Fabrication Method for a TiO₂ Nanofluid with High Roundness and Superior Dispersion Properties

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This study describes the use of a new submerged arc nanofluid synthesis system to fabricate TiO₂ nanofluids. Under vacuum conditions, this system uses the energy produced by an arc discharge to vaporize the desired metal. Then, the vaporized metal is cooled rapidly in a low-temperature dielectric liquid, forming nanoparticles that are evenly distributed inside the dielectric liquid. Experiments show that the fabricated TiO₂ nanoparticles are much better than those fabricated by aerosol methods. In addition, the fabricated nanofluid has high suspension stability. We use X-ray diffraction to analyze the structure of TiO₂ nanofluid. By measuring the Zeta potential of the TiO₂ nanofluid with different pH values, the suspension stability of the TiO₂ nanofluid is demonstrated. To verify the applicability of the TiO₂ nanofluid, this study also analyzes and compares the rheological properties and reaction to light absorption of nanofluids with different average particle sizes.
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1. Introduction

Following the discovery of the photocatalytic splitting reaction of water by a TiO₂ electrode in 1972 by Fujishima and Honda, many chemists, chemical engineers and physicists have studied heterogeneous catalytic reactions by semiconductors to better understand this mechanism.¹⁾ These studies have generally been related to energy renewal or energy storage.^{2,3)}

A photocatalyst is a substance that performs catalytic activity by using light energy, so that a chemical reaction can be stimulated by its surrounding environment. The resulting photocatalytic reaction is a procedure that transforms solar energy into chemical energy by using a semiconductor as the photocatalyst. Common semiconductor materials adopted as photocatalysts include: TiO₂, ZnO, Fe₂O₃, CdS, ZnS and SiO₂. Of these TiO₂ has the advantages of high chemical stability, high refractive index, good ultraviolet absorbency and photochemical reactivity. Thus it is used as a pigment, catalyst, water purification, inorganic film, etc.^{4,5)}

The current methods used to fabricate nanoparticles include metal vapor synthesis, liquid-phase synthesis and ball milling methods.^{6–8)} Most of the previous studies have concentrated on the production of components by submerged arc synthesis system and paid less attention to the production of debris (powder) of various sizes by this method. However, Soni related the formation of debris during rotary electrical discharge machining of titanium alloy and high carbon high chromium die steel.⁹⁾ Many distinct types of spheroidal particles were witnessed and the mechanisms of their formation were discussed. Willey related hollow, dented and cracked particles with solidification from the vapor phase in the dielectric fluid.¹⁰⁾ Murti and Philip analyzed the influence of ultrasonic vibrations on particle shape and size.¹¹⁾ Soni and Chakraverti presented the chemical analysis of debris and found that the debris of die steel was alloyed with the tool electrode material.¹²⁾ All these reports showed

that the produced particles were only in micro particles, not nanoscale.

The main principle for the improved submerged arc nanoparticle synthesis system developed in this study is to convert electric energy into heat energy, which can rapidly melt the electrode. During this processing, the temperature can exceed 10000°C, causing melting and vaporization.^{13–15)} Then, when metallic droplets are scattered into the dielectric liquid, they rapidly condense into nanoparticles, which are dispersed and suspended in the dielectric liquid.

One of the important challenges to industrial applications of nanoparticles is that, since their sizes are too small, the attractive force between the particles can cause them to aggregate. Therefore, nanoparticles need to be dispersed by different methods in order to completely utilize their unique material characteristics. For example, when commercially available powdered TiO₂ nanoparticles are poured into deionized water and then stirred and dispersed by ultrasonic vibration to become a TiO₂ nanofluid, aggregation and precipitation in the TiO₂ nanofluid can commonly be observed within a few minutes. Thus, the suspension stability of the TiO₂ nanofluid that has the powdered TiO₂ nanoparticles simply mixed is not satisfactory, reducing its value for industrial applications. Based on the above findings, the main purpose of this paper is to use the self-developed submerged arc nanoparticle synthesis system to produce a TiO₂ nanofluid with good suspension stability and particle dispersion. In addition, the particles in the synthetic TiO₂ nanofluid developed by the system described in this study have high roundness. Nanoparticles with such high roundness can improve the efficiency of the TiO₂ nanofluid for industrial applications due to its photocatalytic properties, UV resistance, electro-optical effects, tribology properties, etc.

