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Low friction mechanism by carbon-based nanoparticles under mixed lubrication

Yutaka Mabuchi

Utsunomiya University

1. Introduction

The low-friction mechanism of hydrogen-free DLC films, which are becoming increasingly popular, has been analyzed by Isabel et al. [1]. The model is based on an additive-derived -OH group terminating to a carbon atom in the surface layer, which transforms from sp^3 to sp^2 bonds due to sliding, forming a low-shear layer due to hydrogen bonding of the additive with water and -OH groups beyond it. Based on this model, the authors consider the functional group -OH formed on the surface of carbon-based nanoparticles such as nano-diamonds, graphene oxide and fullerenes to be the key, and the formation of a low-shear layer by hydrogen bonding of polar solvents to it to be the main factor causing low friction (Fig.1) [2]. This paper presents the results of an investigation into the low-friction mechanism of carbon-based nanoparticles under mixed lubrication, based on the results of previous research.

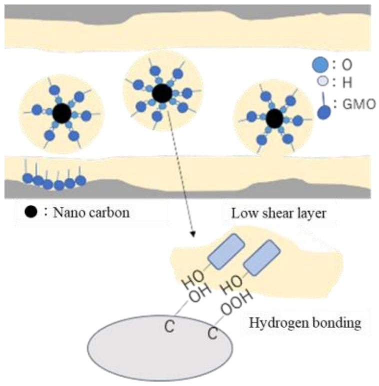

Fig.1 Models of low friction with carbon-based nanoparticles.

2. Requirements for the development of low-friction phenomena

To achieve the low friction model shown in Fig.1, we believe the following three requirements are necessary: 1) The establishment of a formation-dissociation cycle for the functional groups on the nanoparticle surface (ensuring sustainability), 2) Mixed lubrication conditions that allow nanoparticles to enter the interface, and 3) The maintenance of the dispersion state of the nanoparticles.

2-1 Formation and dissociation cycles of functional groups on nanoparticle surfaces

To confirm that the functional group -OH on the surface of GO particles, which exhibits low friction, is replaced by the functional group -OD supplied by the heavy water solvent during the friction test, the GO particles after the test were extracted by centrifugation, as shown in Fig.2, and the functional groups were analyzed using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) [3]. The friction coefficient of pure water is 0.45, while heavy water with 1.0 mass% GO dispersed showed low values of 0.05. Table 1 shows the TOF-SIMS analysis results of the GO particles and steel disk after the friction test in GO-dispersed heavy water. Deuterium (D) and its compounds were detected in the GO particles, as well as in the non-sliding and sliding parts of the disk. The COD/COH ratio calculation revealed that the COD ratio was highest in the GO particles. These results indicate that the functional group -OH, originally present in the surface layer of GO, is not always retained, but when detachment occurs due to friction, it is replaced by functional groups supplied from the solvent, thereby maintaining a balance between formation and dissociation. For this model to be valid, a supply source of the functional group -OH (in this case, pure water or heavy water, or a polar group-containing lubricant in the case of lubricating oil) is necessary.

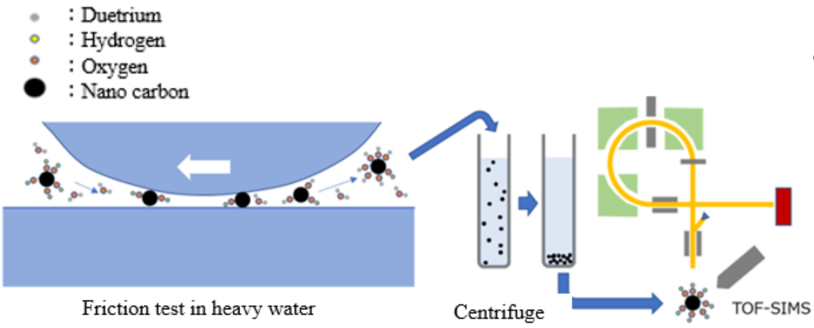

Fig.2 Extraction of nanoparticles from carbon-based nanoparticle dispersion solvents and TOF-SIMS analysis of nanoparticles.

Table 1 TOF-SIMS analysis results for GO particles and Disk specimens tested in heavy water.

