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Additive Effect of Carbon Nanohorn on Grease Lubrication Properties

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Recently, applications of the carbon nanohorn (CNH) have become of great interest in various industrial fields. The load carrying capacity and wear resistance of lithium soap grease containing CNH and heat-treated CNH (HT-CNH) were studied using a Falex friction tester, and compared with those of grease containing reference carbon materials such as graphite, cluster diamond (CD), and graphite cluster diamond (GCD). The load carrying capacity of the greases with carbon materials was always higher than that of the base grease. The greases with CNH and HT-CNH had the same or higher seizure load than those with CD and GCD. In particular, the grease with HT-CNH exhibited good load carrying capacity even at a low concentration of 1 mass%. The grease with 3 or more mass% graphite had the highest seizure load of all greases in this study. The grease with HT-CNH showed the best wear resistance of all greases in this study. The wear resistance of the grease with other solid lubricants was the same or inferior to that of the base grease.

Keywords
Carbon nanohorn, Grease, Wear amount, Load carrying capacity

1. Introduction

Applications of new carbon materials such as fullerene (C_{60}), carbon nanotube (CNT), carbon nanohorn (CNH), and cluster diamond (CD) have been studied in electronics, information processing, nanotechnology, energy, and biotechnology. In tribology, these materials are interesting because of the small particle size, low density, chemical stability, and environmental friendliness. The tribological properties of C_{60}[1)~5)], CNT, and CNH[6),7)] thin films have been studied extensively, but few studies have investigated applications as solid lubricants for lubricating oil and grease[8),9)].

The present study assessed the load carrying capacity and wear resistance of lithium soap grease containing carbon nanohorn and heat-treated carbon nanohorn.

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2. Experimental

2. 1. Samples

Carbon nanohorn (CNH)[10),11)] and heat-treated carbon nanohorn (HT-CNH)[12)] were prepared. **Figure 1(a)** shows transmission electron microscope (TEM) images of CNH produced by CO_2 laser ablation at room temperature without a metal catalyst. CNH is an aggregate of horn-shaped sheaths consisting of single-walled graphene (six-fold-ring) sheets. The diameter of CNH is about 80-100 nm. The density of CNH measured using the high pressure He buoyancy method was about 1.25 g/cm^3 [13)]. Unfortunately, other properties such as hardness, Young's modulus, and thermal conductivity have not been clarified. **Figure 1(b)** shows CNH treated for 5 h at 1960°C. The heat treatment has blunted the horn-shaped tips, and the diameter of individual horn-shaped sheaths has tended to increase[12)]. The bluntness of the horn-shaped tips appeared to slightly reduce the diameter of aggregates of horn-shaped sheaths. The bluntness of the horn tips was probably caused by reduction of defects in the graphene sheets. The density of HT-CNH may be a little higher than that of CNH, because of the reduced aggregate diameter. Graphite (natural flake), cluster diamond (CD), and graphite cluster diamond (GCD) were used as reference materials. The size and density of the carbon particles are summarized in **Table 1**.

Lithium soap grease (**Table 2**) was used as the base grease. Sample particles were added to the base grease at 1, 3, and 5 mass%, and mechanically blended using an agate mortar. **Figure 2** shows photomicrographs of the grease with 2 types of carbon particles. The carbon particles were dispersed fairly well in the grease, although some cohesion was seen.

The worked penetration of base grease and grease with solid lubricants is shown in **Fig. 3**. The worked penetration of grease with solid lubricants, excluding GCD, decreased with higher concentration of solid lubricant. Generally, solid lubricants such as graphite, CNH, HT-CNH, and CD hardly affected the worked penetration, although a slight difference in worked pen-

