

C.K. KIM^{*,**}, G.-J. LEE^{*,#}, M.K. LEE^{*}, C.K. RHEE^{*}

A STUDY ON DISPERSION STABILITY OF NICKEL NANOPARTICLES SYNTHESIZED BY WIRE EXPLOSION IN LIQUID MEDIA

BADANIE STABILNOŚCI DYSPERSJI NANOCZĄSTEK NIKLU WYTWORZONYCH METODĄ WEP W CIEKŁYM MEDIUM

In this study, nickel nanoparticles were synthesized in ethanol using portable pulsed wire evaporation, which is a one-step physical method. From transmission electron microscopy images, it was found that the Ni nanoparticles exhibited a spherical shape with an average diameter of 7.3 nm. To prevent aggregation of the nickel nanoparticles, a polymer surfactant was added into the ethanol before the synthesis of nickel nanoparticles, and adsorbed on the freshly synthesized nickel nanoparticles during the wire explosion. The dispersion stability of the prepared nickel nanofluids was investigated by zeta-potential analyzer and Turbiscan optical analyzer. As a result, the optimum concentration of polymer surfactant to be added was suggested for the maximized dispersion stability of the nickel nanofluids.

Keywords: Nickel nanofluid, Pulsed wire evaporation, Surfactant, Zeta potential, Dispersion stability

1. Introduction

Nanofluid, which is a suspension consisting of nanophase powders and a base liquid, has drawn very strong interest from scientific and industrial communities because of its unique catalytic, electric, magnetic, optical, and thermal properties. Nanofluids have been used in many applications such as automotive, electronic device, medical and heat transfer fluid [1-5]. In particular, nickel (Ni) nanofluids have attracted attention in optical filters, conductive ink, and magnetic fluids because of their good magnetostriction, high electrical conductivity, and high Curie temperature [6,7].

There are two methods used to prepare the nanofluid: a two-step process and a one-step process. In a typical two-step process, nanoparticles are first produced as a dry powder by physical or chemical methods, and then the prepared powders are dispersed in a fluid. In a typical one-step process, the synthesis and dispersion of nanoparticles into the fluid takes place simultaneously. Compared to the two-step process, the one-step process has many advantages such as smaller particle size, less contamination of the particle surface, and process simplicity [8,9]. A promising one-step approach is pulsed wire evaporation (PWE), which is one of the physical methods. The PWE method is favorable to high purity of the nanoparticles, mass production, and cost-effectiveness [8, 10-12].

However, it is difficult to prepare the nanoparticles with long-term dispersion stability in liquid media, since the nanoparticles are easily aggregated due to high surface energy with less surface charge. Therefore, dispersing the nanoparti-

cles uniformly and suspending them stably for a long time are critical for producing nanofluids with high quality and reliability. The key to producing an extremely stable nanofluid is to disperse the nanoparticles before the aggregation of each nanoparticle, using the proper surface treatment.

In this work, an ethanol-based Ni nanofluid was prepared using a portable PWE system. The mean size and particle size distribution (PSD) of the Ni nanoparticles were investigated by transmission electron microscopy (TEM) using image analysis software. A polymer surfactant was adsorbed on the freshly synthesized Ni nanoparticles during wire explosion to improve the dispersion stability of the Ni nanofluids. The dispersion behaviors of the Ni nanofluids as a function of surfactant concentration were observed by zeta potential analyzer and Turbiscan optical analyzer.

2. Experimental

Figure 1 shows the schematic diagram of the portable PWE apparatus in liquid media, which consisted of a pulsed power generator, reaction chamber and wire feeding system. The principle of operation is as follows. The current pulse is driven through a thin metallic wire. Then the current pulse heats the wire and it evaporates. The high-temperature vapors are cooled by interaction with a surrounding solution (deionized water, ethylene glycol, ethanol, hexane etc) and the solution containing nanoparticles is finally obtained.

