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Full Length Article

Stable dispersion of nanodiamonds in oil and their tribological properties as lubricant additives

Gyoung-Ja Lee, Jin-Ju Park, Min-Ku Lee*, Chang Kyu Rhee

Nuclear Materials Development Division, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

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ABSTRACT

Nanodiamonds (NDs) are innovative additives when a combination of mechanical, thermal, tribological, and dielectric properties are required. In this study, a surface modification with oleic acid (OA) is developed for the deaggregation and prolonged dispersion of NDs in oil, and the effect of the NDs as lubricant additives on the tribological properties of a steel substrate is investigated. The OA renders the ND surface hydrophobic and decreases the average particle size from 268.6 to 20.1 nm. The OA-treated NDs exhibit very stable dispersion in oil even after more than 10 days, compared with the untreated NDs. From the analyses of the friction coefficient, wear loss, and worn surfaces using a ball-on-disk wear test, it is concluded that a 0.05 wt% addition of OA-treated NDs in oil lubricant provides excellent friction and anti-wear properties with the friction coefficient being reduced by 23%.

1. Introduction

The addition of solid particles to lubricants has been considered to be beneficial in reducing the wear rate and friction between two rubbing surfaces. For traditional solid additives with micron or submicron sizes, the wear rate increases with increases in the size and concentration of lubricant additives in oil [1,2]. However, nano-sized additives have demonstrated an outstanding tribological performance [3–7] and this lubricating effectiveness becomes more noticeable under aggravated sliding conditions. The commonly used nano-additives such as Cu, graphite, MoS_2, etc. are readily oxidized under a heavy load or at high temperatures; thus, it is necessary to develop new nano-sized solid additives with excellent thermal and chemical stabilities.

Since the first investigation by Tao et al. in 1996 [8], nanodiamonds (NDs) that are produced using an explosive detonation technique have been considered to be promising candidates for improving tribological properties economically and effectively through functioning as ball bearings between two mutually sliding surfaces [9–12]. The NDs possess excellent mechanical properties, superior chemical stability (oxidation resistance), and outstanding thermal stability, all of which are favorable for use as a lubricant additive. However, although the primary particle size of detonation NDs is usually 4–6 nm, a large number of nanoparticles aggregate to form clusters with diameters of hundreds of nanometers or even of several micrometers [13]. In order to further improve the lubricating effectiveness of the NDs using the least amount, preparation of NDs with smaller sizes (from several to tens of nanometers) and more stable, prolonged dispersion in an appropriate solvent (i.e. oil in this work) are very important.

Because the NDs that are commercially produced using the detonation technique are typically hydrophilic due to their high surface-to-volume ratio and non-zero surface charge, it is comparatively easy to disperse the NDs in a polar solution without special physical or chemical treatments, but it is difficult to disperse the NDs in non-polar solutions due to a severe aggregation [14]. Thus, hydrophobic surface modification is required in order to achieve deaggregation and stable dispersion of the NDs in non-polar solutions. A common monounsaturated fatty acid, e.g. oleic acid (OA), is frequently used for the surface modification of nanoparticles in order to introduce a long aliphatic chain, and the OA-modified nanoparticles disperse better in organic solvents.

In this work, in order to use the NDs as lubricant additives in oil, the hydrophobic surface modification of the NDs with OA was conducted. The chemisorption of OA on the ND surfaces was confirmed using Fourier transform infrared spectroscopy (FTIR) analyses, and the degree of hydrophobicity of the untreated and OA-treated NDs was compared through water wettability measurements. The dispersion stability of the oil-containing NDs was investigated using Turbiscan measurements. The friction-reduction and anti-wear properties of oil containing the OA-treated NDs were characterized using ball-on-disk wear tests.

* Corresponding author.
E-mail address: leeminku@kaeri.re.kr (M.-K. Lee).

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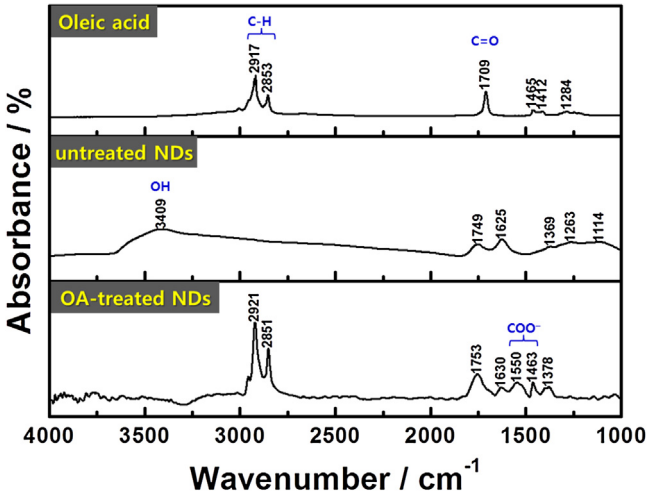

Fig. 1. FTIR spectra of oleic acid, untreated NDs, and OA-treated NDs.

2. Experimental

The detonation ND powder was supplied by Real-Derzinski, Co. (Russian Federation). For the hydrophobic surface modification of the NDs, the ND powder was added to toluene with OA; then, the mixture was homogenized using an ultrasonicator. The mixture was centrifuged at 5000 × *g* for 5 min, and then centrifuged at 3000 × *g* for 5 min again with ethanol after discarding the supernatant. After several cycles of centrifugation and washing, the dried ND powders of which the surfaces were modified with OA were ollected.

