Nanosized Powder Synthesis by Pulsed Wire Discharge in High-Speed Gas Flow

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Copper nanosized powders were successfully synthesized by pulsed wire discharge (PWD) in high-speed gas flow. The maximum pressure of the gas blowing from the gas puff apparatus developed for PWD was 22 kPa at plenum pressure of 0.4 MPa. The experimental results have shown that, by using gas puff at background pressure of 130 Pa, the electrical energy deposition into the wire reached 40 J, which is almost the same as that obtained at pressure of 5 kPa without gas puff. However, the average particle size decreased from 39 nm (at steady pressure of 5 kPa) to 16 nm (at background pressure of 130 Pa with gas puff). Therefore, it has been proved that the gas puff has significant effect in the reduction of average particle size.

Keywords: pulsed wire discharge, gas puff, nanosized powder

1. Introduction

Solid particles with particle size in the range of 1-100 nm are called nanosized powders. Materials of this size have different characteristics from those of the usual bulk due to large specific surface area. In recent years, nanosized powders of particle size less than 10 nm are especially expected as a new material that bears the nanotechnology of the next generation.

Pulsed wire discharge (PWD) is one of the technologies which are used for nanosized powder synthesis. This method is an application of pulsed power technology and is featured by the advantages in high-quality, high-speed, and low cost. It has been understood from previous experimental results that the particle size can be controlled by the pressure of the ambient gas. Since the particle size decreases with reduction of atmosphere gas pressure, it is expected that very small particle size can be obtained at relatively low pressure. However, in the ambient gas of very low pressure, the electrical breakdown between electrodes through the gas instead of the wire prevents efficient wire heating. Thus, the energy for complete wire evaporation cannot be deposited into the wire. For this reason, the minimum particle size of the powders produced by PWD is restricted by gas pressure. In order to solve this problem, we have proposed a new method which is applying gas puff to PWD. The basic idea is using the gas puff to form a dynamic gas pressure so that the wire explosion happens at higher pressure and particle formation occurs at lower pressure.

The gas puff spouts high-density gas to a limited region in vacuum. The gas puff is applied to Z-pinch, molecular-beam, and high-power laser-plasma X-ray sources. The previous study indicated that the instantaneous high pressure provided by the gas puff can prevent electrical breakdown through the gas.

However, the gas puff apparatus has not been installed in and operated with the PWD apparatus for powder preparation. In this paper, we report our preliminary experimental results of PWD with gas puff.

2. Development and Operation of Gas Puff Apparatus

2.1 Experimental Setup

Figure 1 shows the construction of the developed gas puff apparatus. The apparatus consisted of a driver disk, a coil, a body, a spring, a valve, a nozzle, an O-ring and a connecting rod. They were assembled in a cylinder of 380 mm in length, 81 mm in diameter and 0.8 liter in capacity. The valve was connected with the driving disk. The O-ring and the valve that are suppressed by the spring maintain the sealing of the plenum of the gas puff apparatus. The pulsed magnetic field generated by the pulsed current in the coil pushed the disk and opened the valve. The valve opened for a very short time before driven back by the spring.

Figure 2 shows experimental setup for measuring the gas flow from the gas puff apparatus. Electrodes of PWD were covered by insulator in order to prevent the electrical discharge. The top of gas puff nozzle and an acrylic resin tube were located at one of the electrodes. This acrylic resin tube was placed to increase the breakdown voltage. The gas that blew from the gas puff apparatus was sprayed on the electrode and then the gas was temporarily turn into high pressure in the acrylic resin tube.

In the experiment, the current waveform of the circuit was

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![](Fig. 1. The construction of gas puff apparatus)
measured and the time evolution of the pressure in the acrylic resin tube was monitored by a pressure sensor (pressure transducer).