* NUCLEAR MATERIALS DEVELOPMENT DIVISION, KOREA ATOMIC ENERGY RESEARCH INSTITUTE (KAERI), DAEDEOK DAERO 1045, YUSEONG-GU, DAEJEON, 305-353, REPUBLIC OF KOREA

** QUANTUM ENERGY CHEMICAL ENGINEERING, UNIVERSITY OF SCIENCE AND TECHNOLOGY (UST), GAJUNGRO 217, YUSEONG-GU, DAEJEON, 305-350, REPUBLIC OF KOREA

Corresponding author: leegj@kaeri.re.kr

In order to synthesize Ni nanofluids, Ni wire (>99.9%) with the diameter of 0.2 mm was used in the present work. The length of Ni wire feeding into the reaction chamber was 24 mm per explosion and the applied voltage was 320 V. The Ni nanoparticles were synthesized by repeating the wire-explosion 100 times. The detailed experimental conditions can be found in the previous work [13]. Commercially available surfactant, Hypermer KD2 (product of Croda Inc.) was used to improve the dispersion stability of the Ni nanofluids. KD2 was dissolved in ethanol with a concentration of 0 to 2.0 wt.%.

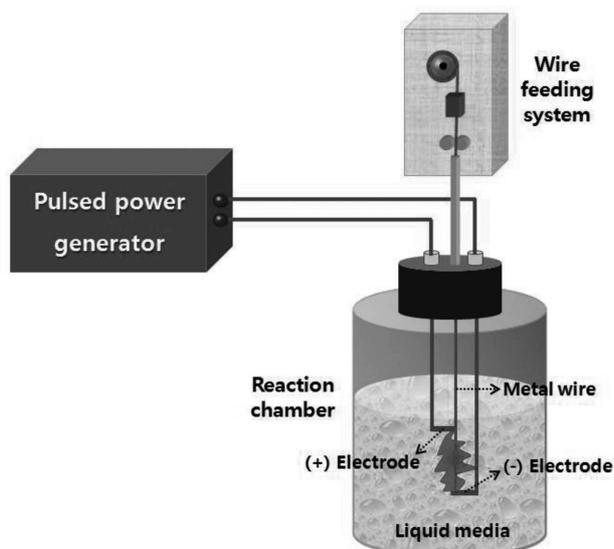
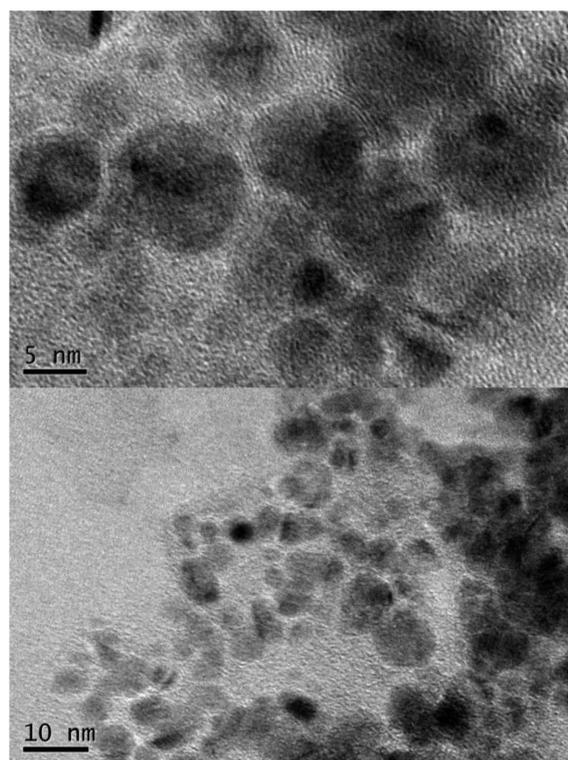


Fig. 1. Schematic diagram of portable pulsed wire evaporation (PWE) apparatus for the synthesis of Ni nanofluids

The particle shape and size of the synthesized Ni nanoparticles were investigated by TEM (JEOL 6300, Japan) and Matrox Inspector software (Matrox Electronic Systems Ltd., Canada). The change in zeta (ζ) potential of the Ni nanofluids as a function of KD2 concentration was investigated by a zeta potential analyzer (Brookhaven Instruments Co., BIC-90 PLUS, USA) using the Smoluchowski relationship. In addition, the dispersion stability of the Ni nanofluids was evaluated with time using a Turbiscan® optical analyzer (Formulation Co., France).

