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This paper proposes a new method—the ultrasonic vibration-assisted arc-submerged nanoparticle synthesis system for preparing TiO$_2$ nanoparticle preparation. In addition to the influence of the ultrasonic amplitude and various process variables such as breakdown voltage, pulse duration, current, and dielectric liquid temperature on particles, this paper will also discuss the relationship between the pH value and the surface potential of the suspension. Experimental results have shown that the proposed method can successfully prepare anatase type TiO$_2$. The TEM image further shows a mean particle size below 10 nm, and that nanoparticle suspension cannot reach a state of stable suspension and starts aggregating under a pH value below 6.4.

(Received August 25, 2003; Accepted January 21, 2004)

**Keywords:** nanoparticles suspension, ultrasonic vibration, TiO$_2$, submerged arc

1. Introduction

Since TiO$_2$ nanoparticle possesses such characteristics as strong reduction and oxidation capability, high chemical stability, harmless to the environment, and low prices, it can be used as a new type of photocatalyst$^1$ and has many applications in areas such as bacteria and fungus resistance, emission purification, air purification, water purification, self-cleaning, and photosynthesis.

The gas condensation method however can often result in the loss of various distinctive qualities of nanoparticles because the condensation process itself can cause nanoparticles to aggregate. According to the basic principles of the gas condensation method, this study has developed an ultrasonic vibration-assisted vacuum Arc-Submerged Nanoparticle Synthesis System (ASNSS) for preparing TiO$_2$ nanoparticle suspension and has investigated into the aggregation phenomenon and the surface potential of nanoparticle. The experiment device mainly comprises a heating system, an ultrasonic system, a pressure control system, and a particle powder spray.

Ultrasonic vibration produces alternating pressure variation which leads to increased hydrostatic pressure variation. When the gap is widened, a large pressure drop causes more molten metal to be removed from the crater. This is because the particles can be effectively removed from the crater, which in turn reduces the probability of the occurrence of carbon deposit and increases the stability of the electric arc. In addition, the energy of ultrasonic vibration can generate minute disturbance and impact on the fusion zone, causing the gasified metal to move away easily from the fusion zone and be cooled down quickly by the low-temperature coolant surrounding it. In the meantime, this can retard the growth rate of nanoparticles after nucleation when the metal is solidifying. Hence, we will be able to obtain better nano-level particles and more dispersed suspension.

Of all the processing capacity of the electric arc, 18% is used to melt the cathode, 8% is used to melt the anode, and the rest 74% is used to grow the electric arc. Throughout the process, the ratio between energy density and electron number density is held constant and is mainly subject to the following two factors: (1) breakdown voltage; and (2) the thermal property of the dielectric liquid. The energy density equation can be expressed as follows$^4$:

$$\rho H = \frac{U_0}{6.317 \times 10^{18}} = H \frac{\sum m_i y_i}{y_e}$$  \hfill (1)

In eq. (1), $\rho H$ (J/cm$^3$) denotes energy density, $n_e$ (electrons/cm$^3$) is the electron number density, $U_0$ is the mean breakdown voltage, $m_i$ is the particle mass, and $y_i$ is the fraction of particle. As eq. (1) shows, the energy density is proportional to the electron number density and mean breakdown voltage. Hence, it requires high mean breakdown voltage to generate great energy density.

The relationship between pulse duration and the size of the craters generated on the surface of metal by the vacuum submerged arc can be expressed as follows$^5$:

$$r_g = 0.788 t_{ON}^{\frac{1}{3}}$$  \hfill (2)

In eq. (2), $r_g$ (µm) denotes the radius of the crater and $t_{ON}$ (µs) is the pulse duration. As the equation indicates, only when pulse duration is lowered would it be able to reduce the size of crater. Eubank and Mukund et al. have used the variable mass, cylindrical plasma model (VMCPM) to simulate the temperature of submerged arc and have found that as the pulse duration $t_{ON}$ increases, the temperature of the submerged arc will drop as a result. Therefore, as long as the size of $t_{ON}$ can be controlled, we will be able to obtain higher submerged arc temperature and finer nanoparticles.