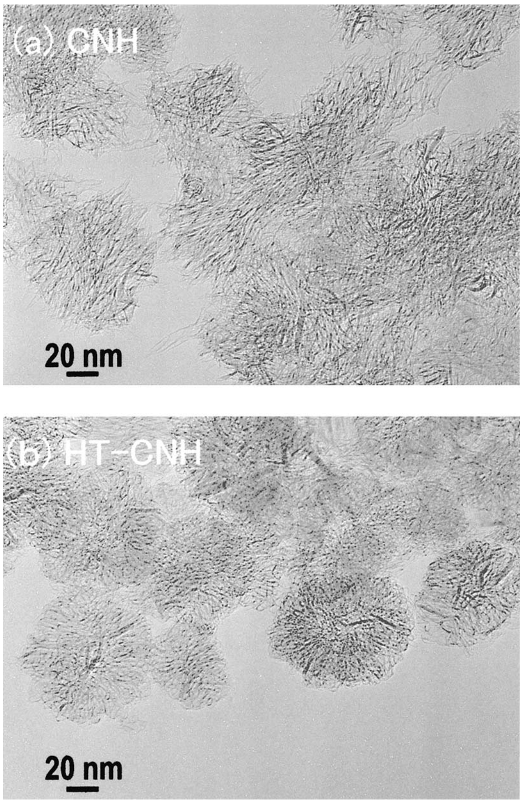

Fig. 1 TEM Images of (a) CNH and (b) HT-CNH

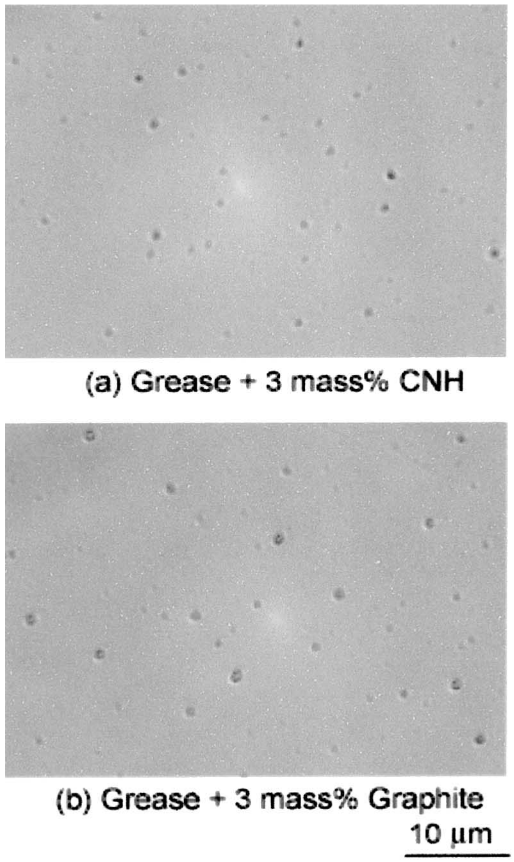

Fig. 2 Photomicrographs of Grease with 2 Types of Carbon Particles

Table 1 Size and Density of Carbon Particles

	CNH	HT-CNH	CD	GCD	Graphite
Size [nm]	80-100	<80-100	5 (average)	20 (average)	600 (average)
Density [g/cm^3]	1.25	>1.25	3.41	3.12	2.23

Table 2 Proportion of Base Grease

Base oil of grease (82 mass%)	High purified paraffinic mineral oil Kinematic viscosity: 102 mm^2/s at 40°C 11.2 mm^2/s at 100°C Viscosity index: 95
Thickener (18 mass%)	Lithium stearate, $C_{17}H_{35}COOLi$
Base grease	Worked penetration (60 W): 280 (No.2) Dropping point: 205°C

