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SYNTHESIS AND MAGNETIC PROPERTIES OF Ni NANOPARTICLES

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Abstract. This study proposes a new method of using the arc-submerged nanofluid synthetic system to fabricate Ni nanoparticles. The proposed system has the advantages of high-power electric arc heating system, excellent stability of the electric arc, and well-developed control technology. This system uses the energy produced by arc discharge to melt and vaporize pure nickel rod under vacuum conditions. The vaporized metal is cooled rapidly inside a low-temperatured dielectric liquid, forming Ni nanoparticles that are evenly distributed inside the dielectic liquid. Experiments prove that the mean particle size of the Ni nanoparticles fabricated by this system is 20 nm. Their size is very consistent and the suspension of fabricated nanofluid is highly stable. This paper further investigates the influence of pH value and Zeta potential of the nanofluid on its suspension stability. Results of inspecting the magnetic properties show that the fabricated Ni nanofluid is similar to a Newtonian fluid, since residual magnetization and coercive force do not exist therein. Moreover, the Ni nanoparticles exhibit superparamagnetism. In addition, when Ni particles are worked under applied magnetic field, the particles would move in the direction of magnetic field. When the magnetic field is removed, the particles stop moving and still remain stably suspend in the dielectric liquid.

1. INTRODUCTION

The applications of nano-magnetic particles have expanded rapidly, for fields including ferrofluids, data storage, biomedicine, *etc*. Magnetic materials are widely applied in daily life, for example in electrical appliances such as electric generators, loudspeakers, adaptor etc. Moreover, even animals carry nano-magnetic materials, for example, bees, migratory birds, salmon, turtles, *etc*. In 2000, Sun *et al*. [1] successfully fabricated FePt magnetic particles with superlattice structure. In 1994, de Herr *et al*. [2] showed that when the temperature lies within the range of 80~1000K, the atomic clusters of super-paramagnetic materials such as iron, cobalt and nickel are composed of from thirty to a few hundred atoms, and the atomic magnetic moment increases to the extent that it is larger than the bulk material. They also found that when the composition of an atomic cluster is less than 30 atoms, its magnetic moment would then be close to the atomic magnetic moment.

However, when the number of atoms increased to 700, the magnetic moment of the particle would approach that of the bulk material. Therefore, the magnetism would change according to the size of the atom cluster. The most commonly seen magnetic material belongs to multi-domain collective body. If the size of the material is too small to identify its magnetic domain, then a single-domain magnetic material would form, enabling the magnetic material to be produced into nano-magnetic particles or a thin film, whereas the mixture of magnetic particles with the solution (liquid carrier) would form a magnetic fluid.

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Table 1. Process variables for production of better Ni nanoparticles.

Working condition	Description
Breakdown voltage (V)	220
Peak current (A)	11~15
Pulse duration (μs)	8
Off time (μs)	8
Pressure (Torr)	20
Temperature of dielectric liquid (°C)	0
Electrode diameter (mm)	5
Dielectric liquid	Deionized water

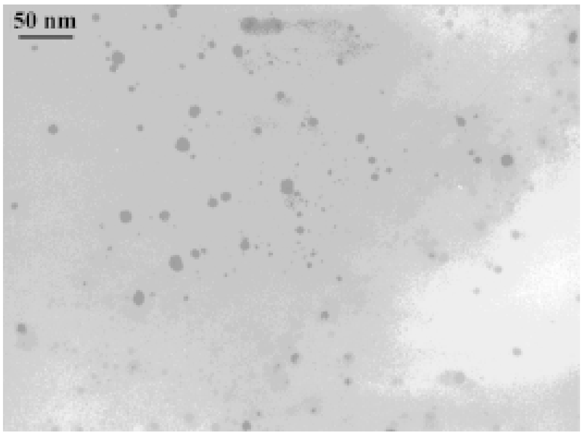

Fig. 1. TEM image of Ni nanoparticle suspension prepared using better process variables.