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In the proposed ASNSS, the vaporized metal is processed through three stages, namely nucleation, growth and condensation, in order to generate nanoparticle suspension. According to the nucleation theory, the nucleating rate of unit volume \( I \) can be described in eq. (3).\(^4,6\)

\[
I = N_v \frac{kT}{h} \exp \left( \frac{- (\Delta G + \Delta g)}{kT} \right)
\]

In eq. (3), \( N_v \) denotes the number of atoms in the raw material, \( \Delta G \) is the change of free energy when new phase is formed, \( \Delta g \) is the required activation energy when atoms pass through interfaces, \( T \) is the absolute temperature, \( h \) is Planck constant and \( k \) is Boltzmann constant. According to eq. (3), \( \Delta G \) is a critical parameter affecting \( I \) when the temperature is kept constant. In addition, \( \Delta G \) also influences the saturation during material transformation from solid to gaseous state. High saturation is dependent on the temperature difference between the arc and deionized water. In other words, high nucleation rate can be obtained when the metal is vaporized in high temperature and condensed rapidly in low temperature. In case of too low the saturation rate, uniform nanoparticles cannot be obtained by the ASNSS. Controlling adequate radiuses of condensation nuclei is significantly essential during the nucleation process because the properties of the particles are mainly determined by this factor. In order to obtain desired nanoparticles, decreasing the critical radiuses of condensation nuclei is important. The radius \( r \) of cluster formed from gaseous state is influenced by the free energy \( \Delta g \) as shown in eq. (4).

\[
\Delta g = 4\pi r^2 \sigma + \frac{4}{3} \pi r^3 \Delta g_v
\]

Nucleation of the metal is followed by particle growth. The diameter of nanoparticles can be governed by eq. (5).

\[
d = \left[ \frac{6}{\pi} \times \frac{c_v M}{N \rho} \right]^{\frac{1}{3}}
\]

where \( N \) is the quantity of produced particle in unit volume of reaction gas, \( c_v \) is the concentration of the vaporized metal, \( M \) is the molecular weight and \( \rho \) is the density. The growth of nucleus determines the desired size of nanoparticles. The growth rate of nucleus is controlled primarily by the concentration of the vaporized metal and the temperature of deionized water. The temperature has a more critical influence on the size of nanoparticles since the growth rate of nucleus is controlled primarily by the temperature. The growth rate of granules and acquire tiny nanoparticles is quick cooling.

The \( \text{TiO}_2 \) nanoparticle suspension synthesized by the proposed method using better process variables demonstrate good dispersion; and even without dispersant, they can still remain in stable suspension for a fairly long time. Moreover, all electric conductor can be used to synthesize different material-based nanoparticle suspension by the proposed method.

