

PULSED VACUUM ARC PLASMA DEPOSITION OF FILMS AND PARTICLES AT DIFFERENT PRESSURES AND TEMPERATURES

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The conditions of powder and film deposition at different pressures in the working chamber and the influence of substrate temperature in using of vacuum arc discharge are investigated. The experiments were carried out on a VAS-1 vacuum arc sprayer with known parameters of discharge circuit. The optimal pressure regime for deposition of thin films of nanoscale thickness was 10^{-3} mbar or below. The calculated estimation time for film deposition ratio was about 1 $\mu\text{m}/\text{min}$. In the experiment the thin layers of copper at pressure 10^{-4} mbar was observed. When a plasma was produced on a cold substrate, a continuous film was not observed. The optimal pressure for producing nanopowders was equal to 10^{-2} mbar; particle agglomeration and the formation of a fractal structure were observed at this pressure. Individual spherical particles with a size of 100–600 nm were deposited at a pressure of 10^{-3} mbar. In their composition, elements of a substrate and electrode materials were found. The recommendations for choosing optimal modes to obtain nanosize coatings by the vacuum arc method and technological conditions for obtaining nanopowders using the pulse installation for industrial application was given.

KEY WORDS: pulsed plasma, arc sprayer, vacuum, deposition, nanoparticles

1. INTRODUCTION

Pulsed plasma sources are promising devices for being used in surface engineering. They have been investigated actively in recent years, because they generate intermittent plasma streams

that have a high flow rate, high energy and particle flux density. As a result, the pulse mode allows controlling the dynamic parameters of the plasma in a wide range by varying the switching time of the discharge current. In addition, reducing the requirement for cooling current-carrying components in the pulse mode, allows achieving higher plasma parameters at a low average power consumption by the installation. Examples of successful application of the pulsed method in nanotechnology are provided by pulsed plasma accelerators (Langner et al., 2000) and by vacuum arc vapor devices (Brown, 1993). They have all the above-mentioned advantages of impulse systems, but also have such a significant drawback as droplet formation. However, in the presence of a beam separation device, they can be successfully used to produce nanomaterials (Gleiter, 2000).

There are many works devoted to the study of stationary arc sources. The first arc devices for coating technology have been investigated in Russia, as is shown in a review of Burrov and Lisenkov (2002), and in Ukraine (Aksenov and Andreev, 1999), simultaneously in the USA (Mattox, 2010) and then in other countries. A simple pulsed device for producing nanopowder by a vacuum arc method was studied by Vershok et al. (2006). Thin films were deposited at a pressure of about 10^{-4} mbar, but the plasma parameters remained unknown. There seems to be a proportional relationship between the capacitance of the anode capacitor and the mass yield of the powder, so that the use of a large capacitance of the order of 1 mF is more perceptive. Similar results were achieved on the installation with a higher anode voltage of about 2000 V (Karpov et al., 2014), however, not all installation parameters were disclosed. According to the authors, other important parameters for industrial pulse devices are the duration of the discharge and the pulse duty cycle. The charge in the pulse and, accordingly, the specific yield of the product depend on them. Typically, the duration of the current pulse in arc discharges is 0.1–100 ms that depends on the electrical parameters of the circuit, as shown in the review of Aksenov and Aksyonov (2014). But at the same time, the duration of the plasma formation itself or the pinching time can be much shorter, of the order of tens of microseconds, which leads to a limitation of the discharge current impact. Correct account for the ratio of electrical and plasma-dynamic parameters should be made when developing pulsed plasma generators, as mentioned earlier (Zhukeshov et al., 2019). The problems of improving the controllability of the arc discharge, as well as the fundamental problems related to the relationship between the plasma parameters and the characteristics of carbon nanostructures are described by Keidar et al. (2011).

Thus, for the wide use of vacuum arc sprayers in industry, it is necessary to investigate the conditions for obtaining a controlled dimension of particles and the mass yield. In the present work, the authors set the task to study the effect of pressure in the working chamber and substrate temperature on the conditions of plasma condensation, as well as to determine the sizes of nanopowder and films for the VAS-1 device with known parameters of the discharge circuit.