The so-called magnetic fluids or ferrofluids are formed by the cladding of the nano-magnetic particles by the surface active agent, so that they can be stably dispersed in solution, and the magnetic particles would not be affected by magnetic or gravitational fields to conglomerate and separate from the solution [3,4]. When the magnetic fluid is placed inside a magnetic field, the nano-magnetic particles would be drawn towards the strong magnetic field. At the same time, the field would drive the solution to move together. Performing the same behavior as strong magnetic solids such as iron and nickel, such fluid can be regarded as strong magnetic substance in liquid state. Therefore, a magnetic fluid is a kind of solution with a behavior that can be controlled by changes of magnetic field, as well as having the characteristics of both magnetism and fluid. The particles of the magnetic fluid are made up of strongly magnetized ferrite, whereas the iron oxides are a complex metal oxide composed mainly of Fe_2O_3. In terms of application, oxides can be divided into soft ferrite and hard ferrite, generally by the intensity of the coercive force (*Hc*). Oxides that can easily lose magnetism are known as soft ferrite, whereas those that maintain it better are hard ferrites. Based on the past definition, *Hc*>200 Oe is a hard ferrite, *Hc*<20 Oe is a soft ferrite and 20 Oe<*Hc*<200 Oe is semi-hard ferrite.

Magnetic fluids are composed mainly of nano-magnetic particles, liquid carrier and surfactant. Herein, the most important element is the material property of nano-magnetic particles, followed by the surfactant, which stabilizes the magnetic particles suspended in the liquid carrier. The selection and use of the liquid carrier depends on the characteristics of the magnetic fluid and its application. Due to the thermal motion of the resting medium elements inside the solution, the magnetic particles inside the magnetic fluid generate Brownian motion. With the irregular Brownian motion inside the liquid carrier, although the magnetic moment of the magnetic particles is fixed at a certain direction, the direction between magnetic particles is not fixed. In other words, there is no magnetic anisotropy or shape anisotropy in the magnetic particles themselves. If the liquid is not affected by an applied magnetic field, the magnetic moment inside the magnetic particles rotates freely because of heat energy. If the magnetic particle is so small to change the direction of the magnetic moment of every magnetic particle by heat energy, then it demonstrates the character of superparamagnetisim [5-7]. Furthermore, when the particle size is smaller than the critical diameter, then the magnetic particles become superparamagnetic, and the coercivity is zero. In other words, there is no residual magnetization, creating a condition without hysteresis [8]. Under the environment of applied an magnetic field, the magnetic particles would act inside the liquid carrier by heat energy, magnetic energy and gravity energy. Under strong magnetic action, gravity energy becomes unimportant. Therefore, if heat energy and magnetic energy conflict with each other, then the magnetic particles can be stably suspended in the liquid carrier. When the particle size of the magnetic particles is smaller than the largest particle size of the suspended particles, then the Brownian motion produces by the heat energy

