Development of Pressure Control Technique of An Arc-Submerged Nanoparticle Synthesis System (ASNSS) for Copper Nanoparticle Fabrication

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The synthesis of nano-materials is one of the crucial techniques towards product and process innovation. In this article, low-pressure control methods for an arc-submerged nanoparticle synthesis system (ASNSS) was proposed and developed for copper nanoparticle fabrication. Two technical advances associated with nanoparticle synthesis were achieved. One is the novel pressure control technique developed for nanoparticle fabrication. The other is the verification that the constant low-operating pressure plays an important role in determining the characteristics of the prepared nanoparticles. From the experimental results, pressure control of the ASNSS was identified as crucial to success of metal nanoparticle synthesis. To achieve the desired pressure control, a vacuum chamber was developed as a nanoparticle accumulator and low-pressure reservoir. The chamber was controlled by the proposed flow-valve feedback control system and integrated with the ASNSS. In this study, the pressure control equipment of the ASNSS was effectively developed to prepare desired copper nanocrystalline particles with well-controlled size.

(Received January 6, 2003; Accepted April 14, 2003)

Keywords: nanoparticle manufacturing, pressure control, cuprum nanoparticles, submerged arc

1. Introduction

Nanotechnology plays an important role in product innovation.¹) A great deal of research and development for new nanoparticle synthesis methods has been proposed and implemented in the past decades.²,³) The Arc-Submerged Nanoparticle Synthesis System (briefed as the ASNSS) is an innovative successful technology for manufacturing metal nanoparticles.⁴,⁵) In the process, a bulk metal applied as the electrode is submerged in dielectric liquid in a vacuum chamber. Applied electrical energy then produces heating source for generating an adequate arc with a high temperature ranging from 6000 to 12000°C. In the development process, a titanium or copper bar is melted and vaporized in distilled water, which is used as an insulating liquid. The vaporized metal powders are then rapidly quenched by the designed cooling system, thus nucleating and forming nano-crystalline powders. The ASNSS is innovative because the raw materials are submerged in dielectric liquid during the process within a vacuum-operating environment and the vaporized metals are condensed in dielectric liquid unservingly.⁶) Nanoparticles can be successfully prepared and uniformly dispersed in dielectric liquid. The suspension with well-dispersed nanoparticles can be used directly in various applications.

In the ASNSS, the key parameters influencing the nucleation of nanoparticles are the pressure and temperature of the operating vacuum chamber.⁷,⁸) The formulated electrical energy heats the distilled water in the vacuum chamber at a low pressure. When the electrical energy produces a high-temperature arc, ranging from 4700 to 19700°C, the pressure inside the vacuum chamber tends to increase rapidly, making it difficult to maintain the vacuum condition of the chamber for stable system operation. Therefore, the pressure is considered as an important process parameter to be controlled for obtaining the desired nucleation and growth of nanoparticles in the ASNSS.

In this article, the new technology for pressure control of the ASNSS is investigated and implemented for nanoparticle synthesis. By integrating direction-control valves and signal feedback practices, important pressure control techniques for operating the vacuum chamber were developed. Our experimental results have verified that the chamber pressure can be effectively controlled and the nanoparticles with desired characteristics can be uniformly dispersed in the dielectric liquid. In addition, with the development of this novel technology, it was feasible to control the process parameters for obtaining the desired system properties of the ASNSS to further improve the overall performance of the particle synthesis.

2. Operating Principle of the ASNSS

The theory of ASNSS is developed from the phase change of metal submerged in the dielectric liquid in low-pressure condition.⁹,¹⁰) Figure 1 illustrates the developed ASNSS, including an electrical power utility, a servo-positioning system, a vacuum chamber, a vacuum pump, a heating source, a cooling system, and a pressure control unit. The vacuum chamber is the place where the temperature and pressure are maintained constant at an adequate level. The heating source generates a submerged arc to vaporize the metals, which are the electrodes. Important process parameters, such as applied electrical current, voltage, duration on and off time, electrode gap and feed velocity of servomotor, are controlled as required. The dielectric liquid in the vacuum chamber is deionized water. Metallic bars are used as the electrodes and positioned at the bottom of the chamber. The constant temperature system is employed to maintain a desired and constant temperature of the dielectric

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liquid, in which the vaporized metal aerosol can be effectively nucleated, thus preventing excessive grain growth. Metal nanoparticles can then be formed and prepared.

