Characteristics of Ternary Metal (Cu-Ni-TiN) Electrodes Used in an Electrical Discharge Machining Process

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Abstract: In the industrial field, electric discharge machining (EDM) is the most commonly used non-traditional machining process because it has the potential to machine electrically conductive materials of high hardness. To satisfy the need for rapid and economical fabrication of EDM electrodes, techniques that use the addition of more metal in the manufacturing process are gaining in popularity. This study presents an investigation of the characterization of ternary metals (Cu–Ni–TiN) for EDM electrodes by using powder metallurgy, which leads to enhancement of the mechanical properties, such as the hardness, electrical properties, and other properties, for the formation of Cu in Ni-TiN electrodes using a cold press at pressures of 18, 20, and 22 MPa. The influences of the parameters of this process were identified for the betterment of Cu–Ni–TiN on the surface. The specimens were calcined in a furnace at 1100 °C for 1 h, with a mixture of argon and hydrogen gas as a controlled gas in the ratio of 95:5. The specimens were investigated in terms of hardness, electric resistivity, apparent density, and porosity. The results show that the 80% Cu–3% Ni–17% TiN electrode at 18 MPa had the highest hardness (124.38 HV) and the lowest electric resistivity (0.39188 cm), while the specimen increased Cu with a ratio of 85% Cu–3% Ni–12% TiN, and a pressure of 20 MPa was found to have the highest density (8.5472 g/cm³) and the lowest porosity (6.2922%). As a further confirmation of the above results, the X-ray diffraction (XRD) patterns of the surfaces of the specimens exhibited major phases that supported the ternary Cu–Ni–TiN phase. However, we also achieved the successful use of Cu–Ni–TiN electrodes as a titanium source (as an alternative to the conventional metal powder) to provide a novel approach to fabricating composite electrodes through the EDM process.

Keywords: powder metallurgy; EDM electrode; Cu–Ni–TiN electrodes; cold press; composite electrodes

1. Introduction

The process of cutting tools for electrical discharge machining (EDM) is considered to be non-traditional and plays a significant role in the die and mold industry. Generally, special machining requires high-priced machines, and the production costs are high. However, the EDM process principle works by releasing electric current through a cutting tool called an electrode. There are many types of electrodes that are commonly used, such as graphite, copper, copper-graphite, copper-tungsten, and brass. In the process of EDM with electrode materials, both solid electrode materials and powder compacted are available [1,2]. The main and essential factors for efficiency in material processing include workpiece material, electrode material, experimental conditions such as duty factor, gap, pulse current and open circuit voltage, fluid dielectric substances, etc. [3,4]. The cutting tools, called electrodes, for the EDM process are essential. It is important to consider the appropriate use for the workpiece material, especially with special hardness material such as tungsten carbide, which is difficult to form due to its high hardness and high melting point [3–5]. Therefore, it is imperative to select the appropriate electrode material in order to obtain good results after processing in terms of precision in both size and surface roughness, as well
as workpiece surfaces free from small cracks [4]. In workpiece material processing with EDM, the selection of electrode materials, both solid and powder sintered, is considered to increase efficiency in optimal processing [5]. However, the EDM process is well-known for parting materials to desired shapes and sizes for use in production systems. Thus, EDM is a popular tool used for the machining of solid material that cannot be fabricated using a conventional machining technique [6–8]. In EDM, the material is transformed by the heat from an electrical spark of a fluid dielectric that extracts material particles (solid, liquid, or gaseous), so the electrode does not contact the specimens [9]. EDM is also known as spark machining, which involves spark eroding material from the conductive workpiece while it is submerged in a dielectric medium [9–13]. For example, the graphite electrode is a popular cutting tool because it has a low wear ratio, light weight, small numbers of microcracks, and a low thermal expansion coefficient, so the size of the workpiece can be controlled. However, the disadvantage of this electrode is that it is expensive because it utilizes a hot isostatic press technique and a high temperature for calcining. Therefore, another efficient cutting tool is required for machining, which results in high costs. One of the alternative electrodes used in the EDM industry is copper graphite, which is popular on the market because it is a good conductor, with a low electrical resistivity and a high melting temperature [14]. However, it is costly to use traditional machining processes on materials that are too difficult to machine, such as copper-based or other alloys [15–18]. The EDM process has been widely used for the manufacturing of molds and dies, as well as in the aerospace and automotive industries [19–23]. Several researchers have conducted investigations in this field. Tsai et al. [24] studied the formation of electrodes at low pressure (20 MPa) and a temperature of 200 °C. The results showed that the surface of the specimens was coated with chromium after EDM. The copper electrode yielded the highest material removal rate, and a higher pressure (30 MPa) yielded a higher material removal rate than that of the low pressure (10 MPa). At low pressure, chromium particles were better dispersed throughout ten specimens because of the stronger bonding between atoms. In addition, Fonda et al. [25] studied the impacts of adding titanium carbide (5–20%) to a copper–tungsten electrode. The results showed that the electrode had the highest density, lowest electric resistivity, highest EDM efficiency, lowest wear rate, and highest material removal rate when 15% titanium carbide was added. Chiyasak et al. [26] also used Ni–TiN binary powder and mixed it with an additive of cobalt elements to produce ternary metal (Ti/Ni/Co) nanocomposites for the application of magnetized materials. Furthermore, Dong et al. [27] studied the properties of composite materials using Cu and Cr metal powder. The metal powder was compressed at 200, 400, and 600 MPa. The shape changed after sintering. The properties of the specimens were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed that a test piece compressed at 600 MPa and sintered at 900 °C for 30 min had a relative density of 82.61%, a conductivity of 40.82%, and a hardness of 116.4 HV. The same results also showed a high hardness and density due to the high temperature used for the manufacturing [28]. However, it is important to consider the selection of electrode materials for the EDM process. The characteristics and properties (electrical conductivity and other properties of the workpiece and materials electrode) are important for the EDM process. In this regard, this study is important in determining the effectiveness of the ternary metal composite powder electrode, based on Cu material, in achieving good conductivity. It was observed that the addition of Ni powder in the ternary composite electrode resulted in increased mechanical properties (hardness and melting point), and compatibility of the copper phase system with other elements. Moreover, nickel is a universally chemically stable metal. Nickel strengthening can be achieved with a wide range of different methods to increase dispersion strengthening, but pure nickel is not used as a structural material because of its high density and relatively low strength. However, its modification allows one to achieve a significant increase in mechanical properties. Furthermore, the use of TiN electrode can result in an increase in corrosion and wear resistance [24–26]. The material removal rate is
also an important consideration, as altering the machining gap can increase the material removal rate, as well as improve surface finish [24].

