Hybrid plasma process for the synthesis of metal nanoparticle-ethylene glycol nanofluids

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Abstract: We present a novel hybrid-plasma process for the synthesis of ethylene glycol-based nanofluids. Nanoparticles are synthesized by means of a pulsed metal vapor arc and are coated with a thin, stabilizing organic film in flight via RF plasma polymerization. The particles are dispersed *in-situ* into the host fluid and the resulting nanofluid is characterized using SEM/TEM, UV-VIS, ICP-OES and dynamic light scattering.

Keywords: Hybrid plasma, nanofluids, coated nanoparticles, pulsed metal vapor arc

1. Introduction

The term nanofluid, coined by Choi & Eastman [1], encompasses all suspensions of nanometric particulates in a liquid. Such suspensions represent a new class of materials because they exhibit several unique properties, many of which have yet to be completely described. Of particular interest are the unusually high heat transfer properties associated with nanofluids. In fact, the thermal conductivity enhancement reported in the literature has yet to be adequately explained by the traditional model. The unique optical properties of nanoparticle suspensions and their potential for use in magnetic pumping applications also offer promising avenues of research. Of significant concern are the issues of suspension stability and process scale-up that have plagued most nanofluid synthesis processes. In the present work, we propose a novel, single-step hybrid plasma process involving the use of a pulsed-arc ablation stage to generate nanoparticles and a RF plasma polymerization stage to provide *in-situ* stabilization of the nanoparticles prior to dispersion in the host fluid.

2. Process description

Whereas other research groups favor the use of resistive evaporation [1,2] or wet chemistry synthesis methods [3, 4] to generate nanoparticles, the present process involves the use of a pulsed-arc evaporation/condensation system for higher throughput. The cathode spot activity on the metal surface leads to a severe local erosion by evaporation, thus forming dense metal vapor clouds near the cathode. The metal vapor supersaturates leading to the formation of metal nanoparticles (copper in the present study). These nanoparticles are then surface-stabilized *in-situ* by means of capacitively coupled radio-frequency (RF) plasma polymerization. In the present study, the RF plasma (13.56 MHz) is sustained in a mixture of the inert quench gas (argon) and the vapors of the host liquid (ethylene glycol). The organic vapors are broken down by the plasma and form radicals that deposit onto the surface of the nanoparticles to form a coating (plasma polymerization). The nanoparticles, passivated by the surface coating, disperse into the host liquid with the help of a gas/liquid contactor. A simplified schematic of the experimental apparatus is presented in Figure 1.

The principal components of the system, following the gas flow direction (from the top of the reactor to the vacuum pump), are: i) The nanoparticle synthesis stage, ii) the in-flight plasma polymerization and gas-liquid contact stage and iii) the nanofluid recirculation unit. An off-gas treatment unit is used to protect the mechanical pump (Leybold, model TRIVAC D90A) that maintains the reactor pressure at the required level. The base pressure of the system is approximately 500 mTorr (when no liquid is present in the reactor). Ethylene glycol is selected as the host fluid because it is already commonly used as a heat transfer fluid and because its low vapor pressure (less than 70 mTorr at 25°C) makes it suitable for use in a vacuum reactor.

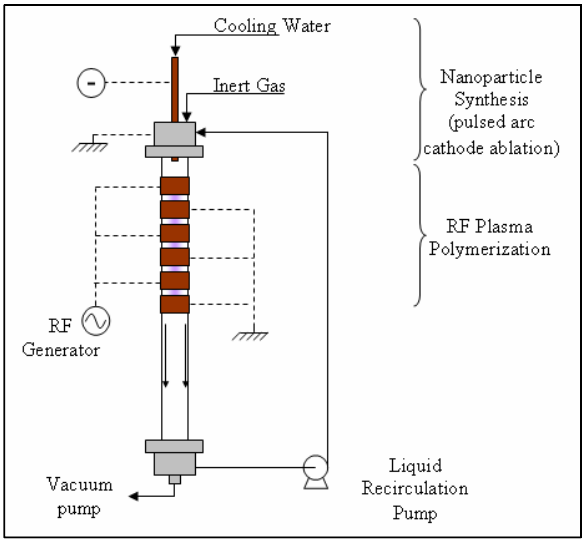

Fig. 1 Schematic of the experimental setup

3. Stability

The most commonly proposed approach to resolve suspension stability issues is the addition of a stabilizing agent, such as a surfactant, to the host fluid in order to prevent agglomeration of the nanoparticles (and, as such, the deterioration of the unique properties associated to their size). However, the addition of surfactants (or other compounds) adds to the chemical complexity of the system and, more importantly, these additives tend to degrade when exposed to high temperatures [5]. Because nanofluids show promise as high efficiency heat transfer fluids, such degradation under “real” conditions of use is unacceptable. In the presented process, the dispersion of nanoparticles into the solvent occurs with greater ease when compared to other processes (often involving ultra-sonification and surfactants) because the organic film deposited onto the nanoparticles acts as an intermediate, chemically compatible layer between the host liquid and the nanoparticles. The working hypothesis is that polar hydroxyl groups from the plasma-radicalized ethylene glycol deposit onto the nanoparticle’s surface, hence rendering the particle “polar” and more compatible with the mildly polar solvent.