2. Experimental

This study uses ultrasonic vibration to enhance the vacuum electric arc discharge system for the preparation of nanoparticles. The experiment device is shown in Fig. 1. The main technique involved in the process includes the use of titanium bulk metal material to be produced as electrode and the integration of the device with an ultrasonic vibrator. The experiment device mainly comprises a heating system, an ultrasonic system, a pressure control system, and a temperature control system. Of which, the heating device can provide stable electric arc to serve as the needed heat source for nanoparticle preparation. In addition, the system allows different settings for important process variables such as electric current, voltage, pulse duration, off time, and gap voltage. The ultrasonic system allows different settings of frequency and amplitude, and with the help of ultrasonic vibration, the disturbance of the dielectric liquid can be increased and the nanoparticles thus produced can quickly come out of the fusion zone. In the meantime, the gasified metal can be quickly cooled down. The pressure control system is used to maintain an appropriate vacuum pressure inside the vacuum chamber, and uses deionized water as the dielectric liquid. When the deionized water is operated within the neighboring region above the triple-phase point of the deionized water, 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 significantly shortened when the operating condition of the ASNSS is close to the triple-phase point of the deionized water within the operation zone. The temperature control system allows different cooling temperature settings, which helps grain nucleation and prohibits the growth of grains. Hence, nanoparticles of smaller size can be obtained.
Figure 2 shows the arc discharge process in the nanoparticle synthesis system. The ultrasonic generator produces a high-frequency electrical signal, this signal is transformed into a mechanical vibration signal of the same frequency by a transducer. A horn amplifies the amplitude and transfers it to the upper electrode. Applying a particular voltage across the working gap generates an electric field between the two electrodes. With the ultrasonic vibration of the upper electrode, the front surface of the upper electrode moves down towards the lower electrode surface and the electric field intensity increases, the resulting electric field causes ultra-fine conductive particles to be suspended and form a bridge across the gap. When the gap reaches a particular, very small size, it results in the breakdown or de-ionization of the dielectric fluid. The voltage falls to a constant value, and the current rises to a value set by the operator. Plasma is created and a vapor bubble forms around the channel. As the front surface of the upper electrode moves away from the lower electrode surface, the voltage begins to rise and the current begins to drop, the discharge channel collapses very rapidly when the gap reaches a particular, large size.7) Regardless of the electrode area, sparking occurs at the point where the gap is the smallest. The current density at this point is high and of sufficient force to erode small particles from the electrodes. This small particles of metal are vaporized by the spark, cooled by the dielectric fluid, and flushed from the gap between the upper and lower electrodes. Ultrasonic vibration of the upper electrode also acts as a gap flushing method. The process begins again when the upper electrode moves down towards the lower electrode again. Briefly, the discharge in the proposed system is formed when a voltage is applied between the two electrodes, which approach and retract periodically by the mechanical vibration of one of them.

This study integrates the ultrasonic vibration system with electrodes by tightening the screw that locks the end of the axis of the ultrasonic system with the titanium rod. The oscillator used in the ultrasonic system is a Lengevin-type piezoelectrical compound transducer with an input working power of 300 W. Since the input voltage of the ultrasonic vibration system is in direct proportion to its amplitude, the amplitude of ultrasonic vibration can be altered through voltage adjustment. In order for the ultrasonic vibration to enhance the process of the vacuum electric arc, the end spot of the titanium electrode has to be the resonance point. By adjusting the frequency of the ultrasonic system, the end of the titanium electrode can be made at exactly the position of a half-wave length. Since it is the resonance point, the ultrasonic microjet can inject into the cavitation bubble at a speed of approximately 110 m/s and can generate a high-pressure injection effect, thereby achieving the best result of ultrasonic vibration.8,9)

The influence of such process variables as breakdown voltage, pulse duration, electric current, and dielectric liquid temperature, as well as the amplitude of the ultrasonic system on the nanoparticles prepared is analyzed and compared through experimentation in order to identify the working conditions conducive to the production of nanoparticles with smaller mean particle size. In addition, the molecule in deionized water can be absorbed onto the surface of the particles via hydrogen bond and other attractions such as van der Waals force, dipole force, and Coulombic force causing TiO$_2$ nanoparticles to carry an electric charge. Since the nanoparticles generated by the system of this study are of suspension type, the surface potential of the particles will have an influence on the stability of the suspension. The surface potential of TiO$_2$ particles will change with the pH value of the fluid, making TiO$_2$ particles aggregate and precipitate within a certain range of pH value. Therefore, the relationship between the pH value of the suspension and the surface potential will also be discussed. The Zeta Potential Analyzer (Zeta Plus) of Brookhaven Instruments Corporation is used to measure surface potentials in the experiment. The pH value of the TiO$_2$ nanoparticle suspension is adjusted by HNO$_3$ and NaOH solutions without constant electrolyte concentration.