Additionally, to the best of our knowledge, there are few works in the literature that have reported the use of ternary metal (Cu–Ni–TiN) powders in the EDM process [27–29]. Padhi et al. and Davim et al. [28,30] explained the results of the additive of Cu doped into plastic electrode and other metal electrodes, which helped to increase the material removal rate and caused less tool wear. Hence, in this work, a novel approach to fabricating a composite electrode by varying the amount of Cu–Ni–TiN as a metal source was studied. The synthesis of composite Cu–Ni–TiN electrodes was analyzed in terms of hardness properties, electric resistivity, apparent density, porosity, and other properties, which are reported.

2. Experimental Procedure

2.1. Material Data

In this work, the as-received metal powders—copper (Cu), nickel (Ni), and titanium nitride (TiN)—were used (Rajamangala University of Technology Krungthep, Bangkok, Thailand) as precursors. The specific details of the properties of Cu–Ni–TiN are listed in Table 1. The melting temperatures of the copper and nickel are obtained by a Cu-Ni binary alloy phase diagram of the American Society for Metals (ASM) handbook Volume 3 [1]. The melting temperatures of TiN is obtained as previously shown in a literature [25]. The differences in the Cu ratios of the mixtures of Cu–Ni–TiN electrodes are presented in Table 2.

Table 1. Properties of the Cu–Ni–TiN electrodes.

| Powder Properties | Cu     | Ni     | TiN    |
|-------------------|--------|--------|--------|
| Purity (%)        | 99.00  | 99.90  | 99.90  |
| Density (g/cm³)   | 8.96   | 8.88   | 5.22   |
| Melting Point (°C)| 1083   | 1455   | 2930   |
| Electric Resistivity (Ω·cm) | 1.70 × 10⁻⁶ | 6.40 × 10⁻⁶ | 6.0 × 10⁻³ |
| Thermal Conductivity (W/m·K) | 383    | 65.5   | 19.2   |

Table 2. The ratios of Cu–Ni–TiN electrodes in this experiment.

| Electrode Code | Composite Electrode Ratio (%) |
|---------------|-------------------------------|
|               | Cu   | Ni   | TiN  |
| A             | 100  | -    | -    |
| B             | 80   | 3    | 17   |
| C             | 85   | 3    | 12   |
| D             | 88   | 3    | 9    |
| E             | 90   | 3    | 7    |
| F             | 93   | 3    | 4    |

