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Evaluating arc spray process parameters to synthesize highly spherical TiO_2 nanoparticles

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Abstract

This work characterizes the metal nanoparticle fabrication process using in situ nanoparticle measurement to obtain the desired geometric sphericity of nanoparticles. Without process characterization and control, the sphericity of prepared TiO_2 nanoparticles varied widely by up to 10% or more of the particle diameter. Therefore, an in situ particle sampling method was employed to collect on-line prepared particles and the particle contours were obtained by FE-SEM. They were analyzed using an image processing approach that had been developed to quantify the sphericity of TiO_2 nanoparticles. Experimental results indicate that the discharge energy parameters, including the operating temperature, vacuum pressure, pulsed peak voltage, pulsed peak current, the pulse on-time and the pulse off-time influence the particles' sphericity. The improved process parameters enhance the average sphericity of the prepared TiO_2 particles by up to 40%.

Keywords: Nanostructured materials; Nanofabrications; Microstructure; Scanning electron microscopy (SEM)

1. Introduction

This study characterizes the synthesis of TiO_2 nanoparticles by a process known as the Submerged Arc Nanoparticle Synthesis System (SANSS) [1,2]. Nanoparticles have potentially useful size- and shape-dependent properties and the synthesis of nanoparticles with desired sizes/shapes is important [3,4]. The application of nanoparticles significantly depends on size-controlled, mono-disperse and shape-controlled (such as sphericity) nanoparticles that are specifically arranged in higher-order structures. However, the reproducible preparation of size and shape-controlled particles using the popular colloid-chemical approach is difficult [4].

The SANSS, shown in Fig. 1, has been developed to prepare nanofluids that contain metal nanoparticles through three stages, namely nucleation, growth and condensation, to generate a suspension of nanoparticles [2,5]. Shape-controlling synthesis of TiO_2 particles with the desired sphericity is vital to obtaining the desired nanomaterial properties.

Without process characterization, preliminary experimental results revealed that the process parameters, such as the operating chamber's pressure, the temperature, the electrical current and the electric energy power markedly influence the sphericity and surface roughness of the prepared TiO_2 nanoparticles, varying by up to 10% of the particle diameter. An in situ particle sampling system was developed and applied to analyze the particle shape and characterize the nanoparticle synthesis. The particle shape contours measured by FE-SEM were also utilized to evaluate the sphericity of the TiO_2 nanoparticles. The following section presents method for sampling and measuring the contours of the particles.

2. Experiment and measurement of particle sphericity

An on-line particle sampling and liquid refilling device, shown in Fig. 1, has been developed to extract TiO_2 particle suspension from the vacuum chamber automatically for on-line particle shape analysis and process characterization [2]. Preliminary predication indicates that the sphericity of nanoparticles could be affected by the operating pressure, temperature, electric current applied in the vacuum chamber, as well as other system parameters [2]. Experiments were conducted on the effect of various process parameters on the sphericity of the prepared nanofluids with TiO_2 nanoparticles.

In the beginning stage of the process, the pure Titanium rod was vaporized by the submerged arc in the heating unit and the control system was deployed to regulate process parameters

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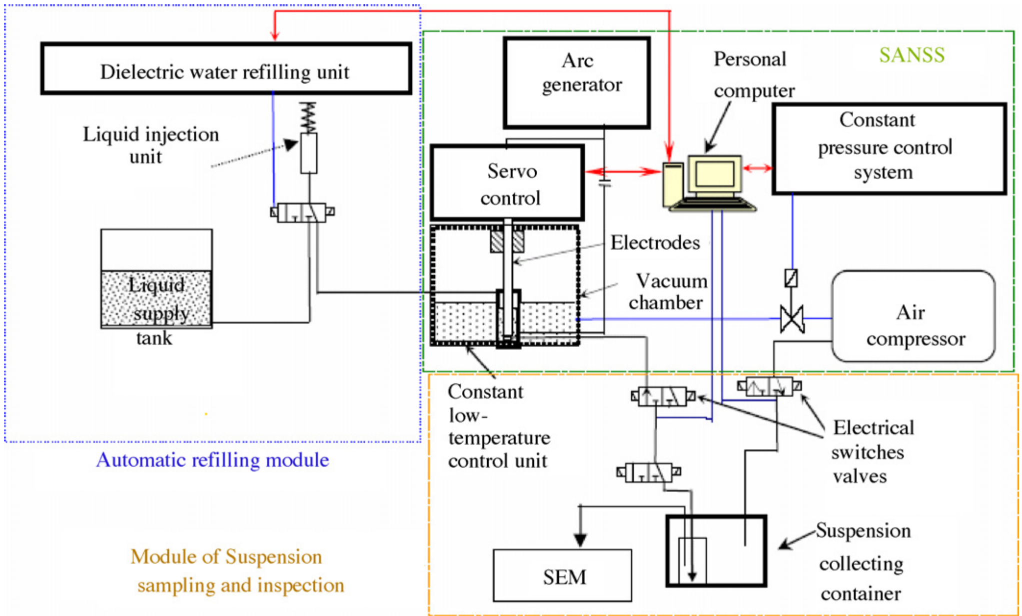