3. Results and discussion

Fig. 2(a) shows the TEM images of Ni nanoparticles synthesized by wire explosion in ethanol. It was observed that the Ni nanoparticles were all of spherical shape with a size smaller than 20 nm. For the detailed analysis of PSD, the TEM images were analyzed using image analysis software, and the resulting PSD of the Ni nanoparticles was shown in Fig. 2(b). It was found from Fig. 2(b) that the sizes of the Ni nanoparticles were distributed from 3.5 nm to 18.5 nm with an average diameter of 7.3 nm. When liquid media is used as a coolant, the size of the nanoparticles is greatly reduced due to more rapid condensation of the metal vapor, comparing to the case that gas is used as a coolant.



(a)

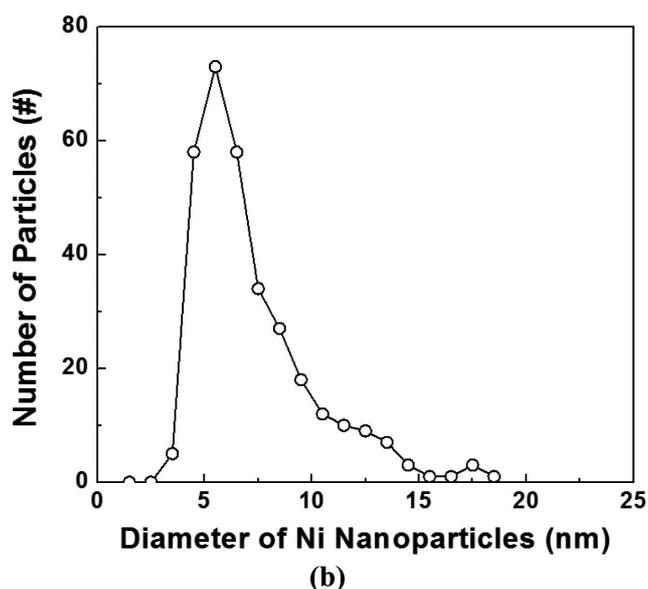


Fig. 2. (a) TEM images of the Ni nanoparticles synthesized by PWE method (experimental conditions: applied voltage, 320 V; wire feeding length, 24 mm) and (b) particle size distribution (PSD) of the Ni nanoparticles obtained from the TEM image analyses

Fig. 3 exhibits the experimentally measured zeta potential of the Ni nanofluids as a function of KD2 concentration. All the nanofluids showed a negative value of zeta potential. The zeta potential of the Ni nanofluid with no surfactant was determined to be -2.7 mV, indicating poor dispersion stability. As the KD2 concentration increased, the zeta potential increased in negative direction, which is attributable that the KD2 is a base material [14]. The zeta potential is an important indicative of ionically stabilized colloid systems. Greater magnitude (usually ± 30 mV) of the zeta potential endows the colloid system with an improved stability against aggregation [15]. It

was noticeable from Figure 3 that the zeta potential reached about -33.9 mV for the KD2 addition of 2.0 wt. %, indicating excellent dispersion stability of the Ni nanofluid.