2.2. Material Setup

The mixed ternary metal powders were calculated to determine the most suitable ratio of Cu–Ni–TiN powders, as described above. The particle size of ternary metal powder was calculated by the average particle sizes (Cu = 20–40 µm, Ni < 25 µm, and TiN < 36 µm) as a precursor, and these were then placed in a grinding mill machine (Herzog, model HSM100A) at 80 rpm for 1 h, as shown in Figure 1. Next, after ensuring thorough grinding, to prepare the electrodes, the ternary metal powders were formed with a hydraulic press with a size of 20 mm × 20 mm × 50 mm (Ward-Forsyth, Sheffield, England) at 18, 20, and 22 MPa, as shown in Figure 2. After compaction, the resultant ternary (Cu–Ni–TiN) metal powders were calcined in a vacuum furnace (Linn, model HT1800 Vac) at temperatures between 1000 and 1250 °C for 1 h (heating rate of 10 °C/min), and were finally cooled.
down in the furnace. In this experiment, all procedures used in the preparation of the Cu–Ni–TiN metal powders are shown in Figure 3.

Figure 1. The mixing machine of the ternary metal powders used in the experiment.

Figure 2. The compaction process of the ternary metal powders used in the experiment.

Figure 3. The procedures for preparing the ternary metal powders used in the experiment.
2.3. Characterization Techniques

Before examining the microstructure, the surfaces of the specimens were polished with a series of silicon carbide papers (400, 600, 800, and 1200), then washed thoroughly with distilled water, and dried at room temperature. The surface morphology imaging and XRD analyses of the Cu–Ni–TiN composites were performed using a scanning electron microscope (SEM, JSM-6610LV, JEOL). The phase determination was carried out through X-ray diffraction (XRD, D8 ADVANCE, Bruker) using Cu-Kα radiation (λ = 1.5406 Å) and 2θ varying from 20° to 80°. The hardness property (MMT-X7, MATSUZAWA) of the specimens was investigated using American Society for Testing and Materials (ASTM) B348. A maximum load of 1 kg was applied to each specimen and the average across all specimens was used to collect the hardness value. The electrical resistivity behavior was assessed by performing an electric resistance scan using an LCR HiTester (HIOKI 3532-50). To measure the electrical resistivity, the two ends of both specimens were coated with silver paint and connected to a silver wire. The Electric Resistivity per unit area (Ω·cm) was calculated using the following equation:

\[ \text{Electric Resistivity} = \rho \times \frac{L}{A}. \]  

(1)

Furthermore, the density was determined with the water displacement technique by measuring the unsaturated dry weight (W_d). The specimen was placed in distilled water, and a vacuum plate and a vacuum pump were used for 1 h to replace the porosity in the specimen with water. Subsequently, the specimen was dried at room temperature, and the saturated weight (W_s) was determined using the weight scales to calculate the bulk density (ρ_B) of both workpieces with the following equation:

\[ \rho_B = \frac{W_D}{W_s - W_{ss}}. \]  

(2)

The apparent density (ρ_A), that is, the density of the whole structural space of the second workpiece, was determined as follows:

\[ \rho_A = \frac{W_D}{W_{D} - W_{ss}}. \]  

(3)

The porosity of the workpiece was determined using the following equation, as suggested by [26].

\[ \% \text{Porosity} = \frac{\rho_A - \rho_B}{\rho_A} \times 100 \]  

(4)