	COH	COD	COD/COH
GO powder	20	5	0.250
Non-Sliding part	140	20	0.143
Sliding part	47	10	0.213
	62	10	0.161
	47	8	0.170

2-2 Lubrication conditions under which nanoparticles can exert their low-friction effect

Mineral oil, mineral oil containing 1 mass% GMO and mineral oil with 0.1 mass% GO (: STD) were used, with a flat surface on the disk side (: SCM1), a surface containing pits on the flat side (: SCM2, 3), a pit surface with manganese phosphate removed (: MnP) and spheroidal graphite cast iron containing pits with graphite loss (: FCD) were tested in combination. The results were organized by the Λ ratio (=hmin/Rrms, hmin: minimum oil film thickness, Rrms: synthetic surface roughness after testing), which is an indicator of the lubrication condition, and are shown in Fig.3 [4]. The effect of GO addition was small in the boundary lubrication zone where Λ was near 0.02, but the effect tended to expand significantly in the mixed lubrication zone. The GMO itself also showed a friction-reducing effect due to physisorption, which is considered to be part of the GO addition effect.

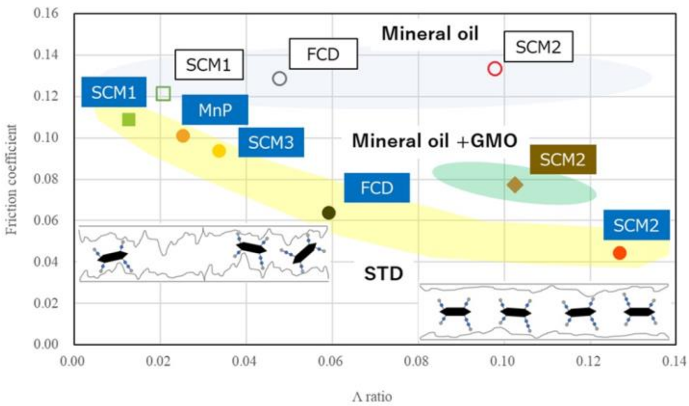

Fig.3 Friction coefficient of GO at different λ ratios.

Reducing the hardness of the disc material [5] and corroding and wearing the steel with the additive ZnDTP [6] are also effective ways to promote the running-in process and maximize the friction-reducing effect of nanoparticle addition. Though the addition of ZnDTP to the lubricating oil creates a 150 nm film on the disc surface, the friction coefficient is rather low, suggesting that film formation by GO is not the main mechanism [6].

2-2 Influence of the dispersion state of nanoparticles

As an example of the influence of the dispersion state of nanoparticles in a solvent, the test results of GO dispersed water are presented [7]. The functional group status was confirmed by XPS analysis for three types of GO and two types of rGO with different structures and functional group statuses. After 0.4 mass% of each GO was stirred into the solvent and left for 30 min, the supernatant solution was collected and the amount of dispersion was measured. Friction evaluation was carried out using a Ring/Disk type friction test. The results of XPS analysis to determine each bond ratio by C1s peak separation are shown in Fig.4. rGO reduced by heat treatment, etc. showed a decrease in C-OH and -C-OOH peaks and an increase in sp^2 bond ratio compared to the three types of GOs. On the other hand, as shown in Fig.5, the concentration of GO/rGO in the supernatant solution tended to be higher when the total ratio of C-O(H) and -C-OOH was higher. The more of these functional groups, the less the nanoparticles settle, suggesting that their dispersibility is maintained.

Based on the model shown in Fig.1, the number of adsorption sites in the polar solvent (water) was calculated as the product of the concentration in the supernatant solution, the secondary particle diameter in the solvent, the ratio of the amount of C in GO/rGO and the total ratio of C-OH and -C-OOH, and the friction coefficient at the end of the test was arranged in Fig.6. A good correlation between the two was observed, validating the model in Fig.1 explaining the lower friction due to GO under mixed lubrication. Based on these results, a more specific model is shown in Fig.7. It shows the importance of the large number of C-OH and -C-OOH functional groups in the nanoparticles to keep the particle size small without sedimentation and to maintain the availability in the narrow areas of the friction zone.

