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Research Article

Influence of WS_2 Nanopowder Addition on Friction Characteristics of ta-C Coating by FCVA Method

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The influence of nano-size WS_2 powders on the tribological behavior of ta-C coatings by the filtered cathodic vacuum arc (FCVA) method under boundary lubrication conditions has been investigated. In order to characterize and understand tribological behaviors of nano-size WS_2 powders added to the synthetic oil (poly-alpha-olefin 6), lubricants with different mixture ratios, ranging from 2 to 8 wt%, have been prepared. ta-C coatings fabricated by FCVA method showed that the G-peak in the obtained Raman spectrum was shifted from 1520 to 1586 cm^{-1}, indicating the sp^3 content increased for samples with the thickness of 156 nm. The average friction coefficient decreased proportionally as the nano-size WS_2 compositions increased up to 4 wt% in PAO6. After the friction test, structures and particle sizes of WS_2 phases were also precisely characterized by using XRD and SEM.

1. Introduction

Various lubricants that contain nanometer sized solid lubricants have received a considerable attention recently due to their improved physical and chemical properties compared to bulk materials or individual molecules [1–3]. The main reason for using nanoparticles is that they are relatively insensitive to a temperature variation and they show higher chemical stability compared with traditional additives [4]. And nanoparticles as additives in lubricating oils as cannot be retained by typical filters [5]. For those reasons, nanoparticle solid lubricants have been synthesized and successfully used in industries. Among solid lubricants, WS_2 powder has been shown to provide a good tribological performance due to its lamellar structure in which there are strong covalent bonds between atoms of the same layer and weaker van der Waals force between layers [6]. Furthermore, the combination of nanometer sized solid lubricants and tetrahedral ta-C can improve the tribological performance in the rubbing state. ta-C is a hydrogen-free carbon coating with 70~80% of sp^3 phase known to show low rates and high abrasion resistance. Moreover, ta-C coating can be synthesized by a relatively convenient method and has a much smoother surface, making the tribological performances of ta-C coating better than those of general DLC [7]. An X-bend filter is one of the powerful methods to remove macro particles streaming from the plasma beam of cathodic vacuum arcs, generally used to fabricate ta-C coating [8]. Furthermore, an X-bend filter is known for a high plasma transmission efficiency, which leads to the reduced macro particle generation, improved deposition rate, and high quality ta-C films with 80% sp^3 bonding. Among various techniques for deposition, FCVA has been most frequently chosen to make ta-C coating suitable for wear resistance applications [9].

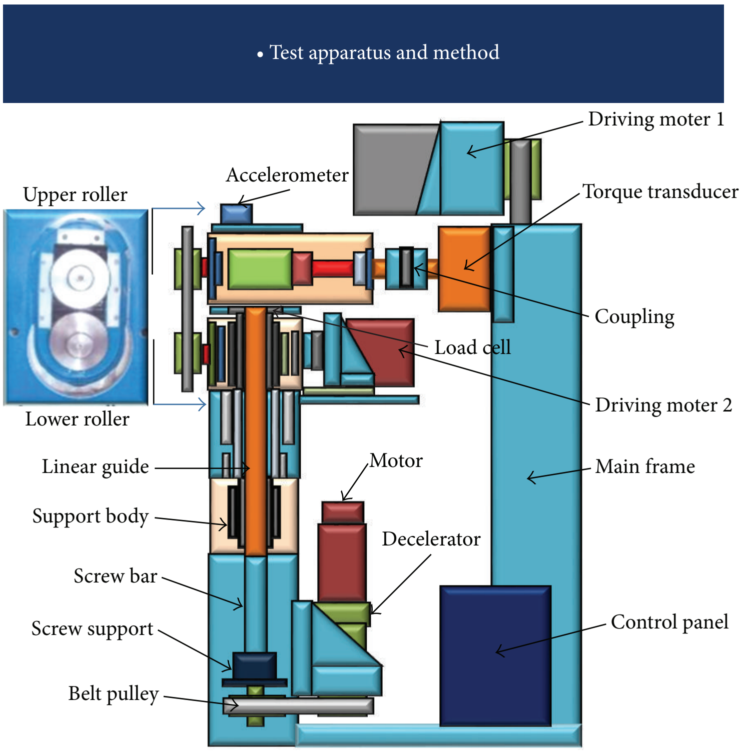


Figure 1: Schematic view of ball-on-disk type friction tester.

