Preparation and Application of Ultrafine Copper Powder

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Abstract. Ultrafine copper powder has the excellent characteristics of both copper and ultrafine particles and has been widely used in industry. Different fields have different requirements for ultrafine copper powder, so various preparation methods have been derived. In this paper, the characteristics of electrolysis, liquid phase reduction, hydrothermal method and polyol method are analyzed. Some new preparation methods with novel ideas are also enumerated. Also, the applications of ultrafine copper powder are described. In electronic industry, ultrafine copper powder can be used in preparing conductive paste of multilayer ceramic capacitor (MLCC) and conductive ink. In catalysts, copper powder can catalyze the reaction alone, can be loaded on other substances and form alloys with other metals for catalysis. In antibacterial materials, copper nanoparticles can distort the DNA of bacteria and interrupt its biochemical process. Finally, the application trend of ultrafine copper powder is prospected, which is helpful to develop new synthesizing methods and applications of ultrafine copper powder.

Keywords: Ultrafine Copper Powder; Preparation; Application.

1. Introduction

Copper has been used for a long time. As early as prehistoric times, copper was excavated and used to make weapons and articles. It is the traditional bulk copper material. However, the traditional bulk copper material is easy to rust in humid air, its hardness is poor and its manufacturing process is complex, limiting its application in some important fields. Therefore, ultrafine copper powder with unique chemical and mechanical properties has gradually attracted the attention of researchers. Like other nanomaterials, copper nanoparticles have some special effects. And copper itself has excellent characteristics such as ductility, conductivity and thermal conductivity. Ultrafine copper powder is widely employed in catalysis, electronics, optics, energy and powder metallurgy industry.

According to the requirements of copper powder properties in different fields, a variety of methods for preparing copper powder have been derived, which can be divided into physical, chemical and biological methods [1]. Physical method can be subdivided into mechanical pulverization method, atomization method, physical vapor deposition method and other methods. Its characteristics are that it does not involve chemical reactions, its principle is simple and it has been maturely applied in industry. However, it is hard to control the structural performance of the powder. Chemical method is the research focus of preparing ultrafine copper powder at present, including electrolysis method, liquid phase reduction method, hydrothermal method and polyol method, among which electrolysis method has been maturely applied in industry. The characteristic of chemical method is that carefully changing the process parameters can control the performance of the powder and the particle size can reach nanoscale. However, chemical method has some disadvantages. The mechanism of some chemical reactions is complex. Some chemical reagents are toxic to the human body or do harm to the environment. The cost of chemical reagents, equipment and pollutant disposal can be very high. Therefore, simplifying the process and reducing the use of toxic and harmful reagents are the research trends of superfine powder preparation by chemical method. Biological method is using plant extracts or microorganisms to prepare ultrafine powder method. The two principles are different: some chemical substances in plant extracts can react with metal salt precursors in liquid phase, the principle is similar to liquid phase reduction method, while the other one is using microbial biochemical reactions to change precursors to ultrafine powders. The advantages of biological method are low cost and reducing the use of dangerous chemicals. However, the research on its reaction mechanism is not in-depth enough and the biological method is still in the laboratory research stage.

Ultrafine copper powder possesses the characteristics of both copper and nanoparticles. Also, different preparation methods can synthesize the powder that can meet the requirements of different fields. Atomization is one of the most commonly used methods in physical method [2]. The ultrafine copper powder prepared by this method performs well in molding and preservation time, and can be used in powder metallurgy and friction materials. But atomized copper powder is easy to be oxidized in humid air, and antioxidant treatment is needed in the later stage. The ultrafine copper powder prepared by chemical method has the following properties. It has small particle size, spherical shape, good dispersion and narrow particle size distribution, which can be applied to conductive paste, conductive ink and battery electrode in the electronics industry. With more pores, the specific surface area increases and the reactivity is higher, making the copper powder used in catalysis. The copper powder synthesized by biological method is often used to prepare antibacterial materials, which can reduce the influence of other chemicals on the properties of antibacterial materials and protect the environment.

In this paper, the characteristics and applications of different preparation methods of ultrafine copper powder are introduced. And its research trend is summarized, hoping to be helpful for developing new preparation technology and broadening application fields.