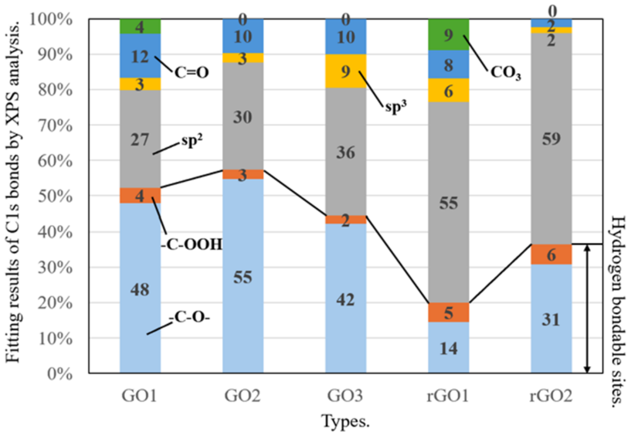

Fig. 4 C1s peak fitting results from XPS analysis of GO/rGO powder.

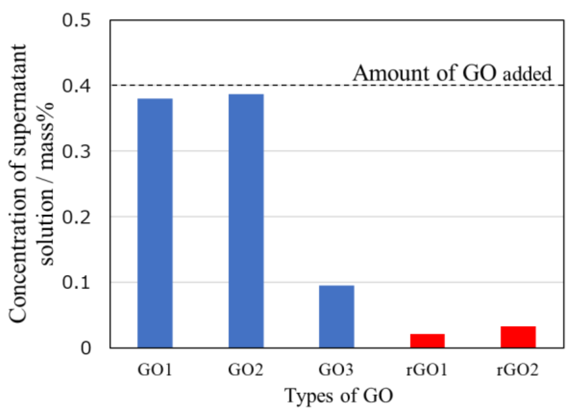

Fig. 5 Concentration of the supernatant of each dispersed water.

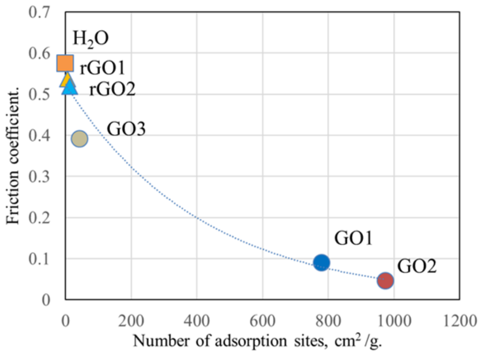

Fig.6 Relationship between the friction coefficient of GO/rGO dispersed water and the number of C-OH,-COOH adsorption sites by the Ring/Disk test.

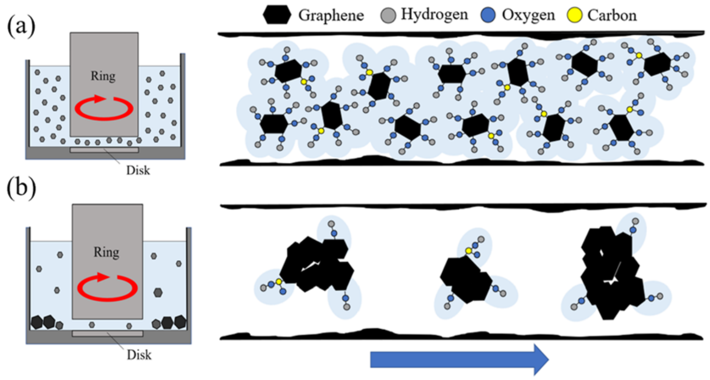

Fig.7 Lubrication mechanisms estimated with GO/rGO dispersed water in the Ring/Disk test (a) GO with good dispersibility, (b) GO/rGO with poor dispersibility.

3. Summary

An analytical case study on low-friction mechanisms using carbon-based nanoparticles is presented. Summaries are as follows,

[1] A solvent that provides functional groups to the nanoparticles is necessary to ensure the sustainability of low friction.

[2] To achieve low friction with nanoparticles, the spacing between the two surfaces should be controlled by running-in process.

[3] For low friction, the nanoparticles should contain -C-OH and -C-OOH functional groups and maintain dispersibility without settling.

Reference

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