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Synthesis of Tin Nanoparticles by Pulse Discharge in Water and Aqueous Gelatin Solution

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High-voltage pulse discharges were generated between underwater two metallic Tin (Sn) wires in order to synthesize nanoparticles. Nanoparticles were synthesized in pure water or aqueous gelatin solution. In pure water, Sn and SnO₂ particles of approximately 5 nm in diameter were synthesized. However, synthetic particles in pure water had a problem of aggregation. The influence of gelatin solution on the particle size and dispersibility of the synthetic particles was investigated. In 10 mg/L gelatin aqueous solution, metallic Sn particles of approximately 40 to 400 nm in diameter were synthesized and were dispersing separately. From the peak width of X-ray diffraction (XRD) spectrum, the particle size was estimated using the Scherrer's equation. As a result, the minimum size was approximately 20 nm at 2 mg/L of aqueous gelatin solution.

金属スズからのナノ粒子合成を目的として、2本の金属スズ線を、先端を対向させて水中に浸漬し、両スズ線間で高電圧パルス放電を発生させた。液体として、純水とゼラチン水溶液を用いた。純水中では、直径約 5 nm の Sn と SnO₂ からなるナノ粒子が合成されたが、粒子の凝集がみられた。10 mg/L のゼラチン水溶液を用いた場合、直径約 40 ~ 400 nm の金属スズナノ粒子が合成され、粒子の凝集はみられず分散していた。合成粒子の X 線回折 (XRD) スペクトルにおけるピークの半値幅から、シェラーの式を用いて粒子径を算出した。その結果、粒子径が最小となるのはゼラチン水溶液が 2 mg/L のときで、そのときの直径は約 20 nm となった。

Key Words

Nano-particle synthesis, Pulse discharge, Water, Gelatin, Tin

1. Introduction

In recent years, there has been an increasing demand for weight reduction and flexibility for electric devices, such as smart phones. Moreover, for the conventional manufacturing, the problems are arising due to the higher cost of the equipment required. Printed electronics is attracting increased attention as a solution to these problems. This is a nano-order wiring technology which uses the technology of an ink-jet printer for application, and metallic nanoparticles for "ink." Moreover, Sn nanoparticles are attracting attention as an alternative bonding material for solder, such as a low-temperature smelting solder alloy with a nano-composite structure, as well as a novel electrode material for lithium ion batteries.

The purpose of this research is to establish the

technique of producing Sn nanoparticles from a bulk Sn material using the in-liquid plasma method. Various processes have been proposed for synthesis of nanoparticles ranging from solution dispersion^{1) 2)}, the chemical reduction method^{3) ~ 5)}, the modified polyol process⁶⁾, laser pyrolysis⁷⁾, sonochemical synthesis^{8) 9)}, the reversed micelle method¹⁰⁾, electrospraying¹¹⁾, to the electrolysis method¹²⁾.

Synthesis of nanoparticles by plasma in a liquid has also been reported^{13) ~ 21)}. In-liquid plasma is generated by applying radio frequency or microwave to generate an active reaction field in the liquid^{22) 23)}. The bulk metal evaporates in the high temperature field of the plasma, and then is rapidly cooled and condensed by the large temperature gradient between the plasma and its surrounding liquid. Thereby, production of nanoparticles is possible. Moreover, it becomes easy to collect the produced nanoparticles because they remain suspended in the liquid. Experimentation on production of nanoparticles by

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inserting metallic wires, using Zn^{16) 17)}, Mg¹⁷⁾, Ag^{17) 19)}, Au¹⁹⁾, and W^{18) 19)} as the raw material, into plasma generated by microwaves or high frequency in a liquid have previously been conducted.

Since among all metals Sn has a relatively low melting point and high boiling point, if synthesis of nanoparticles is attempted by the in-liquid plasma method, the Sn wire melts before evaporation, and forms droplets of several millimeters in size. The droplets sink out of the plasma, solidify and deposited on the bottom of a container. In order to synthesize Sn nanoparticles, a different approach is required. Pulse discharge is an attracting method to synthesize nanoparticles at low temperature. The power applied for pulse discharge in water is usually lower than that of conventional in-liquid plasma which is 100 to 200 W.