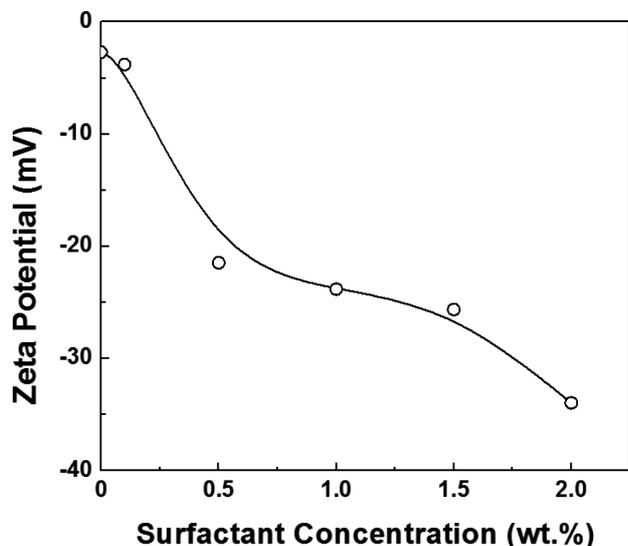


Fig. 3. Plots of zeta potential against surfactant (Hypermer KD2) concentration for the ethanol-based Ni nanofluids

Next, in order to evaluate the long-term dispersion stability of the Ni nanofluids as a function of KD2 concentration, the migration behavior was observed by Turbiscan optical analyzer. The suspension in flat-bottomed cylindrical glass tubes was placed in the instrument, and then the backscattering and transmission signals from monochromatic light ($\lambda = 880$ nm) were periodically measured along the height of sample tube. The transmission detector receives the light going out of the sample at 0 from the incident beam, while the backscattering detector receives the light scattered by the sample at 135 from the incident beam. Then, the delta transmission (ΔT) and delta backscattering (ΔBS) signals were calculated as the differences between T or BS at 0 h and at a given time.

Fig. 4 plots delta transmission, ΔT against sample height of 0 mm to 38 mm for the Ni nanofluids for three days with a change of KD2 concentration. It was found from Fig. 4(a) and (b) that for the case of Ni nanofluids with the KD2 addition smaller than 0.1 wt.%, the value of ΔT was significantly increased up to 70~80%, due to the coalescence between the Ni nanoparticles, and considerable sedimentation phenomena was also observed at the bottom of the sample tubes. For the Ni nanofluids with the KD2 addition higher than 0.5 wt.%, the delta transmission ΔT was greatly reduced (smaller than 5 %) over the whole height of the sample tube, as shown in Fig. 4(c)-(f). This suggests that the long-term dispersion stability of the Ni nanofluids is closely related to the zeta potential. The Ni nanofluid with higher absolute value of zeta potential shows more enhanced dispersion stability with time. It should be also emphasized from Figures 4(e) and (f) that the Ni nanofluids with the KD2 addition of 1.5 and 2.0 wt. % did not show sedimentation phenomena at the bottom of the sample tube.

Fig. 5 plots the mean value of delta transmission, ΔT calculated between 5 mm and 35 mm of the sample tube against analysis time for three days. The Ni nanofluid with no surfactant exhibited the highest mean value of ΔT among the

samples, and the mean value of ΔT dramatically increased up to 63.0% within 1 day and reached 67.2% three days after the dispersion, showing the worst dispersion stability. The mean value of ΔT for the Ni nanofluids with the KD2 addition of 0.1 wt. % considerably increased with time and that value reached 53.8% three days after the dispersion. On the other hand, the initial mean value of ΔT for the Ni nanofluids with the KD2 addition higher than 0.5 wt. % was very low and remained almost constant thereafter. The mean value of ΔT for the Ni nanofluids with the KD2 addition of 2.0 wt. % was only 3.8% three days after the dispersion. It is thus suggested that the addition of KD2 surfactant is highly effective in improving the long-term dispersion stability of Ni nanoparticles in ethanol. Since KD2 surfactant is a cation-type amine derivative with a relatively high molecular weight and many anchoring groups, the zeta potential value of the Ni nanofluids increases in negative direction with increasing KD2 concentration. Higher absolute value of zeta potential indicates greater repulsion between the Ni nanoparticles and therefore that the Ni nanoparticles remain dispersed for a long period of time.