Fig. 1. Schematic diagram of SANSS automatic on-line particle sampling and measurement device.

for suspension preparation. The control modules operated by the SANSS include an arc generating source, a constant pressure system and an isothermal system, in which the governing parameters for synthesizing TiO_2 particles are the breakdown voltage (V), the applied electric current (I), the electric energy frequency with various pulse on-time (T_{on}) and off-time duration (T_{off}), the pressure of the vacuum chamber (P) and the temperature (T) of deionized water. To conduct an effective process analysis, the modulated range of the process parameters was designed to include their full variation range.

The TiO_2 particle suspensions can be automatically sampled using the on-line sampling system, for shape analysis, which includes analysis of size, structure and circularity. The circularity is analyzed by high-resolution FE-SEM (field emission scanning electron microscopy, $\times$100k magnification). The distribution of the secondary particle diameters can also be measured using a dynamic light scattering particle-size analyzer and X-ray diffraction (XRD) is utilized to determine the structure of the nanoparticles.

Fig. 2 reveals that the circularity of particles measured using particle image obtained by FE-SEM, image processing techniques and the least-squares method. The contrast of particle image is enhanced using low-pass filtering through Fourier transformation (Fig. 2(b)). The image is then segmented using an adaptive thresholding algorithm to identify the particle boundary [6]. Accurate particle contours are detected by Laplacian edge detection. The circularity of each particle contour is then calculated using a least squares circle-fitting algorithm. The circularity of contours can be defined as the difference between the maximum and minimum radii of the circles enclosed in the detected contour. However, this value is generally proportional to the diameter of the particle, so the following more useful parameter is proposed to represent the circularity of particle.

$$C = r/d \quad (1)$$

where r is the roundout of the particle contour and d is the mean particle diameter.

In each experiment, more than 30 measurements of particle circularity are made. They are used in a statistical calculation of particle sphericity. The sphericity calculation is based on a 95% confidence level and the standard deviation is determined to ensure data accuracy.

3. Results and discussion

3.1. Analysis of composition of nanoparticle suspension

The nanoparticle suspension is prepared by SANSS at high temperature and vacuum; the nanoparticles have only three constituent elements—Ti, O and H. Fig. 3 shows the XRD results of sampled particles. The prepared nanoparticles are TiO_2 in the form of anatase. The reason for forming TiO_2 rather than pure Ti nanoparticles was that titanium can react with oxygen, which is dissolved from deionized water or air. Consequently, the sampled suspension appears grey at the beginning of the sampling process, and slowly turns white after presence in air for a period of time.

3.2. Effect of temperature of deionized water and pressure in the vacuum chamber on shape of nanoparticles

Fig. 4 presents four FE-SEM images of the samples prepared at four different temperatures of the deionized water—0, 5, 10 and 20 °C. Clearly, sphericity of particles prepared at low temperature tends to be superior to those prepared at high temperature. The particles tended to be incomplete and break into pieces as the temperature is increased. The temperature critically affects the quality of the formed particles, because the metal transfer frequency from gaseous state (β) to solid state (α) on the interface significantly affects the growth rate