3. Results and Discussion

This study uses the ultrasonic vibration-assisted ASNSS to prepare TiO$_2$ nanoparticles and adopts X-ray diffraction
(XRD) to confirm the lattice structure of particles. The nanoparticles produced from the process are anatase type TiO$_2$. Among the heat source variables in the electric arc discharge, the magnitude of the pulse duration is found to have an influence on the submerged arc temperature and the crater radius. Hence, the change in the pulse duration will have a direct effect on the size of the nanoparticles produced. In order to further investigate the influence of the change of pulse duration on nanoparticle preparation, the experiment sets the current at 2.25 A, breakdown voltage at 220 V, and pulse durations at 4 $\mu$s and 200 $\mu$s, respectively. Figure 3 is the FESEM image derived at pulse durations of 4 $\mu$s. The FESEM images prove that under larger pulse duration, the size of particles prepared is also greater.

From eq. (1), we find that breakdown voltage can directly affect the density of the discharge energy of the electric arc. Preparing electric arc under different energy densities will cause the material to form particles by fusion or gasification, which will then affect directly the size of nanoparticles thus produced. In the experiment, the pulse duration is set at 2 $\mu$s, with breakdown voltage set at 220 V, 210 V, and 90 V, respectively. Figure 4 shows the relationship between the current and mean particle size under different breakdown voltage settings. The particle size in the figure is measured by HORIBA LB500 particle size distribution analyzer. As seen in Fig. 4, when the breakdown voltage is set at 90 V, the particle size is significantly larger than that with a breakdown voltage of 220 V and 210 V. In addition, when the breakdown voltage is 220 V with a current between 4 A and 6 A, a higher rate of nanoparticles can be derived.

In order to gain an insight into the influence of the amplitude of ultrasonic vibration on nanoparticle preparation, the experiment sets the pulse duration at 2 $\mu$s, breakdown voltage at 220 V, and amplitude at 5 $\mu$m and 10 $\mu$m, to identify the relationship between the current and the nanoparticles prepared under different amplitudes of ultrasonic vibration. As shown in Fig. 5, when the current falls below 8 A, the size of particles prepared under amplitude of 10 $\mu$m is larger than that under amplitude of 5 $\mu$m. Generally speaking, large amplitude requires large energy density. However, high current can exert a great influence on nanoparticles. Therefore, the combination of smaller ultrasonic amplitude with smaller current should be the best way to prepare more ideal nanoparticles.

The most effective way to prohibit the growth of grains and to obtain fine nanoparticles is to cool it rapidly. The experimental result reveals that the size of particles prepared under a dielectric liquid temperature of 273 K is significantly smaller than that under a dielectric liquid temperature of 292 K.

This study employs the ultrasonic vibration-assisted ASNSS for nanoparticle preparation and finds that the energy of the ultrasonic vibration can successfully prepare fine TiO$_2$ nanoparticles and that the particles in the suspension are evenly dispersed. The comparison between the above-mentioned experiment result and that under different working conditions shows that when the processing current is set between 2.25 A and 6 A, a higher rate of nanoparticle can be
produced, and that an current of 4.5 A can prepare relatively smaller nanoparticles. Table 1 summarizes the working conditions conducive to the preparation of ideal nanoparticles. Figures 6(a) and (b) are the TEM image of the nanoparticle suspension prepared using the process variables in Table 1. As shown in Fig. 6(a), with aid of ultrasonic vibration which indicates good nanoparticle dispersion with a mean particle size below 10 nm. Figure 6(b) shows the result without the use of ultrasonic vibration. Comparing Figs. 6(a) with 6(b) shows that the size of nanoparticles obtained without ultrasonic vibration is larger than that with and that some nanoparticles aggregate together, implying a relatively poor dispersion.

During the time of discharge, current is converted into heat, the surface of the electrode being heated very strongly in the area of the plasma channel, this high temperature causes the melting and vaporization of the electrode materials. In ASNSS, with the ultrasonic vibration of the electrode, the electrode makes the gap vary very rapidly, and a high frequency alternate pressure variation is generated. During the decreasing phase of the gap, the pressure is increased and the growth in the diameter of the plasma channel is slowed, whilst during the increasing phase of the gap, a large pressure drop occurs and an increase in material evaporation should arise owing to a decrease in the evaporation temperature. The ultrasonic vibration of the electrode prevents the sedimentation of the nanoparticles in the working gap and results in their animated suspension in the deionized water, which improves the deionized water circulation. These features increase the discharge efficiency substantially and improve the state of dispersion of nanoparticle suspension.

