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A GALVANIC-CHEMICAL METHOD FOR PREPARING DIAMOND CONTAINING COATINGS

by

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1 Introduction

The formation of a composite coating layer containing diamond on the surface of materials is a method to prepare surfaces with higher hardness and wearability. Methods of producing abrasive surfaces, grinding belts and other metal-based tools by introducing diamond into a metal surface through a gas stream or plasma are known [1-5]. When using a gas-thermal or plasma-chemical methods to produce diamond-containing composite coatings, pre-clad powders of synthetic or natural diamond are used [5-7]. Metallisation of diamonds grains induces a significant improvement of their performance when in the coating layer, especially at elevated processing conditions. Micro-cracks present in diamond grains are filled and the grains are encased in a metal shell, such coatings increase the strength of diamond powder, which leads to enhanced productivity of the tools [8,9].

An alternative method to prepare composite coatings containing diamonds is electroplating. In such process the non-metallic phase (diamond), in the form of dispersed particles, is distributed in an electrolyte solution, and, when it reaches the surface of the cathode, it undergoes metalisation. In this way, diamonds containing copper, nickel and chrome have been produced [10-13]. The disadvantages of the electrochemical process for producing composite coatings include the need for intensive mixing of the electrolyte, which complicates the design of the plating bath; difficulty in obtaining coatings with high content of non-metallic phase and the need for filtration of the electrolyte.

One of the important properties of diamond is its high biocompatibility compared to the other substances. This has led to the use of different kinds of natural and synthetic diamond in medicine [14-16]. For these purposes, diamond-like coating (DLC), obtained by high-temperature decomposition of hydrocarbons, have found widespread use. These carbon-based materials are not pure diamond, but they have the structure and physicochemical properties similar to them [17-18]. Surfaces of prosthetic devices and implants having a

diamond or diamond-like coatings are chemically inert, non-toxic for cells and do not cause inflammation or pathogenic processes [19].

In this work, we present an inventive method to introduce diamonds in a composite coating, based on the preliminary fixing of the diamonds on the surface of the product and a subsequent overgrowth by metal, adapting previous approaches based on the generation of a sorption layer of copper sulphate on the surface of metallic or non-metallic products, subsequently this layer is treated with gaseous phosphine resulting in the formation of a metal-like copper phosphide layer on the product surface [20,22].

2 Materials and methods

2.1 Chemicals and substrates

To study the process of obtaining diamond-containing composite coatings flat copper samples with a width of 2 cm, length of 6 cm and a thickness of 0.5 cm were used; when immersed in the respective solutions the working height was of 5 cm.

Synthetic diamond powder ACM grade 5 (Russia), which is produced by sympathetic detonation were used as the non-metallic phase of the composite coating; the composition of the diamond crystals is presented in Table 1. From Figure 1 it is clear that this powder comprises prismatic particles with an average size of 0.5-1.0 μm. Table 1 shows the results of spectral analysis of diamond crystals, which exhibit a relatively high purity diamond powder.

2.2 Diamond containing coating formation

The process of obtaining composite coatings is schematised in Figure 2 and consisted of the following consecutive steps:

- preconditioning of samples;

- creation of a surface layer of copper sulfate solution;

- deposition of diamond powder onto the sample surface;

- consolidation of diamond particles;

- application of a layer of a metal.

For the preconditioning of the samples degreasing and etching operations were performed as in other electroplating methods [20]. A surface layer of $CuSO_4$ solution was achieved through dipping the samples for 3-5 sec in a $CuSO_4$ solution (200 g/l) followed by shaking to remove liquid excess.

Spraying of diamond powder onto the surface sample was conducted with the device shown in Figure 3.. To prevent any premature drying of the surface film of $CuSO_4$ solution, the spraying time did not exceed 20-30 seconds. The mass of the diamond powder sprayed was 1.6-1.9 mg/cm^2.