Table 1: Physical and chemical properties of nano-size WS_2 powder.

Purity	More than 99.9%
APS (Average Particle Size)	Below 120 nm
SSA (Specific Surface Area)	$30\ m^2/g$
True density	$7.50\ g/cm^3$

However, tribological performance of ta-C coatings under lubricated conditions and their interaction with lubricating additives are strongly affected by the hydrogen content, chemical stability, sp^2/sp^3 ratio, and environmental conditions [10]. Furthermore, the maximum coating thickness for ta-C is limited to less than 1 um due to its high intrinsic stress, low load bearing capability, and brittleness [11]. Hence, more research on their tribological performance with nano-size WS_2 particle additives will be beneficial for successful operations under lubricated conditions.

The object of this paper is to investigate the effect of nano-size WS_2 additives on the lubrication performance of X-bend filtered ta-C coatings when rubbed against AISI 52100 depending on the load and the concentration of nano-size WS_2 solid lubricants added to PAO6 under the boundary lubrication condition.

2. Experiments

2.1. ta-C Coating with X-Bend Filtered of FCVA. For this research, ta-C coatings were deposited on polished Si (100) wafer by FCVA. The Si surface was cleaned with r.f. ion beam using Ar prior to deposition. The ultimate pressure and the working pressure in the main chamber were 1.7×10^{-4} Pa and 1.7×10^{-2} ~4.0×10^{-2} Pa, respectively.

During the deposition, the substrate holder was rotated to achieve a uniform film thickness. To reduce the high residual stress, ta-C coating was deposited between hard and soft coatings by controlling the bias voltage. The ta-C coatings were deposited with the arc voltage in the range of 200~1350 V and the arc current of 40 A at room temperature. Each ta-C sample's thickness was about 156 nm to avoid a high level of intrinsic stress. The hardness test of ta-C was measured with a nanohardness tester using a Berkovich diamond indenter. The measured hardness of ta-C coatings with X-bend filtered of FCVA was found to be 50 GPa in this study.

2.2. Characterizations. A commercially available nano-size WS_2 powder was purchased from Hanshin-Metal Co., Ltd., Korea. The physical and chemical properties of the nano-size WS_2 powders used in this study were described in Table 1.

The base lubricants investigated in this work include pure poly-alpha-olefin oil of viscosity grade 6 (known as PAO6) chosen mainly because of its higher operating temperature and good resistance to oxidation [12]. Nano-size WS_2 powders were blended into PAO6 with different mass percentages of 2, 4, 6, and 8 wt% for tribo-testing. The physical and chemical properties of PAO6 were shown in Table 2.

XRD data for the nano-size WS_2 powders were acquired using a PANalytical Pro MPD X-ray diffraction machine with *CuKa* radiation (wavelength $\lambda = 0.154$ nm) over a range of 0–70°, a step size of 0.02°, and a time step of two seconds for

Table 2: Physical and chemical properties of base oil.

Item	PAO6
Viscosity index	137
Kinematic viscosity (cSt) at 40°C	28.50
Kinematic viscosity (cSt) at 100°C	5.50
Pour point (°C)	−54.0

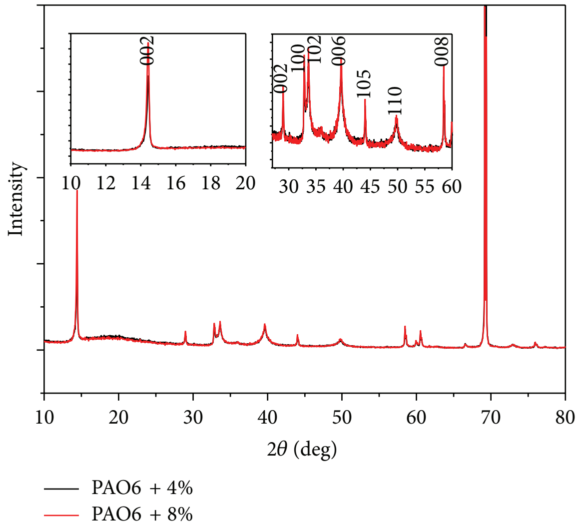


Figure 2: XRD analysis of 4 wt% and 8 wt% WS_2 powders in PAO6.

normal scans. A Tescan scanning electron microscope (SEM), operated at 20 keV, was used to visualize the thickness of ta-C samples. The structures of ta-C were analyzed by Raman spectroscopy.