4. Analysis of the nanofluid

A nanofluid sample was deposited onto a grid on which carbon fibers had been grown [6]. After the solvent was evaporated away, a FE-SEM micrograph was obtained showing that copper nanoparticles had precipitated out of the liquid sample. It is presented as Figure 2. As a proof-of-concept, ethylene glycol vapors were introduced into a reactor normally used to coat nanoparticles by means of a radio-frequency plasma sustained in a mixture of an inert gas and an organic monomer. A TEM image of the collected powders (Figure 3) shows that plasma polymerization is in fact possible with ethylene glycol vapors. Previous work by Qin & al. has shown using XPS and FTIR that the coating deposited on the surface of the metal nanoparticles is chemically bonded to the surface [7,8].

The typical sample size is 500 mL and the obtained liquid usually exhibits a color change, becoming yellow or green (pure ethylene glycol is clear). This change in physical appearance can be attributed to the presence of secondary products (yellow) as well as copper in solution (green when oxidized). Large particulates are visible and quickly sediment. Secondary products generated in the fluid are identified by means of GC-MS and UV-VIS spectrometry. The principal by-product identified in these investigations is 1,4-dioxane. Additional compounds, such as diphenyl ether, have been detected in the produced nanofluid. However, these additional compounds are most likely a product of the reaction of benzene, a contaminant found in commercial-grade ethylene glycol. Three theories are proposed to explain the by-product generation: (i) the host liquid is sensitive to the ultra-violet light given off by

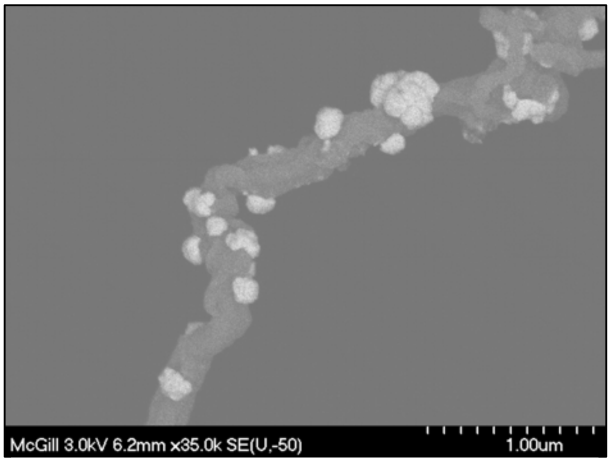

Fig. 2 FE-SEM (BSE) image showing agglomerated copper nanoparticles precipitated from a nanofluid onto a carbon fiber

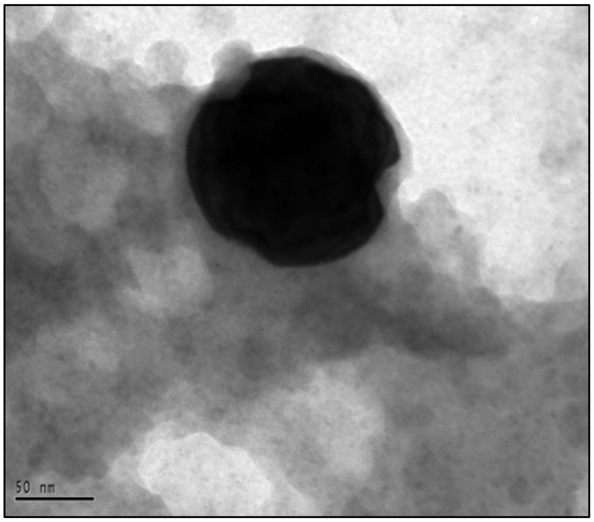

Fig. 3 TEM image of a Cu nanoparticle covered with an organic coating plasma-deposited from ethylene glycol

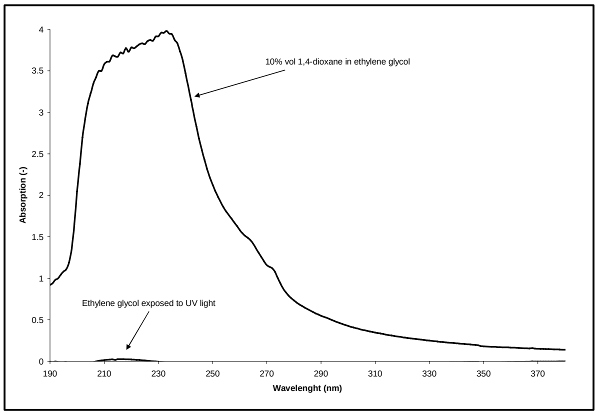

Fig. 4 Comparison of the absorbance of a solution of 1,4-dioxane in ethylene glycol and a sample of ethylene glycol exposed to UV light

either one of the plasma sources, (ii) the metallic nanoparticles act as catalyst sites for chemical reactions to occur within the ethylene glycol and/or (iii) the direct contact between the RF plasma and the ethylene glycol induces chemical reactions within the fluid. Using the UV-VIS spectrometer, the absorbance of a sample of 1,4-dioxane in ethylene glycol (10%) was compared to that of a sample of ethylene glycol that had been exposed to the light of two UV lamps for 3 hours (Ster-L-Ray Germicidal Lamps, 10 watts each, approximate total UV output of 50 microwatts). The results are presented in Figure 4. Although its absorbance is low, the UV-exposed sample does show the production of some 1,4-dioxane (the experiment was replicated to confirm the results). Although this fact does not exclude the second and third theories listed, it clearly shows that UV radiation plays a role in the formation of secondary products.

