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Growth of single-crystalline particles of metallic copper

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ABSTRACT

Most of ultrafine particles of metallic copper reported so far were of polycrystalline structures. Here, some ultrafine particles of metallic copper of single-crystalline structure were synthesized in gas phase. Some mixtures of a raw copper powder (about 79 μm) and sodium chloride powder were used as the precursor materials. The materials were chlorinated by dry chlorine at 400 °C. Some anhydrous eutectics composed of copper chlorides and sodium chloride were thus obtained. The eutectics were first heated in situ up to 900 °C and then carried to a gas space by evaporation using a flowing Argon, where they met H_2 and were reduced to metallic copper particles. It was found that all these copper particles prepared were of single-crystalline structure irrespective of the molar ratio of raw copper and sodium chloride. When the molar ratio of NaCl to Cu in the precursor materials was 1 to 3, some dispersed octahedral particles of single-crystalline copper with an average size of 776 nm were prepared. However, when the ratio was increased to 4 to 1, some dispersed spherical particles of single-crystalline copper with a size of 92 nm were obtained. No impurities from the two shapes of copper particles were detected. The mechanisms involved in controlling the shape and size of copper particles were proposed.

1. Introduction

Compared with the usual bulk metal of polycrystalline structure, the bulk metal of single-crystalline structure have the advantages of low transition temperature of plastic and brittle and having no grain boundary destruction at high and low temperatures. These properties significantly improve the stability, reliability and working life of the metallic parts [1]. Thus, the bulk metals of single-crystalline structure are widely used in electronics, electrical, mechanical, instrument manufacture, and nuclear power industry etc.

Compared with the single-crystals of bulk metals, the single-crystals of ultrafine particles of metals have scarcely been reported so far. Most of ultrafine particles of metallic copper reported so far were of polycrystalline structures, the ultrafine particles of metallic copper having single-crystal structure were rarely reported [2,3]. At present some ultrafine metal particles of high quality, such as the single-crystal of ultrafine copper particles, are needed for 3D printing. In addition, the ultrafine copper particles of high quality are currently used as the inner electrode of multilayer ceramic capacitor (MLCC) [4]. The copper nanoparticles are also expected to be used for high temperature solders required for high power density of semiconductor devices used for hybrid electric vehicles or renewable energy sources [5]. The successful synthesis of ultrafine copper particles will lead to an increased use of copper powder in many industries, such as electronics, lubrication, optics, filler modification of polymers, antibacterial and so on, which are currently dominated by the use of ultrafine particles of gold, silver, and platinum group metals [6,7]. However, the synthesis of not oxidized, dispersed, ultrafine copper particles has been proved to be very difficult, partially because of the propensity of ultrafine copper particles for oxidation and agglomeration under the reaction temperatures. Owing to the high oxidation reactivity of ultrafine copper particles, some strong reducing agents such as toxic hydrazine in combination with an elevated reaction temperature are required to reduce a typical copper precursor (e.g., cupric sulfate, nitrate, acetate, chloride) to metallic copper [8]. In addition, the ultrafine particles of metallic copper freshly prepared tend to be oxidized by water under the elevated synthesis temperatures [9–11]. Partially for the reason of avoiding the oxidation of metallic copper, some Cu-organic chemical vapor deposition methods (MO-CVD) were developed to synthesize the nanoparticles of metallic copper [9,10,12]. The produced nanoparticles of copper were deposited and collected on the surfaces of some substrates such as TaN or Si [8,9,11]. However, it seems that only Cu nanowires or nanorods instead of Cu nanospheres were obtained by MO-CVD methods [9,10,12]. To the best of our knowledge, most of these ultrafine particles (wire or rod) of metallic copper reported so far were of polycrystalline structures. The

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initial aim of this work was to prepare ultrafine single-crystalline spherical particles of metallic copper for some special usages such as 3D printing so on.

2. Experimental details

2.1. Materials

A commercial raw copper powder with a purity of about 99.7 wt% was used as copper precursor. The contents of O, Pb and S in the raw copper powder were 0.2 wt%, 0.05 wt% and 0.006 wt%, respectively based on a chemical analysis with a X-ray fluorescence spectroscope (XRF-1800, Shimadzu). The average particle size of the copper powder was 79 μm based on one measurement with laser size distribution analyzer (LMS-30, Japan). The gases of argon, chlorine and hydrogen all having a purity of over 99.99 (v/v)% were used in this work. The powder of sodium chloride of analytical grade was used in this work and its particle size ranged from 106 to 149 μm. Before use, it was dried at 500 °C for 2 h and then preserved in a tightly closed desiccator filled with anhydrous calcium chloride.

