Electrochemical recycling of diamond and precious metals from used diamond tools

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Abstract. The recycling of used diamond tools, which contain a large amount of unused diamond particles and precious metals, can not only realize the reuse of resources, but also reduce the pressure of environmental protection. In this paper, diamond particles were recovered by acid dissolution of aqua regia, and the current density, complexing agent concentration and pH value of the acid dissolution system were adjusted to recover Cu and Co by electrodeposition. Scanning electron microscope and energy spectrometer were used to study the changes of the composition and morphology of the plated layers, and the effects of the parameters such as current density, complexing agent concentration and pH on the organization and composition of the alloy plated layers were analyzed. The results showed that at the current density of 40 mA/cm², pH 4.5 and complexing agent concentration of 10 g/L, uniformly distributed, dense and moderately thick Cu-Co alloy plating was obtained, and the weight percentages of Cu and Co reached the peak respectively. The Cu and Co in the waste diamond tools can be recovered under this condition with good recovery effect.

Keywords: diamond, used diamond tools, precious metals, Co, electrodeposition.

1. Introduction

Diamond tools are high-performance cutting tools consisting of synthetic diamond, tungsten carbide matrix and metal binder[1]. During the use of diamond tools, about 15% of diamond tools must be replaced after a period of time in order to protect the saw body from damage. However, used diamond tools contain a large amount of unused diamonds and precious metals. Directly discarding used diamond tools not only causes waste of resources, but also brings pressure to the environment[2].

According to the survey, used diamond tools contain a large amount of Cu and Co. These two metals have a wide range of applications and demands in the fields of catalysts, electronic information, energy, and environmental protection[3,4]. For example, as raw materials for electronic devices, wires, pipes and magnetic materials, superalloys, batteries, coatings, and many other products. Meanwhile the reserves of both are lower than the global production and the rapid generation of end-of-life products has become an important resource for both[5].

According to the International Energy Agency (IEA)[6] and the U.S. Energy Information Administration (EIA)[7], the global consumption of Cu in 2022 is 24.5 Mt and the global consumption of Co is 146,000 tons, while the global consumption of Cu in 2023 is expected to be 25.1 Mt, an increase of 2.4% from 2022, and the global consumption of Co is expected to be 152,000 tons, an increase of 2022, an increase of 4.1%. With the recovery of the global economy and the promotion of low-carbon transition and the development of new energy industry Cu and Co demand will maintain high growth[7]. Most of the existing Cu and Co comes from mineral smelting, tailings recovery and other recycling of Cu and Co containing waste materials. If effective recycling of waste diamond tools can be realized, it will not only make Cu and Co recycling, reduce the waste of resources and promote the economic development, but also optimize the production capacity structure, reduce the pressure on the environment, reduce the environmental pollution and improve the living environment of people. Therefore, the development of effective recycling technology is of great significance to alleviate Cu and Co resource tension and environmental pressure[8,9].

At present, the acid dissolution method[10] is commonly used for the recovery of used diamond tools, which takes advantage of the difference in solubility of metal and diamond in acid to separate them. However, this method has low recovery efficiency and complicated operation. Compared with other conventional recovery methods, the accuracy and efficiency of electrochemical metal recovery has the

advantages of being environmentally friendly, free of secondary pollution, requiring no further redox agents, easy to use in combination with other methods or substances, simple process, high product purity and showing flexibility at various temperatures or electrolytes[11]. However, some problems and challenges are faced, such as the selection and optimization of electrolyte, the study of reaction mechanism and kinetic model, scale up production and cost-benefit analysis. Therefore, the aim of this paper is to explore a simple, low-cost, high-efficiency and environment-friendly recycling technology to provide new ideas for the resourceization of used diamond tools.