In this study, synthesis of Sn nanoparticles by pulse discharge between the tips of two Sn wires in pure water was conducted. Moreover, in order to synthesize dispersed Sn nanoparticles, we used the aqueous gelatin solution, instead of pure water. The discharge characteristics and the synthesized particles were investigated.

2. Experimental

The experimental apparatus is shown in Fig. 1. A commercial ignition coil from a gasoline engine connected to an ordinary car Pb battery of 12 V was used, and was connected to a wave generator (WF1941, NF circuit) to turn the circuit on and off by transmitting a rectangle wave signal. The frequency, duty ratio and amplitude of the rectangle wave were set to 50 Hz, 25% and 5 V, respectively. A high-voltage pulse is generated from the ignition coil by mutual induction when the circuit was turned off at the

Fig. 1 Experimental apparatus

rectangle wave drops.

As electrodes, two metallic Sn wires of 1 mm in diameter are inserted from the top and bottom of the standing polycarbonate pipe with an inner diameter of 20 mm filled with pure water or aqueous gelatin solution. The bottom electrode is connected to high-voltage pulse circuit, while the top electrode is grounded and fixed to a XYZ-axis stage in order to adjust the distance between the electrodes. Voltage between the electrodes and current in the grounded electrode are measured using an oscilloscope (DPO4104, Tektronix). Voltage and current of the battery were also measured using the same oscilloscope, and the power consumption as calculated from these values was 15 W when the pulse was generated. The experiments were conducted at room temperature and atmospheric pressure.

3. Results and Discussion

The voltage and current waveform of the high voltage pulse in pure water is shown in Fig. 2 (a). In pure water, the high voltage is generated on the negative

(a) Pure water

(b) Gelatin 10 mg/L

Fig. 2 Voltage and current of pulse

side at approximately $-14 \mu\text{s}$ and falls down to -10 kV . Hereinafter the absolute value of the voltage is named “discharge voltage”. At $t = 0$, the first discharge occurred and the voltage return to 0 kV or higher. After that, the voltage kept dropping and then the second discharge occurred. The discharge repeated several thousand times approximately in 1 ms. In Fig. 2, each noise-wise spike of the current waveform shows discharge. It was confirmed using a photo-diode (S5973-02, Hamamatsu). The signal of the photo-diode which was faced to the discharge was fully synchronized with spike of the current waveform.

The voltage and current waveform of the high voltage pulse in aqueous gelatin solution of 10 mg/L is shown in Fig. 2 (b). While the voltage falls down to the discharge voltage, weak discharges occurred several times. These discharges are considered to occur due to black substances generated between the electrodes by long time discharges. The discharge voltage was approximately 3 kV, which was less than that in pure water.

The relationship between the discharge voltage and the distance between electrodes is shown in Fig. 3. When the distance is approximately 1 mm or less, discharge voltage increases to 20 kV, and when the distance is longer than 1 mm, discharge voltage increases more slowly. At a distance is 6.8 mm, the discharge voltage reaches 27 kV.

The changes of breakdown voltage with the elapsed time for different initial distances between electrodes (0.05, 0.80 and 1.75 mm) are shown in Fig. 4. For initial distances of 0.05, 0.80 and 1.75 mm discharge occurred until 900, 120 and 120 s, respectively, and then stopped spontaneously as the distance increased to 0.50, 0.85 and 1.80 mm, respectively.

The distance between the electrodes increases with elapsed time because the discharge transforms the Sn electrodes into nanoparticles. The discharge breakdown

Fig. 3 Discharge voltage as a function of distance between electrodes

Fig. 4 Discharge voltage as functions of elapsed time

voltage decreased with time when the initial distance is 0.80 and 1.75 mm, while the breakdown voltage increased until 650 s and decreased slightly after that when the distance is 0.05 mm. The increase of breakdown voltage with time is caused by an increase of the distance between the electrodes as they are worn down by the discharge, previously mentioned regarding Fig. 3. On the other hand, the decrease of breakdown voltage with time is caused by changes in the characteristics of the liquid. In fact, when the liquid is exchanged with fresh pure water without changing anything else after generating the discharge, the breakdown voltage becomes larger than that before the water was exchanged. However, the physical mechanism of the decrease of breakdown voltage has not been clarified yet.