To verify that the TiO₂ nanofluid synthesized in this study has high suspension stability, good particle dispersion and high roundness, the instruments and spectroscopy listed below are used for measurement and material property evaluation of the TiO₂ nanofluid. Furthermore, this study uses a TiO₂ nanofluid synthesized by the aerosol method for

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Fig. 1 Schematic figure of the improved submerged arc nanofluid synthesis system (ISANSS).

comparison. XRD is used to analyze the composition and structure of the fabricated nanoparticles, Zeta potential is used to analyze their suspension stability, TEM and FE-SEM are used to observe the appearance and size of the particles, and a rheometer is used to analyze the rheological properties of the nanofluid.

2. Experimental

This study uses the improved submerged arc nanoparticle synthesis system (ISANSS) to produce nano-scaled metallic particles.^{16,17)} The major difference between the improved SANSS developed in this study and the previous systems is the reduced equipment size and improved stability of the proposed system. Since the previous machine is a modification of the Electric Discharge Machine (EDM), it is very large. However, in ISANSS, the arc spray control system is first modified to increase the energy density of electrical discharge and the arc stability. To improve pressure control, the original accumulator is enlarged to increase the pressure stability and allow it to be as close as possible to the vacuum chamber. The size of the vacuum chamber is reduced, and the seal of the vacuum chamber is improved by using a more precise O-ring. The interior of vacuum chamber is re-designed to contain as much coolant as possible. The system parameter adjustment and stability of the improved machine is more precise and stable. Moreover, due to the size reduction of the system, the pressure control system and coolant circulation system are more stable during fabrication control.

The basic principle of this type of fabrication is to use the nano metallic material intended to be produced as electrode, and use the energy produced by high temperature of the submerged arc to vaporize the metal. The metal that is being vaporized is instantly condensed by the low-temperature dielectric liquid to yield nanoparticles. Figure 1 shows the experimental equipment, consisting of arc spray system, pressure control system, temperature control system, vacuum chamber and control system. In this system, the arc discharge device can provide a stable submerged arc as the heat source for the production of nanoparticles. At the same time, this system can set important processing parameters such as electric current, voltage, pulse duration, and off-time. A pressure control system is used inside the vacuum chamber to maintain suitable vacuum pressure. Inside the vacuum chamber, deionized water is used as the dielectric liquid.

For proper arc discharge machining, two titanium rods of the same size are used as upper and lower electrodes inside the chamber, and these are automatically controlled by a servo control system to maintain the proper gap. The temperature control system can set different cooling temperatures, allowing the nucleation of the particles and at the same time suppressing their growth, thereby producing smaller nanoparticles.

Based on the fundamental theory of gas condensation method, this study develops an improved submerged arc nanoparticle synthesis system, which is a method and equipment for nanoparticle fabrication. The overall set of equipment includes pressure control system, vacuum chamber system, arc spray control system, servo control system, cooling system and parameter control system. The pressure control system can maintain suitable vacuum pressure of around 3325~4655 Pa inside the vacuum chamber. Within the vacuum chamber, deionized water is used as the dielectric liquid, in which the upper and lower titanium electrodes are submerged, so that the generated nanoparticles can evenly be distributed in the dielectric liquid. The arc starter system can provide a stable arc as the heat source. The generated temperature is high enough to vaporize the material, so that the vaporized material can condense inside the dielectric liquid, becoming the nano-metallic particles. The cooling system can maintain a stable low temperature of around 0~2°C for the dielectric liquid of the vacuum chamber, which is beneficial for the nucleation of the metallic particles, and also suppresses the particle growth to yield smaller nanoparticles. Since the submerged arc nanofluid synthesis system developed in this study directly fabricates the nanofluid, not a dry powder, during the collection and continued application of nanoparticles, powder suspension in the air can be avoided, thereby reducing the danger of inhaling nanoparticles. After several trials, it can be observed that the process variables contributing to the production of a superior TiO₂ nanofluid are: breakdown voltage of 220 V, peak current of 6 A, pulse duration of 2 μs, off time of 2 μs, vacuum pressure of 3325~4655 Pa and dielectric fluid temperature of 1°C.