Fourier transform infrared (FTIR) spectroscopy analyses were performed using a NiCOLET 6700 spectrometer (ThermoFisher Scientific, USA). The as-received (untreated) and OA-treated ND powders were dispersed in a commercial oil (Shell Helix HX7, The Netherlands) using a portable homogenizer. The particle size distribution of the NDs in the oil was measured using a laser particle size analyzer (LPSA, BIC 90Plus, USA). The morphology and particle size of the detonation NDs before and after the surface treatment were observed using a high-resolution transmission electron microscopy (HRTEM, JEOL 6300, Japan). The powder wettability of the untreated and surface-treated NDs were investigated by water absorption capability measurement using a tensiometry (KSV Sigma700 tensiometer). The long-term dispersion stability of the 0.5 wt% ND-dispersed oils was measured using a Turbiscan Lab® Expert (Formulaction Co., France) based on the multiple light scattering method. The mean variation of the delta transmission (ΔT) signal was calculated as the transmission difference between the initial time (0 h) and a given time at the sample height of 30–40 mm.

The tribological performance of the oil lubricants containing 0, 0.01, and 0.05 wt% NDs was evaluated using ball-on-disk wear tests with an SKD11 steel disk. The test was conducted at an ambient temperature under a normal load of 20 N against a Al_2O_3 ball (6 mm diameter), over a sliding distance of 1000 m. After the wear test, the worn surfaces were observed using an optical microscope (OM; OLYMPUS B202, Japan).

3. Results and discussion

Fig. 1 presents the FTIR spectra of the oleic acid, untreated NDs, and OA-treated NDs. In the spectrum of pure oleic acid, the two sharp bands at 2917 and 2853 cm^{-1} resulted from the asymmetric C—H stretch and symmetric C—H stretch, respectively, which are known to be characteristic bands of CH_2 groups in oleic acid. The intense peak at 1709 cm^{-1} was derived from the existence

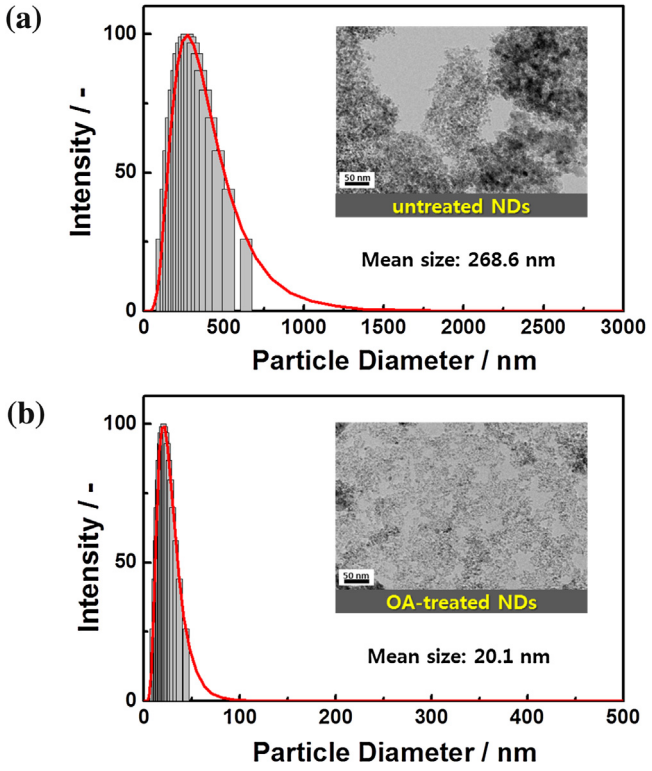

Fig. 2. Particle size distributions and TEM images of the (a) untreated and (b) OA-treated NDs.

of the C=O stretch for the COOH species [15–17]. The bands at 1462 and 1284 cm^{-1} confirmed the presence of the O—H in-plain and C—O stretch, respectively. The analyses of the FTIR spectra for the untreated (as-received) NDs have been provided in more detail elsewhere [14]. In the spectrum of the OA-treated NDs, it should be noted that the C—H stretches of oleic acid were not significantly affected, but the carbonyl stretching peak at 1709 cm^{-1} was no longer observed. Instead, two prominent peaks appeared at approximately 1463 and 1550 cm^{-1}, which are characteristics of symmetric and asymmetric carboxylate (COO^-) stretches [17,18], and this indicated that the oleic acid was chemisorbed to the ND surfaces via its carboxylate ion. It was also noticeable that the peak at 3409 cm^{-1} in the spectrum of the untreated NDs that corresponds to the stretching —OH vibration stretch peak was not observed in the spectrum of the OA-treated NDs. This implies that the oleic acid coating changes the ND surfaces from hydrophilic to hydrophobic.

Fig. 2 presents the particle size distributions of the untreated and OA-treated ND powders dispersed in oil with 0.05 wt%. The particle size of the untreated NDs was distributed from 100 to 700 nm with an average size of 268.6 nm, which resulted from severe aggregation of the primary nanoparticles, as seen in the HRTEM image (Fig. 2(a)). It is clearly demonstrated from Fig. 2(b) that after the surface treatment with OA, the ND aggregates were broken into smaller sized particles in the range from 10 to 90 nm and the average particle diameter of the OA-treated NDs decreased to 20.1 nm. This indicates that the surface treatment with OA is highly effective in breaking down the ND aggregates into smaller sized particles in the oil solution.

Wettability is an important criterion for measurement of the surface property of a power, which influences the dispersion stability. The wetting behavior of the powders was characterized through measuring the weight gain due to the test liquid penetrating the powder bed as a function of time. The water or oil adsorption capability depends on the hydrophilic or hydrophobic surface nature.

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