It was confirmed that synthesis speed increased with decrease of the distance between electrodes. The speed is related to the electric field which can be roughly estimated by dividing the voltage by the distance. The estimation applying the result in Fig. 3 gives an answer that larger electric field is generated at smaller distance.

Synthesis speed of nanoparticles can be obtained by comparing the length of the electrodes using photographs of the tip portion of the two electrodes taken before and after discharge. Both electrodes are worn down. The sequential pictures are shown in Fig. 5, and the synthesis speed is found to be 0.5 mg/min from these pictures. It is supposed that the yield is almost 100%, because observable particles, whose size is larger than sub-millimeter order, were not generated during synthesizing nanoparticles and there are no particles whose diameter is larger than $1 \mu\text{m}$ in TEM images.

TEM images of particles synthesized in pure water and aqueous gelatin solution of 10 mg/L are shown in Fig. 6 (a) and (b), respectively. The sample was provided by drying

a drop of the residual liquid on a collodion membrane. In pure water, the synthesized particles were approximately 5 nm, and each particle were agglutinated. On the other

Fig. 5 Sequential pictures of the gap between electrodes for high-voltage pulse discharge in water. The white lines indicate the gap distance before and after discharge

hand, the synthesized particles were approximately 40 to 400 nm in diameter and almost particles were dispersing separately.

The crystal structure of the particles was analyzed using XRD. As a sample, the synthesized particles were collected by drying the residual liquid in a drying oven of 343 K. The diffraction spectrum of the particles synthesized in pure water and aqueous gelatin solution of 10 mg/L is shown in Fig. 6 (c) and (d), respectively. The main compounds of particles synthesized in pure water were Sn and SnO₂. In the case of aqueous gelatin solution, the main compound was Sn. From this, it is considered that oxidation of the synthesized particles could be suppressed by adding gelatin.

The size of the synthesized particles is obtained from Sn peaks of the XRD spectrum. The minimum of the particle diameter is calculated using the Scherrer's equation from the full width at half maximum (FWHM) of each peak. The Scherrer's equation is expressed as follows.

(a) TEM image (pure water)

(b) TEM image (gelatin 10 mg/L)

(c) XRD pattern (pure water)

(d) XRD pattern (gelatin 10 mg/L)

Fig. 6 Synthesized particles

Fig. 7 Diameter of the particles calculated using the Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the minimum diameter of particles, β is the value of the FWHM in radian, θ is the Bragg angle and λ is the wavelength of the X-ray. K represents the Scherrer's constant of 0.9.

The size of the particles is shown in Fig. 7. The horizontal and the vertical axis represent the concentration of the gelatin and the particle size, respectively. In the case of pure water, the particle diameter was the maximum at approximately 80 nm, and when the aqueous gelatin solution was 2 mg/L, the particle diameter was the smallest at approximately 20 nm. Comparing the particle size calculated using the Scherrer's equation with that in the TEM image, the minimum of the particle diameter is almost the same as approximately 40 nm at 10 mg/L of the gelatin aqueous solution. Meanwhile, at 0 mg/L of the gelatin aqueous solution, which is pure water, the values between the two disagree. In the TEM image, although the individual size of particles is approximately 5 nm, the aggregates size of the particles seems to be close to 80 nm.

4. Conclusions

Nanoparticles were synthesized from metallic tin wires by high-voltage pulse discharges in water or aqueous gelatin solution using an ignition coil, and the following conclusions were provided.

In pure water, the synthetic rate was 0.5 mg/min. The diameter of the synthesized nanoparticles was approximately 5 nm and most of particles adhered each other. Synthesized nanoparticles mainly consist of Sn and SnO₂.

In order to disperse the particles synthesized by underwater pulse discharge, aqueous gelatin solutions were used. When the aqueous gelatin solution was 10 mg/L, the particles of approximately 40 nm were synthesized and dispersed. The discharge voltage was approximately 3 kV, and the main compound was metallic tin. The particle size

obtained from XRD was the smallest at approximately 20 nm when the aqueous gelatin solution was 2 mg/L.

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