2. Processes and experimental methods

The basic principle of electrochemical method to recover metals from scrap diamond tools is to dissolve the metals in scrap diamond tools in a suitable electrolyte using electric current or potential as a driving force[12], and then separate the dissolved metals from the electrolyte by electrodeposition. In this paper, used diamond tools were used as raw materials. The acid-dissolution-electrochemical method was used to recover the diamond and precious metals from the waste diamond tools. Firstly, the used diamond tools were acid-dissolved with aqua regia to filter out the diamond particles, and then the types and contents of precious metal ions in the solution were analyzed by ICP spectrometer. Finally, the metals were deposited on graphite electrodes by electrodeposition method. SEM and EDS were used to study the morphology and composition of the plated layers, and the effects of parameters such as current density, complexing agent concentration and pH on the plating properties were investigated. The process flow diagram used for the experiments is shown in Figure 1 below.

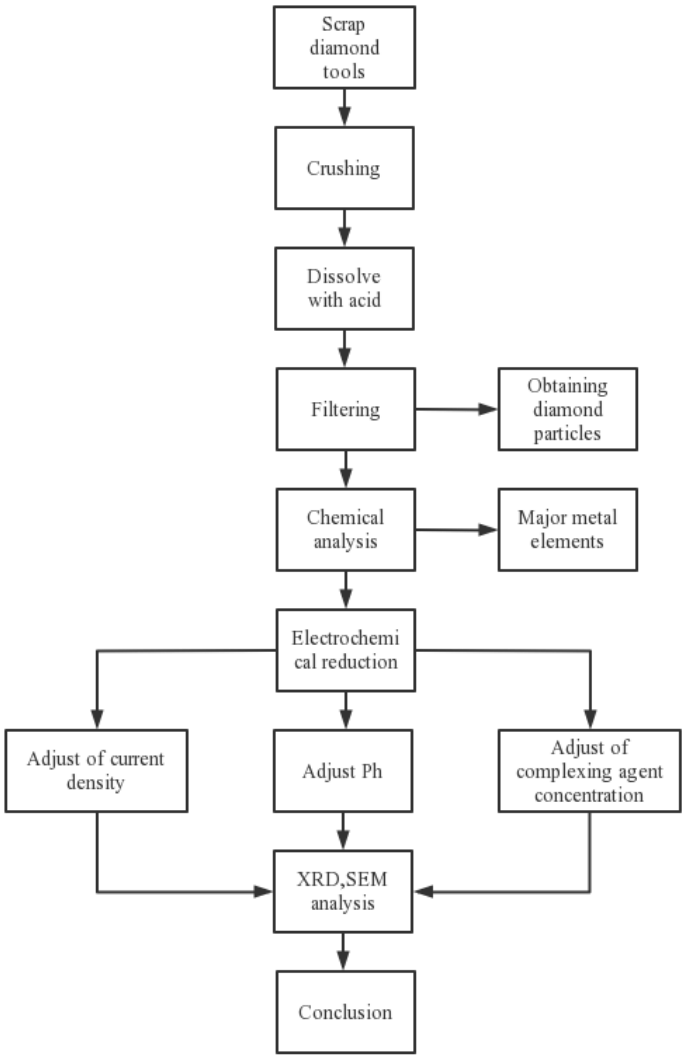


Fig. 1 Process flow diagram

2.1. Acid dissolution of used diamond tools

Since the hot pressing process used in the processing of diamond tools makes the metal binder more dense, this experiment intends to use the aqua regia system for the decomposition of diamond tools. A certain amount of crushed used diamond tools were put into the aqua regia system at 96°C for 2h and subsequently filtered, and the chemical composition of the obtained solution is shown in Table 1:

Table 1. Composition of aqua regia leachate of used diamond tools after filtration (wt%)

Co	Cr	Cu	Hg	Mn	Ni	Pb	Tl	V	Fe
41.395%	0.004%	26.645%	0.012%	0.023%	0.066%	0.011%	0.347%	0.006%	31.492%

From the above table, it can be seen that the main components in the leachate of this system are Co, Fe and Cu. The filtrate was filtered and washed to recover diamond particles and tungsten carbide.