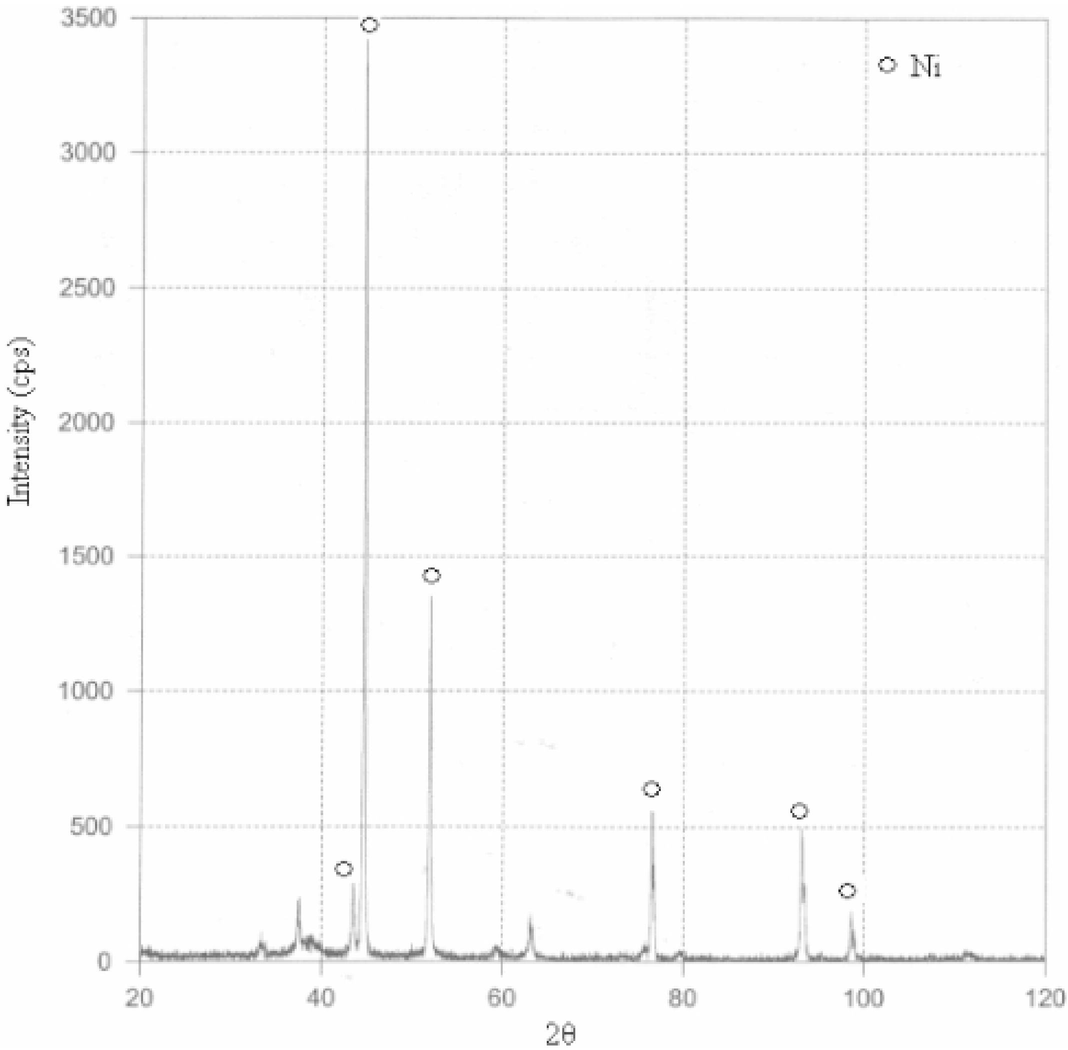

Fig. 2. XRD pattern of Ni nanoparticles prepared by the proposed system.

contends with attraction action generated by the magnetic field, and the particle size can be stably suspended [9,10].

The main purpose of this paper is to use the self-developed arc-submerged nanofluid synthetic system to produce a Ni nanofluid with smaller particle size and good suspension stability. This paper further investigates the influence of pH value and Zeta potential of the nanofluid on its suspension stability. Furthermore, this study will also discuss the magnetic properties of the prepared Ni nanoparticle suspension.

2. EXPERIMENTAL

A great deal of research and development for new nanoparticle synthesis methods has been proposed and implemented in the past decades. This study proposes a new method using an arc-submerged nanofluid synthetic system to fabricate Ni nanoparticles [11-13]. The experimental device is comprised mainly of an electrical power utility, servo-positioning system, vacuum chamber, vacuum pump, heating source, cooling system, and pressure control unit. The vacuum chamber maintains the temperature and pressure constant at an adequate level [14]. The heating source generates a submerged arc to vaporize the metals, which are the electrodes. Important process parameters, such as applied electrical current, voltage, duration on and off time, electrode gap and feed velocity of servomotor, are controlled as required. In the process, a bulk metal applied as the electrode is