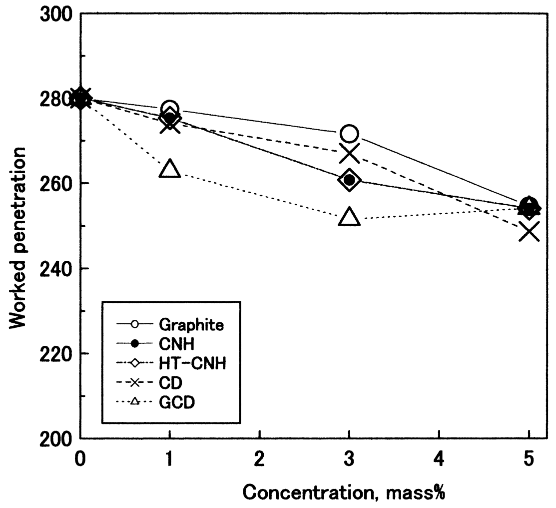

Fig. 3 Effect of Addition of Solid Lubricant on Load Carrying Capacity

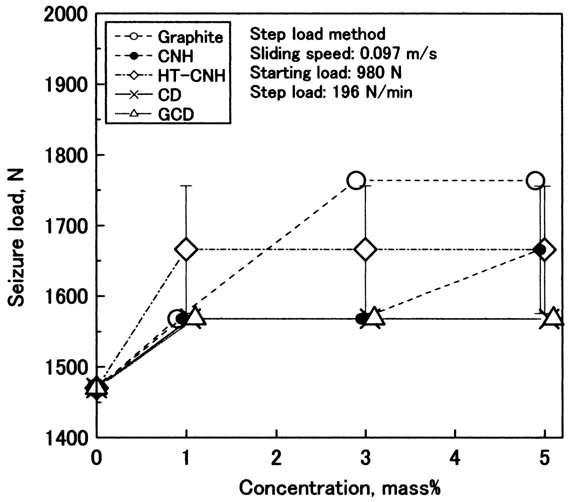

Fig. 4 Worked Penetration of Base Grease and Grease with Carbon Particles

Table 3 Specifications of Pin and Vee Block Specimens

Pin (SNC-236)	diameter: 6.37 × 31.75 mm *Ra*: 0.1-0.3 μm HRB: 87-91
Vee block (SUM-41)	diameter: 12.81 × 10.16-10.41 mm V-angle: 96 ± 1° *Ra*: 0.1-0.3 μm HRC: 20-24

etration was seen for grease with 3% solid lubricants. The dependency of worked penetration on the concentration of GCD was unclear, although the worked penetration at 1 and 3 mass% seemed to be a little smaller than that for other carbon particles.

2. 2. Measurement of Seizure Load

A Falex pin-vee block tester was used for the seizure tests based on the ASTM D 3233 standard (**Table 3**). Test pieces were cleaned ultrasonically for 10 min in toluene and acetone, and then dried prior to testing. Rotation was set at a constant 290 rpm (sliding speed 0.097 m/s). The friction test was carried for 1 min with an initial load of 980 N and the load was increased at 196 N/min until seizure occurred at room temperature (25 ± 2°C). The tester was designed to stop automatically when the frictional torque exceeded 588 N·cm. The load at which the tester stopped was defined as the seizure load. Two measurements were made for the base grease and the greases with solid lubricants and the mean was taken as the seizure load.

2. 3. Wear Test

Wear tests were carried out for 6 min at room temperature (25 ± 2°C) under constant 980 N and 290 rpm. The weight loss of the pin and vee block was measured after the test, and the mean of 3 measurements was used as the wear amount. The friction surfaces of the pins and vee blocks were observed under the scanning electron microscope (SEM) after the test.

3. Results and Discussion

Figure 4 shows the seizure load as a function of the concentration of solid lubricant. The vertical bars in this figure show the scatter range of data. Addition of solid lubricants improved the load carrying capacity of the base grease even at a concentration of 1 mass%. The load carrying capacity of HT-CNH was better than that of graphite at a low concentration of 1 mass%, but was inferior at concentrations exceeding 3 mass%. CNH was not as effective as HT-CNH at low concentrations, but the grease with 5 mass% CNH was similar to that with 5 mass% HT-CNH. The good load carrying capacity of the grease with 1 mass% HT-CNH may be related to the small size and more spherical shape of HT-CNH particles, compared with those of CNH and graphite. CD and GCD did not show any concentration dependency of seizure load. The graphite-containing grease showed superior seizure load at concentrations exceeding 3 mass%, compared with grease containing other solid lubricants.

Wear as a function of the concentration of solid lubricant is shown in **Fig. 5**. The vertical bars in this figure show the scatter range of data. The wear resistance of the grease with HT-CNH seemed to improve with increasing concentration, although the scatter of data was large. In contrast, the wear resistance of the grease with other solid lubricants was similar or inferior to that of base grease. In particular, addition of 5 mass% CNH considerably deteriorated the wear resistance of the grease.

As mentioned in section **2. 1.**, the particle size of HT-CNH was smaller than that of CNH and graphite.

Moreover, the horn-shaped tip of HT-CNH was more rounded than that of CNH, and the shape of HT-CNH was more spherical than that of CNH as well as graphite. These characteristics may be related to the easy penetration into the sliding interface and low abrasion of HT-CNH particles, compared with CNH and graphite, and the clearly superior wear resistance of the grease with HT-CNH compared to grease containing CNH or graphite. Moreover, the high concentration of HT-CNH powders on the sliding surface may improve the wear resistance of the grease with HT-CNH. CD and GCD particles are very hard and have high abrasion, although the size is very small. A similar explanation may account for the improvement of seizure load.