2.2. Electrochemical reduction of leachate

Since the standard potential difference between Cu and Co is large, i.e., 0.337 VSCE for Cu^{2+}/Cu and -0.277 VSE for Co^{2+}/Co[13], an appropriate amount of complexing agent should be added and used to bring the deposition potentials of Cu and Co closer. Therefore, trisodium citrate was used as the complexing agent and the leaching aqua regia system was used as the plating solution to complete the co-deposition of Cu-Co plating on the graphite rod surface.

3. Results and Discussion

3.1. Effect of current density on the microscopic morphology and composition of Cu-Co alloy plating

The current density greatly affects the precipitation efficiency and precipitation composition of the plated layer. At pH=4.5, t=20min, and complexing agent concentration of 10g/L, changing the current density from 20 to 120mA/cm² affects the microscopic morphology and precipitation composition of the plated layer.

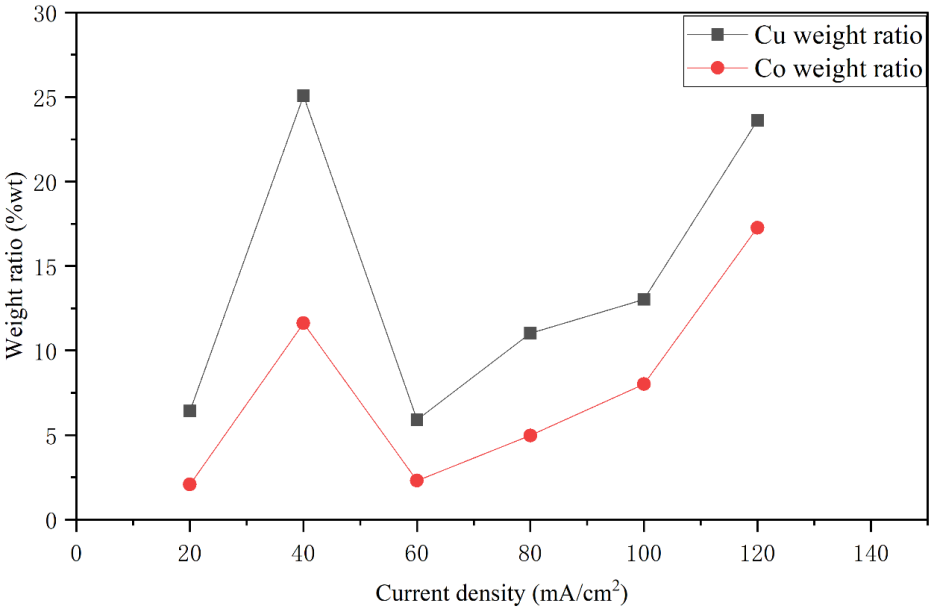


Fig. 2 Weight ratio of plating elements at different current densities

Figure 2 shows that the weight share of Cu and Co peaks at a current density of i=40mA/cm², so the analysis may be that a current density of i=40mA/cm² is the optimal precipitation current density for Cu and Co. At the current density of i=60-120mA/cm², the weight percentage of Cu and Co, with the increase of current density, once again showed a rapid and consistent increase. Therefore, it is assumed that the

optimal precipitation current density of Cu and Co is i=40 mA/cm² and the current density i>120 mA/cm² will have a larger current density of Cu and Co by weight.