In addition, the dielectric liquid is vaporized by part of the submerged arc rapidly while the metal electrodes are heated. Water vapor with high pressure is generated by the inertia force of the surrounding dielectric liquid (deionized water). The vapor promotes effectively a rapid removal of the vaporized aerosol from the electrodes. Then, the vaporized aerosol present in the dielectric liquid changes its current phase state through the nucleating, growing and solidifying stages, and eventually becomes metal nanoparticles dispersed in the dielectric liquid. Because the dielectric liquid is controlled at a low and constant temperature level, the vaporized metal can be condensed in the dielectric liquid simultaneously by the submerged arc. Meanwhile, since the submerged arc is generated steadily and the pressure of the vacuum chamber and the temperature of the dielectric liquid are controlled at a desired level, the vaporized metal gas can be effectively transformed into particles in nano-scale through particle nucleation and grain growth.

The first step in applying the pressure control technique to the vacuum chamber is the manipulation of the pump control system. Because the pressure in the vacuum chamber may not be stable and the vacuum suction time may be too excessive, a balance tank is used and the control algorithm is shifted from the pump control to the valve control. The pressure variation of the vacuum chamber and the system responding time can be reduced significantly.

Apart from the pressure control, another important issue to be dealt with in the ASNSS is constant temperature control. In the ASNSS, the temperature in the vacuum chamber is mainly controlled by the cooling water. The heating source is placed in the vacuum chamber and a volume of 5000 mL of deionized water is applied as the dielectric cooling liquid. The water removes heat from the vacuum chamber and maintains a temperature ranging from 25 to 30 °C in the chamber. However, such a working temperature level is actually too high to produce the nanoparticles because it cannot maintain a steady submerged arc for the vaporized aerosol to nucleate and grow desirably. Therefore, an additional thermal control unit is designed to obtain a low and constant temperature. The temperature of the deionized water used in the vacuum chamber is controlled constantly within the range of 2 to 5 °C.

3. Preparation of Copper Nanoparticle Suspension

As described above, a pure copper bar, used as the electrode, is melted and vaporized in the dielectric liquid. The vaporized metal aerosol is directly quenched by the dielectric liquid, and cuprum nanoparticles are nucleated and formed in the deionized water.

The cuprum nanoparticle preparation is described below. A Cu bulk bar, used as the electrode, is submerged in the deionized water. After setting the proper parameters of the process, electrical energy is inputted to the electrode. The electrical energy is determined according to the applied electrical current and breakdown voltage. The waveform, pulse intensity and on-time period of the electrical current and voltage are shown in Fig. 2. Since the electrical energy produces the submerged arc with a high temperature ranging from 6000 to 12000 °C, metal vaporization occurs in the vicinity of where the arc is generated and the Cu metal bar is vaporized rapidly.

Because both the metal aerosol and the deionized water vapor are under a high temperature and pressure condition, their volumes expand rapidly and enormously. As a result, the vaporized aerosol is removed rapidly from the arcing zone by the evaporating water. When the metal aerosol moves through the non-vaporized deionized water, it can be immediately quenched and then solidified without excessive particle growth. Therefore, the vaporized metal aerosol is nucleated and grown into nano-scale particles.

The phase diagram for the deionized water is shown in Fig. 3. Without the pressure control in the ASNSS, the pressure variation of the vacuum chamber is obviously large, ranging from $13 \times 10^{-4}$ to $43 \times 10^{-4}$ MPa. The working pressure is normally above the liquid-vapor saturation line of the phase diagram. Figure 3 illustrates the operation zone (the black area) between the working temperature and pressure of the vacuum chamber. When the deionized water is operated...
within this zone, the phase of the water can be rapidly changed between its liquid and vapor state so that the metal aerosol can be moved, quenched, and then solidified without excessive particle growth. The solidification time of the metal aerosol can be shortened when the operating condition of the ASNSS is close to the triple-phase point of the deionized water within the operation zone.

In the case when no pressure control system is employed in the ASNSS, as shown in Fig. 4, the vacuum chamber is connected to a two-ways-two-positions direction control valve through a pipe. The frequency margin (−3 dB) of the two-ways-two-positions direction control valve is 10 Hz. The control algorithm is implemented with the PWM feedback control theory. Without the pressure control, the average length and width of metal particles may grow above 200 and 60 nm, respectively. Figure 5 illustrates the system diagram of the modified pressure control system and its associated valve control unit. The block diagram of the control algorithm and its important system components is shown in Fig. 6. Figure 7 shows that the working pressure ($P$) of the ASNSS is controlled and maintained at a constant level ($26.6 \times 10^{-4}$ MPa) along the time frame. The average length of the metal particles prepared is less than 80 nm while the average width is less than 10 nm.