In order to fix the particles of diamond powder onto the sample surface was treated by phosphine-containing gas by the technique described in our previous work [22]. This briefly requires the placing of the sample in a hermetically sealed chamber that is filled with phosphine-containing gas produced by acid decomposition of zinc phosphide

$$Zn_3P_2 + 6HCl \rightarrow 3ZnCl_2 + 2PH_3 \uparrow \tag{1}$$
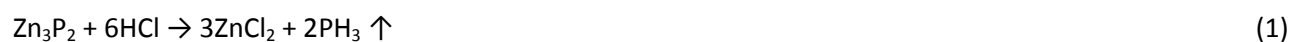
During this step, gaseous phosphine (at room temperature) reacts with copper sulphate in the liquid phase generating copper phosphide according to the following reaction:

$$6\ CuSO_4 + 3PH_3 + 3H_2O \rightarrow 2\ Cu_3P + 6H_2SO_4 + H_3PO_3 \tag{2}$$
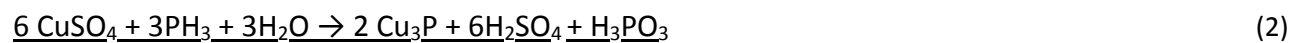
usually, the process required 7-10 minutes and the remaining unreacted phosphine-containing gas was neutralized by blowing through a solution of potassium dichromate.

The final copper plating was carried out using a solution of $CuSO_4 \cdot 5H_2O$ g/l and H_2SO_4 g/l as electrolyte: the current density was 100 A/m^2 and temperature of 20 °C.

2.3 Kinetics of conversion of copper phosphate with phosphine and copper phosphine film thickness determination

The reaction rate of transformation of copper sulfate into copper phosphide was determined using the apparatus schematically shown in Figure 4. Its working principle is that the reduction of the water level in the surge vessel 7, over a certain period of time, is linked to the amount of phosphine consumed; this is also dependent on the amount of copper phosphide formed in reaction 2. According to this reaction, the formation of 1 g of copper phosphide requires 150 cm^3 (in normal conditions) of phosphine.

The average thickness of the copper-phosphine coating was calculated as:

$$\delta = \frac{m}{S \cdot \rho}$$ (3)

where:

δ coating thickness

m mass precipitated copper phosphide

S sample surface

ρ copper phosphide density (7.0 g/cm^3)

2.4 Coated materials hardness characterisation

Hardness measurements were performed using a coating hardness-2 Temp on samples of 50 mm thick lapped to a flat steel plate 500x500x10 mm by grease "litol." The hardness values were calculated as the mean of 5 measurements.

To investigate the composite of the coatings scanning electron microscope ISM-6490-LV (JEOL, Japan) was performed. This device allows to obtain electronic images of the surface at the same time as elemental composition of both overall and individual spectra.

3   Results and discussion

The deposited diamond particles were fixed on the surface layer of copper sulfate solution through the transformation of copper sulfate into the solid phosphide using phosphine gas. The concentration of $CuSO_4$ g/l is optimal since it allows the introduction on the surface of the product of a sufficient amount of copper phosphide, moreover, it does not result in the formation of crystals of copper sulphate leading to inhomogeneity of the coating [20-22]. Calculations showed that the film thickness of the solution remaining on the surface of the sample was 50-70 µm.

The kinetic of the conversion process, measured through the volume of adsorbed phosphine, is presented in Figure 5 and it is evident that the process ended after 2-3 minutes; therefore, allowing to carry out such conversion process without shedding diamond particles due to drying of the aqueous solution in the chamber during the course of the transformation reaction. Furthermore, these data show that the introduction of the diamond particles did not substantially affect the absorption rate of phosphine (Figure 5). Consequently, the deposition of diamond particles did not create additional diffusional difficulties for the chemical process. Additionally the thickness of the copper phosphide was estimated to be about 4 µm from the amount of phosphine used (Equ. 3).