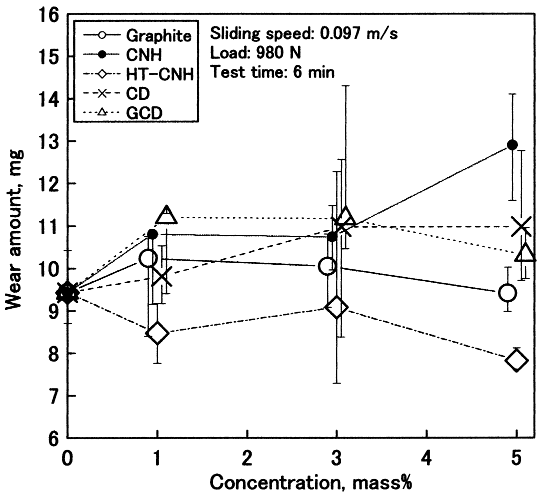

Fig. 5 Effect of Addition of Solid Lubricant on Pin Wear

Both wear of pin specimens and worked penetration of grease decreased with higher HT-CNH concentration. However, the wear of pins tended to increase with higher CNH concentration, and the worked penetration decreased. These results suggest that the worked penetration of grease has no correlation with the wear behavior of pin specimens.

Figure 6 shows SEM images of the pin surfaces after wear tests using the base grease and grease with 5% solid lubricants. The worn surfaces for the grease with solid lubricant, except for grease containing CNH, were smoother than that for the base grease. CD and GCD with higher hardness and finer particle size appeared to cause smooth worn surfaces by microabrasion, but promoted wear (**Fig. 5**). The worn surface for HT-CNH seemed to be similar to those for CD and GCD. In contrast, the surface for CNH was not so smooth and had some scraped parts in the direction of friction. The grease containing 5% CNH which caused the rough worn surface also caused high wear of pins compared with the grease containing other lubricants (**Fig. 5**). **Figure 7** shows the SEM micrographs of the worn surfaces on vee blocks. No clear difference between the solid lubricants was observed. Similar features were seen on the worn surfaces for grease containing 1 or 3% solid lubricant.

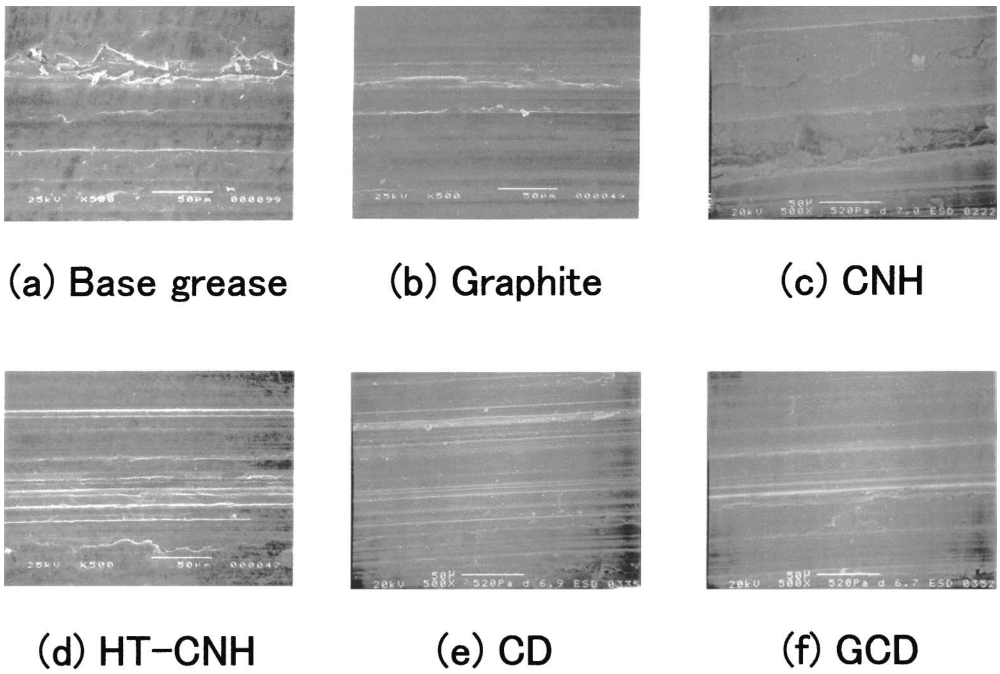

Fig. 6 SEM Images of Worn Surfaces of Pins Lubricated by Base Grease and Grease with 5 mass% Carbon Particles