3. Results and Discussion

3.1. Structural Analysis Results

The suitable temperature for Cu–Ni–TiN electrode manufacturing and the results of the analysis of the electrode compositions obtained via sintering at 1000, 1050, 1100, and 1250 °C are presented in Figure 4a,b. Figure 4a,b shows good and bad specimens after sintering. After the sintering at each temperature, the workpieces showed the characteristics of the different specimens. We found that the specimens sintered at 1100 °C resulted in a completely homogeneous substance and high mechanical properties, as also shown in [27,28]. However, the specimens obtained via sintering at other temperatures showed longitudinal cracks on their surfaces, and the interiors of the samples could not be used as electrodes [27–29].
The interior of each sample was investigated using surface analysis techniques and chemical dispersion with SEM–EDS (energy dispersive spectroscopy) instruments after calcination. We found that each element was dispersed throughout the specimen, and more copper melted when the material was sintered at temperatures under 1250 °C. Thus, the melting of elements in the different electrodes at different temperatures is presented in Figures 5 and 6. Figure 6 shows the chemical dispersion in the electrode, which was detected with the EDS pattern. The Cu–Ni–TiN electrodes and their elemental compositions were determined and analyzed to identify the electrode with the best properties. The analysis of the Cu–Ni–TiN electrode with the main elemental composition—Ti, Cu, Ni, and Co—revealed that Cu represented the dispersion of clusters, whereas Ti was found in the agglomerates of Cu. Conversely, Co and Ni were dispersed across the whole surface. Moreover, the Cu concentration decreased because of the melting and evaporation of Cu during sintering, whereas the Ti concentration increased due to the decreases in the concentrations of other elements. The results of the analysis of the dispersion of the elements in the Cu–Ni–TiN electrode specimens are presented in Table 3. Cu and Ti occurred in small compound particles that connect with Co and Ni; these particles were generated on the dispersed atoms throughout the whole sample during sintering [30,31]. In addition, the phase transformation of the Cu–Ni–TiN electrode was detected through XRD, which is displayed in Figure 7. Figure 7 shows the diffraction peaks of the Cu peak in the Cu–Ni–TiN electrode located at 2θ of 43.4, 50.5, and 74.1° (JCPDS No. 03-065-9743). Among the indicated diffraction peaks, 2θ was located at 24.1, 33.0, 41.0, 62.0, and 71.5°, which indicates the TiNi B2 crystal structure (JCPDS No. 00-003-1154). Based upon these XRD results, we concluded that the addition of copper resulted in the formation of the Cu-Ni-TiN B2 crystal structure from determination using the Scherrer equation to calculate average crystallite sizes (23.16 ± 0.46 nm). However, the oxide phases of Ti and Ni were also observed in the Cu–Ni–TiN electrode. This is probably the result of an incomplete reaction during the calcination process. The existence of this Cu–Ni–TiN B2 crystal structure (crystalline size particles) arose from the calcination conditions (more than 500 °C for 1 h at a heating rate of 10 °C/min), which were lower than in other studies [32–34]. The addition of nickel and titanium in a Cu electrode resulted in greater hardness properties compared with those of the pure Cu electrode as shown in the results of hardness (Figure 8) and the related density and porosity properties, which is discussed later on.
Table 3. The chemical composition of the Cu–Ni–TiN electrodes in this experiment.

| Elements (wt.%) | Cu    | Ni    | Co    | Ti    |
|----------------|-------|-------|-------|-------|
|                | 80.17 | 3.02  | 0.81  | 16.00 |
3.2. Hardness Property Results

Figure 8 shows the results of the hardness analysis of the Cu–TiN electrodes manufactured at different pressures. The 80% Cu–3% Ni–17% TiN electrode to which the pressure of 18 MPa was applied had the highest hardness of 124.38 HV, whereas the 80% Cu–3% Ni–17% TiN electrode that was fabricated using a pressure of 22 MPa had the lowest hardness, with a value of 101.34 HV. Other electrodes showed similar hardness values, which were higher than that of the 100% Cu electrode. These results indicate that the hardness depends on the composition, that is, the addition of Ti to the mixture, as well as the pressure used for the manufacturing of the electrode [35].

3.3. Electric Resistivity Results

The electric resistivity values of the Cu–Ni–TiN electrodes depending on the pressure are shown in Figure 9. The results indicate that the 80% Cu–3% Ni–17% TiN electrode
manufactured at a pressure of 18 MPa had the lowest electric resistivity (0.39188 Ω·cm), and was thus the best conductor compared with the other electrodes [36].

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**Figure 9.** Electric resistivity values of the Cu–Ni–TiN electrodes.

**3.4. Density/Porosity Results**

Analysis of the electrode density shows the effects of density on porosity. Electrodes with a high density have a low porosity because of the expansion that occurs during sintering, or the dispersion of other compounds, which results in a new phase in that area. However, other factors influence the electrode properties. Figure 10 shows that the 85% Cu–3% Ni–12% TiN electrode fabricated at a pressure of 18 MPa had the lowest porosity (6.2922%). Note that the porosity depends on the change in the shape of each metal powder and other electrode factors. Figure 11 shows the densities of the Cu–Ni–TiN electrodes. The values are similar, except for the 85% Cu–3% Ni–12% TiN electrode fabricated at a pressure of 20 MPa, which had the highest density (8.5472 g/cm³). The 80% Cu–3% Ni–17% TiN electrode fabricated at a pressure of 18 MPa exhibited a density of 5.89439 g/cm³. The different densities are due to the different properties and shapes of the metal powders, as well as the sintering process [37,38].