2. Different preparation methods for ultrafine copper powder

2.1. Electrolysis

Electrolysis method is to electrolyze the solution or molten salt containing metal ions in an electrolytic cell to obtain the required metal powder. The advantages are the maturity of the process, including the wide availability of raw materials and the simultaneous preparation and purification of metal powders. Its disadvantages are high power consumption and high cost. In the traditional electrolysis method, copper powder needs to be scraped off from the cathode plate every 10~20 minutes to prevent the particles from growing up, which greatly increases the labor intensity [1]. Therefore, some researchers tried to improve this method. For example, Orhan et al. used rotating cylinder electrodes to efficiently prepare ultrafine copper powder [3].

The raw materials of copper powder prepared by electrolytic method are widely available. Copper salt can not only use general copper salt precursor, but also comprehensively use waste devices. The electrolyte can choose acid, alkali and ionic liquid. Deng et al. electrolyzed waste circuit board and obtained the particle size of about 4.9 μm, high purity, good oxidation resistance and circular ultrafine copper powder [4]. Wu et al. used the leaching solution obtained by leaching waste circuit board with ammonia solution as the electrolyte for electrolysis, and obtained dendritic micron Cu powder with high purity [5]. Ke et al. obtained dendritic micron Cu powder with good oxidation resistance by using copper as anode, titanium sheet as cathode and DES ionic liquid as electrolyte [6].

The key of electrolysis is the setting of process parameters. Orhan et al. also investigated the influence of parameters on the performance of copper powder, such as current density, copper ion concentration, electrode rotation speed and electrolysis temperature [3]. The reaction mechanism of electrolysis is also one of the research hotspots. Popov et al. started with experiments and then carried out mathematical modeling to systematically study the how parameters affect the structural performance of copper powder [7-10]. Saremi et al. focused on the oxidation resistance and corrosion resistance of copper powder prepared by AC electrolysis [11]. Yue et al. studied the surface structure of electrolytic copper powder by using non-ionic surfactants [12].

2.2. Liquid phase reduction

Liquid phase reduction method reacts reducing agents with metal ions in solution to obtain the required ultrafine powder. Hydrazine hydrate, ascorbic acid and glucose are commonly used. Its advantage lies in easy access to raw materials and simple operation of equipment. However, with high chemical activity, copper powder is easy to agglomerate and oxidize in the preparation, so it is generally necessary to add surfactants in the solution to prevent this situation.

Liquid phase reduction method can be divided into one-step and two-step method. In the one-step method, copper ions are directly reduced to copper powder in solution by using reductants with certain reducing power. In the two-step method, the copper salt is first reacted to form an intermediate (such as copper oxide or cuprous oxide), and then the intermediate reacts with the reducing agent to form copper powder. Therefore, the two-step method can control the reaction better. Wu used $CuSO_4$ as the precursor to prepare intermediate $Cu(OH)_2$, then further reduced the intermediate to copper powder and applied it in multilayer ceramic capacitors (MLCC) [13]. Wen et al. prepared ultrafine copper powder by one-step and two-step method respectively [14]. The results showed that the ultrafine copper powder synthesized by two-step method had better monodispersity and more uniform particles.

2.3. Hydrothermal method

Hydrothermal method is a derivative of liquid phase reduction method. Hydrothermal method is a method in which water is used as the solvent and the powder is dissolved and recrystallized in the closed system at high temperature and pressure, which is quite different from the methods used at room temperature and pressure. The advantages of this method are that it can dissolve the insoluble material in water and the grains obtained by the reaction are well-developed, evenly distributed, small in size and good in dispersion, which is especially suitable for the preparation of ceramics. Hu et al. prepared ultrafine copper powder with high crystallinity and good dispersion under hydrothermal conditions using $CuSO_4$, NaOH and formaldehyde as raw materials [15].

The disadvantages of hydrothermal method are that under high temperature and high pressure, the reaction kettle is easy to explode and hurt people and some reaction reagents are toxic and may cause pollution, so extra care should be taken when preparing powder by hydrothermal method.

2.4. Polyol method

The polyol method was proposed by Fievet, Lagier and Figlarz in the 1980s [16]. It has the following advantages. Polyol can play the role of solvent, reducing agent and dispersant at the same time, which is conducive to controlling the structural performance of particles. The prepared powder surface is coated with a layer of organic film so that the powder has good antioxidant performance. The process conditions and equipment are simple, the reaction temperature is not high and easy to control. Polyols have various kinds and strong adaptability of raw materials. Different process routes can be designed according to different solution systems and target products, and by-products are easy to be comprehensively utilized [17].