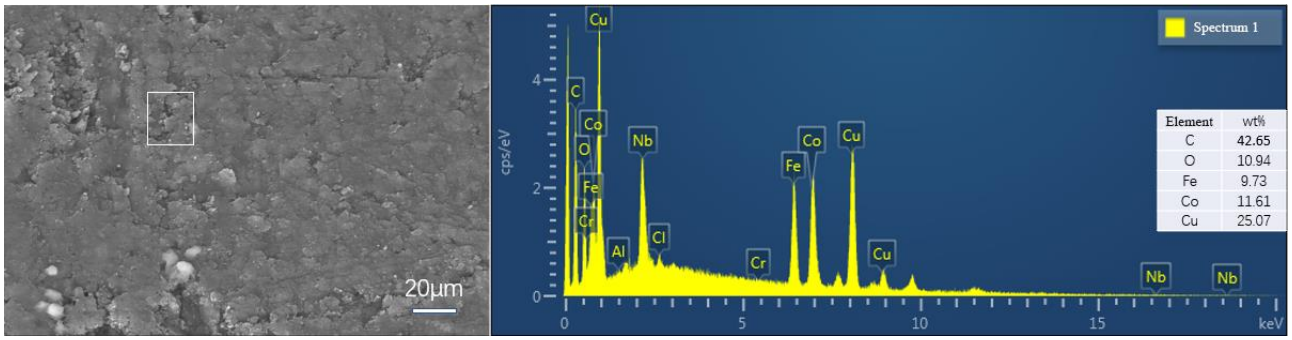


Fig. 3 Microscopic morphology and EDS analysis of the plated surface at i=40 mA/cm² current density

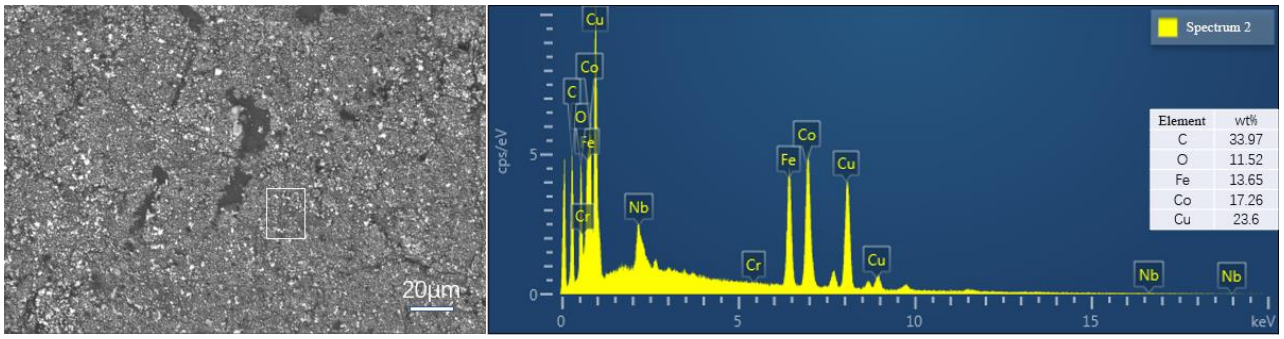


Fig. 4 Microscopic morphology and EDS analysis of the plated surface at i=120 mA/cm² current density

It can be seen from Figure 3 that at a current density of 40mA/cm², the surface of the plating appears fine cracks, the plating is thin and dense, but relatively uniform, the substrate is partially exposed, the plating is black and white, and the weight of Cu and Co accounts for a higher percentage at this time.

It can be seen from Fig. 4 that at the current density of 120mA/cm², the plating layer is thicker, laying flat on the surface of the substrate, the surface of the plating layer is relatively uniform and dense, the substrate is partially exposed, and the plating layer is black.

At low current densities, the deposition rates of Cu and Co are slower and are more affected by diffusive polarization[14,15,16], resulting in thinner, non-uniform layers with defects such as cracks and exposed substrate. As the current density increases, the deposition rate of Cu and Co accelerates, diffusive polarization decreases, and the layer becomes thicker, denser, and flatter. At the critical current density (40mA/cm²), the deposition rates of Cu and Co reach equilibrium, and the weight ratio of Cu and Co in the plating layer reaches the maximum. At this time, fine cracks appear on the surface of the plated layer, which may be caused by the stress generated during the deposition process. When the current density increases, the equilibrium of deposition rate of Cu and Co is broken, and the weight ratio of Cu and Co in the layer decreases sharply. However, as the current density increases further, the deposition rate of Cu and Co approaches another deposition equilibrium point, so the weight ratio of Cu and Co in the layer increases again with the increase of current density when it exceeds the critical current density (40mA/cm²).

