Effect of Surface Modification of Carbon Nanotubes on the Properties of High-Strength and High-Conductivity Copper Matrix Composites

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The use of carbon nanotubes (CNTs) as the reinforcing phase to prepare copper-based composite materials can improve the strength and high conductivity of copper-based conductors. In order to analyze the effect of surface oxidation modification on the structural properties of carbon nanotubes and its strengthening effect on composite materials, this article combines heterogeneous copolymerization liquid phase mixing method and spark plasma sintering molding method; prepares the carbon nanotubes/copper composite materials using carbon nanotubes under different oxidation treatment conditions as the reinforcing phase (the volume fraction of carbon nanotubes is 3%); and characterizes the microstructure, mechanical properties, and electrical and thermal conductivity of the composite material. Studies have shown that the tensile strength and hardness of composite materials first increase with the increase of CNT oxidation treatment time and then decrease with the increase of oxidation treatment time. When the oxidation treatment time is 4 h, CNTs are uniformly dispersed in the matrix while maintaining good structural integrity and load-bearing capacity, and the composite material has the highest mechanical properties. The tensile strength of the composite material made of 80-nm CNTs reaches 452.4 MPa, which is 1.6 times that of pure copper, and the hardness reaches 127.4HV, which is twice that of pure copper. The electrical conductivity and thermal conductivity of the composite material first increase with the increase of the oxidation treatment time of carbon nanotubes and then decrease with the increase of the oxidation treatment time. The 80 nm CNT reinforced composite material has better CNT dispersion performance and higher conductivity than that of 15 nm CNT preparation. The electrical conductivity of the composite material reaches the maximum value of 92% IACS when the CNT oxidation treatment time is 4 hours, which is 95% of the pure copper sample, and the electrical conductivity is significantly better than that of the CNT/Cu composite material and copper alloy prepared by other methods. The thermal conductivity of composite materials is lower than that of pure copper. The thermal conductivity of carbon nanotubes with an oxidation treatment time of 2 h decreases most obviously, indicating that the thermal resistance generated by the interface and agglomeration phases in the composite material affects its thermal conductivity.

1. Introduction

Copper and copper alloys are one of the important materials in the field of structural and engineering applications. They have excellent electrical and thermal conductivity and corrosion resistance and have many advantages such as easy processing and low cost. Therefore, they are widely used in electronic devices, high-energy facilities, aerospace,
transportation, and other fields [1, 2]. With the rapid development of industrial technology, modern industry has put forward higher and higher requirements for this type of material, requiring not only excellent electrical and thermal conductivity, but also high room temperature and high-temperature mechanical properties and good formability while maintaining high toughness during use [3].

Defects such as insufficient strength and wear resistance of copper and copper alloys limit its wider application. The current preparation methods of high-strength and high-conductivity copper alloys are mostly to improve the mechanical properties of materials under the premise of sacrificing conductivity to a certain extent [4, 5]. Compared with copper and copper alloys, copper-based composite materials can maintain the high electrical and thermal conductivity of the material while enhancing its mechanical properties [6]. A new type of high-strength and high-conductivity copper (alloy)-based composite material with excellent comprehensive performance has been developed, which is one of the hot research objects in material development with a wide range of application prospects [7].

As a typical one-dimensional nanomaterial, carbon nanotubes have attracted the attention of many researchers with their unique structure and excellent performance. Carbon nanotubes have a high aspect ratio and super mechanical properties (high strength and high rigidity), high electrical and thermal conductivity, low thermal expansion coefficient, strong acid and alkali resistance, and high-temperature oxidation resistance [8]. At present, the preparation of carbon nanotubes has become more and more perfect, and high-quality, high-yield carbon nanotubes have moved from the experimental stage to the application field.