Example of SEM image of a sample having a surface coated with a layer of diamond particles cemented in copper phosphide is shown in Figure 6. It reveals that the diamond particles were relatively uniformly distributed over the surface of the sample. However, some particles were not fully immersed in the copper solution, for these, only the surface closer to the metal surface was immersed, hence on their surface copper phosphide was absent. Some of these partially-hardened particles were weakly bound to the metal substrate, so they could be removed by shaking. Typically, the amount of such particles was 5-7% of the total deposited diamond particles; these particles could be re-used for spraying.

For the production of coatings with improved physical and mechanical properties it is necessary to achieve absence of gaps, cracks, etc. between the dispersed particles and the metal of the matrix. In our process, the dispersed diamond particles were already deposited on the surface of the product and cemented there by a layer of copper phosphide. Also, the surface of most of diamond particles was coated with an electrically conductive film of phosphide. Therefore, a gap between metallic matrix and the diamond particles should not be present. The small number of particles, which were not covered by layer of copper phosphide (as discussed above) would also be embedded in metal [13].

We studied the effect of the galvanically deposited copper film onto the diamond particles at different thickness. When the coating was applied at a thickness of 1 μm (Figure 7) the surface layers of the diamond practically did not change, the presence of coating due to deposition of copper is imperceptible. Consequently, the copper deposition started from the layers closer to the surface of the initial (untreated) sample; this happens because the specific electrical conductivity of copper phosphide is 20 % IACS (International Annealed Copper Standard) [20]. Moreover, the cross-section of these layers is greater than thin layers of copper phosphide, which covered with diamond particles. The electrical conductivity of the layers closer to the surface of the initial (untreated) sample is higher than the electrical conductivity of the thin copper phosphide covering diamond particles. Hence, in accordance with Ohm law the current distribution in the lower layers is substantially higher than in the upper layers.

A noticeable leveling of coating surface occurred when applying of a layer of copper in an amount resulting in a coating in thickness of 4 μm (Figure 8). In this case, the surface was composed mainly of copper has shown by the spectra. The majority of the diamond particles were covered by the copper coating. The presence of phosphorus in the spectra indicated that, due to the small thickness of the coating, on some parts the scanning spot partially intercepted the signals of the lower layer of copper phosphide. Besides, it is more likely that copper phosphide was covering the particles and not the copper phosphide located directly on the surface of sample. A further application of copper was impractical because it led to a decrease in content of the diamond in the final composite coating.

We obtained a copper-diamond coating of overall thickness equal to 10 μm in which the content of the diamond was 27% (w/w) or 47% (v/v); this is significantly higher amount of diamonds in coating compared to existing methods where diamond content in the coating does not exceed 1-2% [13]. Another virtue of the process presented here is that, unlike gas-thermal and gas-flame techniques, it does not require high temperatures (on the order 700-1000 °C) and special expensive equipment.

The hardness testing of samples showed that the diamond-containing composite coating increased the hardness of the sample of 52 units HB (Figure 9). It should be noted that the copper phosphide also positively influenced the hardness of the coating, but this effect was not significant, whilst the copper layer did not have any effect on the surface roughness. Such results were expected in virtue of the well known hardness of the individual components of the composite.

It should be noted that obtaining a diamond containing coatings with matrix of other metals (such as nickel, chromium, iron) does not principally differ from the given technology. For example, the catalytic properties of copper phosphide also allow the use of metal electroless nickel plating process to build the matrix.

4   Conclusions

We proposed a novel method of embedding diamond particles in a composite coating, at first diamond particles are fixed on the surface of the metal substrate, and then these particles are coated with a metal matrix.

In the first part of the process on the substrate surface a sorption layer of copper sulfate solution is created by dipping the sample in a corresponding solution. Then diamond powder is sprayed onto this surface layer; the quantity of retained powder depends only on its wettability. In this case, a flat surface of 1 cm^2 sample hold 1.6-1.9 mg diamond powder. Then, a low temperature gas-phase reaction between the phosphine and copper sulfate leads to the formation of metal-like copper phosphide in the spaces between the individual diamond particles. In this case the diamond particles are completely or partially submerged in solid phosphide. . Pre-consolidation of the diamond particles on the surface allows the electrodeposition of the matrix in conventional electroplating baths.Electrodeposition of a metal matrix follows; electroplating proceeds easier on the surface layers, where the layer of phosphide provides higher conductivity. In the outer layers, diamond particles that do not exhibit the phosphide coating are covered mechanically. The resulting composite coating has a thickness of about 10 microns, and it has high hardness. Repeating of the above operations can produce coatings with thickness of several tens of microns.