In order to verify that the TiO₂ nanofluid described in this study is superior in particle dispersion and roundness, this study uses TiO₂ nanoparticles synthesized by a commonly available aerosol method for comparison. The preparation conditions of the TiO₂ nanoparticles synthesized by aerosol method are briefly described as follows. A solution of titanium(IV) n-butoxide (Ti(O-Bu)₄) in isopropyl alcohol (*i*-PrOH) was used as the molecular precursor of TiO₂. The water used for hydrolysis in solution with *i*-PrOH was added gradually under mechanical stirring. The reaction condition was carefully controlled to obtain a white precipitate of titanium oxyhydroxide, which was then washed with water several times. The molar ratio of these reactants was: Ti(O-Bu)₄ : H₂O : *i*-PropOH : Acetylaceton(acac) = 1 : 100 : 2 : 0.01. The final solution was peptized by adding HNO₃, followed by refluxing at 85°C for 8 hr to give a sol of pH ~ 2.5. During optimization of processing conditions in the early stage of this work, the important role of the pH value in the control of the size of the TiO₂ particles was revealed. The as-prepared titania hydrosol was gelled by drying at 100°C for

Fig. 2 XRD pattern of the nanoparticles (a) immediately after fabrication and (b) after 15 days of settling time.

3 hr, then calcinated in a vacuum oven (1 Pa, NeyTech Qex-JFF 2000) at various temperatures (400–700°C) to yield TiO₂ powder.^{18,19)}

3. Results and Discussion

By using an x-ray single crystal diffractometer (XRD), the crystal structure of the fabricated TiO₂ nanoparticles can be understood. When producing the samples, a vacuum funnel is first used to filter out the particles from the nanofluid. After dessication, the acquired dessicated powder can act as the production sample. Two samples are available for this examination, one is the nanoparticles fabricated by the ISANSS, and the other is the nanoparticles that had been kept for 15 days of settling time. By comparing the XRD pattern after examination with the standard spectrum of a JCPD card, it can be seen that the crystal structure of the fabricated particles is TiO (JCPD no. 8-117), as shown in Fig. 2(a). This figure shows that the TiO₂ nanofluid synthesized in this study would oxidize into TiO within one day upon the completion of preparation. The crystal structure of the fabricated particles that were kept for 15 days of settling time are TiO₂ of anatase (JCPD no. 21-1272), as shown in Figure 2(b). It

Fig. 3 (a) TEM image of the TiO₂ particles fabricated by the proposed method and (b) roundness of the TiO₂ particles measured by Midfun Protech 2500 optical measurement method.

can be seen from the analysis of this examination that when the nanofluid changes to milky white from the original bluish-black color, the particle structure will also change.