2. METHODS

Pulse plasma sputtering and deposition was carried out on the VAS-1 installation, created by Zhukeshov et al. (2016) and shown in Fig. 1. The main parts of this device are electrodes mounted in the vacuum chamber, DC power supply with energy store unit (capacitor battery), and pulse ignition units. The electrode system of VAS-1 consists of the removable cathode 1

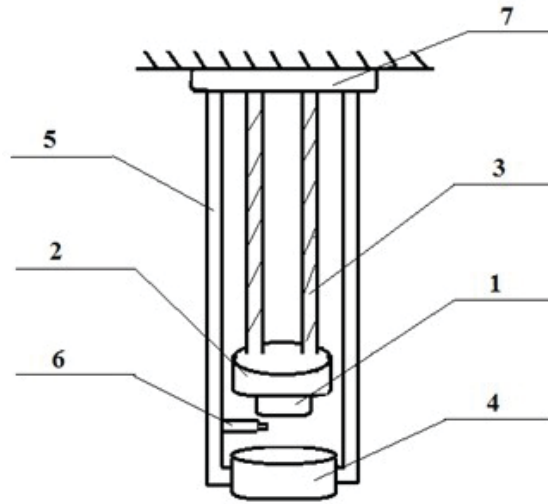


FIG. 1: The electrodes of pulse vacuum arc accelerator VAS-1

of diameter $D = 50$ mm, which is mounted on cathode holder 2 of cylinder shape, connected to cooling system 3. On the cathode axis, there is an orifice anode ring 4 with $D = 125$ mm, which is connected to the power supply interface 7 through a copper conductor placed inside ceramic insulation 5. The other conductor is connected to the vacuum arc ignition electrode 6. The ignition electrode is fixed at a distance of 50 mm from the cathode surface. The plasma, formed at the anode outlet, is deposited onto the substrate on the holder placed below the anode ring.

The power supply source of VAS-1 consists of the capacitor battery with the capacity of 600 μF , 5000 V, DC source for 500 V, 10 A, and a pulse generator with the passing frequency of 5–50 Hz. Ignition of the arc discharge is provided by the impulse supply with an amplitude of ~ 10 kV to the igniter electrode with energy of 5–6 J.

The measurements of average pulse current of this device were carried out earlier (Zhukeshov et al., 2020). For the average mass transfer for copper cathode $100 \mu\text{g}/\text{Q}$, determined by Kimblin (1973), and current value of 0.15 A, at a frequency of 5 Hz, we obtain mass yield for copper of 0.015 mg/s. So, for the deposition of thin copper layer with thickness of 40 μm the estimated time was about 40 min.

3. RESULTS AND DISCUSSION: INFLUENCE OF WORKING PRESSURE

At first, the temperature of substrates at any vacuum increases up to about 80–100°C. The aim of the study was to find out what should be the gas pressure in the working chamber to produce metal powders or formation of continuous films. In the VAS-1 device the pulse frequency was 5 Hz, the voltage of the anode was 470 V. A copper sample was used as the cathode. Three pressures, $\sim 10^{-2}$, 10^{-3} , and 10^{-4} mbar, differing by the order of magnitude, were selected for comparison. Substrates of ordinary steel of the same size were placed on a uncooled holder and processed for 30–40 min. According to SEM images, the deposition