Carbon nanotubes are considered to be an ideal reinforcing phase for the preparation of high-performance composite materials. Carbon nanotubes are added to metal substrates such as Cu, Al, Mg, Ti, etc. to improve the strength, hardness, wear resistance, and thermal stability of the metal [9]. However, due to the nanowire-shaped structure of the carbon nanotube itself and the chemical inertness of the surface, the carbon nanotube is very easy to agglomerate, especially when used as a reinforcement in a composite material, which often leads to the uneven performance of various parts of the composite material [10]. The preparation methods of copper-based composite materials mainly include powder metallurgy, composite casting, internal oxidation, liquid metal in-situ method, and mechanical alloying method. These preparation processes are mainly through the introduction of a high-performance second phase into the copper matrix to make up for the lack of mechanical properties of the copper matrix, so that the composite material can achieve the best match of mechanical and electrical properties. The main strengthening methods are dispersion strengthening, fine-grained strengthening, deformation strengthening, and solid solution strengthening [11, 12].

As the reinforcing phase of high-strength and high-conductivity copper-based composite materials, carbon nanotubes and copper matrix have achieved a perfect match in terms of mechanical properties and electrical conductivity [13]. The excellent mechanical properties of carbon nanotubes can make up for the lack of strength and hardness of the copper matrix at room temperature and high temperature. In terms of electrical conductivity, since the mean free path and electronic energy state density jointly determine the electrical conductivity of the material, the combination of the larger mean free path of carbon nanotubes and the higher electron density of the copper matrix can achieve breakthroughs in the application of composite materials in conductive applications [14–16].

Synthesizing carbon nanotube/copper composite materials through a reasonable preparation method is an effective method for simultaneously achieving the high-strength and high-conductivity properties of copper-based conductors [17]. In this article, according to the structural and performance characteristics of CNTs and Cu, a carbon nanotube/copper composite material is prepared by powder metallurgy. The preparation process is mainly divided into two stages: the powder mixing stage and the composite material curing and molding stage [18]. The powder mixing stage directly affects the uniformity of the CNT distribution in the composite material. Therefore, this article adopts the heteropolymerization liquid phase powder mixing method to realize the liquid phase mixing of carbon nanotubes and copper powder [19].

The dispersibility of the oxidized carbon nanotubes in the solution directly affects the uniformity of the liquid phase mixing powder. At the same time, the degradation of the CNT structural integrity caused by the oxidation process will also affect the mechanical, electrical, and thermal properties of the carbon nanotubes, which in turn affects the mechanical properties and electrical and thermal conductivity of composite materials [20]. Based on this, this article analyzes the mechanical, electrical, and thermal properties of the prepared composite materials; explores the effect of surface oxidation modification conditions of carbon nanotubes on the performance of copper-based composites; and tests and analyzes the effect of the volume fraction of CNTs on the properties of the reinforced composite material properties.

2. Materials and Methods

2.1. Experimental Materials and Reagents. In this article, two original carbon nanotubes with aspect ratios are selected. The carbon tubes are prepared by chemical deposition, and the copper powder is prepared by evaporation. The raw material parameters are shown in Table 1.

Chemical reagents include nitric acid (analytical purity, >99.5%, for surface treatment), absolute ethanol (analytical purity, >99.7%, for cleaning and as a solvent), and acetone (analytical purity, 66%, for cleaning).

2.2. Experimental Equipment and Methods. The experimental equipment includes the following: an analytical balance (used to weigh the mass of the sample), an ultrasonic cleaner (used for the dispersion of carbon nanotubes and
micron copper powder in absolute ethanol, the mixing of composite powders, and the cleaning of bulk samples), a vacuum drying box (used for the heating process of carbon nanotube oxidation modification and the drying process of carbon nanotubes and composite powder; the optimum temperature of oxidation modification of carbon nanotubes is 190°C and 220°C, and the drying temperature is 60°C), a spark plasma sintering furnace (for carbon nanotubes/ copper composite material sintering molding), manual press (used for the demolding process of carbon nanotube/copper composite block after sintering), an ion thinner (used for carbon nanotube/copper composite material transmission sample preparation), and so on.