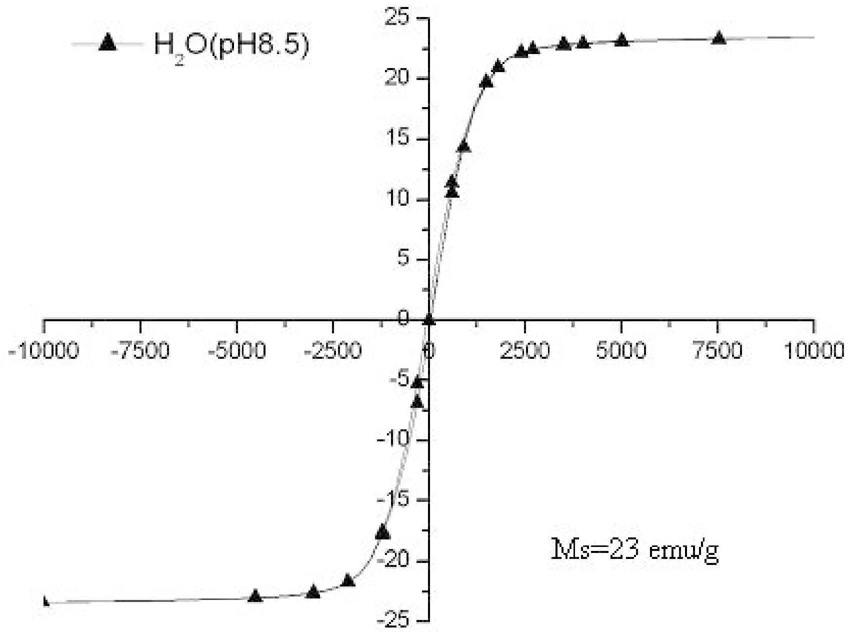

Fig. 3. Hysteresis loops of the magnetic particles in the magnetic fluid.

submerged in dielectric liquid in a vacuum chamber. Applied electrical energy then produces heating source for generating an adequate arc with a high temperature ranging from 6000 to 12000 °C. In the development process, a Ni bar is melted and vaporized in distilled water, which is used as an insulating liquid. The constant temperature system is employed to maintain a desired and constant temperature of the dielectric liquid, in which the vaporized metal aerosol can be effectively nucleated, thus preventing excessive grain growth. Metal nanoparticles can then be formed and prepared. The proposed system is innovative because the raw materials are submerged in the dielectric liquid during the process within a vacuum-operating environment and the vaporized metals are condensed in dielectric liquid. Nanoparticles can be successfully prepared and uniformly dispersed in the dielectric liquid. The suspension with well-dispersed nanoparticles can be used directly in various applications.

This paper mainly investigates the processing method by vacuum submerged arc as well as the effect of the important processing parameters such as peak current, voltage, pulse duration, off time, temperature of dielectric fluid towards the production of nanoparticles, so as to find the best processing parameters. Based on the best processing parameters, after centrifugal and still placement screening, there is further analysis to investigate the properties of the fabricated nanoparticles, such as the particle shape, structure, magnetism as well as the Zeta potential of the nanofluid. XRD and EDX are used to analyze the structure and composition of the nanoparticles produced by the experimental equipment, and TEM, FE-SEM and PSA are used to observe the particle size and the distribution of the particle size. A Zeta potential meter is used to measure the Zeta potential, and a Superconducting Quantum Interferences Device Magnetometer (SQUID) is used to analyze the magnetic properties of the nanoparticles.

3. RESULTS AND DISCUSSION

From the analysis of a few experiments, the results show that process variables including breakdown voltage, pulse duration, off time, peak current and temperature of dielectric fluid can all affect the preparation of nanoparticles. The Ni nanoparticle suspension prepared under better process variables identified throughout different conditions in the experiment is summarized in Table 1. In sum, nanoparticles with a mean particle size