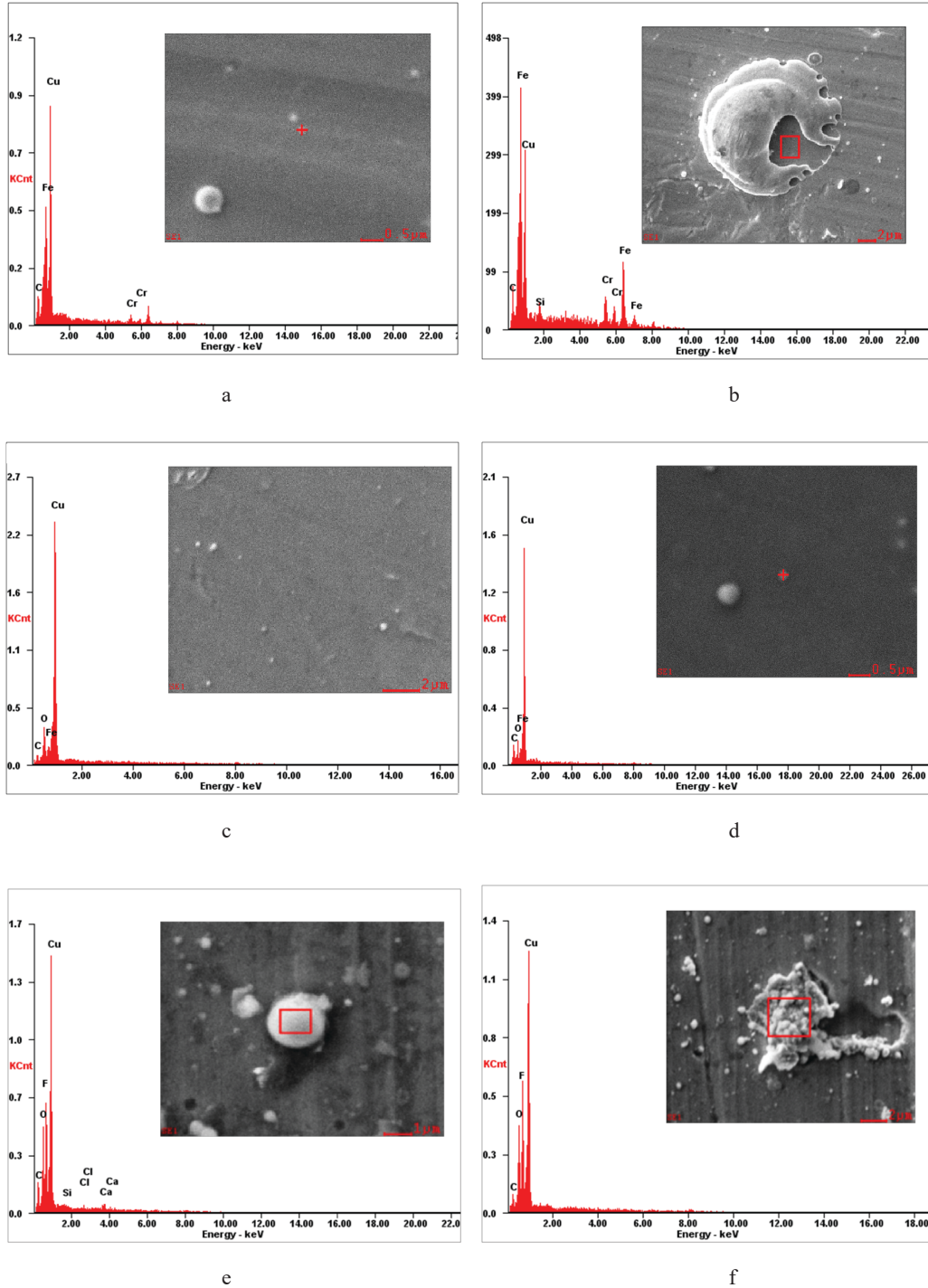


FIG. 2: The surface and RSA data of substrates processed at: a, b) 10^{-4} mbar; c, d) 10^{-3} mbar; e, f) 10^{-2} mbar

products, depending on the gas pressure in the vacuum chamber, were thin films, agglomerates of dust-like formations, and spherical particles. Figure 2a,b shows the surfaces of substrates, which were processed at a pressure in a vacuum chamber of 10^{-4} mbar, and next to it shows the RSA spectra of the surface composition. According to the RSA, at this pressure, solid, very thin films with a copper content of 12–25 at.% were deposited on the substrate surface. There are also copper nanoparticles with dimensions of 100–500 nm, which contain up to 29.5% copper. Obviously, the presence of iron and chromium is due to the emission of secondary electrons from the steel matrix, and the presence of a large amount of carbon indicates the ingress of oil from the vacuum system. No magnetic system was used to separate the droplets from the stream, so some 100 at.% copper droplets were observed (b). At a pressure of 10^{-3} mbar, the formation of a thicker copper film with a copper content of 26–49 at.% was detected, as well as the formation of spherical particles of the order of 100 nm containing up to 41 at.% of copper according to the RSA. The sizes of spherical particles were 100–600 nm (Fig. 2c,d).

At a pressure of 10^{-2} mbar (Fig. 2e) the thinner copper film did not change with the amount of copper of 30–37 at.%, but the color became greenish, which indicates the oxidation of the copper film with oxygen, the presence of which was observed up to 27% according to the RSA. At low pressure, agglomerates of small spherical formations consisting of 30–42 at.% copper were observed. Figure 2f shows the characteristic surface areas of the steel substrate with conglomeration of particles and globular formations at a pressure of 10^{-2} mbar in the device chamber. Table 1 contains data on the composition of the film on the surface of the above samples. The absence of chromium and iron at a ratio of 10^{-3} mbar and below can be explained by the fact that the thickness of the copper film layer becomes greater than the depth of the secondary electrons exiting from the steel surface, usually ~ 10 nm. This fact, due to the pressure of gas in the vacuum chamber, plays an important role in the deposition process.