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Table 1. Element analysis of diamond powder ACM brand 5

Element	Content, %(weight)
C	99.6
Si	0.25
Ca	0.20
Fe	0.04

5 Figures caption

Figure 1. SEM of diamond powder ACM brand 5

Figure 2. Scheme of diamond-containing composite coatings formation.

Figure 3. Scheme of the apparatus for applying diamond powder on the sample surface. 1 - vessel with a conical bottom, 2 - cover of the vessel, 3 – sample, 4 - diamond powder, 5 - compressor, 6 - venting

Figure 4. Apparatus for determining the length of the conversion process of copper sulfate into the phosphide. 1 - reaction vessel; 2 - a cover of the vessel; 3 - sample; 4 - sealed sample chamber; 5 - cork; 6 - Vessel with phosphine gas; 7 - surge vessel; 8 - tap; 9 - stem to open tube; 10 - dimensional surge vessel.

Figure 5. Phosphine absorption rate during the flow conversion reaction of copper sulfate into phosphide. Circles for coated diamond powder and squares for samples not coated with diamond powder. Open symbols for 200 g/l solution of copper sulfate and filled symbols for 100 g/l solution of copper sulfate.

Figure 6. SEM of sample surface after applying of diamond powder and fixing (cementing) by copper phosphide.

Figure 7. SEM of sample surface after applying a layer of copper, which provides on a smooth surface coating in thickness of 1 μm.

Figure 8. SEM of sample surface after applying a layer of copper, which provides on a smooth surface a coating in thickness of 4 μm. (On the right the results of spectral analysis)

Figure 9. Influence of coating composition on Brinell hardness of samples.

☐ copper base uncoated

▨ copper phosphide (10 μm)

▨ copper phosphide (4 μm) + copper (6 μm)

■ copper phosphide + diamond + copper (total 10 μm)