2.3. Surface Oxidation Modification of Carbon Nanotubes. In this experiment, the acid steam oxidation method is used to oxidize and modify the carbon nanotubes, and at the same time, the carbon nanotubes are purified and functionalized. First, 300 mg of carbon nanotubes was weighed and placed in a self-made sand core glass container, then 3 mL of HNO3 was dropped into the 50-mL polytetrafluoroethylene hydrothermal reaction vessel, and then the abovementioned sand star glass container with carbon nanotubes was placed into it. The inner container of the hydrothermal kettle with HNO3 is put into the corresponding hydrothermal reaction kettle, sealed, and heated to a certain temperature (190°C, 220°C) in an oven and maintained for a certain reaction time. Under higher reaction temperature conditions, HNO3 is put into the corresponding hydrothermal reaction kettle, sealed, and heated to a certain temperature (190°C, 220°C) in an oven and maintained for a certain reaction time. Under higher reaction temperature conditions, HNO3 evaporates to form HNO3 vapor in a closed container. The sand core glass container can avoid direct contact between carbon nanotubes and liquid HNO3 and at the same time can promote the contact reaction of HNO3 vapor and carbon nanotubes to achieve acid evaporation oxidation modification. After the reaction, the oxidized carbon nanotubes are taken out of the reaction device and placed in a funnel filter device and directly filtered and washed with absolute ethanol several times. The cleaned carbon nanotubes are placed in a drying box at a temperature of 60°C. After drying under vacuum for 6 hours, the functionalized carbon nanotubes are collected. The acid steam oxidation process is shown in Figure 1.

3. Result

3.1. Conductivity of Carbon Nanotubes. In order to analyze the conductivity of CNTs under different oxidation treatment time conditions, this experiment made CNTs into thin films. The resistivity of the CNT thin films can be measured by the four-probe method, which reflects the conductivity of the corresponding CNTs. Table 2 shows the thickness of the CNT film and its resistivity test results.

When the oxidation treatment time is longer than 4 h, the thickness of the CNT film is very similar, but the thickness of the CNT film with the oxidation treatment time of 2 h is significantly larger. In the process of filtering the film, it is easy to agglomerate, resulting in the carbon nanotube film with more voids and insufficient density. Therefore, the film thickness is large, and the measured resistivity is much higher than that of the other three CNT films. For the film made of carbon nanotubes with an oxidation treatment time of 4–6 h, the resistivity of the film is basically only affected by the conductivity of the CNTs due to the similar thickness and the similar film structure. As the oxidation treatment time increases, the increase in the resistivity of the film indicates that the decline in the structural integrity of CNTs has led to the decline in its own conductivity.

3.2. Preparation of Carbon Nanotube/Copper Composite Material

3.2.1. Preparation of Composite Powder. In this experiment, the carbon nanotube/copper composite powder is prepared by the heteropolymerization liquid phase powder mixing method. First, a certain amount of and a certain amount of copper powder are ultrasonically dispersed in absolute ethanol for 50 minutes to obtain a carbon nanotube dispersion with a concentration of 1 g/L and a copper powder slurry with a concentration of 20 g/L. A certain amount of each is mixed in a water bath ultrasonic environment. As we mix, we place the copper powder slurry in an ultrasonic cleaner, disperse the carbon nanotubes, and add the copper powder slurry while stirring and mixing the surface. After stirring for 30 minutes, the mixture is removed and left to stand for some time at room temperature. The carbon nanotubes and copper powder are charged differently in ethanol, so they can undergo electrostatic self-assembly and co-precipitation under the action of electrostatic force to achieve particles with different densities. The supernatant liquid is completely transparent, indicating that there is no single carbon nanotube in the supernatant liquid. The carbon nanotubes and copper particles are fully mixed and settled. The supernatant liquid can be removed to obtain carbon. The nanotube/copper mixed slurry is directly placed in a vacuum oven and dried at a temperature of 60°C for 8 hours to obtain a carbon nanotube/copper composite powder. The preparation process of the composite powder is shown in Figure 2.