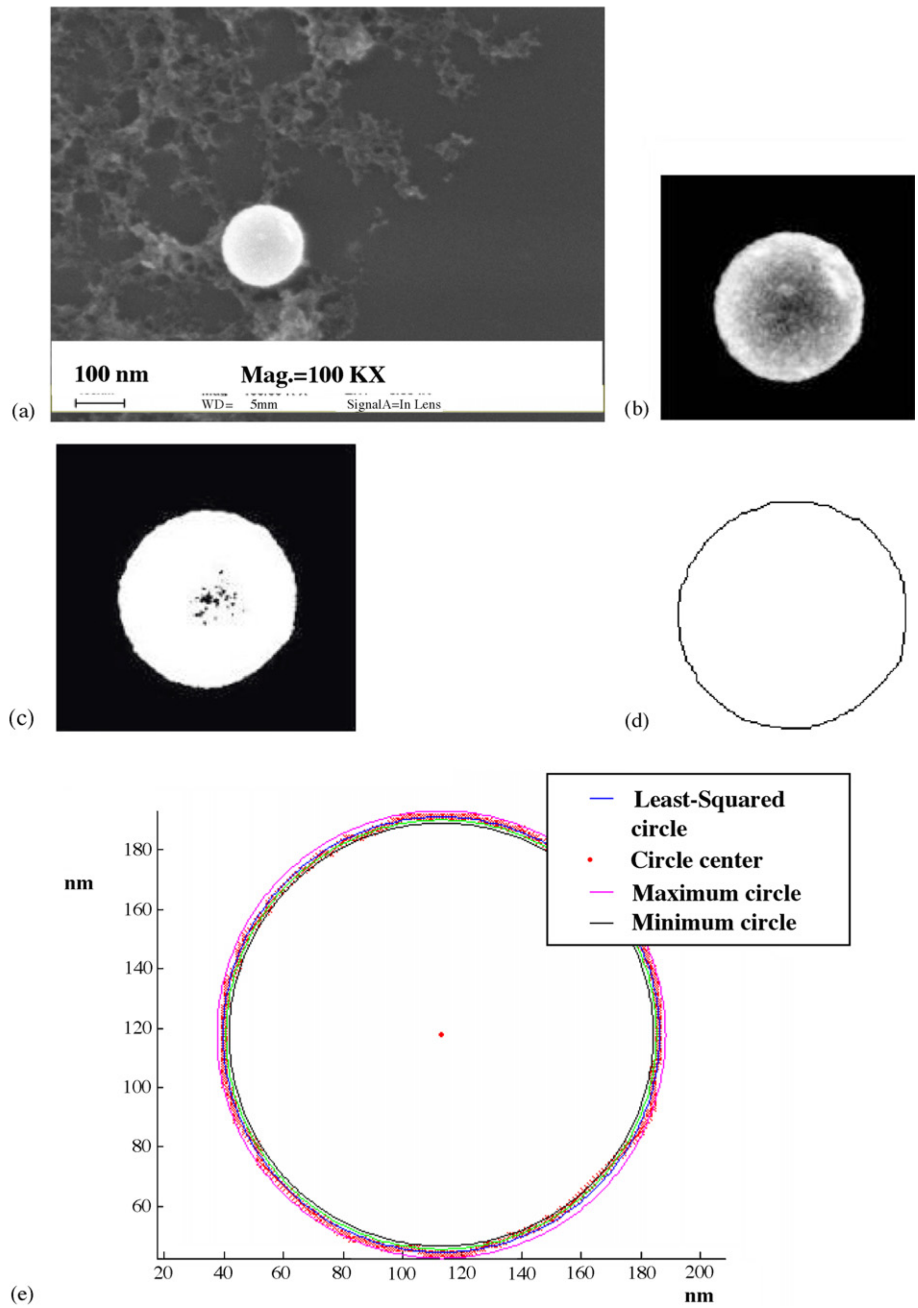

Fig. 2. Determination of contour circularity of the particles: (a) capture image of detected TiO_2 nanoparticle using FE-SEM; (b) enhance image by low-pass filtering; (c) segment the image; (d) identification of particle contours; (e) identification of roundout.

of the nuclei. Comparable results were obtained when a low vacuum pressure was used in the SANSS. Fig. 5(a and b) reveal that increasing operating pressure increases irregularity of shapes.

3.3. Effect of breakdown voltages on shape of nanoparticles

Fig. 6 plots the variation in sphericity at four breakdown voltages when other process parameters are held constant. The results demonstrate that a higher breakdown voltage tends to produce particles of better sphericity. Average sphericity, calculated from over 30 samples, improved from 4.37 to 2.91% as the breakdown voltage was increased from 90 to 220 V. Thus, particle sphericity was improved by more than 30% as the breakdown voltage rose by 130 V.

3.4. Effect of applied electric current on shape of nanoparticles

Fig. 7 plots the variation in sphericity of the TiO_2 nanoparticles prepared at four different electric currents. A lower electric current tends to prepare particles of better sphericity. The mean sphericity of the particles was improved from 4.87 to 2.91% as

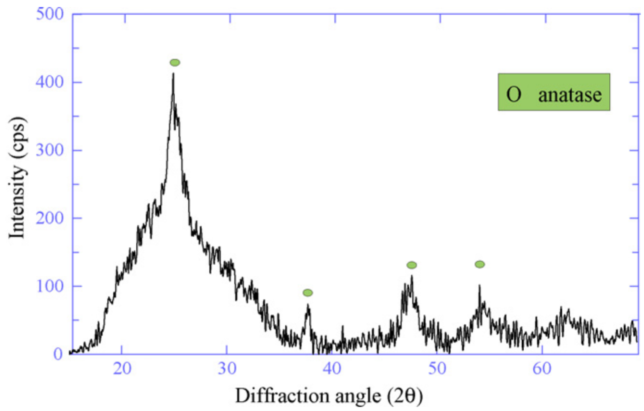

Fig. 3. XRD pattern of prepared TiO_2 particles.

the current applied to the ASNSS was reduced from 6 to 1.5 V. Sphericity was thus improved by over 40%. A maximum threshold value was maintained to control the particle shape within the desired range.