However, the reducing ability of polyols is weak, and the reaction time is too long or the reaction product is not pure. Therefore, sometimes auxiliary reducing agents and surfactants need to be added to improve the reaction efficiency. Common auxiliary reducing agents are sodium phosphite, ascorbic acid, hydrazine hydrate, sodium borohydride (potassium) and sodium citrate. As for surfactants, PVP is the most commonly used. Engels et al. reacted the ethylene glycol solution of PVP with $CuSO_4$, $Cu(CH_3COO)_2$, $CuCl_2$ respectively, adding auxiliary reducing agents (hydrazine hydrate, sodium hypophosphite or sodium borohydride) in the reaction, and studied the effects of the types of auxiliary reducing agents on the chemical reactions in the solution and the properties of copper powder [18]. Finally, the ultrafine copper powder with good oxidation resistance was obtained. Park et al. prepared ultrafine copper powder with $CuSO_4$, diethylene glycol, PVP and sodium hypophosphate as raw materials, and analyzed the effect of sodium hypophosphate on the reaction [19].

Some researchers also use polyols without additives to prepare ultrafine copper powder, which simplifies the process, reduces the risk of reaction and prevents the introduction of impurities. Sinha et al. reacted CuO, $Cu(CH_3COO)_2$ and $Cu(OH)_2$ with glycerol to prepare ultrafine copper powder with submicron particle size and good monodispersity [20]. Carroll et al. reacted $Cu(CH_3COO)_2$, $CuCl_2$, $Cu(OH)_2$ with EG, DEG, and TEG respectively to produce copper powder with different shapes [21].

Since the research of polyol method is still in the laboratory stage and each copper precursor reacting with a different polyol is a specific case, researchers need to study the reaction mechanism in depth. At present, the reaction mechanism between EG and various copper salts is studied. Teichert et al. investigated the effect of EG reduction reaction with different copper salts in detail, and they found that the nature of the anion itself greatly affected the reaction [22]. $CuCl_2$ and $CuSO_4$ are not suitable for the preparation of copper powder directly and the reaction conditions need to be improved. The reason is that $CuCl_2$ will be converted into complex or monovalent copper instead of elemental copper, while $CuSO_4$ will be converted into a mixture of Cu and Cu_2O when directly reacting with EG. $Cu(NO_3)_2$ reacts with EG at low temperature to produce Cu_2O and toxic gas NO. At high temperature, elemental copper can be obtained, but it is easy to be oxidized. $Cu(OH)_2$ reacts with EG at low temperature to form a complex and at high temperature to produce elemental copper, but the agglomeration is serious. $Cu(CH_3COO)_2$ reacts with EG at low temperature to form a complex and only elemental copper can be obtained at high temperature.

2.5. Other methods

In microemulsion method, the pre-reaction body solution is uniformly dispersed in the liquid phase which is insoluble with it to form an emulsion. After the reaction, the precipitate is separated, the surfactant and oil on the surface are removed, and then the ultrafine powder is obtained by drying. It is easy to control the reaction, uniform particle size and good dispersion of powder particles. Its disadvantages are that emulsifier and oil consumption is large, production is small and industrialization is difficult to achieve. As a result, it is still in the laboratory research stage. Chen et al. prepared ultrafine copper powder by microemulsion method, reacted copper sulfate pentahydrate with sodium borohydride to obtain spherical ultrafine copper powder and recycled surfactant and organic solvent to reduce the cost [23].

In sputtering method, two pieces of metal are placed in argon in parallel, and hundreds of volts are applied, so that the metal atoms on the surface of the cathode are evaporated and aggregated to form high purity ultrafine powder. Kim et al. prepared ultrafine copper powder by sputtering method and systematically characterized the surface structure and oxidation resistance of copper powder [24]. Electric explosive wire method is to heat the metal wire under the current of 500~800 kA. After the wire is broken, the high voltage discharge will make the molten metal heated and evaporated and settle into ultrafine powder under the inert atmosphere. Its advantages are high production efficiency and uniform particle size distribution. Using 0.1 mm in diameter and 74 mm in length copper wire as raw material, Li et al. prepared ultrafine copper powder with a diameter of 15~75 nm by electric explosive wire method [25].