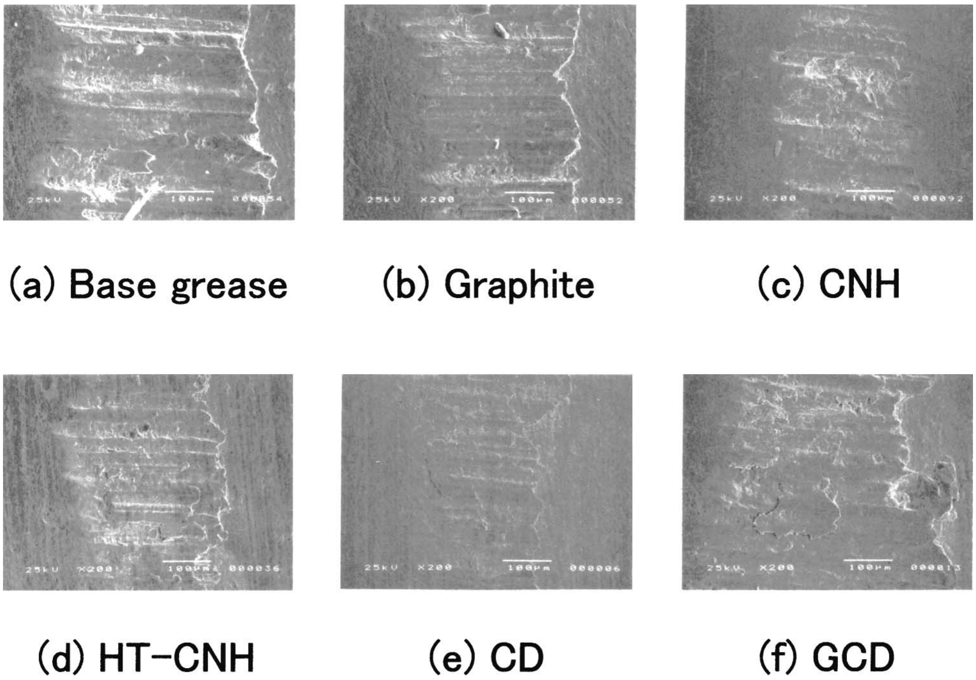

Fig. 7 SEM Images of Worn Surfaces of Vee Blocks Lubricated by Base Grease and Grease with 5 mass% Carbon Particles

4. Conclusion

The load carrying capacity and wear resistance of lithium soap grease containing CNH and HT-CNH were studied using a Falex friction tester, and compared with those of grease containing reference carbon materials such as graphite, CD, and GCD. The following results were obtained:

(1) The load carrying capacity of the greases with carbon materials was always higher than that of base grease. The greases with CNH and HT-CNH showed the same or higher seizure load than those with CD and GCD. In particular, the grease with HT-CNH exhibited good load carrying capacity even at a low concentration of 1 mass%. The grease with 3 or greater mass% graphite had the highest seizure load in this study.

(2) The grease with HT-CNH showed the best wear resistance in all greases determined in this study. The wear resistance of grease with other solid lubricants was similar or inferior to that of the base grease.

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要　　旨

グリースの潤滑性能に対するカーボンナノホーンの添加効果

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新しいナノカーボン材料であるカーボンナノホーン（CNH）が最近様々な産業分野において注目されている。本研究では，このCNHをグリースに添加した場合に，焼き付きや摩耗に関してどのような特性が得られるかを調べた。グリースにはリチウム石けんグリースを用い，添加物にはCNHおよび熱処理したナノホーン（NT-CNH）のほかにグラファイト，クラスタダイヤモンド（CD），グラファイトクラスタダイヤモンド（GCD）を用いた。試験はFalex型摩擦試験機により行った。いずれの添加物の場合にも添加により焼き付き荷重は増加した。CNH添加グリースの場合，CDおよびGCDを添加したグリースの場合と同程度かより優れた耐焼き付き性を示したが，耐摩耗性に関しては添加の効果は見られなかった。一方，HT-CNHに関しては，1 mass％ だけグリースに添加するだけでも，CDやGCDを添加したグリースの場合よりも優れた耐焼き付き性を示した。さらに，HT-CNHを添加したグリースでは耐摩耗性も明らかに向上した。添加量が多くなると，グラファイト添加グリースが最も良い耐焼き付き性を示した。