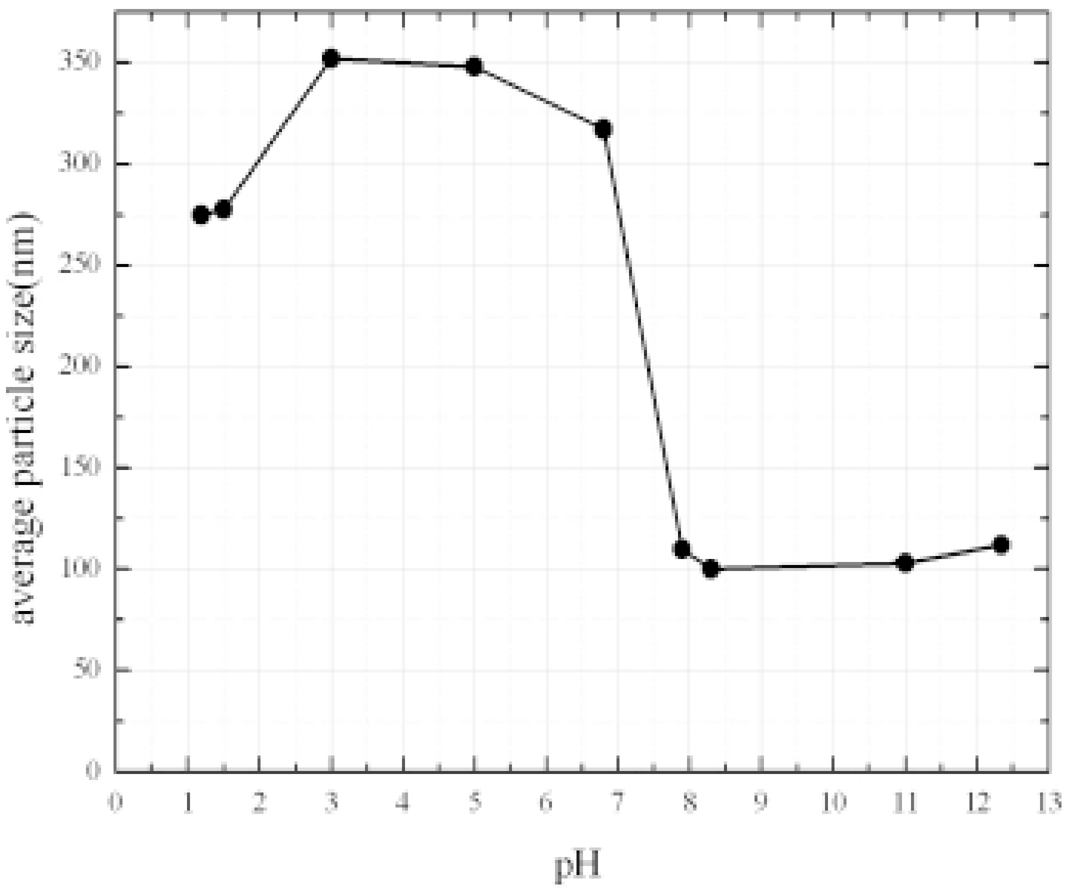

Fig. 4. Relationship between the pH value and the mean particle size of the magnetic fluid.

of less than 20 nm can be prepared using process variables within their respective scopes listed in Table 1, and particles with the smallest mean size can be achieved under a current of 13 A. As shown in Fig. 1, with process variables listed in Table 1, there can be good nanoparticle dispersion with a mean particle size below 20 nm. Furthermore, the particle size distribution under volume distribution derived from the HORIBA particle size distribution analyzer, indicates a mean particle size of 25 nm.

Furthermore, based on single Ni nanoparticle, EDX analysis is used to analyze the ingredients of its composition, indicating that the fabricated nanoparticles contain elements of Ni and O. Besides, EDX analysis result shows that, the weight percentage of O is 4% only, whereas that of Ni is as high as 96%. Then upon the comparison of XRD analysis, as shown in Fig. 2, the fabricated nanoparticles have a high percentage of pure nickel, as well as small quantities of NiO. Therefore, the fabricated magnetic fluid contains mainly pure nickel particles and very small quantities of oxidized nickel exists.

The authors adopt SQUID, as manufactured by Quantum Design Company of the U.S, is frequently used for the experiments on magnetic measurement. As shown in Fig. 3, the magnetic fluid is initially dried into powder, and then put in the capsule container to measure the hysteresis loops of Ni nanoparticles at room temperature of 25 °C, and magnetic strength of -10^4 ~ $+10^4$ Gauss. From the magnetic measurement results of Figure 3, it is found that the saturated magnetization Ms of the fabricated Ni nanoparticles is 23 emg/g, and its saturated magnetic strength is 2760 Oe. In addition, the experiment shows that its residual magnetism and coercive force is close to 0, confirming that the magnetic particle is superparamagnetic particle. In other words, when the particle is small enough, and the anisotropy energy is too small to be identical with the heat motion, the direction of magnetization would no longer be fixed and the