3.2.2. Composite Material Molding. In this experiment, the spark plasma sintering method is used to prepare carbon nanotube/copper bulk composites. Spark plasma sintering has a high heating rate. The sintering and pressurizing processes can be carried out at the same time. The plasma generated by the pulse current can make the sintering process proceed at a lower temperature. The sintering process is fast and clean. The resulting bulk composite material is high density. Figure 3 is a schematic diagram of the spark plasma sintering process. First, the carbon
nanotube/copper composite powder obtained by heterocopolymerization and mixing is placed inside the graphite abrasive tool. Graphite paper is placed in the graphite abrasive tool in advance to prevent the sample from sticking to the mold during the sintering process. The inner diameter of the abrasive tool is 28 mm. The composite powder is slightly shaken in the abrasive tool to ensure even distribution, compacted with a graphite indenter, checked to see whether the abrasive tool leaks powder, and then placed into the spark plasma sintering furnace after compaction. The corresponding heating, pressurizing, heat preservation, and cooling procedures are set to start pressing and sintering.

The parameters of the spark plasma sintering process are set as follows: the sintering temperature is 550 °C, the holding time is 5 min, the sintering pressure is 50 MPa, and the heating rate is 50 °C/min. In order to prevent the carbon nanotube structure from being damaged at high-temperature and affecting the performance of carbon nanotubes, this experiment selects a lower sintering temperature of 550 °C. Considering the maximum pressure strength that the mold can withstand, and at the same time, to ensure the density of the sample, the sintering pressure is set. The increase in holding time promotes the grain growth and the densification process of the sample, but too long holding time will destroy the carbon nanotube structure, so the holding time is set at 5 min. Increasing the heating rate will reduce the sintering time and is not conducive to the densification process. But at the same time, it will also accelerate the increase of current density, thereby increasing the excitation effect on the plasma and accelerating the sintering process. Therefore, the heating rate is set at 50 °C/min in this experiment.

3.3. Analysis of Mechanical Properties of Carbon Nanotube/Copper Composite Material. Figure 4 shows the tensile strength and hardness of pure copper samples prepared under the same conditions, which are 288 MPa and 66 HV. It can be seen from Figure 4 that the tensile strength and hardness of the composite material have been improved by different degrees compared with pure copper. The tensile strength and hardness increase with the oxidation treatment time. When the oxidation treatment time is higher than 4 h, the tensile strength and hardness of the composite material decrease with the increase of CNT oxidation treatment time. When the oxidation treatment time reaches 4 h, the tensile strength and hardness of the composite material prepared by CNTs of two diameters reach the maximum value. For composites made of CNTs with an oxidation treatment time of 2 h, due to the serious internal macroscopic agglomeration, the CNT agglomerated phase will act as a matrix weakness and cause the composite material to fail and fracture faster under tensile stress. The agglomerated phase also affects the load transfer in the composite, resulting in low tensile strength and hardness.

When the oxidation treatment time continues to increase, the structural integrity of the carbon nanotubes will be destroyed under strong oxidation. When the oxidation degree reaches a certain saturation value, the mechanical properties of the carbon nanotubes will be severely affected and its carrying capacity in the matrix will be affected. Therefore, the mechanical properties of composite materials decrease accordingly. Among them, the composite material prepared with 80 nm carbon nanotubes under the same oxidation treatment time exhibits higher dispersibility, and the CNT reinforcement phase also has higher structural integrity. Therefore, the strength and hardness of the composite material are higher than 15 nm CNT reinforced composite material. In summary, 80 nm CNTs with an oxidation modification time of 4 h have the highest mechanical properties. Its tensile strength is as high as 452.4 MPa, which is 1.6 times that of pure copper under the same preparation conditions, and its Vickers hardness reaches 127.4 HV, which is twice that of pure copper.

