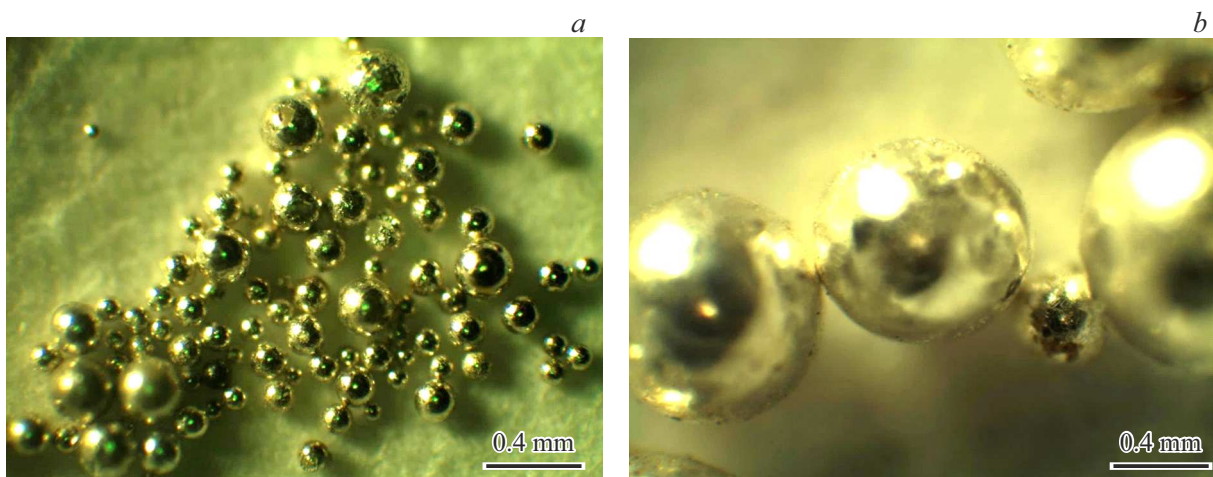
Element	Atomic concentration, %	Mass concentration, %
Cu	63.72	87.54
O	26.78	9.26
C	8.73	2.27
Fe	0.77	0.93

It should be noted that spherical particles were also obtained using copper wires of smaller diameters (0.5–1 mm) with the same conductivity of the solution (240 mS/cm) and current (1–5 A) and voltage (270–320 V) parameters. The elemental composition of spherical particles obtained by plasma spraying of the copper cathode (copper wire) is presented in Table 1.

The presence of carbon is likely attributable to the fact that transformer oil was used in the same container where a discharge with copper wire was later performed; however, it may also be attributed to other contaminants in the scanned region.

Examples of particles produced from the fine silver cathode by the liquid anode discharge method at the same discharge voltage of 270–320 V are shown in Fig. 3, *a* (for an electrolyte conductivity of 240 mS/cm) and Fig. 3, *b* (for 31.85 mS/cm). In both cases, the sprayed wire had a diameter of 0.3 mm.

It is evident that particles of different diameters are obtained at a fixed discharge voltage and different electrical conductivities of the electrolyte. With a higher electrical conductivity of the electrolyte, spherical particles normally have a smaller diameter than those obtained with the electrolyte of a lower conductivity (in this case, pellets with a typical diameter over 0.5 μm are produced). The



**Figure 3.** Spherical particles obtained with an electrolyte conductivity of 240 mS/cm (*a*) and pellets obtained with an electrolyte conductivity of 31.85 mS/cm (*b*) in a discharge with a silver cathode.

**Table 2.** Elemental composition of spherical particles obtained by plasma spraying of a silver cathode

Element	Atomic concentration, %	Mass concentration, %
Ag	95	99.23
O	5	0.77

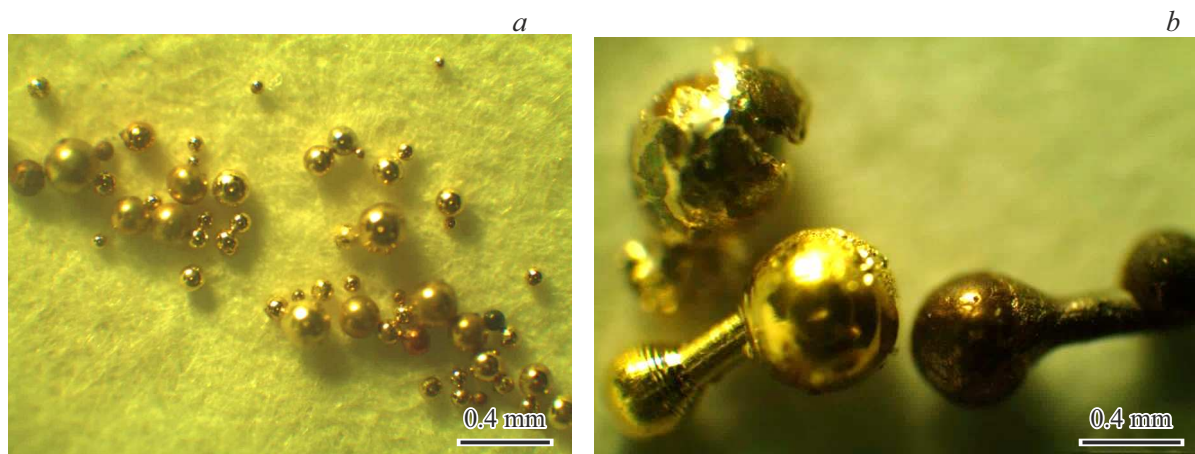
elemental composition of spherical particles obtained by plasma spraying of the silver cathode is presented in Table 2.

The results of an experiment on sputtering fine gold on the liquid anode at an electrolyte conductivity of 240 and 31.85 mS/cm are presented in Figs. 4, *a* and 4, *b*, respectively. In both cases, the sprayed wire had a diameter of 0.2 mm. The elemental composition of spherical particles is listed in Table 3.

**Table 3.** Elemental composition of spherical particles obtained by plasma spraying of a fine gold cathode

Element	Atomic concentration, %	Mass concentration, %
Au	59.90	95.04
O	19.81	2.55
C	16.69	1.61
Cl	1.27	0.36
Na	2.33	0.43

Sodium and chlorine in the composition are likely to originate from dried traces of the liquid anode solution containing table salt. As was the case with copper, the presence of carbon is probably attributable to the fact that transformer oil was used in the same container where a discharge with gold wire was later performed; however,



**Figure 4.** Spherical particles obtained with an electrolyte conductivity of 240 mS/cm (*a*) and non-spherical particles obtained with an electrolyte conductivity of 31.85 mS/cm (*b*) in a discharge with a fine gold cathode.

it may also be attributed to other contaminants in the scanned region. To eliminate such impurities, one needs to wash samples more thoroughly (e.g., in an ultrasonic bath) and use separate containers for liquid anode electrolytes of different compositions.

Increasing the electrical conductivity of the liquid anode, we managed to obtain spherical particles, which have a size range suitable for additive manufacturing, by spraying metals with a high thermal conductivity coefficient: copper, silver, and gold. Elemental analysis of the produced spherical particles was also carried out using energy-dispersive X-ray spectroscopy.

The discussed production technique is more technologically advanced than the liquid cathode method [1], since lower voltages are required to obtain spherical particles using the liquid anode method. It also differs from the methods for synthesis of spherical particles of the nanometer range (see, e.g., [5,8,10]) or 1–10  $\mu\text{m}$  in size [11,12,14] and is simpler than the method detailed in [16,21]. However, it provides a higher impurity concentration than the technique [16] of copper reduction with graphite.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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