**Figure 10.** The porosity of Cu–Ni–TiN electrodes.

**Figure 11.** The density of the Cu–Ni–TiN electrodes.

**3.5. Material Removal Rate Results**

The material removal rate of the 80% Cu–3% Ni–17% TiN electrode compressed at 22 MPa reached up to 0.0038 g/min, whereas that of the 85% Cu–3% Ni–12% TiN electrode manufactured at 18 MPa was the lowest (0.0007 g/min), as shown in Figure 12. The results depend on the compositions of the electrodes in material removal rate, as shown by similar studies [33–35]. Therefore, when sparking a workpiece of tungsten carbide with high hardness, this effect is caused by higher heat energy generation, resulting from the ability to remove much of the workpiece as well, which is comparable to the amount of the mixed elements in TiN electrode type with a lower quantity value. Similar results of the materials removal rate were reported by Jeswani [39], who described that the addition of graphite electrode into binary metals powder (such as Ti, Ni, Cu, and others) in the EDM process helps to increase material removal rate and increase wear resistance.
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3.6. Electrode Wear Ratio Results

The electrode wear ratios differed depending on the EDM conditions and material mixtures. The wear ratio of the 90% Cu–3% Ni–7% TiN electrode obtained at a pressure of 18 MPa was less than 9.46%. Because the electrode had good physical and mechanical properties, the bonding of the metal powder particles was quite good, as shown in Figure 13. In addition, the electrode had a relatively low surface roughness [36]. However, the electrode wear rate decreased as TiN content decreased when the use of compression force in the workpiece was small, so the wear rate was less compared with the compression of other electrodes. This is explained by the amount of molten metal that can be flushed away by the fluid dielectric being constant, which also affects electrode wear constantly [40,41]. Therefore, as heat energy from the electrode is transferred into the workpiece as the pulse-on duration increases, the dielectric is increasingly unable to clear away the molten material, and so it builds up upon the surface of the workpiece and eroded electrode [42,43]. Similar results showed that the use of Cu powder can be increased with an increase in the concentration of the system due to a decrease in the time lag, whereas the use of Ti and Ni powder exhibits more improvement in surface finish than caused by pure Cu powder [37,38].
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Figure 13. Electrode wear ratios of the Cu–Ni–TiN electrodes.

3.7. Surface Roughness Results

The average surface roughness of these materials under the sparked surface of the Cu–Ni–TiN electrode was found. The average surface roughness was minimal when the spark of the 80% Cu–3% Ni–17% TiN electrode obtained at 22 MPa was equal to 1.183 µm. The roughness depends on the amount of material between the discharge electrode and the workpiece [35–37]. The removal of the material with the spark causes the erosion of the surface, which leads to unequal surface roughness, as shown in Figure 14.

Figure 14. Average surface roughness of the Cu–Ni–TiN electrodes.
4. Conclusions
A ternary Cu–Ni–TiN electrode was successfully prepared using the electrical discharge machining process, leading to the following conclusions of this study:

1. The appropriate calcination temperature for yielding the highest hardness (115.43 HV) was determined to be 1100 °C.
2. The 80% Cu–3% Ni–17% TiN electrode obtained at a pressure of 18 MPa had the highest hardness of 124.38 HV and the lowest electric resistivity of 0.39188 Ω·cm.
3. The 85% Cu–3% Ni–12% TiN electrode manufactured at a pressure of 20 MPa showed the highest density of 8.5472 g/cm³ and the lowest porosity of 6.2922%. The main elements were continuously dispersed throughout the electrode, and the element concentration reflected the ratio after sintering.
4. The porosities and densities of the electrodes differed because each metal had a different melting temperature. Therefore, there was an imbalance in the mass transfer during diffusion, which depended on the temperature and duration of sintering, leading to different levels of homogeneous substance.
5. The lowest material removal rate of 0.0038 g/min was obtained for the 80% Cu–3% Ni–17% TiN electrode manufactured at 22 MPa, and the lowest electrode wear ratio of 9.46% was detected in the 90% Cu–3% Ni–7% TiN electrode compressed at 18 MPa.
6. The average surface roughness of the tungsten carbide surface obtained by machining with the Cu–Ni–TiN electrode was the lowest (1.183 µm) because the melting temperatures of TiNi and TiCu yielded similar results, leading to the smallest wear ratio and a good surface quality.

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