In order to further analyze the enhancement mechanism of carbon nanotubes, this experiment analyzed the surface micro-morphology and fracture morphology of the copper-based composite material prepared by 80 nm CNT oxidized for 4 h. According to the TEM grain morphology map, this experiment has performed statistics on the grain size of the composite material and pure copper, and the statistical results of the grain size are shown in Figure 5.

By comparing the statistical results of the grain size of the composite material and pure copper in Figures 5(a) and 5(b), it can also be concluded that under the action of CNTs, the
average grain size of the composite material is significantly lower than that of pure copper, and CNTs can strengthen the mechanical properties of composite materials through fine-grain strengthening. According to the high-resolution TEM morphology of the interface in the composite material, there is no gap at the interface between the carbon nanotubes and the copper matrix, and the two are completely wetted and tightly bonded under the action of the residual stress in the sintering process. The interface is clean and free of impurities, and the interface is strongly bonded which is conducive to the effective transfer of load between the carbon nanotubes and the matrix and can ensure the high load-bearing efficiency and effective reinforcement of the carbon nanotubes.

It can be seen from Figure 6(a) that the tensile strength of the CNT/Cu composite material first increases with the increase of the volume fraction of carbon nanotubes. This is because the strength of CNTs is much higher than that of the copper matrix. The addition of CNTs has a significant effect on the copper matrix. The strength of the composite material increases with the addition of CNTs. However, when the volume fraction of CNTs is higher than 4%, the tensile strength of the composite material begins to decrease. This is caused by the agglomeration phenomenon of CNTs. The agglomerated carbon nanotubes do not play a reinforcing role, but also act as a weak phase in the matrix and act as a source of cracks when the composite material is loaded to cause damage and fracture of the material. When the volume fraction of CNTs is higher than 5%, the tensile strength of the CNT/Cu composite material decreases rapidly. According to the observation results of the metallographic microstructure, the CNT agglomerated phase size in the composites with CNT volume fractions of 7% and 10% is significantly larger, and the number is significantly larger. The composite material is prone to cracking at the large-size agglomerated phase under tensile stress, resulting in early failure of the material.

Figure 6(b) is a graph showing the change of the Vickers hardness of the composite material with the volume fraction of CNT. The changing trend for Vickers hardness and tensile strength is similar. When the CNT volume fraction is lower than 4%, the Vickers hardness of the composite material increases with the increase of the CNT volume fraction due to the reinforcement of CNTs. As the volume fraction of CNT increases, when the volume fraction of carbon nanotubes increases to 5% and above, the composite material begins to agglomerate, and the agglomerated phase may form a network structure around the matrix grains, forming a weaker interface bonding area. Under the action of external stress, these positions are more prone to grain slip and material deformation. Therefore, the composite material exhibits a lower Vickers hardness when the CNT volume fraction is higher than 5%.

3.4. Conductivity Analysis of Carbon Nanotube/Copper Composite Material. Figure 7 shows the electrical conductivity of the CNT/Cu composite under different oxidation
treatment time conditions. The test results are in accordance with the international annealing copper standard. The experiment also tests the electrical conductivity of the pure copper sample, and the result is 98% IACS. Compared with the pure copper samples prepared under the same conditions, the electrical conductivity of the composite material has decreased to different degrees. This may be due to the following two reasons: the order of magnitude of the resistivity of the carbon nanotubes is $10^{-3} \Omega \cdot \text{cm}$, while the order of magnitude of electrical resistivity of the pure copper is $10^{-6} \Omega \cdot \text{cm}$, and the electrical resistivity of the copper matrix is one-thousandth of that of the carbon nanotubes. Therefore, adding carbon nanotubes as a reinforcing phase will reduce the electrical conductivity of the copper matrix to a certain extent. Compared with pure copper, the carbon nanotubes/copper composite material has a smaller grain size, so there are more grain boundaries inside the material. Since carriers are easily scattered at the grain boundaries, the presence of the grain boundaries will affect the internal charge transfer of the material, so the conductivity of the composite material is reduced.