Plasma method is to use plasma to evaporate metal to form gas, physical or chemical reactions, and finally condense and grow into copper powder. It is fast to prepare ultrafine copper powder by this method. Jin et al. took basic copper carbonate as raw material and added hydrogen into the reactor (to convert it into hydrogen plasma) for reduction reaction and the spherical submicron copper powder was obtained [26]. The methods above have novel ideas and high production efficiency, but they are still in the laboratory research stage, and researchers need to conduct further research on the reaction mechanism and performance control.

3. Applications

3.1. Electronic industry

Since the 1990s, the electronic industry has developed rapidly, which has driven the development of the ultrafine powder preparation and application. However, as the price of precious metals continues to rise, which makes the production of electronic products more expensive, researchers are trying to produce ultrafine powders with cheaper base metals instead of precious metals. As an alternative to superfine precious metal powder, superfine copper powder has been widely used in MLCC, integrated circuit technology, battery, conductive ink, conductive adhesive and other fields.

The application progress of MLCC ultrafine copper powder is as follows. MLCC is made of ceramic dielectric films with printed electrodes stacked in a dislocated way, and a ceramic chip is formed by high-temperature sintering and then a metal layer is sealed at both ends of the chip to form a structure similar to a single stone, so it is also called a single stone capacitor. Electrode is an important part of MLCC, which is made of conductive paste sintered at high temperature. The conductive paste is mainly composed of metal powder, glass powder and organic carrier, and its composition determines its performance. The metal powder accounted for 75% of the conductive paste, which mainly plays the role of conduction. Although silver has the best conductivity among metals, it is prone to electron migration under the action of electric field, which makes the conductivity of MLCC decrease and the cost is high. However, copper is second only to silver in electrical conductivity among metals, with extremely low resistivity and high melting point, which is not easy to occur electron migration and has no effect on the dielectric properties of ceramics. Therefore, copper is cheap and easy to obtain, making it an ideal metal for preparing conductive paste. MLCC copper powder needs to meet the following requirements: (1) Under the oxidizing atmosphere sintering, copper powder is easy to oxidize, so copper powder is required to have good oxidation resistance, high crystallinity and moderate specific surface area. (2) With the progress of technology, the dielectric layer and electrode layer of MLCC become thinner, and the diameter of metal powder required for the thickness of 2~3 μm inner layer is between 200 and 700 nm. (3) The powder should be spherical or spherical and the particles are uniform, which is conducive to the uniform dispersion of the powder in the slurry, tiling to form an electrode layer, and good contact of metal particles after sintering. (4) High vibration density is conducive to the formation of uniform thickness electrode layer [27]. Wu et al. prepared ultrafine copper powder for MLCC with good oxidation resistance by liquid reduction method, and the terminal electrode prepared with this ultrafine copper powder had a good connection effect with the chip [13].

Ultrafine copper powder has the advantages of low sintering temperature, small particle size, good electrical conductivity and low cost, which can be used to prepare conductive ink. Zhang et al. prepared ultrafine copper powders with good oxidation resistance and narrow particle size distribution by polyol method and applied them to the preparation of conductive inks and the assembly of integrated circuits [28-29], as shown in Figure 1. Tang et al. investigated how various technological parameters on the performance of Cu powder while preparing copper conductive ink [30].



Figure 1. Printed Cu pattern [29]

3.2. Catalysts

Due to volume effect, surface effect and quantum size effect, ultrafine copper powder has more pores and large specific surface area, which contributes to its high surface activity and excellent catalytic performance. In addition, copper catalyst has small particle size, good oxidation resistance and simple process, which can be used in a variety of catalytic reactions. According to the

characteristics of the catalyzed substance, copper powder can be used to catalyze the reaction alone, can be loaded on other substances and form alloys with other metals for catalysis.

Lee et al. studied the catalytic capacity of copper [31]. They prepared ultrafine copper powder with good oxidation resistance using CuSO4, ethylene glycol, PVP, sodium hypophosphate and ascorbic acid as raw materials. They first studied the catalytic capacity of copper powder for 4-nitrophenol reduction at different temperatures. The whole process of the reaction was characterized by UV-VIS. The results indicated that the absorption peak changed significantly in the presence of some copper nanoparticles and NaBH4, indicating that 4-nitrophenol first changed into p-nitrophenol sodium and then into p-aminophenol in the reaction. Secondly, the electrocatalytic effect of nano-copper on nitrite was studied. They used cyclic voltammetry to conduct experiments. By observing the changes of current waves, it can be seen that GCE/Nf/CuNPs can promote the electrocatalytic reaction. This provides technical support for the preparation of electrochemical sensors for nitrite detection.

