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Original Research Paper

The formation mechanism and morphology of the nickel particles by the ultrasound-aided spark discharge in different liquid media

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ABSTRACT

Spark discharge is widely applied in the fabrication process of the particles with very small sizes. The ultrasound-aided spark discharge process is based on the electrical discharge in the liquid media of the electrical discharge machining (EDM). In this paper, the morphology, element composition, and crystal structure of the Nickle particles produced by the ultrasound-aided spark discharge were observed and analyzed by SEM, EDS and XRD respectively. The EDS and XRD indicated that the purity of the nickel particles generated in pure water is higher than that in kerosene. Meanwhile the effects of dielectric media on the size distribution were also investigated. It was found that the size distribution of the particles in pure water is narrower than that in kerosene, but when the ultrasound was introduced into the generating process, the size distributions of the particles in both media have remarkable improvements (both became narrower). Based on the attaching and entrapping processes, the formation mechanism of different structural particles was also presented. Following the study on the changes of the effective densities and the ratios of the closed hollow particles in different experiments (with and without ultrasound), we found that, with the aid of ultrasound, the ratio of the closed hollow particles increased about 10–15%. In overall, the results in this paper provide a foundation for the some future research, such as the study on the control of the particle properties (in size and morphology) by improving the experimental conditions.

1. Introduction

In recent years, the demands of metallic micro/nanoparticles have been constantly increasing in various science and engineering areas, from semiconductor industry to environmental industry. Particularly, because metallic micro/nanoparticles have the sizes on micro scale or Nano scale, they have been broadly used in the fields such as nanoelectronics, sensor technology, linear optics, catalysts, hydrogen storage and solar technology [1–2]. Different physical methods/techniques have been developed and applied to produce various kinds of metallic micro/nanoparticles, and the common techniques include gas-evaporation, vapor condensation, plasma, laser ablation, and spark discharge [3–6]. Spark discharge has been receiving more and more attention due to its simple and low cost in the setup and operation of the metallic micro/nanoparticles producing process. This technique uses periodic spark discharge to vaporize electrode materials and subsequently generates micro/nanoparticles in the process of nucleation and condensation. During the spark discharge, the breakdown voltage enables a discharge channel instantaneously generate in the dielectric fluid between the electrode gaps, and the subsequently formed plasma enables the local temperature of the sparks reach about 10,000–18,000 K [7]. Material is removed through the thermal erosive actions of the electrical discharges between the two electrodes. Each individual spark discharge can melt and evaporate a small amount of material from both electrodes. Most of the molten metals and vapor clusters are ejected, and when they come across and contact with the cold dielectric media, finally form into the particles with very small sizes.

Many researchers have devoted their efforts on the study of producing metallic micro/nanoparticles by using spark discharge. Nguyen et al. [8] produced high purity magnetic particles by spark erosion. Hontanon et al. [9] synthesized the copper micro/nanoparticles in the pure nitrogen between two electrodes by electrical discharges, and they found that the mass output rate and the particle size distribution were mainly determined by the electrical gap and the gas flow rate. Schmidt-Ott et al. [10] investigated the

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characterizations of Silicon nanoparticles produced by spark discharge and they also summarized the relationship between the purity of the nanoparticles and the synthesizing conditions. Messing et al. [11,12] produced Pd particles in the aerosol generator and characterized the particles by different photoelectric devices, and they also claimed that the small size dispersion and particle surface coverage could be controllable. Tabrizi et al. [6,13,14] used the microsecond spark discharge generator to synthesize bimetallic nanoparticles with a flexible mixing ratios on nanoscale. Voloshko et al. [15,16] numerically investigated the physical mechanisms involved in the formation process of metallic nanoparticles by spark discharge at atmospheric pressure, and they also demonstrated that their calculation results can indicate the favorable conditions for the nanoparticle yield increase and also for the particles size reduction. Allagui et al. [17] synthesized Ni and Pt nanomaterials in acidic and alkaline solutions by glow discharge and showed the co-existing of the two synthesis mechanisms of nanomaterials. Dvornik [18] used spark erosion to produce microstructured particles and carbonized them in CO gas to synthesize nanostructured particles. It is worth pointing out that the researchers above mainly used a high voltage (over than 1 kV) to generate energy and also the gas or liquid flows to take away the primary particles, and finally form the nanoparticles after the nucleation and condensation. Therefore these methods are highly dependent on the sealed chambers, where the generated turbulence of the gas or liquid flows can eject the primary particles from the heating region. Meanwhile, the insulation of the chamber should be carefully treated due to the high voltage. On the other hand, some researchers also used electrical discharge machining (EDM) to fabricate particles in the low voltage condition (less than 200 V). Sahu et al. [19] used micro-EDM to prepare the copper micro/nanoparticles with different operating parameters in de-ionized water with the stabilizers. Tseng et al. [20] used the EDM device to fabricate the silver nanoparticles in pure water at room temperature.