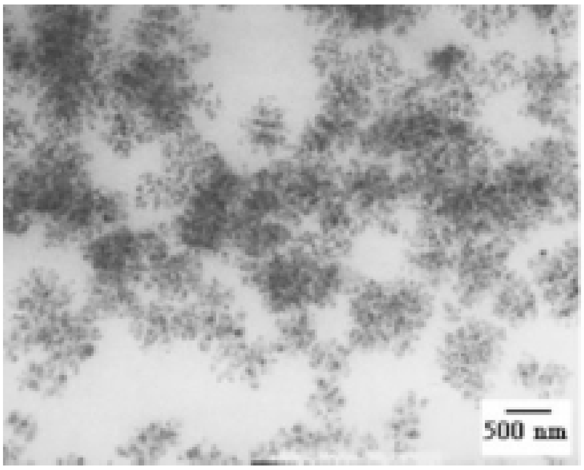

Fig. 5. TEM image of Ni nanofluid with pH value of 3.0.

direction of easy magnetization would change irregularly, causing the phenomenon of superparamagnetism [15].

Apart from the influence of the form and ingredients of the particles, the mutual action between the particles and all kinds of fluids in the environment is also an important factor affecting the application of magnetic fluids. When the surface of a particle contacts the fluid, it will stick to the molecules of the fluid and chemical ingredients that are different from the interior of the particles exist. Therefore, researchers use strong acid (H_2SO4) and strong alkaline (NaOH) to mix the *p*H value of the solution, so as to observe the effect of the pH value of the liquid carrier (environment) towards the particles. Experimental results show that, when the pH value of the magnetic fluid lies within the range of 1.2~1.5, Ni particles would rapidly conglomerate and precipitate within a few hours, and it is fastest is when the magnetic fluid has a 3.0 pH value, whereas a 6.8 pH value will precipitate only after still placement for a week. A magnetic fluid of 7.9 pH value will slightly cluster after approximately 3 weeks and that of ph value?8.0 carries good suspension ability. Therefore, the authors consider that the critical point of the pH value of the magnetic fluid is pH 8.0, so a fluid of over pH 8.0 would not conglomerate. Fig. 4 shows the relationship between the pH value and the mean particle size of the magnetic fluid, Fig. 5 is the TEM image of acid suspension fluid of pH 3.0. It is known from the image that clustering occurs towards the Ni particles inside the strong acid fluid, and its mean particle size is larger than 200 nm.

The first problem that needs to be solved when nanoparticles are in a liquid carrier is their clustering and precipitation, especially in a magnetic fluid. In addition to the properties of stable dispersion and suspension, the fluid has to carry magnetic and mobile properties, so the phenomenon of clustering and precipitation of the particles needs more attention. The zeta potential is an important parameter reflecting the colloid behavior of the particles. When it is at isoelectric point, the surface of a particle does not carry an electric charge. At this moment, particles inside the fluid would be prone to conglomerate. However, the farther away that the Zeta potential of the particle is from the isoelectric point, the better the dispersion ability. In other words, when the density of the electric discharge of the particles is higher, the particle carries higher Zeta potential and the high electric discharge density on the surface of the particle would produce a larger repulsive force of the static electricity between the particles, leading to a higher stability of the suspension fluid. The current experiment firstly mixed the pH value of the magnetic fluid, so as to change the property of the liquid carrier environment and make the surface of the magnetic particles to form a certain amount of surface electric discharge, producing a double electric layer. The repulsive force between the double electric layers offset the mutual attractive action between the particles, which is beneficial to their dispersion. Fig. 6 shows the Zeta potential of Ni nanofluids with different pH values.