2.2 Experimental Conditions The experimental conditions for gas puff are shown in Table 1. The electrode distance was 25 mm. The distance from the top of gas puff nozzle to the electrode was 8 mm and the distance from gas puff nozzle to the pressure sensor was 50 mm. The acrylic resin tube was 55 mm in length and 9 mm in diameter. The slit of the acrylic resin tube was 2 mm in width and 25 mm in length. The initial pressure in chamber was 130 Pa.

2.3 Experimental Results Figure 3 shows a typical current waveform of this gas puff apparatus. The beginning of the increase in current was defined as time \( t=0 \). The peak current is 10 kA at \( t=10 \) \( \mu \)s and the circuit inductance of 5.3 \( \mu \)H is obtained.

Figure 4 shows the time evolution of pressure in the acrylic resin tube at each plenum pressure. The pressure rising started to rise at \( t=0.4 \) ms after the start of the discharge. The time of peak pressure at each plenum pressure was about \( t=2.0 \) ms. Additionally, the peak pressure increased as the plenum pressure was increased.

On the other hand, the opening duration of valve decreases. The maximum pressure in the acrylic resin tube was obtained to be 22 kPa at plenum pressure of 0.4 MPa.

3. Synthesized Nanosized Powders

3.1 Experimental Setup Figure 5 shows the experimental setup for applying gas puff to PWD. This experimental equipment was composed of the gas puff system, a PWD system, and a nanosized powder preparation chamber. The nanosized powders were made with and without gas puff. The configuration of the electrodes, acrylic resin tube and the gas puff nozzle was same as that in Fig. 2.

The experiment was conducted in the following procedure. The chamber was evacuated after the wire was located between the electrodes. Then, the chamber and the gas puff apparatus were filled with gas and the capacitors of the PWD and the gas puff system were charged by high-voltage DC power supplies. The spark gap switch in the gas puff system was closed. At that time, the gas in the gas puff apparatus was sprayed on one of the electrodes and a photo-detector detected the flash of the spark gap switch installed in the gas puff system. The photo-detector signal, delayed by the delay generator, was used to trigger the spark gap
switch of PWD so that the wire was exploded during the gas puff. After the discharge, the nanosized powders floating in the ambient gas were collected by pumping the gas though a membrane filter.

In the experiment, the voltage between electrodes and the current waveform of PWD system were measured by an oscilloscope using high voltage probes and a current transformer when nanosized powders were synthesized. The voltage waveform was obtained from subtraction between two probe signals obtained at inlet and outlet electrodes. The energy deposition of the wire was calculated from these voltage and current waveforms\(^{(19)}\). The synthesized nanosized powders were analyzed by X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET) method and transmission electron microscopy (TEM). From the peak positions in XRD patterns, phases in the powders were identified. The volume fractions for the phases were determined by the following process. First, the structure factors were calculated from the crystal structures for the phases. Secondly, peaks were deconvoluted using the structure factors by assuming Gaussian curves with one to three grain sizes ranging from 2 to 61 nm. Finally, the volume fractions for the phases were determined. In this process, absorption of X-ray in the phases assumed to be comparable. The BET measurements were carried out for the estimation of specific surface area. The average particle sizes were calculated by the specific surface area and the density that was obtained by the volume fraction of the phases in the nanosized powders. The TEM images revealed the morphology of synthesized nanosized powders.

3.2 Experimental Conditions The experimental conditions for applying gas puff to PWD is shown in Table 2. The copper wire was 0.2 mm in diameter, 25 mm in length and 99.9% in purity. The vaporization energy of this wire is 43.3 J and the melting energy is 4.7 J. The pressure in the chamber was fixed at 130 Pa with gas puff and it was changed from 130 Pa to 79.8 kPa without gas puff. In the case with gas puff, we set this pressure to investigate the influence of electrical breakdown between electrodes in low pressure with the gas puff. The delay time was kept to be 1100 \(\mu\)s, which is the time delay of the spark gap switch of PWD relative to that of the gas puff system.