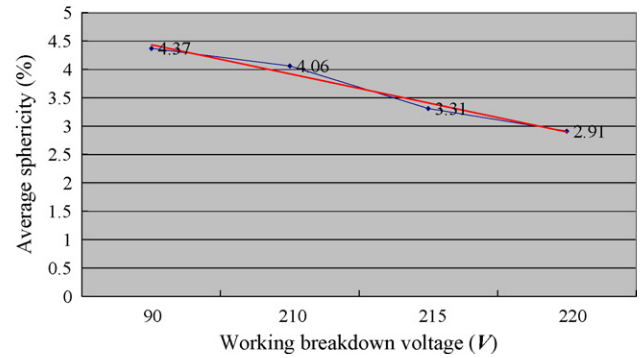

Fig. 6. Relationship between applied breakdown voltage (*V*) and particle sphericity.

3.5. Effects of on-time and off-time of pulse on shape of nanoparticles

The duration of the pulse of the applied electric discharge determines the heating pattern (magnitude and frequency) of

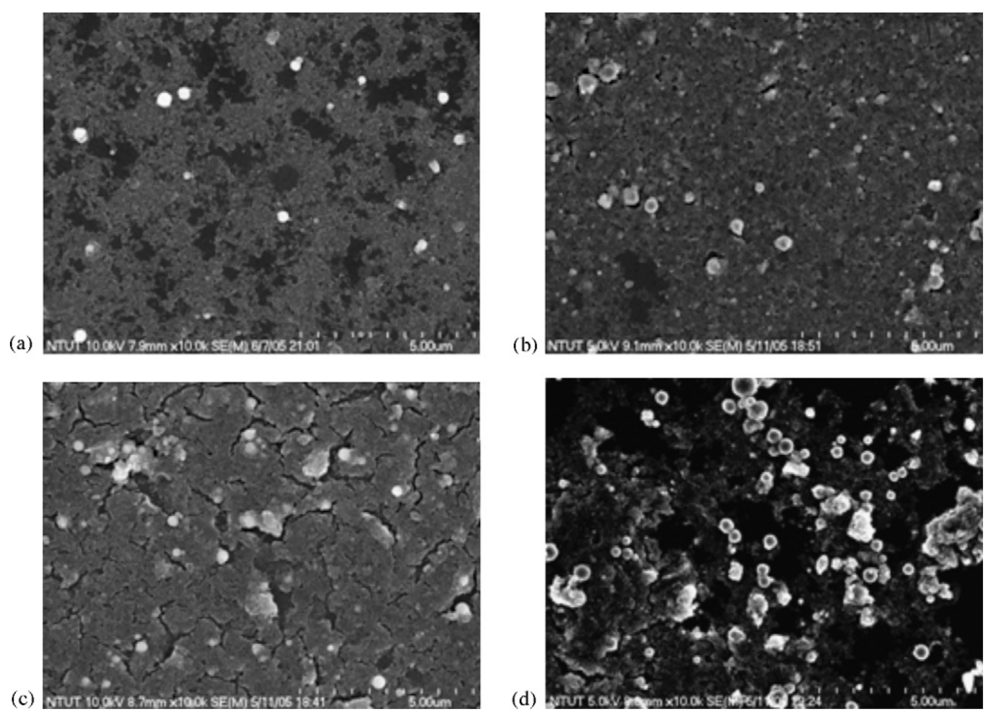

Fig. 4. Effect of temperature (*T*) of suspension on particle shape: (a) 0 °C, (b) 5 °C, (c) 10 °C and (d) 20 °C.