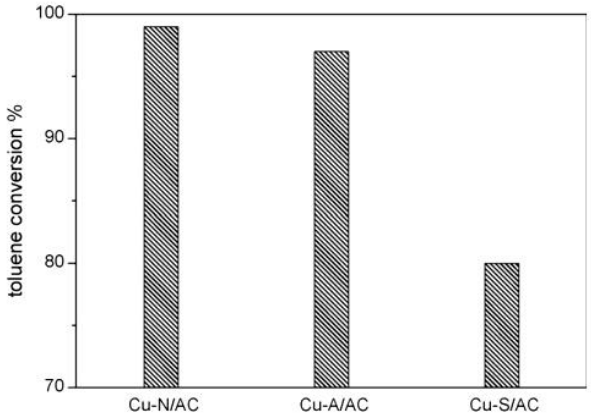


Figure 2. The effect of precursors on toluene conversion [32]

Copper nanoparticles loaded with carbon are common in catalysis field. Lu, Wey and Chuang et al. used activated carbon or carbon nanotubes as substrates to prepare a carbon-supported copper catalyst [32-34], as shown in Figure 2, 3 and 4. For the catalytic oxidation reaction of toluene, copper catalyst prepared by copper nitrate had the highest catalytic efficiency (toluene conversion rate of 98% when catalytic temperature was 270 ℃). For the reaction between CO and O_2, the catalyst prepared with a microwave power of 700 W and no PVP was the best, with a CO conversion efficiency of 41.3% when catalytic temperature was 150 ℃. In the catalytic removal of NO from NH_3, the copper nanoparticles prepared by microwave polyol method combined with activated carbon pretreated with HNO_3 had the best catalytic effect, and when the ratio of NH_3 to NO was 2:1, the conversion rate of NO can be close to 100%.

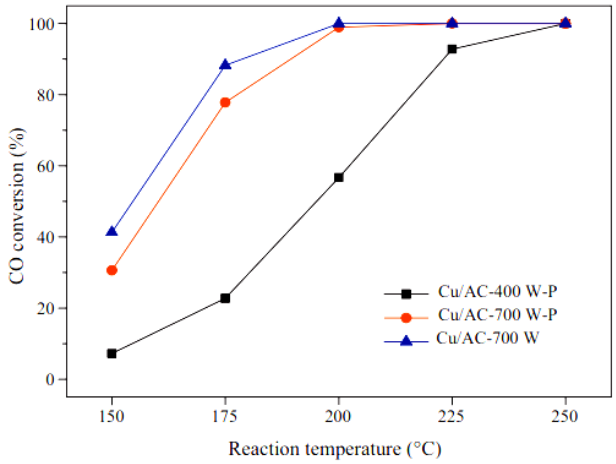


Figure 3. The effect of microwave power and PVP on CO conversion [33]

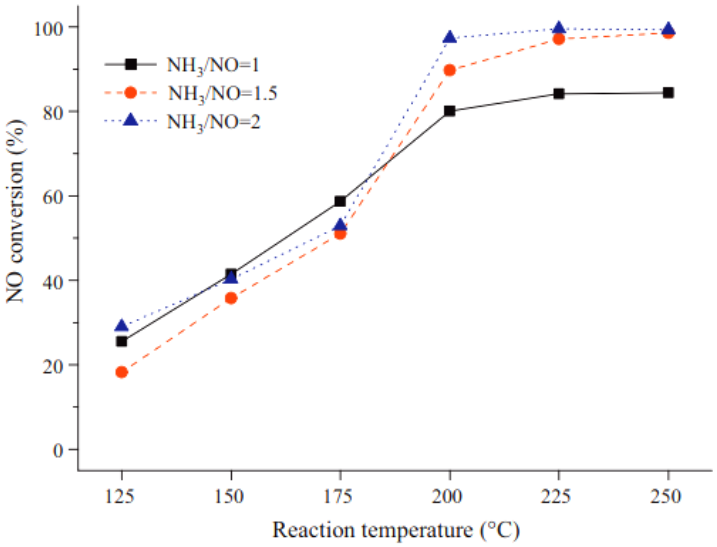


Figure 4. The effect of the ratio of NH_3 and NO on NO conversion [34]