To assess the roundness of the nanoparticles, TEM is first used to measure the appearance of the particles. Figure 3(a) is the TEM of the TiO₂ particles fabricated herein, whereas Fig. 3(b) is the roundness of the TiO₂ particles measured by

the Midfun Protech 2500 optical measurement system. The process variables contributing to the production of TiO₂ nanofluid in Fig. 3 are: breakdown voltage of 220 V, peak current of 6.5 A, pulse duration of 4 μ s, off time of 4 μ s, vacuum pressure of 3325~4655 Pa and dielectric fluid temperature of 1°C. The least squares circle method is used to measure the roundness of the prepared TiO₂ nanoparticles. The definition of the least squares circle is: the least of the sum of the square of the radial distance between the target measurement profile shape and the least squares circle. Upon calculation, the average roundness of the TiO₂ particles is 1.2 nm. In comparison, this kind of nano-scale TiO₂ particle with such a high roundness is far superior to those fabricated by a chemical method, and has rarely been noted in the literature. Since the fabricated TiO₂ particles have a high roundness and also good dispersion, the material properties of the nano TiO₂ can be enhanced, significantly improving its further application. Figure 4(a) shows the TEM of the TiO₂ single particle fabricated by this processing method, Fig. 4(b) is a TiO₂ particle for commercial use fabricated by aerosol methods, Fig. 4(c) is the TEM of the roundness measurement of the particles of Fig. 4(A). The synthetic conditions contributing to the production of TiO₂ nanofluid in Figs. 3 and 4 are the same. The roundness determined by the optical measurement system is 0.32 nm. By comparing Figs. 4(b) and (c), it can be clearly seen that the TiO₂ particles fabricated by the aerosol methods do not have sufficient roundness.

Zeta potential is a referential value that can indicate how steady the particles can be suspended and dispersed in the suspension liquid due to the electrostatic repulsive force. It has an important relation with its surface charge density. Although surface charge density cannot be directly measured, it can be estimated by the changes in its Zeta potential.

Generally speaking, if the Zeta potential of a colloidal system is smaller than 20 mV, aggregation occurs between particles, so that they cannot maintain long-term suspension stability. A colloidal system can maintain long-term suspension stability only when its Zeta potential is larger than 35 mV.

When a colloidal system has Zeta potential higher than 40 mV, its electrostatic repulsive force can generally be stabilized and the fluid will show even dispersion.²⁰⁾ By adjusting the pH value, the surface of the particles will generate a certain amount of surface charge, forming an electrical double layer. The repulsive force occurring between this electrical double layer can neutralize the mutual attractive action between the particles, ensuring a more stable TiO₂ nanofluid. Before the Zeta potential measurement, HCl and NaOH are mixed with deionized water into a 0.1 kmol/m³ concentration to adjust the pH value of the TiO₂ nanofluid. The secondary mean particle size of the TiO₂ nanofluid used herein is 45 nm, and its pH value is 7.35. Its fabrication conditions are 250 V breakdown voltage, 6 A current and 15 days of settling time. The Zeta potential of the TiO₂ nanofluid is measured by a Zeta potential meter. The secondary mean particle size is acquired by a particle size distribution analyzer (HORIBA LB-500). The acquired experimental data is shown in Figs. 5 and 6. The measurement results indicate that when the pH value of the TiO₂

(a)

(b)

(c)

Fig. 4 TEM image of a single TiO₂ particle fabricated (a) by the proposed method, (b) by the TiO₂ particles for commercial use, and (c) upon measuring its roundness.

nanofluid is approximately equal to 3.5, the potential carried on the surface of the particle is equal to zero, which is the isoelectric point. When the pH value is larger than 3.5, the particle surface is negatively charged, and when it is smaller than 3.5, it is positively charged. Figure 6 shows the relation between average particle size and pH value, indicating that when the pH value is between 2.5 to 4.5, aggregation occurs between particles, which clearly enlarges the average particle

Fig. 5 Relation between Zeta potential and pH value.