Before the properties of the colloid of the magnetic fluid fabricated by a better process parameter had not been affected by the pH fluid, its average Zeta potential was -1.625 m.V. Figure 6 shows that when the pH value is 3.0, the Zeta potential of Ni nanofluid was close to the isoelectric point. Comparing this figure with Fig. 4, it can be seen that the mean particle size of the magnetic fluid with pH value of 3.0 is also larger. When the magnetic fluid tends to be alkaline, the Zeta potential increases clearly and the particles do not conglomerate easily. Therefore, it can be seen that when the pH value of the magnetic fluid is larger than 8.0, and the Zeta potential is below -1.5 mV (which is farther away from the isoelectric point), then the suspension ability of the particles of the magnetic fluid would be better. However, if surfactant is added into Ni nanofluid, then the Zeta potential would be greatly

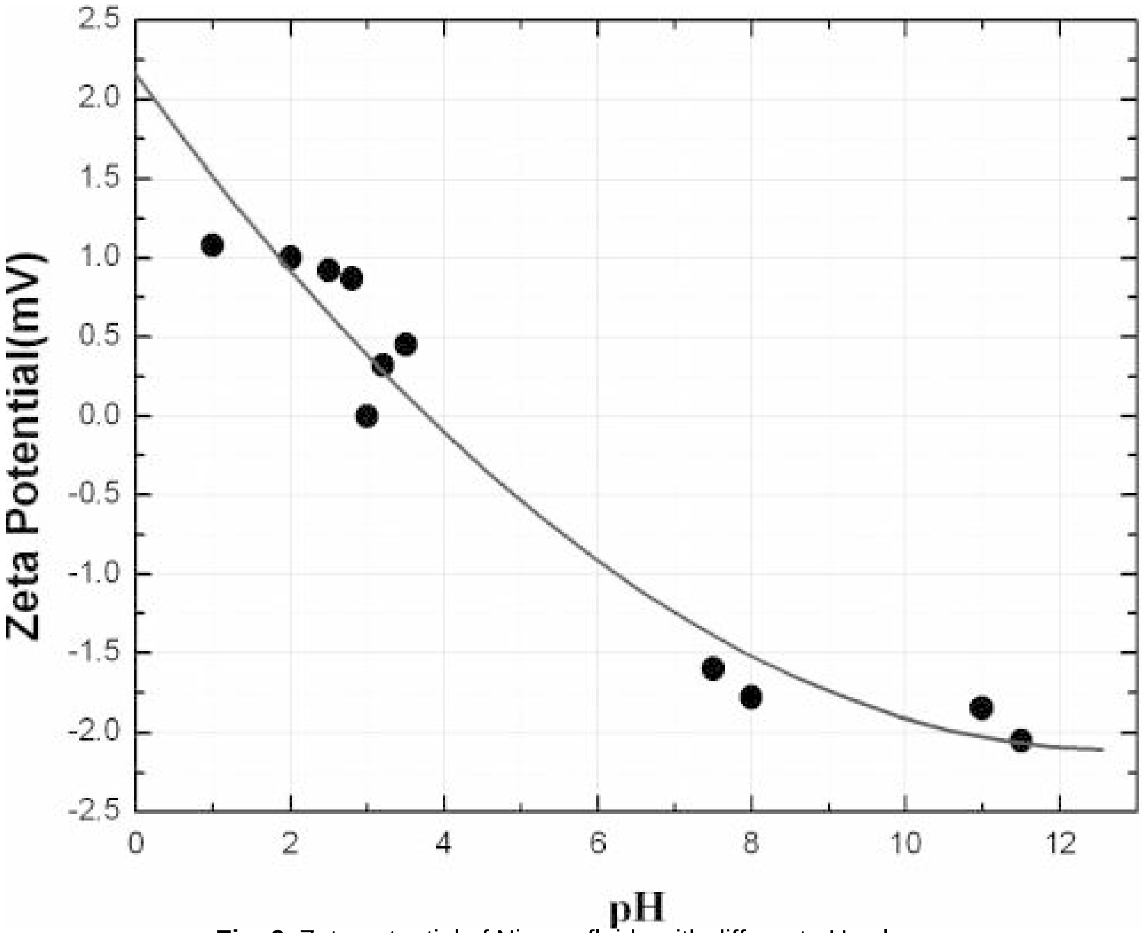

Fig. 6. Zeta potential of Ni nanofluids with different pH values

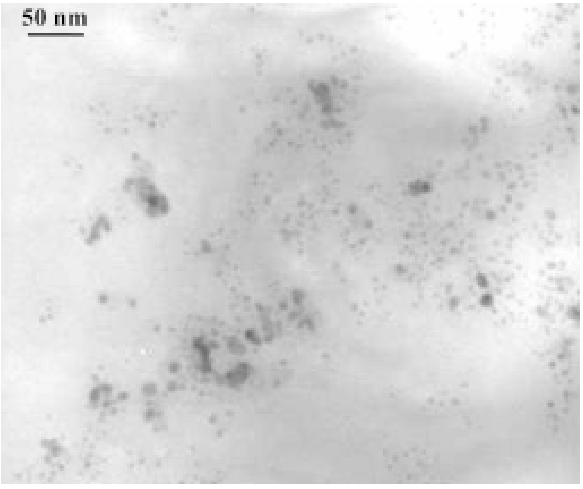

Fig. 7. TEM image of Ni nanofluid after the action of applied magnetic field.

increased, leading to much better suspension and dispersion properties.

This study develops a magnetic environment system to simulate an environment having applied magnetic field imposed onto the fluid [16]. It further investigates the stability of the Ni nanofluid under the influence of applied magnetic fields. Two pairs of magnets, which are capable of creating the same magnetic field, are installed on the platform. They are then set at magnetic fields (3000 Gauss) for comparative studies. The magnetization frequency is controlled by the rotation speed that is pre-set by the motor. Then, 15 cm^3 of Ni nanofluid, which is prepared by the process variables as shown in Table 1, are extracted and poured into a cylindrical test tube made of glass with a diameter of 10 mm and length of 100 mm. The test tube is then placed on a fixed position at the center of a turntable. After the testing of the experiment, it is found that when the magnetic fluid that has added with surfactant is placed under the action of applied magnetic field, its magnetic particles and liquid carrier would create a consistent motion because of the magnetic attraction, forming the phenomenon of consistent motion between particles and fluid. As to the magnetic fluid without adding the surfactant, the liquid carrier would not be pulled by the magnetic particles, causing the particles inside the liquid carrier to be static, and thereby losing the meaning of magnetic fluid. Affected by the intermittent static magnetic field, the magnetic