2.2. Synthesis and characterization of Cu particles

A commercial raw copper powder with average particle size of 79 μm was used as copper precursor. The synthesis of copper powders was carried out in a horizontal tubular furnace (Fig. 1). The length of the heating zone of furnace is 60 cm. A quartz tube 10 (Fig. 1) with an outside diameter of 60 mm was inserted in the furnace. Typically, about 1.5000 g of weighed raw copper powder was adequately mixed with 5.5300 g of sodium chloride powder as copper precursor material. The molar ratio of NaCl/Cu was 4.0 in this case. The copper precursor material was put in a quartz boat. The quartz boat was placed at the center of furnace. The quartz tubes 5, 6 and 7 (Fig. 1) were evacuated simultaneously for 20 min with a water pump, then an argon gas with a flow rate of 100 mL/min was passed through three quartz tubes 5, 6 and 7 (Fig. 1), respectively, for 0.5 h. Then the furnace temperature was raised to 400 °C gradually and maintained at this temperature for 30 min. The three tubes of Ar were kept at 100 mL/min during the furnace heating process. After that the Ar in tube 7 was switched to a dry chlorine with a flow rate of 40 mL/min meanwhile the Ar in tubes 5 and 6 were maintained at 100 mL/min. After 1 h, the chlorine in tube 6 was switched to an argon gas with a flow rate of 40 mL/min meanwhile the furnace temperature was quickly raised to 900 °C. After reaching 900 °C for 1 h, three ways of gases of H_2, Ar and Ar were passed simultaneously through the quartz tubes 5, 6 and 7, respectively, in the flow rates of 60, 300 and 400 ml/min for 2 h. After that the furnace was cooled down to room temperature meanwhile only the Ar in tube 3 was kept at a flow rate of 60 ml/min. Red copper powder was found to be produced and mostly deposited on the inner wall of the narrow section of the quartz tube 10 outside the furnace heating region, which had a temperature about 50 °C during the hydrogen reduction process. The copper powder deposited on the tube 10 were then flushed off the tube using anhydrous acetone and collected in a beaker. Then the copper powder contained in acetone was transferred to several 90 mL of centrifuge tubes and then centrifuged at $5534 \times g$ for 15 min in order to separate copper powder and acetone solution. The copper powder deposited at the bottom of centrifuge tubes was washed with water and anhydrous ethanol sequentially and then centrifuged for three times. Finally the copper powder deposited at the bottom of centrifuge tubes was transferred to an anhydrous acetone solution, which was preserved in a glass bottle with tightly-screwed plastic lid. Then the glass bottle was kept in a refrigerator at -18 °C.

The SEM samples were prepared by dropping the acetone solution containing copper powder on one side of double-sided carbon conductive tape. The other side of the tape was supported on a pure copper block. The SEM observation was performed with Zeiss Ultra 55. The statistical analysis of the particle size showed in the SEM images was performed using a software named as Nano Measurer 1.2. The TEM samples of the copper particles were prepared by dropping the acetone solution containing copper particles on some smooth carbon-coated copper grids. TEM observation of the copper particles was carried out with FEI TECNAI G2 F30. Electron diffraction images of the copper particles were also obtained using the TEM device. The copper particles contained in an anhydrous acetone solution was placed in a dry quartz tube and dried in flowing argon at room temperature for 2 h before sending it to do X-ray diffraction (XRD) characterization. XRD patterns of the samples were recorded with a Simens D5000 X-ray diffractmeter equipped with a Cu Kα radiation source (λ=0.15405 nm). The sample patterns of XRD were analyzed using software of MDI Jade 5.0 with the aid of JCPDF database. For the XRD characterization, the XRD pattern background was stripped first, then the pattern was smoothed, $K\alpha_2$ line contribution was stripped and the pattern was simulated sequentially. In this way, the lattice parameters (*abc*) for the samples were thus obtained.

3. Results

3.1. Synthesis of single-crystalline copper particles of octahedral shape

The SEM images of the product sample synthesized for the Cu

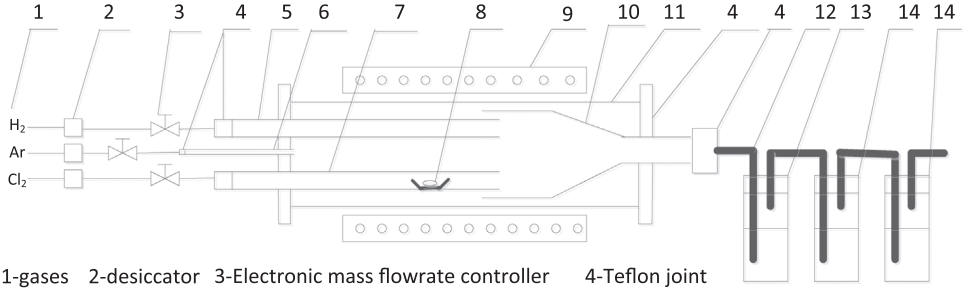

Fig. 1. Schematic diagram of the reactor used to synthesize Cu powder in gas phase.