3.3 Experimental Results and Discussion Figure 6 shows the waveforms of voltage, current and the energy deposition of the wire at the ambient gas pressure of 130 Pa and 5.33 kPa. The beginning of the increase in the current was defined as time \(t=0\). The voltage between the electrodes (Fig. 5) should be expressed by the following equation:

\[
V(t) = Ri(t) + L \frac{di(t)}{dt} \tag{1}
\]

where \(V(t)\), \(R\), \(L\) and \(i(t)\) are respectively the measured voltage, circuit resistance in the chamber, circuit inductance in the chamber which is 300 nH and the current of PWD system. Because of the effect of the inductance, the voltage maintains a value of about 1 kV during the risetime of the current (Fig.6. (a)-(c)).

In the case of \(p=130\) Pa with gas puff, the voltage waveform has two peaks which are a broad peak of 2.5 kV at \(t=3.0\) \(\mu\)s and a sharp peak of 5.8 kV at \(t=3.8\) \(\mu\)s and the current decreased rapidly at \(t=3.8\) \(\mu\)s (Fig.6. (a)). In the case of \(p=130\) Pa without gas puff, the waveforms were almost the same as those of short-circuit, while, with gas puff, the voltage waveform had a small peak of 1.5 kV at \(t=2.5\) \(\mu\)s (Fig.6. (b)). In the case of \(p=5.33\) kPa without gas puff (conventional PWD condition), the voltage and current waveforms are those of typical wire discharge. The voltage waveform had a peak of 4.6 kV at \(t=3.9\) \(\mu\)s (Fig.6. (c)), which are typical in the PWD process\(^{(15)}\).

The voltage-rise was caused by the increase in resistance of the wire due to the vaporization. The voltage drop was caused by the decrease in resistance due to the formation of plasma. Thus, the energy deposition in the wire \(W_n\) was defined by the following equation:

\[
W_n = \int_0^{t_2} V_n(t) \times i(t) \, dt \tag{2}
\]

where \(V_n(t)\) and \(t_2\) are respectively the voltage of the wire and the time of the voltage peak. The voltage of the wire \(V_n(t)\) was calculated by Eq. (1), assuming \(V_n(t) = Ri(t)\). Here, we also assume that the resistance of circuit in the chamber was small enough compared with the resistance of the wire. Thus, the resistance \(R\) was equal to the resistance of wire.

### Table 2. Experimental conditions of the PWD with gas puff apparatus

<table>
<thead>
<tr>
<th>PWD System</th>
<th>With Gas Puff</th>
<th>Without Gas Puff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire</td>
<td>Cu, φ 0.2×25 mm</td>
<td></td>
</tr>
<tr>
<td>Vaporization Energy</td>
<td>43.3 J</td>
<td></td>
</tr>
<tr>
<td>Capacitance</td>
<td>10 (\mu)F</td>
<td></td>
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<tr>
<td>Charging Voltage</td>
<td>4.0 kV</td>
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<tr>
<td>Gas Species</td>
<td>(N_2)</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>130 Pa</td>
<td>130 - 79800 Pa</td>
</tr>
<tr>
<td>Gas Puff System</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitor</td>
<td>20 (\mu)F</td>
<td></td>
</tr>
<tr>
<td>Charging Voltage</td>
<td>4.0 kV</td>
<td></td>
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<tr>
<td>Gas Species</td>
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<tr>
<td>Pressure</td>
<td>0.4 MPa</td>
<td></td>
</tr>
<tr>
<td>Delay Time</td>
<td>1100 (\mu)s</td>
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</tr>
</tbody>
</table>

![Fig. 6. Voltage, current and the deposited energy waveforms during discharge: (a) with gas puff, (b) and (c) without gas puff. The pressure of (a), (b) 130 Pa and (c) 5.33 kPa](image-url)
In the case of $p=130$ Pa, the deposited energy in the wire was about 5 J at $t_p=2.5$ ms without gas puff and 40 J at $t_p=3.8$ ms with gas puff, respectively. In the case of $p=5.33$ kPa, the deposited energy in the wire was about 40 J at $t_p=3.9$ ms without gas puff. From these results, the energy deposited in the wire at $p=130$ Pa with gas puff was same as that obtained in ambient gas at $p=5.33$ kPa.