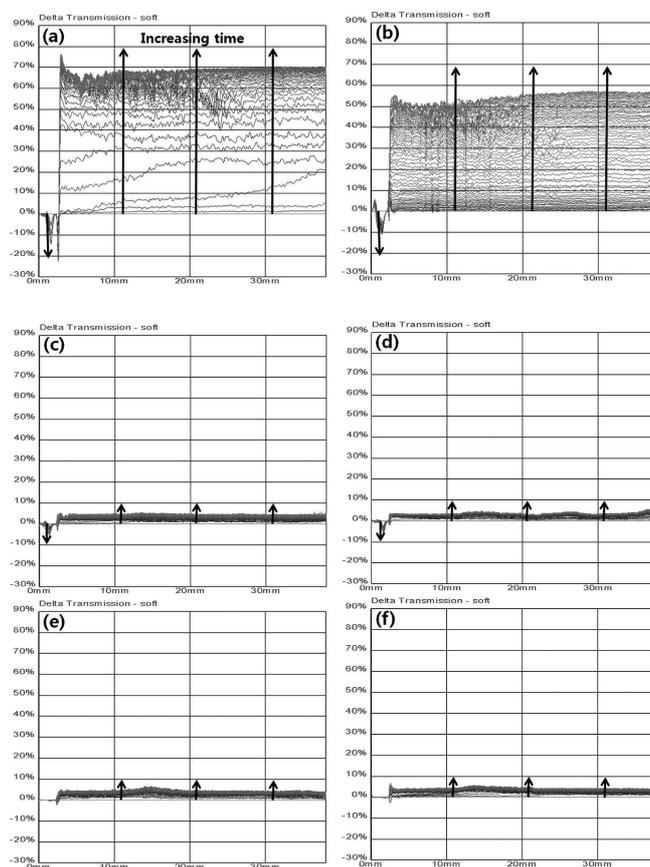


Fig. 4. Delta transmission, ΔT profiles for the Ni nanofluids with surfactant (Hypermer KD2) concentration of (a) 0 wt.%, (b) 0.1 wt.%, (c) 0.5 wt.%, (d) 1.0 wt.%, (e) 1.5 wt.%, and (f) 2.0 wt.%

As a result, it is concluded that the long-term dispersion stability of colloidal suspension is closely related to the value of zeta potential. High zeta potential usually means more stable suspension, although this is only a rough correlation. As a working rule, it is considered that a zeta potential of at least 30 mV in absolute value is necessary for long-term dispersion stability [16]. In this work, the optimum concentration of KD2 surfactant to be added was determined to be 2.0 wt. % for the

highest zeta potential and the maximized dispersion stability with time. However, the use of higher surfactant concentration can induce a loss of the dispersion stability due to micelle depletion flocculation [17,18], and also give detrimental effects on thermal property, viscosity, electrical conductivity, etc. Therefore, it is necessary to optimize the surfactant concentration to produce a nanofluid with high dispersion stability and good fluid performances.

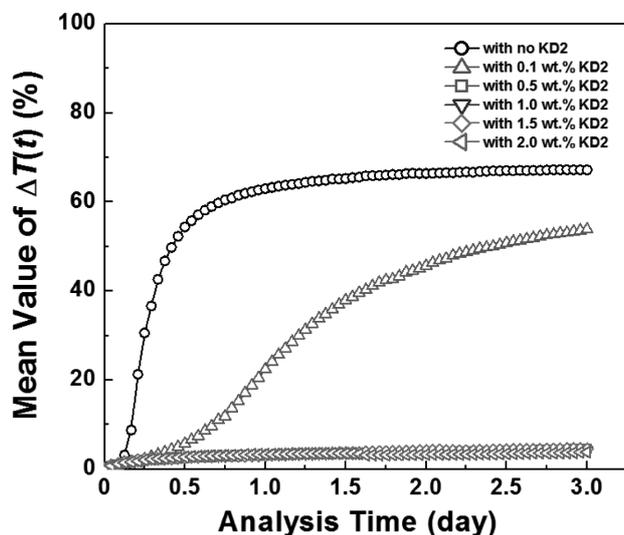


Fig. 5. Mean value of ΔT as a function of time at a sample height of 5 mm to 35 mm for the Ni nanofluids with various surfactant (Hypermer KD2) concentrations