3.2. Effect of pH on the microscopic morphology and composition of Cu-Co alloy plating

Fixed current density i=20mA/cm², t=40min, complexing agent concentration 10g/L, varying different pH values, EDS tests were performed and plotted as curves for the weight percentage of Cu and Co in the plated layer, as shown in Figure 5:

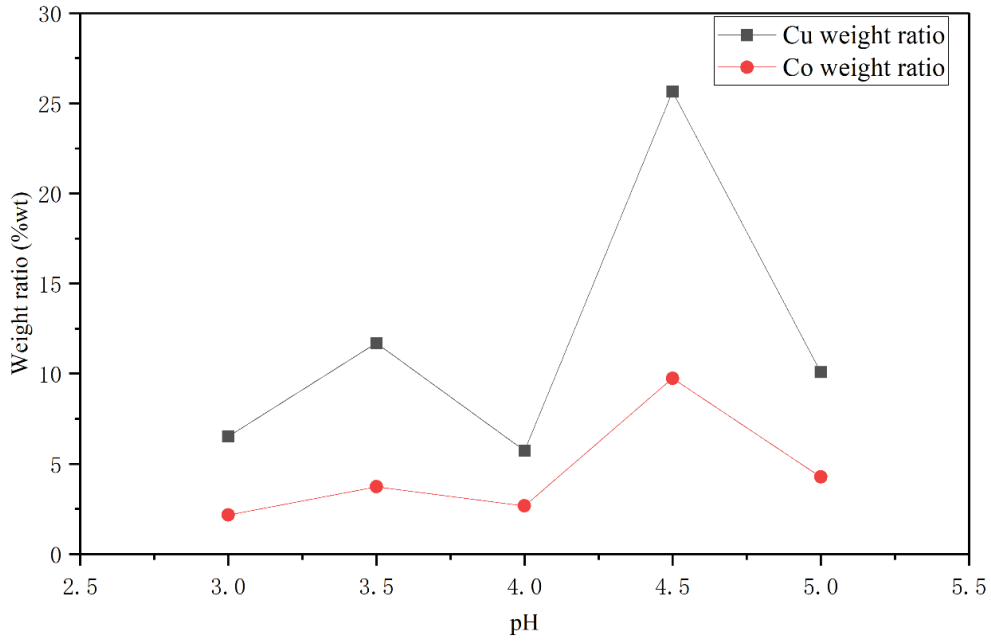


Fig. 5 Weight percentage of plated elements at different pH values for a complexing agent concentration of 10 g/L

And the surface micromorphology and EDS analysis of the plated layer obtained at the current density i=20mA/cm², t=40min, complexing agent concentration 10g/L, pH=4.5, were obtained as shown in Figure 6:

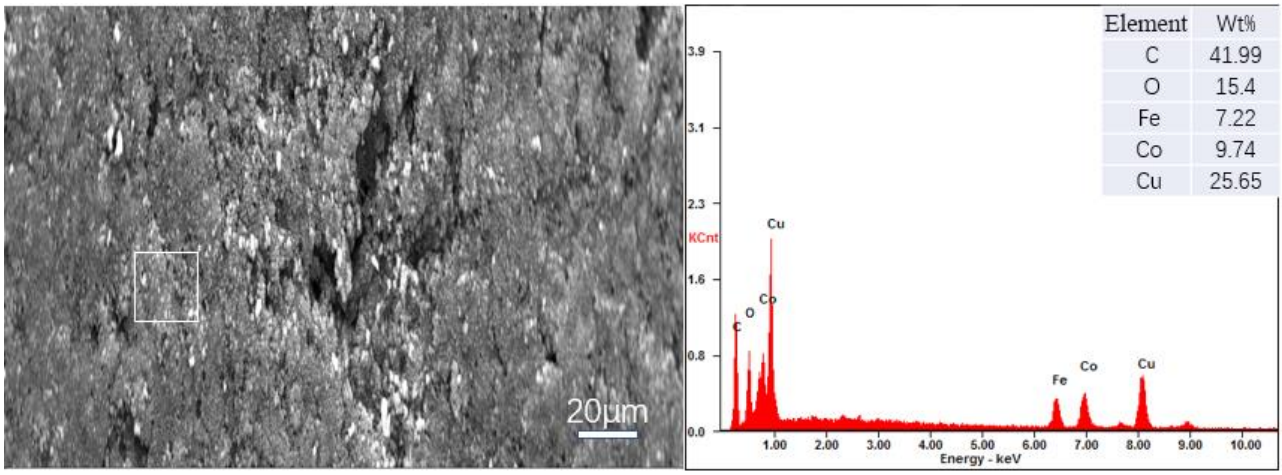


Fig. 6 Microscopic morphology and EDS analysis of the plated surface at a complexing agent concentration of 10 g/L and pH=4.5

From Fig. 5 and Fig. 6, it can be seen that under the conditions of i=20mA/cm², t=40min, and complexing agent concentration of 10g/L, with the increase of pH, the Cu and Co weight ratio increased slightly and reached the first smaller peak at 3.5, then with the increase of pH the Cu and Co weight ratio decreased slightly, when pH=4.5, the Cu and Co weight ratio reached the peak, at this time The plating is uniformly distributed and dense, with thicker plating, less cracks, and a small part of the substrate exposed.

Within a certain pH range, the stability of the plating solution and the crystallinity of the plating layer are better, which is conducive to the formation of high quality plating layer. If the pH value is too high or too low, it will lead to the decomposition or precipitation of the plating solution, which will affect the uniformity and denseness of the plating layer. At the same time, the crystallinity of the plating layer will also be affected by the pH value, which will affect the grain size and crack formation of the plating layer.

Cu^{2+} is almost completely complexed with citrate in the plating solution at pH 4~6[17], while Co^{2+} is present as a simple ion, drawing the deposition potential of Cu^{2+} and Co^{2+} closer to achieve Cu-Co alloy

co-deposition. At a certain current density, the deposition rate of Cu^{2+} and Co^{2+} is influenced by the pH value. With the increase of pH, the complexation of Cu^{2+} increases and its deposition rate decreases, while the deposition rate of Co^{2+} is relatively stable or slightly increases. Therefore, the content of Cu and Co in the plated layer changes at different pH values. The deposition rates of Cu^{2+} and Co^{2+} are best matched when the pH reaches an optimum value of 4.5, resulting in the highest content of both elements in the plating.

Because of the large potential difference between Cu and Co, a certain degree of polarization effect occurs during electrodeposition[18], i.e., the accumulated metal atoms on the electrode surface inhibit the reduction of subsequent metal ions as the deposition time increases. As the pH increases, the complexation of Cu^{2+} increases and its deposition rate decreases, thus partially suppressing the polarization effect making a small peak in the percentage of Cu at pH 3.5. As the pH increased, the balance between the slowing down of deposition rate and the suppression of polarization effect was broken, resulting in a slight decrease in the Cu percentage. However, the balance between the two reached a more stable equilibrium with further increase of pH, and the deposition rates of Cu^{2+} and Co^{2+} also reached an equilibrium value at the same time when pH reached 4.5, so that the weight ratios of both Cu and Co reached a peak.