However, all of these researches above did not discuss the formation mechanism of solid or hollow particles. Compared with the solid micro/nanoparticles, the hollow micro/nanoparticles have larger specific surface area, higher specific surface energy and higher catalytic activity. The hollow micro/nanoparticle also have different properties from the conventional solid particles, such as optics, magnetics, mechanics, electricity, and chemical activity [21]. Therefore, it is necessary to study the formation mechanism of the particles. Particularly the preparation of hollow metallic micro/nanoparticles has attracted more and more attention in very recent years. In our previous research [22,23], we found that the hollow monometallic particles could be fabricated by the EDM device with the assist of the ultrasound. Peng et al. [24] fabricated the hollow Ni microspheres by means of silicon powder-mixed spark discharge and they mainly focused on the size distribution analysis in different operation conditions. Byeon et al. [25] used the spark plasma to synthesize bimetallic hollow micro/nanoparticles in ambient gas, and they also investigated the biocompatibility and lithium storage capacity of the generated particles. Berkowitz and Nersessian et al. [26,27] attempted to produce hollow alloy particles in nitrogen surrounding by spark discharge technique, but they didn't pay more attention on the formation mechanism of hollow particle, the mean size of their produced particles was large. In overall, the existing research is far from being enough for understanding the formation mechanism and morphology of different structural particles, especially for the hollow metallic particles.

In this paper, we mainly investigated the formation mechanism and morphology of the hollow Ni micro/nanoparticles generated by ultrasound-aided Spark Discharge. In order to analyze the purity of the particles generated in different dielectric media (pure water and kerosene), the composition of the elements and the lattice structure of the samples were detected by EDS and XRD respectively. To discuss the positive effect of ultrasound on the size of particles, the relationship between the cavitation collapses and the properties of dielectric media was studied by analyzing the influence of surface tension, viscosity, and vapor pressure on the cavitation. It was found that higher purity and narrower size distribution were obtained in pure water, in comparison with the experiment results in kerosene. Based on the attaching and entrapping processes, the formation mechanism of different structural particles was also interpreted. In particular, the formation mechanism of hollow particles was described in detail. Finally, the effective density of Ni particles were measured by the gas volume replacement method and the effect of ultrasound on the ratio of the closed hollow particles was studied.

2. Experiments

The schematic diagram of our ultrasound-aided EDM experimental setup for Ni particle generation is shown in Fig. 1. The system mainly consists of a spark discharge generator and an ultrasound generator. The spark energy was controlled by the EDM machine E46PM (from Jiangsu Excellent Numerical Control Equipment Co., Ltd., Jiangsu, China) with variable electrical currents (ranging from 1.5 to 60 A), variable pulse widths (ranging from 2 to 1200 μs), and variable gap voltages (ranging from 30 to 120 V). The servo system controlled the tool electrode to maintain the optimal distance on micrometer scale. The ultrasound oscillators were attached on the opposite sides of the stainless steel processing box. We conducted the high purity Ni rods (with purity higher than 99.9%, supplied by Tianjin Chengshuo Steel Trading Co., Ltd., Tianjin, China) as the two-electrode, i.e. the tool electrode (cathode) and the workpiece electrode (anode).

The investigation was conducted in a laboratory environment in two different liquid dielectric media, i.e. in pure water and in kerosene. The boiling point of kerosene ranges from 180 to 310 °C and density is 0.780 g/cm^3 at 25 °C. The density of pure water is 1 g/cm^3 at 25 °C. The physical properties of the two dielectric medium are shown in Table 1.

Twenty groups of experiments were carried out by ultrasound-aided spark discharge and each group consists of two experiments, one in pure water and the other in kerosene, and we call these groups as control groups. Meanwhile, another twenty groups of experiments were carried out by spark discharge only (without ultrasound), likewise, in pure water and in kerosene separately, and we call these groups as reference groups. The selection of experimental parameters is based on the orthogonality relation principle. The currents were from 4.5 to 60 A, the pulse widths were from 15 to 300 μs, and the variable gap voltages were from 15 to 90 V. The range of ultrasound powers were from 0 to 900 W and the frequencies were selected at 28, 56, and 126 KHz. It is worth pointing out that we found that the results from the all forty experiment groups had very similar tendency and characteristic, so we only select five control groups and five reference groups to explain the tendency and changing characteristic in the following section. The experimental conditions of the selected reference groups are shown in Table 2.

The electric parameters of the selected control groups (called as Sample1$^{\#}$ to 4$^{\#}$) are the same as those of the selected reference groups, but with the extra parameters of the ultrasound at 900 W of power and 28 KHz of frequency. Each group was applied with fixed 1 h time duration.

The gelatinous precipitates were filtered through a vacuum filter. In particular, the samples generated in kerosene were washed and cleaned by petroleum ether (melting (II), AR, boiling point 60–90 °C, 500 mL, supplied by Hangjia Bio-pharmaceutical Technology