particles inside the liquid carrier would be attracted by the magnetic line and the magnetic particles would concentrate on the magnet position. When the magnet is taken away, the magnetic particles would disperse immediately within the fluid. By TEM inspection of the magnetic fluid after the action of applied magnetic field, whose TEM image is shown in Fig. 7, it can be seen that by eliminating the effect of magnetic field, the Ni nanoparticles would not tend to cluster, and there is no tendency for their mean particle size to increase. In other words, the suspended particles would not be attracted by the mutual magnetic force and thereby reduce the repulsive force of the molecules of the surfactant that is adhered to the surface of the particles. As a result, the suspended particles can still be suspended stably within the liquid carrier.

4. CONCLUSIONS

This study proposes a new method of using the arc-submerged nanofluid synthetic system to fabricate Ni nanoparticles. After performing and analyzing several experiments, the best process parameters of fabricating Ni nanoparticles are determined. According to property examination such as analyzing the shape, structure, ingredient, magnetism of the material, as well as the Zeta potential of the particles, the following conclusions are made:

1. The main process parameters for the fabrication of ideal Ni nanoparticles include: peak current of 13A, pulse duration of 8 μs, breakdown voltage of 220 V, off time of 8 μs and temperature of dielectric liquid of 0 °C.
2. When the pH value of the magnetic fluid is 3.0, clustering clearly occurs because the Zeta potential is 0. Under this situation, the suspended particles would rapidly precipitate. With higher the pH value of the magnetic fluid (>8.0), the value of Zeta potential is further from the isoelectric point, and so the suspension and dispersion ability of the particles is better.
3. The saturated magnetization (*Ms*) of the fabricated Ni nanoparticles is 23 emu/g, and the saturated magnetic strength is 2760 Oe. Furthermore, its residual magnetism and coercivity all approach 0. This confirms that the magnetic particles are superparamagnetic. particle.
4. Affected by the magnetic line, the magnetic particles would move along with the magnetic field. When the static magnetic field is removed, the particles would remain suspended in the fluid. After removing the applied magnetic field, the Ni nanoparticles do not carry residual magnetism and coercive magnetic force. Therefore, it can be confirmed that the particles can be stably suspended and the magnetic particles are superparamagnetic.

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