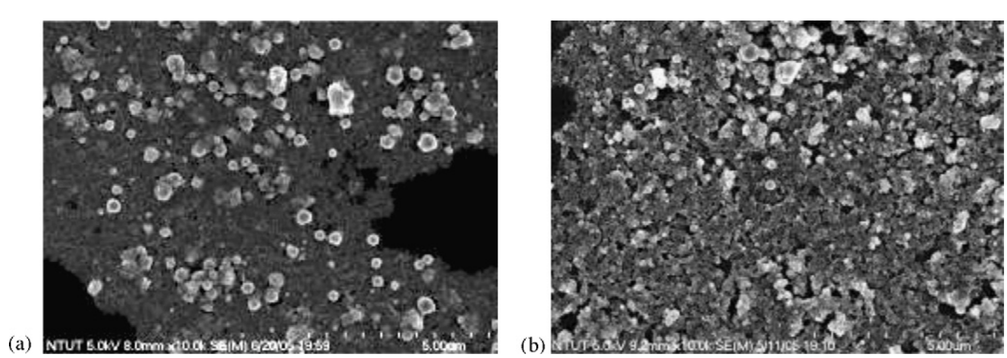

Fig. 5. Effect of pressure (*P*) of vacuum chamber on particle shape; (a) 30 Torr and (b) 1 atm.

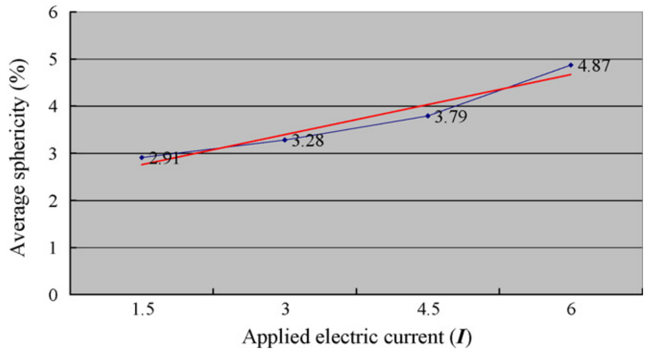

Fig. 7. Relationship between applied electric current (I) and particle sphericity.

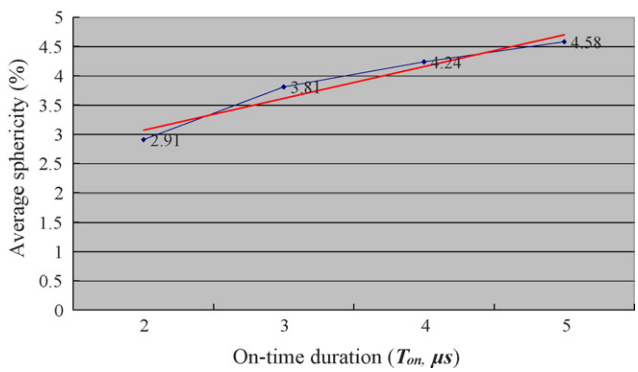

Fig. 8. Relationship between on-time duration (T_{on}) of pulse and particle sphericity.

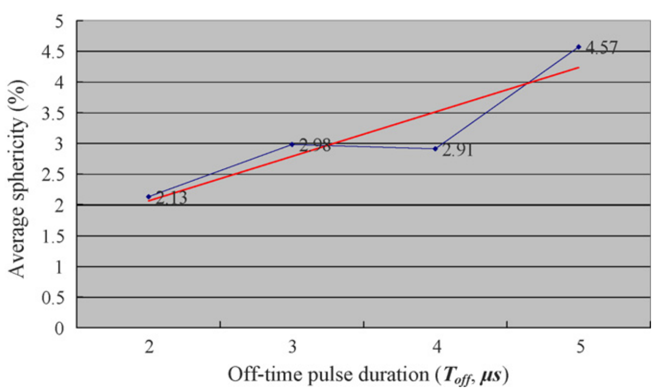

Fig. 9. Relationship between off-time duration (T_{off}) of pulse and particle sphericity.

the SANSS. The mechanism of preparation clearly differs between large and short pulse. The melted and vaporized depth zone is deeper when the electrode is machined using longer pulses. Shorter pulses create shallower vaporized zone than longer pulses. Accordingly, the pulse on-time and off-time durations were set at different levels to explore the effect of pulse-duration on particle size. The experimental results reveal that the particle sphericity varies with the pulse-duration. The increase in the average sphericity (Fig. 8) was 36% as the on-time duration was decreased from 5 to 2 μs. Comparable results were obtained when lower off-time duration was applied (Fig. 9).

4. Conclusions

SANSS was used to investigate the preparation of titanium dioxide nanoparticles with a desired sphericity. The process parameters, such as applied electric current, breakdown voltage, pulse-duration, operating temperature and chamber pressure are used to improve sphericity of TiO_2 nanoparticles. Sphericity was improved with high breakdown voltage, low electric current and a high frequency of the electric energy pattern. The temperature of the deionized water and the chamber pressure used in the process also crucially affect the shape of the formed particles.

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