Fig. 6 Relation between average particle size and pH value.

size. The main reason for this phenomenon is that, when the repulsive force of the surface electrical double layer cannot neutralize the mutual attractive action between particles, a stable TiO_2 nanofluid cannot be acquired, thereby enlarging the particle size. But when the Zeta potential is lower than -40 mV, a stable suspension can be obtained. The pH value of the TiO_2 nanofluid produced by this processing method is 7.35, and the Zeta potential is -45 mV, so the suspension liquid has excellent suspension. Figure 7(a) is the FE-SEM image of the TiO_2 particle fabricated by this processing method. The process variables contributing to the production of the superior TiO_2 nanofluid in Fig. 7(a) are: breakdown voltage of 220 V, peak current of 6 A, pulse duration of $2\ \mu\text{s}$, off time of $2\ \mu\text{s}$, vacuum pressure of 3325~4655 Pa and temperature of dielectric fluid 1°C . By calculation, the average roundness of the TiO_2 particles is 0.3 nm. Figure 7(b) is an FE-SEM image of TiO_2 particles for commercial use fabricated by an aerosol method, showing that the TiO_2 particles fabricated by the proposed processing method have far superior dispersion.

Rheological properties are mainly related with the shear stress, shear rate and viscosity of the fluid. Figure 8 shows the measurement result of the rheology properties of three samples of 45 nm and 121 nm of TiO_2 nanofluid with the weight concentrations of 0.1%, as well as of deionized water. The mean particles sizes of two samples are acquired by HORIBA LB-500 particle size analyzer, and 45 nm and

(a)

(b)

Fig. 7 (a) FE-SEM image of TiO_2 particles fabricated by the proposed method and (b) FE-SEM image of the TiO_2 particles for commercial use.

121 nm are the secondary particle sizes. The process variables contributing to the production of TiO_2 nanofluid with mean particle size of 45 nm in Fig. 8 are: breakdown voltage of 210 V, peak current of 5.5 A, pulse duration of $2\ \mu\text{s}$, off time of $2\ \mu\text{s}$, vacuum pressure of 3325~4655 Pa and dielectric fluid temperature of 1°C . The process variables contributing to the production of TiO_2 nanofluid with mean particle size of 121 nm in Fig. 8 are: breakdown voltage of 200 V, peak current of 7 A, pulse duration of $4\ \mu\text{s}$, off time of $6\ \mu\text{s}$, vacuum pressure of 3325~4655 Pa and dielectric fluid temperature of 1°C . The curve slope of Fig. 8(a) is acquired by shear stress and shear strain, and a steeper slope indicates higher viscosity. In this figure, the nanofluid shows a linear relation, not a parabolic shape, confirming that the TiO_2 nanofluid fabricated in this experiment is a Newtonian fluid. Moreover, since the experimental sample is Newtonian fluid, based upon Newton's Law of Viscosity, the ratio of the shear stress and shear strain of any experiment sample should be a fixed value, as shown in Fig. 8(b). This figure shows that under the condition of any strain rate, the viscosity of a fluid with nanoparticles is higher than that of deionized water. This figure also shows that when the nanofluid has a larger secondary mean value, its viscosity value is also larger, but it can still maintain the property of a Newtonian fluid.

Fig. 8 Rheological properties of TiO₂ nanofluids and deionized water: (a) relation between shear stress and strain rate and (b) relation between viscosity and strain rate.

4. Conclusions

This study presents a nanoparticle fabrication method using an improved vacuum arc-submerged nanofluid synthesis system. The conclusions, based on experimental results and analysis, are as follows:

- (1) By means of XRD patterns analysis, the dark blue liquid first fabricated is TiO. After 15 days of settling time, this liquid turns milky white and becomes TiO₂ with anatase structure.
- (2) TEM images clearly show that the TiO₂ particles fabricated herein have outstanding roundness, which is calculated to be 0.3 nm.
- (3) When the Ph value of the fabricated TiO₂ is 3.5, the potential carried on the surface of the particle is zero. When the Ph value is larger than 3.5, the surface of

the particle has a negative charge. The pH value of the TiO₂ nanofluid fabricated herein is 7.35, and its Zeta potential is lower than -40 mV, indicating a stable suspension.

- (4) The fabricated TiO₂ nanofluid is a Newtonian fluid. When the nanofluid has a larger secondary mean value, its viscosity value is also larger.

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