In this way, it is possible to indirectly estimate the thickness of the copper film on the surface. Another question to be answered is the presence of large amounts of iron, carbon, and oxygen in nanoparticles, formed at a pressure of 10^{-3} mbar and below. Data on the composition of spherical particles deposited at a low pressure of 10^{-4} – 10^{-3} mbar, as well as particles of both types deposited at 10^{-2} mbar, are given in Table 2. The presence of

TABLE 1: Composition of the films deposited at different pressures, at.%

Element, at. %	10^{-4} mbar	10^{-3} mbar	10^{-2} mbar
Cu	24.82	49.24	37.89
Fe	44.69	9.30	34.78
Cr	10.53	—	—
C	18.75	22.30	—
O	—	19.16	27.33

TABLE 2: Composition of the particles deposited at different pressures, at.%

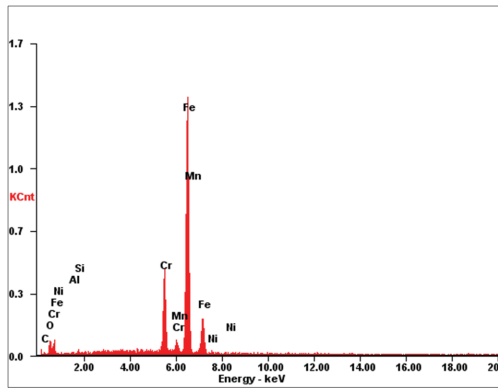
Element, at.%	10^{-4} mbar	10^{-3} mbar	10^{-2} mbar	
			spherical	agglomerate
Cu	29.03	37.13	42.31	29.79
Fe	31.61	7.52	18.39	26.34
Cr	6.59	—	—	—
C	32.77	39.43	22.83	21.62
O	—	15.92	16.48	22.25

iron on all samples confirms the fact that the plasma exposure occurs in partial sputtering of the substrate surface. The presence of oxygen and carbon is due to the ingress of gases from the vacuum system. The presence of iron on all materials can also be due to the atomization of the anode, which is also made of steel.

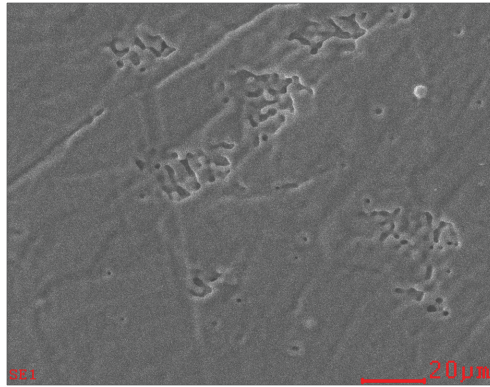
With regard to the question of the mass composition of nanoparticles, it can be concluded that in RSA spectra the copper mass content is greater, and in films, the atomic content of elements is greater than the mass one. This state indicates that these particles contain mainly heavy copper and a small amount of iron, carbon, and oxygen, i.e., they are composites. Therefore, we can talk about the formation of copper composites, although we did not do it deliberately. Obviously, by mixing reaction gases and using other electrodes, we can form composites of the desired composition.

4. INFLUENCE OF SUBSTRATE TEMPERATURE

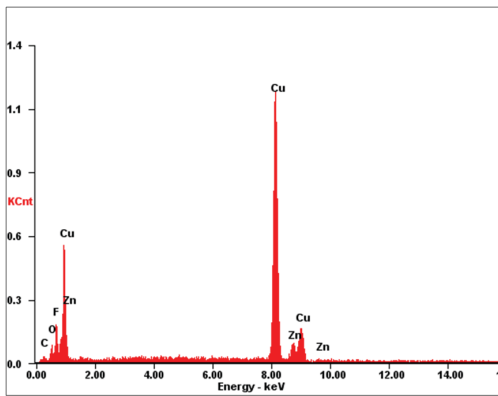
In this experiment, deposition of copper cathode sputtering products was carried out on stainless steel substrate, cooled by running water. So, the temperature at this condition was about 10°C . The pressure in the vacuum chamber was 10^{-2} mbar. The aim of the experiment was to realize the condition for condensation of nanoparticles from dust plasma in contact with a cold substrate. Figure 3 shows the surface morphology of the substrates and the surface RSA spectra. In the image, sample No. 1 is the surface of the original stainless steel substrate. Sample No. 2 is the surface with a deposited copper coating. Sample No. 3 is the copper powder, removed from the surface. From the analysis of the morphology of the substrates, it may be concluded that when using a cold substrate, intense condensation of the plasma in the form of a powder on the surface occurs. The sizes of large particles reach $10\text{ }\mu\text{m}$ and more, but the minimum sizes of particles cannot be determined. The structure of the powder in the form of fractals is the result of the process of agglomeration of individual spherical nanoparticles into larger ones and further formation of a loose thick film. According to the RSA, the composition of agglomerates consists mainly of 80% copper, and includes up to 19% carbon and up to 1.5% oxygen. Secondary zinc electrons can explain the presence of zinc on sample No. 2 from the gal-