It can be seen from Figure 7 that the electrical conductivity of the composite material first increases with the increase of the oxidation treatment time of CNTs and reaches the highest value at the oxidation treatment time of 4 h. Then, the electrical conductivity of the composite material decreases with the increase of the oxidation treatment time. First of all, for the composite material prepared by oxidatively modified 2 h CNTs, because there are more agglomerated phases inside, the agglomerated phase can reduce the conductivity of the composite as the center of carrier scattering. Due to the poor dispersion and many agglomeration phases, the conductivity of the composite material is generally lower than that of the composite material prepared by 80 nm CNTs. Second, in view of the phenomenon that the conductivity of the composite material decreases with the increase of the oxidation treatment time, when the oxidation time exceeds 4 h, the conductivity of carbon nanotubes themselves decreases as their structural integrity decreases.

Therefore, although the uniformity of the dispersion of CNTs in the composite material is improved, in the oxidation process, the conductivity of the composite first increases and then decreases, and the overall conductivity of the composite is lower than that of pure copper. The 80-nm carbon nanotubes with the oxidation treatment time of 4 h have the highest mechanical properties, while the electrical conductivity also reaches the maximum 91% IACS. The experiment has compared the results with the electrical conductivity of CNT/Cu composites prepared by other methods and some copper alloys. For comparison, the comparative results are shown in Table 3. In this experiment, the conductivity of the CNT/Cu composite prepared by the method of reasonably controlling the surface oxidation modification process of CNTs, combining heteropolymer powder and spark plasma sintering, is significantly better than other methods. Due to the uniform distribution of the structurally complete reinforcing phase in the matrix and the close bonding of the composite material interface without impurities, these factors greatly reduce the interface resistance caused by the electronic boundary scattering of the internal interface of the composite material, and thus the reduction of the conductivity of the composite can be prevented to the greatest extent. At the same time, the excellent electrical conductivity of the carbon nanotube reinforcement phase also makes the electrical conductivity of the composite material significantly better than other copper alloys. Table 3 also shows the mechanical properties of some composite materials and copper alloys. The comparison results show that the optimized CNT/Cu composite material has high tensile strength, hardness, and electrical conductivity at the same time and realizes the comprehensive performance of high strength and high conductivity.
Figure 5: Material grain size distribution histogram ((a) carbon nanotube/copper composite material; (b) pure copper grain).

Figure 6: The tensile strength and Vickers hardness of carbon nanotube/copper-based composites change with the volume fraction of carbon nanotubes ((a) tensile strength; (b) Vickers hardness).

Figure 7: The electrical conductivity of carbon nanotube/copper composite material changes with the time of carbon nanotube oxidation treatment.
Figure 8 shows the relationship between the electrical conductivity of the CNT/Cu composite and the volume fraction of CNT. Since the conductivity of CNTs itself is lower than that of pure copper, the addition of CNTs may reduce the conductivity of the composite to a certain extent. In addition, the voids generated by the weakly bonded interface and the agglomeration of carbon nanotubes will also cause carrier scattering and affect the electrical conductivity of the composite material. Therefore, when the CNT volume fraction is higher than 3%, as the amount of CNTs increases, the agglomeration of CNTs increases, the interface bonding between CNTs and the matrix becomes weaker, and the electrical conductivity of the composite material decreases in a linear trend. For composite materials with a volume fraction of CNTs of 1%, due to insufficient filling of the voids of copper powder by CNTs, the density of the composite materials is not improved to a greater extent than that of pure copper. While there are CNTs that reduce its electrical conductivity in the composite material, there are also certain gaps. Two reasons affect the electrical conductivity of the CNT/Cu composite material at the same time, making the conductivity of the CNT/Cu composite with a CNT volume fraction of 1% lower than that of the CNT/Cu composite with a CNT volume of 3%.