Without a thermal control unit in the ASNSS, the working temperature of the deionized water usually increases up to 45°C or more. It is clear that a constant temperature system (also called isothermal system) is required to control the operating temperature when the vaporized metal is condensed and a great deal of heat is released in the vacuum chamber. The isothermal system is used to keep the temperature of deionized water constant. It consists of a heat exchanger, a condenser and a pump. After the desired temperature is set, the feedback signal of the thermocouple is fed through the A/D converter and the controller drives the relay and the pump to maintain the deionized water with a desired temperature level by using the feedback principle. Figure 8 shows that the temperature of deionized water can be effectively controlled. The variation of the working temperature of the deionized water is less than ±2°C.
4. Experimental Results and Discussion

The prepared Cu Nanoparticles are illustrated in Figs. 9 and 10. The experimental results show that more uniform and smaller Cu nanoparticles can be prepared when applying the pressure and temperature control systems in the ASNSS. In addition, uniformly distributed and well-controlled size of nanocrystalline powders can be prepared by the ASNSS with the proposed control systems.

As shown in Figs. 9 and 10, the gray lump images with the shape of bamboo leaves are identified to be individual Cu nanoparticles, while the black lump images are clusters of Cu nanoparticles. Figure 9 illustrates that the nanoparticle size in length can increase up to more than 200 nm when no pressure control is implemented in the ASNSS. In other words, a higher pressure variation allows for a greater growth of the size of the nanoparticles. This is because the nucleating cell of metal aerosol has more time to grow before solidification when there is a higher pressure variation of the deionized water in the operating chamber. In order to further clarify the above hypothesis, the TEM images were used to observe and characterize the particle size in the deionized water. Two TEM photos of the prepared particles were taken and are shown in Figs. 9 and 10. Figure 9 shows the nanoparticles produced from the ASNSS with the original pump control system. As can be seen, the average length and width of metal particles are above 200 and 60 nm, respectively, while they appear like coarse bamboo leaves. As seen in Fig. 10, with the modified pressure control system and the valve control system applied, the average size (length by width) of the Cu nanoparticles prepared is reduced to less than 80 by 10 nm, while the Cu nanoparticles look like fine bamboo leaves. Comparing the two figures reveals that the size of the particles is influenced significantly by the pressure inside the vacuum chamber. An operating chamber with a low and stable vacuum pressure can produce fine Cu nanoparticles.

Two important technical advances were achieved in this study. The first was the new control technique to keep the low and stable pressure in the vacuum chamber for nanoparticle preparation. The second was the important finding that the operating pressure is one of the key factors in determining the form of the prepared nanoparticles. The second point was clearly verified by the TEM results of the Cu nanoparticles with different system pressure conditions. As seen in the photos of the samples, shown in Figs. 9 and 10, the morphological shape of the nanoparticles is clearly influenced by the operating pressure condition. By inspecting the XRD results of the prepared Cu nanoparticles (shown in Fig. 11), it is also verified that the peaks of the data curves with and without the system pressure control appeared in the same 2θ. This indicates that there was no new substance produced when the pressure condition was manipulated between different variations.

Figure 7 illustrates the pressure variation of the vacuum chamber when the pressure control system was applied to the...
ASNSS. It clearly indicates that the deviation of the pressure variation without the constant pressure control system is almost 10 times as that equipped with the pressure control system. Smaller and more uniform nanoparticles can be prepared under a constant pressure condition than those prepared under a larger pressure variation. The experimental results indicate that the nanoparticles can be prepared when the operating pressure is kept constant at $26.6 \times 10^{-6}$ MPa. However, the shape of particles remains unchanged whether the pressure varies or not.

5. Conclusions

The pressure control techniques used in the ASNSS have been successfully developed with the developed balance-operating vacuum chamber as a working reservoir for copper nanoparticle fabrication by integrating direction flow valves and the feedback control algorithm. It has been identified that the pressure in the vacuum chamber can be maintained at a stable condition, which is crucial to the successful fabrication of nanocrystalline particles. More importantly, two technical contributions associated with nanoparticle synthesis were achieved in this study. One was the novel pressure control technique to keep the low and stable pressure in the vacuum chamber for nanoparticle preparation. The other one was the verification that the operating pressure is one of the key system parameters for determining the physical form of the prepared nanoparticles.

Acknowledgement

The study is supported by the National Science Council of Taiwan, the Republic of China through grant NSC 90-2212-E-027-010.

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