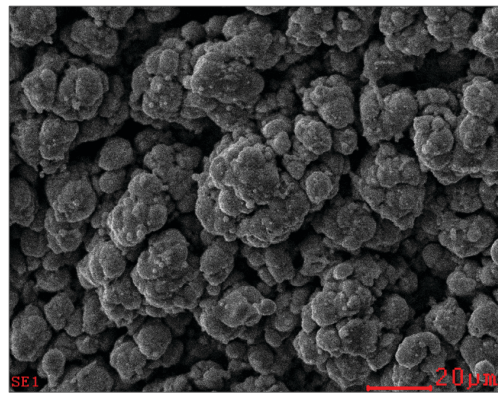
a



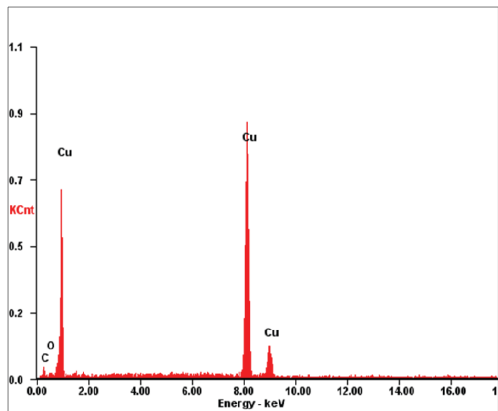
b



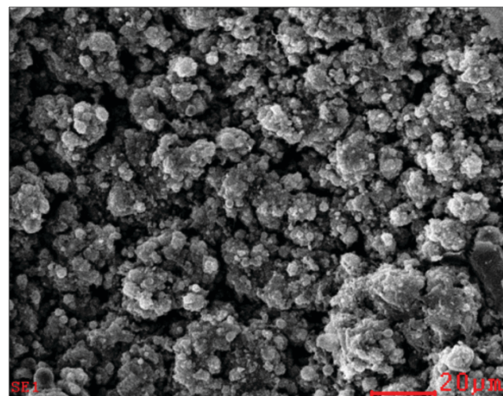
c



d



e



f

FIG. 3: The surface image and RSA data of initial substrate (#1), powders deposited on cool substrate at 10^{-2} mbar (#2), and free powder (#3)

vanized cooler of substrate. At the same time, the pure powder on sample No. 3 does not contain zinc.

5. CONCLUSIONS

Thus, when the pressure variation in the working chamber of the order 10^{-2} – 10^{-3} mbar, is the formation of individual particles of copper powder with dimensions of 0.1 to 1 μm , and with the use of additional cooling, they agglomerate into a powder with a structure size of more than 10 μm . It is obvious that there is an optimal pressure in the vacuum chamber, when the sprayed material is deposited mainly in the form of individual particles of a spherical shape. At a higher pressure, individual particles are formed into agglomerates, and at a lower pressure, solid thin films are obtained.

The optimal pressure regime for deposition of ultrafine films of nanoscale thickness is a pressure below 10^{-4} mbar. The calculated estimation time was 1 $\mu\text{m}/\text{min}$, but the experimental deposition rate value was more than 1 nm/min. Thus, the calculations was applicable only to estimation of higher level of deposition rate and at below pressure.

On the other hand, when deposited on a cold substrate, it is possible to get rid of a continuous film. The optimal pressure for obtaining nanopowder is 10^{-2} mbar, since at this pressure, particle agglomeration occurs. This result is confirmed in similar works of other authors (Keldar et al., 2011; Kimblin, 1973), where agglomeration usually occurred during deposition on an oil tank. This indicates that the substrate should be placed away from the anode, so that condensation of particles in the gas environment occurs before reaching the substrate.

These results can be used to choose for optimal modes in the development of technology for obtaining nanosize coatings by the vacuum arc method and to develop recommendations for industrial application of the pulse installation for obtaining nanopowders. So, to obtain thin films, provided that there is no drop formation, it is necessary to do a deep vacuum cleaning. The absence of erosion of the anode and other elements of the vacuum chamber is another necessary condition for obtaining clean films. To do this, it is necessary to arrange the anode so that it does not get a large electronic current or carry it into the plane of the cathode. To obtain a pure nanopowder, it is necessary to exclude particle agglomeration, for example, using mechanical mixing systems. To increase the mass yield, it is necessary to increase the anode current so that there is no significant heating of the cathode and an increase in droplets.

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