To confirm the presence and concentration of copper in solution, ICP-OES experiments were carried out. For a 90-minute batch experiment, the detected loading is on the order of 200-300 ppm (0.02-0.03% wt). The emission spectrum obtained about copper's characteristic wavelength of 327.45 nm is presented in Figure 5. An additional indication of the amount of metal present in the liquid is obtained by weighing the eroded cathode before and after an experiment. For the experimental run discussed, 314 mg of copper were ablated by the pulsed arc, which would lead to an expected loading of 0.056% wt (the collection efficiency of the gas liquid contactor is therefore on the order of 50%).

A particle size distribution was obtained using a dynamic light scattering apparatus (ZetaSizer) and is presented in Figure 6. The obtained size distribution shows a small peak around 200 nm that is somewhat consistent with the electron micrograph images. However, a broader peak is also obtained around 900 nm which may be due to the presence of the larger sediment particles mentioned previously. It is also possible that the secondary products in the fluid caused fluorescence and abnormal absorbance in the sample, which could skew the size distribution.

5. Conclusion

We have developed a novel, hybrid plasma process that tackles the issues that have affected the synthesis of nanofluids. This scalable process addresses the issue of stability and its proper operation has been demonstrated. Work in progress involves optimizing the reactor conditions in order to attenuate the agglomeration of the arc-produced nanoparticles, studying the effect of the nature of the plasma polymerization gas on the coating properties and suspension stability and characterizing to a greater extent the heat transfer properties of this new material and the secondary products that are generated.

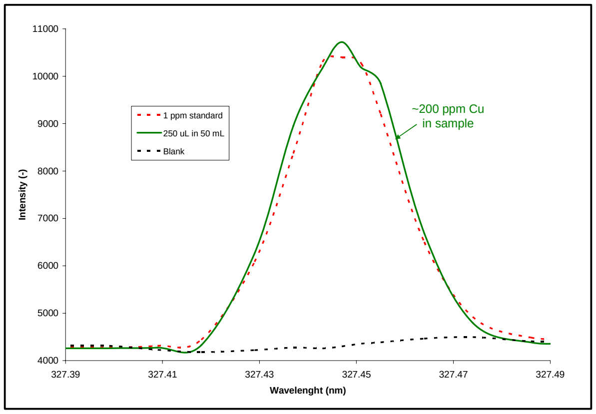

Fig. 5 ICP-OES output of sample obtained after a 90 min. batch experiment diluted by a factor of 200 and compared to a 1 ppm standard

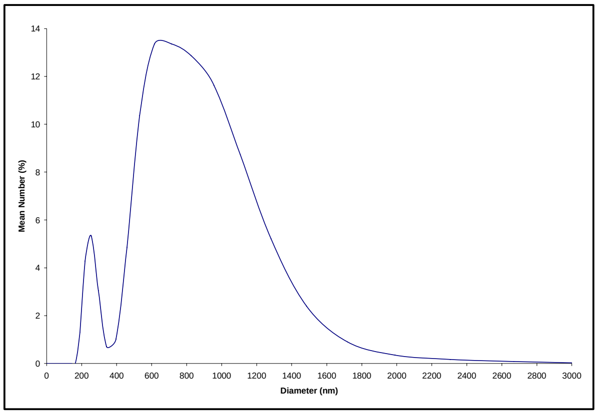

Fig. 6 Particle size distribution of discussed sample obtained using the ZetaSizer dynamic light scattering apparatus (average of six measurements)

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References

[1] J.A. Eastman, S.U.S. Choi, S. Li, W. Yu, L.J. Thompson, Applied Physics Letters, 2001, 78(6), p.718-720

[2]. C. Tsung, C.S. Jwo, H. Chang, K.C. Wang, International Journal of Advanced Manufacturing Techniques, 2005

[3]. Y. Lin, H. Zhu, Y. Yin, Journal of Colloid and Interface Science, 2004, 277, p. 100-103

[4]. C. Zhang, H. Zhu, Y. Yin, Institute of Physics Publishing: Nanotechnology, 2005, 16, p. 3079-3083

[5]. D. Wen, Y. Ding, Journal of Thermophysics & Heat Transfer, 2004, 18(4), p.481-485

[6]. L. Rao, N.K. Reddy, S. Coulombe, J.L. Meunier, R. Munz, Journal of Nanoparticle Research, 2006, *in press*
[7]. C. Qin, S. Coulombe, Materials Letters, 2006, 60, p. 1973-1976
[8]. C. Qin, S. Coulombe, Plasma Sources Science & Technology, 2007, 16, p. 240-249