3.5. Analysis of Thermal Conductivity of Carbon Nanotube/Copper Composite Material. Figure 9 shows the thermal conductivity test result of the copper-based composite prepared by 80 nm CNT. The thermal conductivity test result of the pure copper sample under the same preparation conditions is 346.5 W·m⁻¹·k⁻¹. It can be seen from the figure that the thermal conductivity of different CNT-enhanced CNT/Cu composites is lower than that of pure copper samples. In the heat transfer process of the composite material, the conduction of heat in the copper matrix is controlled by electrons, and the conduction of heat in the carbon nanotubes is controlled by photons. The photon-electron coupling conducts heat at the carbon nanotube/copper composite interface, and the interface position of the composite material is more prone to energy scattering. Due to the small size of carbon nanotubes, there are a large number of interfaces in the composite material, which affects the heat transfer. The existence of interface thermal resistance greatly reduces the thermal conductivity of the composite material. In addition, the presence of grain boundaries will also cause a decrease in thermal conductivity. The composite material matrix has more grain boundaries than pure copper due to grain refinement, which affects its thermal conductivity. The thermal conductivity of the composite material prepared by CNT with an oxidation modification time of 2 h has the most serious decline. The voids formed inside the agglomerates also affect heat transfer. For composite materials prepared from CNTs with a better dispersibility and oxidation treatment time of 4.5 hours, the damage to the carbon nanotube structure caused by the long-term oxidation treatment will affect its own thermal

| Synthetic method (alloy type) | Tensile strength (MPa) | Vickers hardness (HV) | Electrical conductivity (%IACS) |
|-----------------------------|----------------------|----------------------|-------------------------------|
| Present study               | 451                  | 123                  | 91                            |
| CNT/Cu composites           | Electroless deposition + SPS | —                  | 76                            |
|                             | Electrodeposition    | —                    | 88                            |
| Flake powder metallurgy     | —                    | —                    | 75                            |
| Cu-based alloys             | Cu–Mg–Ca            | 540                  | 74.3                          |
|                             | Cu–Fe–P             | 464                  | 70.7                          |
|                             | Cu–Cr               | 458                  | 77.5                          |
|                             |                      |                      | 71.1                          |

Table 3: Comparison of mechanical properties and electrical conductivity of carbon nanotube/copper composites prepared by different methods and different copper alloys.
4. Conclusion

(1) The tensile strength and hardness of composite materials first increase with the increase of CNT oxidation treatment time and then decrease with the increase of oxidation treatment time. When the oxidation treatment time is 4 h, CNTs can be uniformly dispersed in the matrix while maintaining good structural integrity and bearing capacity. The tensile strength of the composite material prepared with 80 nm CNTs is as high as 452.4 MPa, which is 1.6 times that of pure copper, and the hardness is as high as 127.4 HV, which is 2 times that of pure copper.

(2) The electrical conductivity of the composite material increases first with the increase of the CNT oxidation treatment time and then decreases with the increase of the oxidation treatment time. The electrical conductivity of the composites prepared by CNTs with two diameters reaches the maximum when the oxidation treatment time is 4 h. The conductivity of 80 nm CNTs reinforces composite material is significantly better than 15 nm CNTs due to the high reinforcement dispersion. The conductivity is up to 91% IACS, which is 95% of the pure copper sample. The electrical conductivity is significantly better than that of copper alloys prepared by other methods.

(3) The thermal conductivity of composite materials first increases with the increase of CNT oxidation treatment time and then decreases with the increase of oxidation treatment time. The thermal conductivity of carbon nanotubes with an oxidation treatment time of 2 h decreases most significantly, indicating that the existing interface and the thermal resistance of the agglomerated phase in the CNT/Cu composite are the main factors affecting the thermal conductivity of the composite. When the oxidation treatment time is 4 h, the thermal conductivity of the composite reaches its best.

Data Availability

The figures and tables used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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