Figure 1

Initial copper sample

Layer of CuSO$_4$ solution

Diamond particles deposited on the film of aqueous CuSO$_4$

Layer of copper phosphide obtained transforming CuSO$_4$
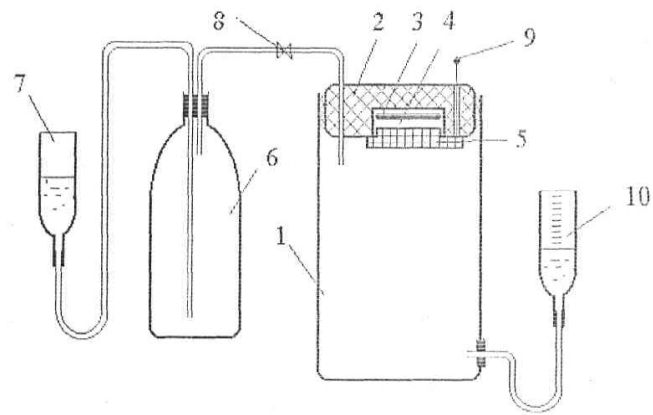
Metal matrix completely covering the diamond particles
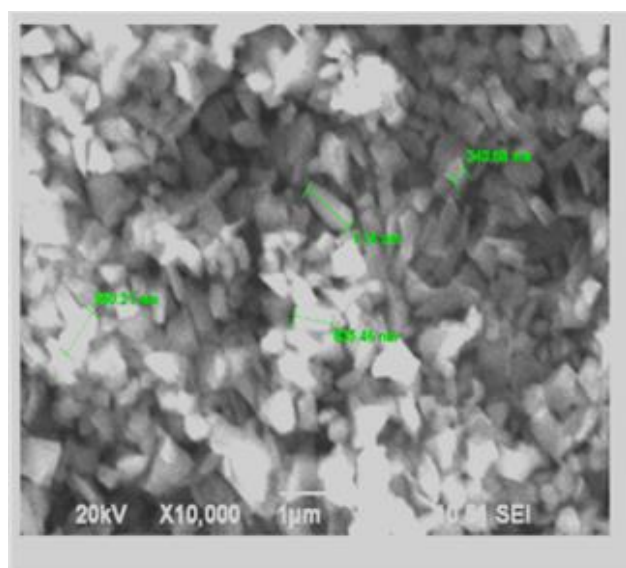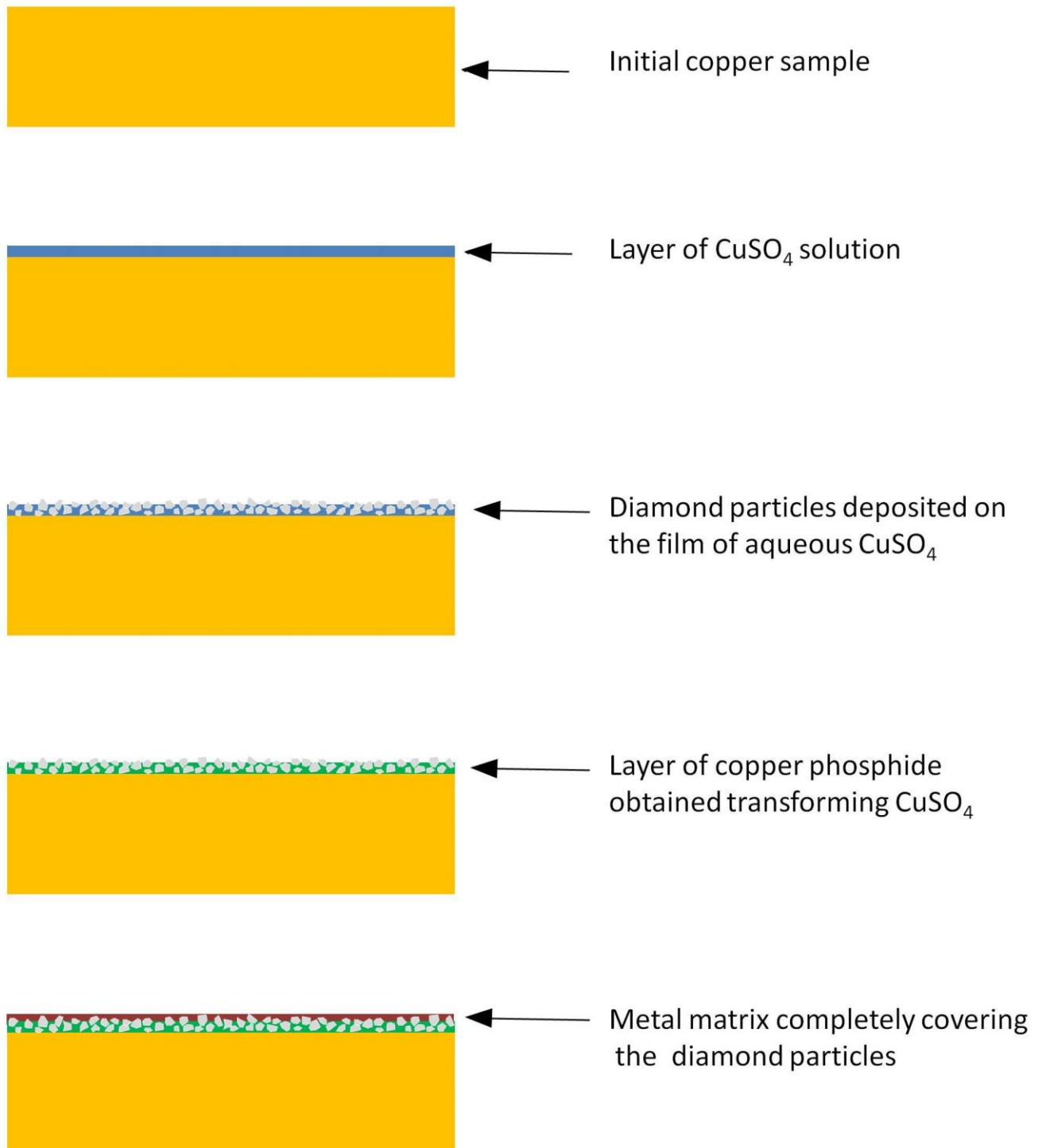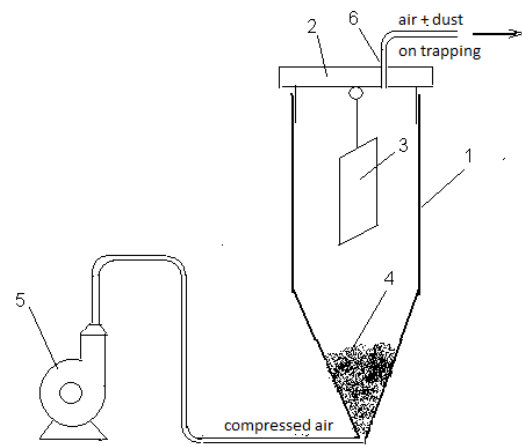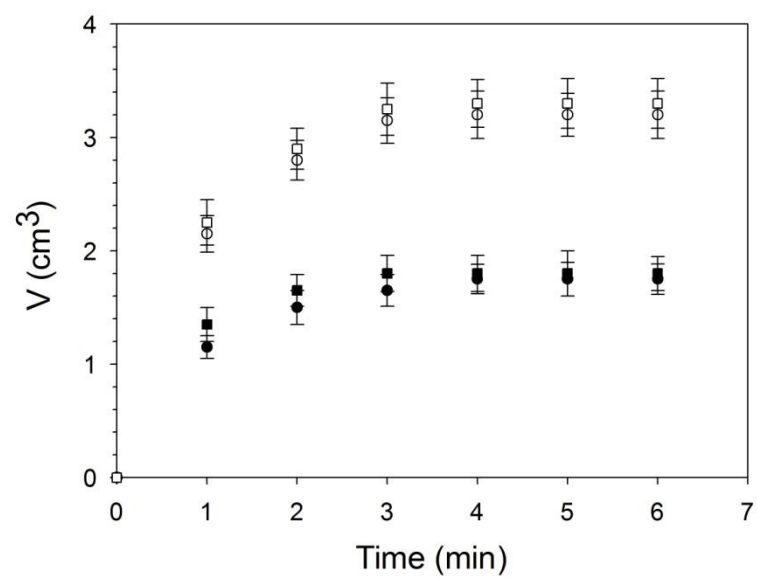
Figure 2