3.3. Effect of complexing agent concentration on the microscopic morphology and composition of Cu-Co alloy plating

At a fixed current density i=20mA/cm², t=40min, pH=4.5, the EDS test was performed and plotted as a curve by varying the concentration of different complexing agents and thus the weight percentage of Cu and Co in the plated layer, as shown in Figure 7:

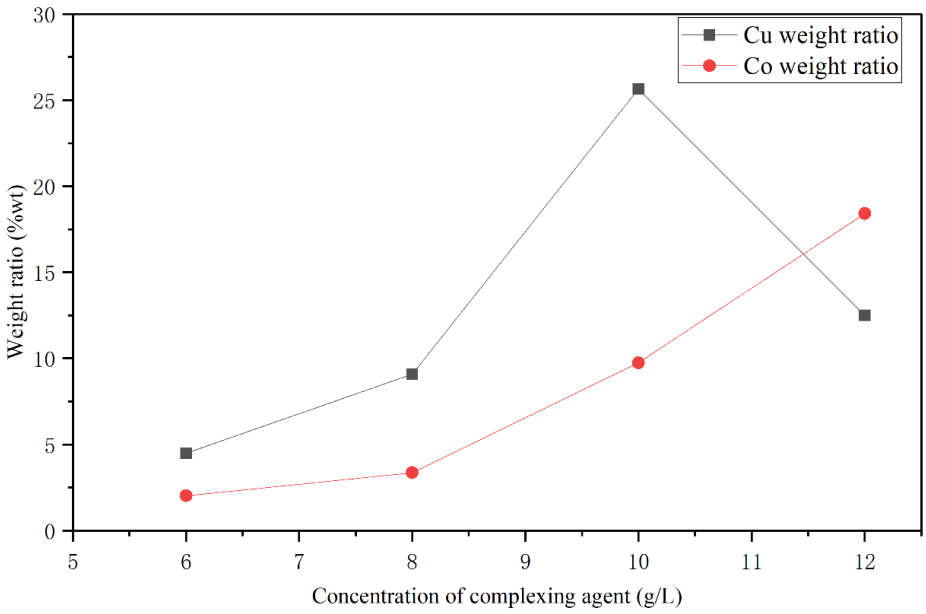


Fig. 7 Weight percentage of plated elements for different complexing agent concentrations at pH 4.5

And the surface micromorphology and EDS analysis of the plated layer obtained at the current density i=20mA/cm², t=40min, pH 4.5, and complexing agent concentration 10g/L were obtained as shown in Figure 8:

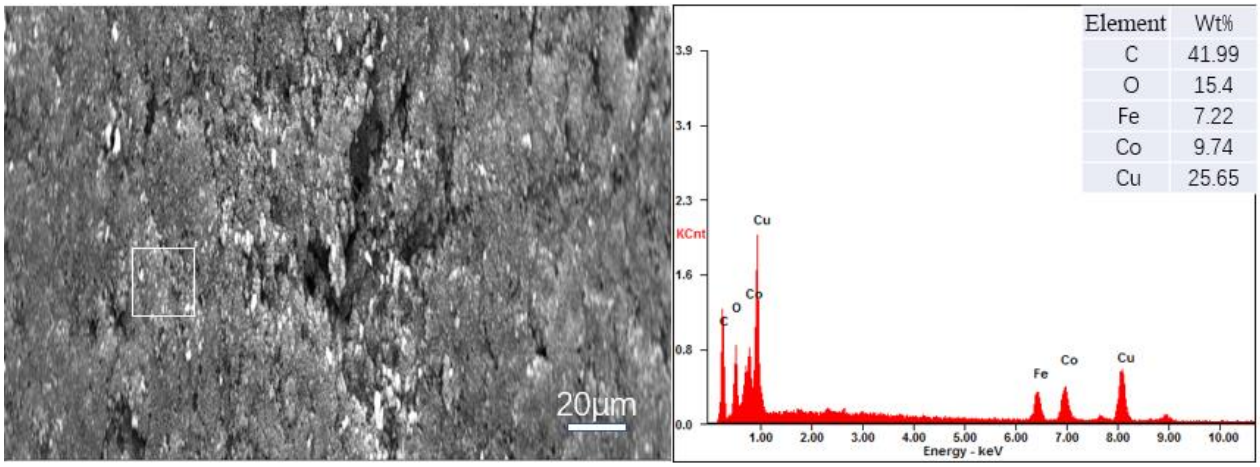


Fig. 8 Surface microscopic morphology and EDS analysis of the plated layer at pH 4.5 and complexing agent concentration of 10 g/L