Figure 7 shows the deposited energy in each ambient gas pressure. The energy increases with the increase in ambient gas pressure. The deposited energy in the wire exceeded the vaporization energy of the whole wire (Table II) at the ambient gas pressure higher than about 5.33 kPa.

The deposited energy in the wire was increased by using gas puff. It was thought the sharp peak in the voltage waveform indicated the beginning of the vaporization of the wire(10). In Fig. 6 (a), at the sharp voltage peak, the deposited energy in the wire reached 40 J, which was comparable to the vaporization energy of the whole wire (43.3 J). From this result, most of the copper wire was thought to be vaporized by PWD and nanosized powder synthesis became possible even at low pressure. It was considered that the gas that was temporarily accumulated in the acrylic resin tube and around the electrode increased the breakdown voltage. In the case of $p=5.33$ kPa, it was considered that the breakdown voltage was same as $p=130$ Pa with gas puff because the deposited energy in the wire was same as $p=130$ Pa with gas puff.

After PWD discharge, the wire between electrodes disappeared both with and without gas puff at the pressure of 130 Pa. However, no nanosized powders were collected without gas puff at 130 Pa. Because of the deposited energy in the wire exceeded the fusion energy of the wire (4.7 J), the wire was dispersed to the chamber after the fusion. We considered that it was caused by insufficient energy deposition in the wire.

Figure 8 shows XRD patterns of the powders synthesized at various ambient gas pressures. The vertical straight lines in Fig. 8 show the International Centre for Diffraction Data (ICDD). In the case with gas puff, the nanosized powders synthesized have XRD peaks at copper (Cu) and copper oxides (CuO and Cu$_2$O). On the other hand, the nanosized powders synthesized without gas puff were identified as pure Cu (Figs. 8(b)-(f)).

Figure 9 shows the deconvoluted X-ray peaks of the nonosized powders synthesized at the background pressure of 130 Pa with gas puff corresponding to Cu, CuO and Cu$_2$O. The solid lines of Fig. 9 show the ICDD powder diffraction data. The volume fraction of the nanosized powder determined by measuring the integrated intensity of Cu, CuO and Cu$_2$O were 82 %, 15 % and 3 %, respectively.

From Figs. 8 and 9, the nanosized powders synthesized with gas puff.
puff contained oxides. We considered the following two reasons from the oxidation. The oxides were synthesized from the remaining oxygen in chamber or the gas puff apparatus. Alternatively, very small particles were oxidized in air after the preparation.

Figure 10 shows dependence of the specific surface area and the average particle size on the ambient gas pressure. The specific surface area decreased with increasing ambient gas pressure. In the case with gas puff, the specific surface area was larger than those obtained without gas puff. The average particle sizes were 16 nm at pressure of 130 Pa with gas puff and 39 nm at pressure of 5.33 kPa without gas puff. As far as the authors know, Cu nanosized powder with grain size of 16 nm is the finest one prepared by PWD.

Figure 11 shows the bright field TEM images of the nanosized powders prepared with (in background pressure of 130 Pa) and without gas puff (steady pressure of 5.33 kPa). The particle size obtained with the gas puff was smaller than that obtained without the gas puff and at the same energy deposition in the wire (40 J).

4. Conclusion

We carried out preparation of Cu powders by PWD with gas puff and obtained the following conclusions.

(1) The maximum pressure of the gas blowing from the gas puff apparatus developed for PWD was 22 kPa at pressure 0.4 MPa.

(2) With the gas puff apparatus, all of the Cu wire was evaporated and nanosized powders were synthesized at low pressure by PWD.

(3) The average particle size of prepared nanosized powders with gas puff was 16 nm which was the smallest size of the Cu nanosized powders produced by PWD so far.

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References


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