Figure 3

Figure 4

Figure 5
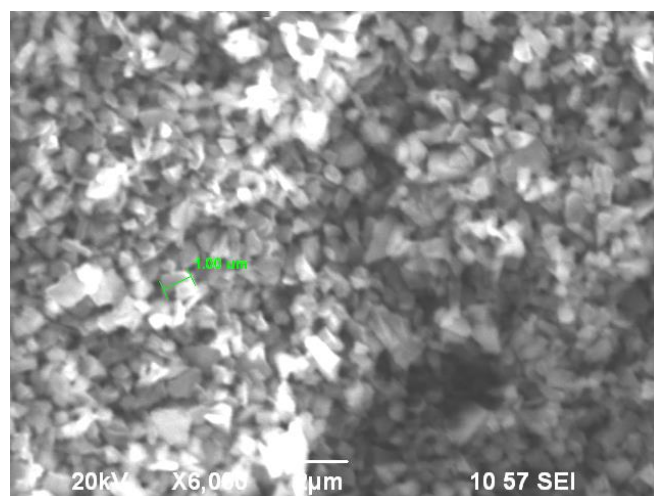
Figure 6
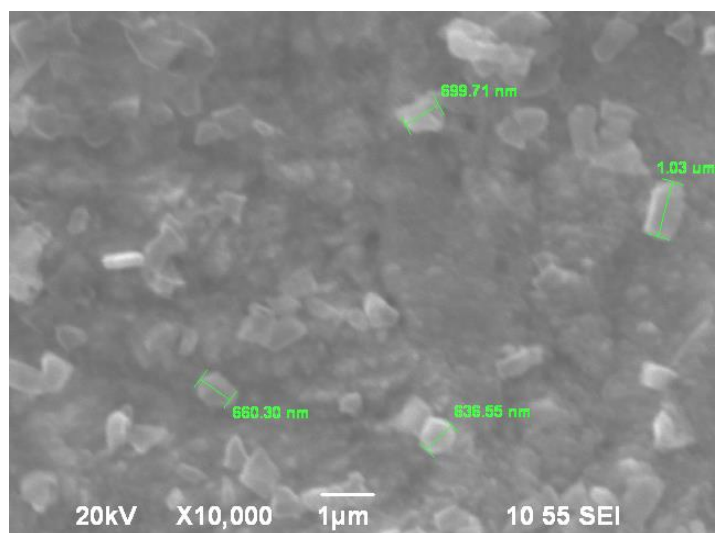
Figure 7
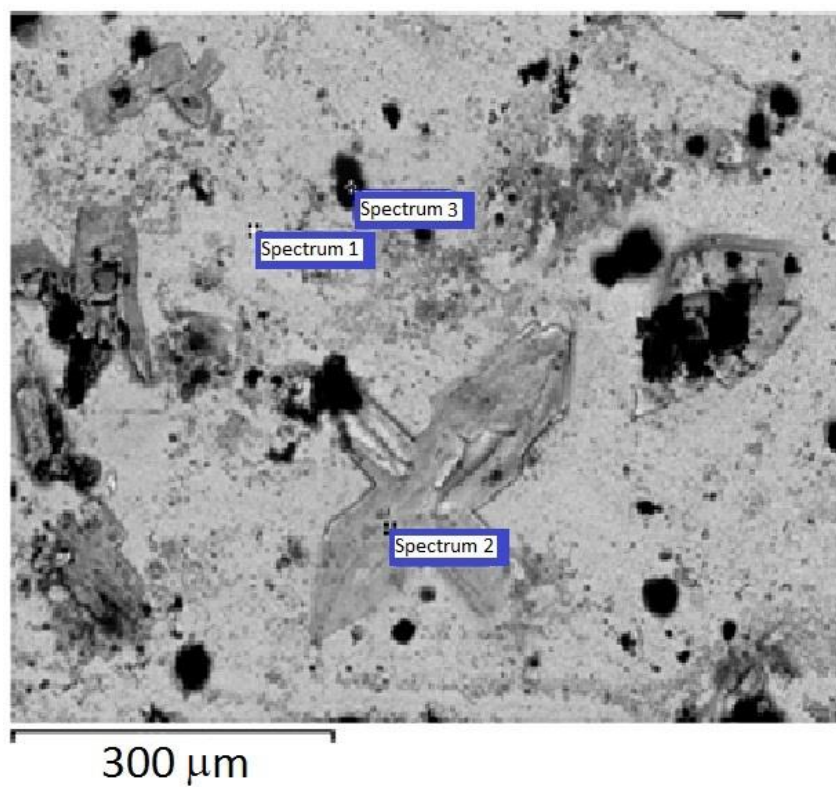
Elementary composition

Spectrum 1

Element	Weigth (%)
P	2.2
Cu	97.7

Spectrum 2

Element	Weigth (%)
P	11.5
Cu	88.5

Spectrum 3

Element	Weigth (%)
C	99.9

Figure 8

Figure 9