Solid oxides in aqueous suspension generally possess electrical charge due to the amphoteric dissociation of surface hydroxyl groups, the adsorption of $\text{H}^+$/OH$^-$/ ions, or metal hydroxo compounds from the hydrolysis of solid material. The resultant surface charge is pH dependent. The pH was controlled by the addition of HNO$_3$ and NaOH in our investigation. As shown in the surface potential measurement in Fig. 7, the surface potential of the particles is zero when TiO$_2$ is at a pH value of 3.8. The isoelectric point is rather low compared with those of TiO$_2$ particles prepared by conventional chemical fabrication. Because the Ti rod is melted and vaporized in the region with a high temperature between 5000 K and 20000 K where the arc is generated, the surface of TiO$_2$ particles tends to generate a passive layer which may affect the ions exchange and result in a lower isoelectric point. The farer the pH value is from the isoelectric point (pH 3.8), the less the TiO$_2$ particles tend to aggregate. Figure 8 shows the average size of TiO$_2$ particle as a function of pH value. The zone of maximum particle size is located within the pH range 2.5–4.5, which practically coincides with the pH value of TiO$_2$ isoelectric point. It is noted that in this pH range, the particles tend to precipitate and become larger. This observation indicated the rapid coagulation of TiO$_2$ particles as suggested by the pH dependent surface potential. The original pH of the prepared suspension is 7.1, which is much higher than the pH of i.e.p. Hence, even before the use of alkaline solution to adjust the pH value of the solution, the nanoparticle suspension already

<table>
<thead>
<tr>
<th>Working condition</th>
<th>Description</th>
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<tbody>
<tr>
<td>Breakdown voltage (V)</td>
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<tr>
<td>Peak current (A)</td>
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<tr>
<td>Pulse duration (μs)</td>
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<tr>
<td>Off time (μs)</td>
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<td>Pressure (Pa)</td>
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<td>Temperature of dielectric fluid (K)</td>
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<tr>
<td>Ultrasonic frequency (kHz)</td>
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<tr>
<td>Amplitude (μm)</td>
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</tr>
</tbody>
</table>

Fig. 6 TEM image of TiO$_2$ nanoparticles suspension prepared using better process variables (a) with the aid of ultrasonic vibration (b) without the aid of ultrasonic vibration.
possesses electrostatic stability properties. The strong repulsive force among charged particles reduces the probability of coalesce and thus more stable suspension can be formed in alkaline media. This can be also confirmed by Fig. 8. that the mean particle size of the TiO$_2$ nanoparticles does not change significantly when the nanoparticle suspension has a pH higher than 6.4. The nanoparticle suspension prepared using this method can be stabilized for a period of time longer than six months.

4. Conclusions

From the experiment result and the discussion above, this study has derived the following conclusions about the nanoparticles prepared using the proposed method.

1. The TiO$_2$ nanoparticle suspension already possesses good dispersion; and even without dispersant, they can still remain in stable suspension for a fairly long time.
2. Ultrasonic vibration can effectively improve the state of dispersion of nanoparticle suspension and obtain smaller nanoparticles.
3. In process variables, higher breakdown voltage, smaller pulse duration, lower dielectric liquid temperature, and smaller ultrasonic amplitude are found to be conducive to the production of fine nanoparticles, and that a current setting between 2.25 A and 6 A contributes to a higher rate of nanoparticle yield.
4. The TiO$_2$ nanoparticles suspension with an i.e.p. of 3.8. When the pH of the suspension reaches above 6.4, the TiO$_2$ nanoparticles become stably suspended.

Acknowledgement

This study is supported by the National Science Council of Taiwan, Republic of China under grant NSC 91-2212-E-027-003.

REFERENCES