From Fig. 7 and Fig. 8, it can be seen that the weight ratio of Cu and Co increases significantly with the increase of complexant concentration at the current density i=20mA/cm², t=40min, and pH 4.5, and the weight ratio of Cu reaches the peak at the complexant concentration of 10g/L, and the weight ratio of Co will be higher when the complexant concentration is above 10g/L. Meanwhile, at the complexing agent concentration of 10 g/L, the plating is uniformly distributed and dense, with thicker plating, less cracks, and a small part of the substrate exposed.

The complexing agent can increase the solubility and reducing activity of Cu^{2+} and Co^{2+}[19,20] and close the potential difference between them, thus promoting their co-deposition. When the complexing agent concentration is low, the degree of Cu^{2+} complexation is low, so the deposition rate of Cu^{2+} is higher than that of Co^{2+}, resulting in a higher weight percentage of Cu. However, when the deposition rate of Cu^{2+} is too fast, it will produce polarization effect and thus inhibit the further deposition of Cu^{2+}. Therefore, as the concentration of complexing agent increases, the weight percentage of Cu continues to increase under the combined effect of complexation degree and polarization effect. When the concentration of complexing agent is high, Cu^{2+} is almost completely complexed, which makes the deposition rate of Cu^{2+} greatly reduced, and the deposition rate of Co^{2+} is higher than that of Cu^{2+} at this time, resulting in the increase of the weight proportion of Co. When the concentration of complexing agent was 10g/L, the deposition rate of Cu^{2+} and the polarization effect reached a balance so that the weight ratio of Cu reached a peak, and the deposition rate of Co^{2+} was also higher at this time, and the deposition rates of both were similar, so that the weight ratios of Cu and Co both reached a high value.

During the electrodeposition process, grains of different sizes and shapes appear on the surface of the plating, and stresses and cracks are generated as the grains grow[21]. When the complexing agent concentration is low, large and inhomogeneous grains appear on the surface of the coating due to the high number of Cu atoms in the coating, which leads to increased stress and cracks in the coating, uneven distribution of the coating, reduced denseness and thickness, and increased exposure of the substrate. When the concentration of the complexing agent is higher, smaller and uniform grains appear on the surface of the plating due to the high content of Co atoms in the plating, resulting in reduced stress and cracks in the plating, uniform distribution of the plating, increased densities and thicknesses, and reduced exposure of the substrate. When the complexing agent concentration is 10 g/L, moderate and homogeneous grains appear on the surface of the plated layer due to the considerable amount of Cu and Co atoms in the plated layer, which leads to the least stress and cracks in the plated layer, the most uniform distribution of the plated layer, the most moderate densities and thicknesses, and the least exposure of the substrate[21,22].

4. Conclusion

(1) In this paper, the effects of current density, pH and complexant concentration on the microscopic morphology and composition of Cu-Co alloy plating were investigated, and the plating was characterized by scanning electron microscopy and energy spectrometry.

(2) At a current density of 40 mA/cm², a pH of 4.5 and a complexing agent concentration of 10 g/L, a uniformly distributed, dense and moderately thick Cu-Co alloy layer was obtained, and the weight ratios of both Cu and Co reached high values. The Cu and Co in the used diamond tools can be recovered under this condition with good recovery effect.

(3) The formation mechanism of Cu-Co alloy coating may be related to the complex stability of Cu^{2+} and Co^{2+} in the electrolyte, potential difference, polarization effect, deposition rate, and grain growth and crack formation on the surface of the coating.

(4) This paper provides an effective electrochemical method for efficient recovery of Cu and Co, but further studies are needed to investigate the effects of different parameters on the plating properties, as well as the feasibility of optimizing the process conditions and large-scale production.

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