4. Conclusions

In this study, a facile one-pot method was developed to synthesize ethanol-based Ni nanofluid with high dispersion stability. From the analysis of the TEM images, it was found that the sizes of the Ni nanoparticles synthesized by wire explosion in ethanol were distributed from 3.5 nm to 18.5 nm with a mean diameter of 7.3 nm. Comparing to the wire explosion in gas atmosphere, the wire explosion in liquid media is beneficial to decrease a particle size due to more rapid condensation of the metal vapor. The absolute value of zeta

potential increased from 2.7 to 33.9 mV as the KD2 concentration increased from 0 to 2.0 wt. %. From the analyses of Turbiscan results, it was concluded that the Ni nanofluid with the KD2 addition of 2.0 wt. % exhibited the smallest mean value of ΔT (only 3.8% three days after the dispersion), indicating the highest long-term dispersion stability.

Acknowledgements

This study was supported by the Korea Atomic Energy Research Institute (KAERI) Project, Republic of Korea.

REFERENCES

- [1] H.E. Patel, S.K. Das, T. Sundararajan, A.S. Nair, B. George, T. Pradeep, *App. Phys. Lett.* **83**, 2931 (2003).
- [2] Y. Xuan, Q. Li, *J. Heat Trans.* **125**, 151 (2003).
- [3] O.P. Siwach, P. Sen, *Mat. Sci. Eng. B* **149**, 99 (2008).
- [4] P. Cheng, S. Choi, Y. Jaluria, D. Li, P. Norris, R.D.Y. Tzou, *J. Heat Trans.* **131**, 030301 (2009).
- [5] K.V. Wong, O. Deleon, *Adv. Mech. Eng.* (2010), DOI:10.1155/2010/519659 (in press).
- [6] J. Philip, T. Jaykumar, P. Kalyanasundaram, B. Raj, *Meas. Sci. Technol.* **14**, 1289 (2003).
- [7] C.F. Goh, H. Yu, S.S. Yong, S.G. Mhaisalkar, F.Y.C. Boey, P.S. Teo, *Thin Solid Films* **504**, 416 (2006).
- [8] E.J. Park, S.W. Lee, I.C. Bang, H.W. Park, *Nanoscale Research Lett.* **6**, 223 (2011).
- [9] H.J. Kim, I.C. Bang, J. Onoe, *Opt. Laser. Eng.* **47**, 532 (2009).
- [10] C.K. Kim, G.-J. Lee, C.K. Rhee, *Kor. J. Mater. Res.* **19**, 468 (2009).
- [11] W.H. Lee, *Nanoscale Research Lett.* **6**, 258 (2011).
- [12] G.J. Lee, C.K. Kim, M.K. Lee, C.K. Rhee, *Rev. Adv. Mater. Sci.* **28**, 126 (2011).
- [13] C.K. Kim, G.-J. Lee, C.K. Rhee, *Spring Conference of the Kor. Powder Metall. Inst.*, P-25 (2011).
- [14] E.M. DeLiso, A. Bleier, *J. Am. Ceram. Soc.* **76**, 81 (1993).
- [15] S.Y. Lin, S.H. Wu, C.H. Chen, *Angew. Chem. Int. Ed.* **45**, 4948 (2006).
- [16] L. Wang, G. Tang, Z. Xu, *Ceram. Int.* **35**, 487 (2009).
- [17] R. Pool, P.G. Bolhuis, *Phys. Chem. Chem. Phys.* **12**, 14789 (2010).
- [18] A.B. Jódar-Reyes, A. Martín-Rodríguez, J.L. Ortega-Vinuesa, *J. Colloid Interface Sci.* **298**, 248 (2006).