3.3. Antibacterial materials

Ultrafine copper powder is also used in biological applications. Among them, the preparation of antibacterial materials is more reported. Although the antibacterial ability of nano-copper is slightly weaker than that of nano-silver, nano-copper has low cost and is easy to prepare, so nano-copper antibacterial materials have gradually become a research hotspot. The antibacterial mechanism of copper nanoparticles is that metal ions released by particles may enter the bacteria. After that, metal ions will interact with DNA, distort DNA and interrupt its biochemical process [35]. This is the oxidative stress effect. Thiruvengadam et al. used green chemical method to prepare Cu nanoparticles [36]. After testing, the antibacterial rate of Cu nanoparticles against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* was more than 70%, while the antibacterial rate of plant extract against these bacteria was less than 70%, indicating the antibacterial efficiency of Cu nanoparticles was good. Suresh et al. prepared nano-copper antibacterial materials and cultured Gram-bacteria on the antibacterial materials. By observing the morphological changes of the bacterial film by SEM, it can be seen that there was no bacterial growth on the membrane [37]. By contrast, in the control group, the bacterial growth was good. It indicated that the antibacterial effect of nano-copper antibacterial materials was good. Yano et al. prepared copper nanoparticles by polyol method and studied their inhibitory effect on *Escherichia coli* [38], as shown in Figure 5. They divided bacterial cultures into control group 1 (blank group), control group 2 (culture medium containing ethylene glycol) and experimental group (culture medium containing both nano-copper and ethylene glycol). They found that the number of bacteria in control group 1 and 2 increased explodes within 24 hours, while in experimental group, the number decreased to zero within 6 hours. Even if the culture medium containing nano-copper was diluted 10 times, the experimental effect could still be obtained, indicating that nano-copper has very strong antibacterial properties.

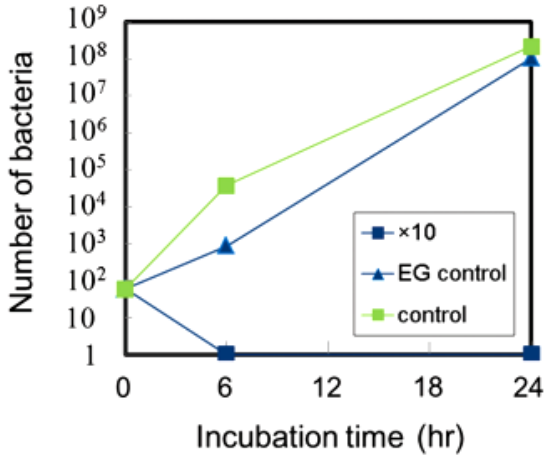


Figure 5. The change of the number of bacteria in 24 h [38]

3.4. Other applications

In lubricants, ultrafine copper powder is dispersed in them to form a protective layer, which can effectively reduce the friction force. Nanoparticles can be filled in scratches on the device surface, significantly reducing wear and extending the device life.

Copper has unique optical properties, so researchers are using it to make optoelectronic materials. Al-Sagheer et al. studied the optical applications of copper powders. Using copper acetate and polyvinyl alcohol as raw materials and adding purslane extract as auxiliary reducing agent, they prepared ultrafine copper powder [39]. The optical and luminescence characteristics of copper powder were characterized, which provided technical support for the development of optical remote sensing, waveguides, transmitting antennas and optical filters.

4. Conclusions

The preparation method of ultrafine Cu powder varies with the practical application requirements in different fields, but usually requires high purity, high oxidation resistance, better dispersion, uniform particle size distribution and specific morphology. Chemical method has been widely applied to prepare ultrafine copper powder. The key lies in how to change the process parameters to control the performance of copper powder. Among the chemical methods, electrolysis has been maturely applied in industrial production. China has also formulated the quality standard of electrolytic copper powder. Liquid phase reduction method is a hot research topic because of easy availability of raw materials and its simple process. Hydrothermal method and polyol method have novel ideas and good application prospects. However, due to the lack of in-depth research on the reaction mechanism, they are still in the laboratory research stage.

With the outstanding properties of both copper and nanoparticles, ultrafine copper powder has been employed in electronics, catalysis, antibacterial, photoelectric and lubrication materials. The application trend of ultrafine copper powder is that: (1) Combining the advantages of various ultrafine copper powder preparation methods to produce copper powder with better performance and meet the requirements of related fields. (2) Simplifying the process and reducing the use of toxic chemical reagents to prepare ultrafine copper powder with better performance. (3) Exploring potential excellent characteristics of ultrafine copper powder and broadening their application fields.

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