2.3. Ball-on-Disk Type of Tribo-Tester. The tribological tests were conducted at room temperature (approximately 25°C) according to ASTM D5183-2005. The wear and friction properties of lubricating oils containing nano-size WS_2 powders were investigated at the rotational speed of 300 rpm and at different normal loads ranging from 2 to 8 N (maximum Hertzian contact pressure of 0.83 to 1.32 GPa, resp.) for 30 min. During the test, the friction coefficient was monitored continuously as a function of number of cycles. All tests were conducted 5 times for each condition for high reliability. A schematic view of the ball-on-disk type friction tester used in this study is shown in Figure 1.

The wear traces and extracted nano-size WS_2 powders including wear debris were investigated by field emission scanning electron microscopy (SU 8020, Hitachi).

3. Results and Discussion

3.1. Effect of Nano-Size WS_2 Concentration on Friction and Wear. XRD analysis recorded for PAO6 with 4 and 8 wt% WS_2 is presented in Figure 2 showing sharp peaks indicating a high quality crystalline structure, with (002) as the strongest peak. Furthermore, the two peaks representing (100) and (101) that indicate the planes of hexagonal WS_2 are clearly observed in Figure 2. It is noted that another research article reported [12] that (002) peaks indicate both a smaller size and fewer layers for WS_2 sheets. This sheet structure may enhance its own lubricity to provide a good low friction and antiwear behavior.

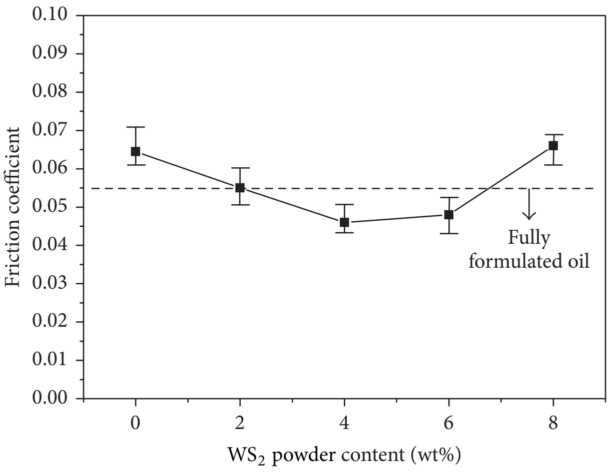


Figure 3: Variation of the average friction coefficient of PAO6 with increasing contents of nano-size WS_2 powders. (load = 4 N, rotational speed = 300 rpm for 30 minutes).

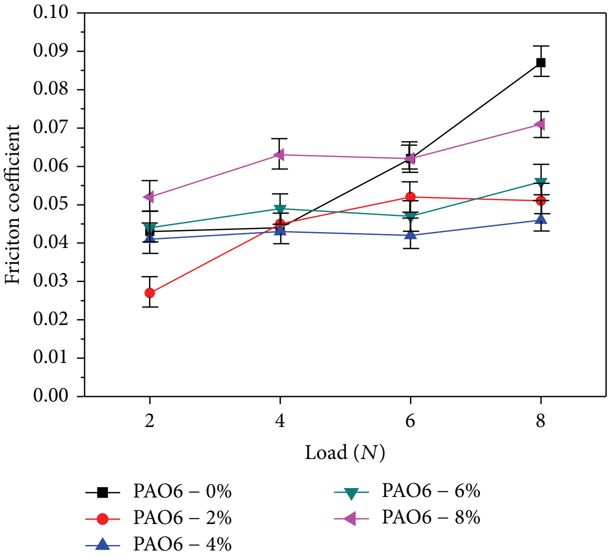


Figure 4: Effect of load on the friction properties of PAO6 containing different nano-size WS_2 powder contents.

Figure 3 shows the variation of the average friction coefficient of PAO6 with increasing contents of nano-size WS_2 powder. As expected, pure PAO6 without nano-size WS_2 powders yielded the highest friction coefficient of 0.065 during the ball-on-disk test. The average friction coefficient proportionally decreased from 0.065 to 0.045 with the increasing nano-size WS_2 powder concentration up to 4 wt%. The lowest friction coefficient measured with 4 wt% WS_2 content in PAO6 showed a better frictional performance than the conventional oil (0.065) used in this study.

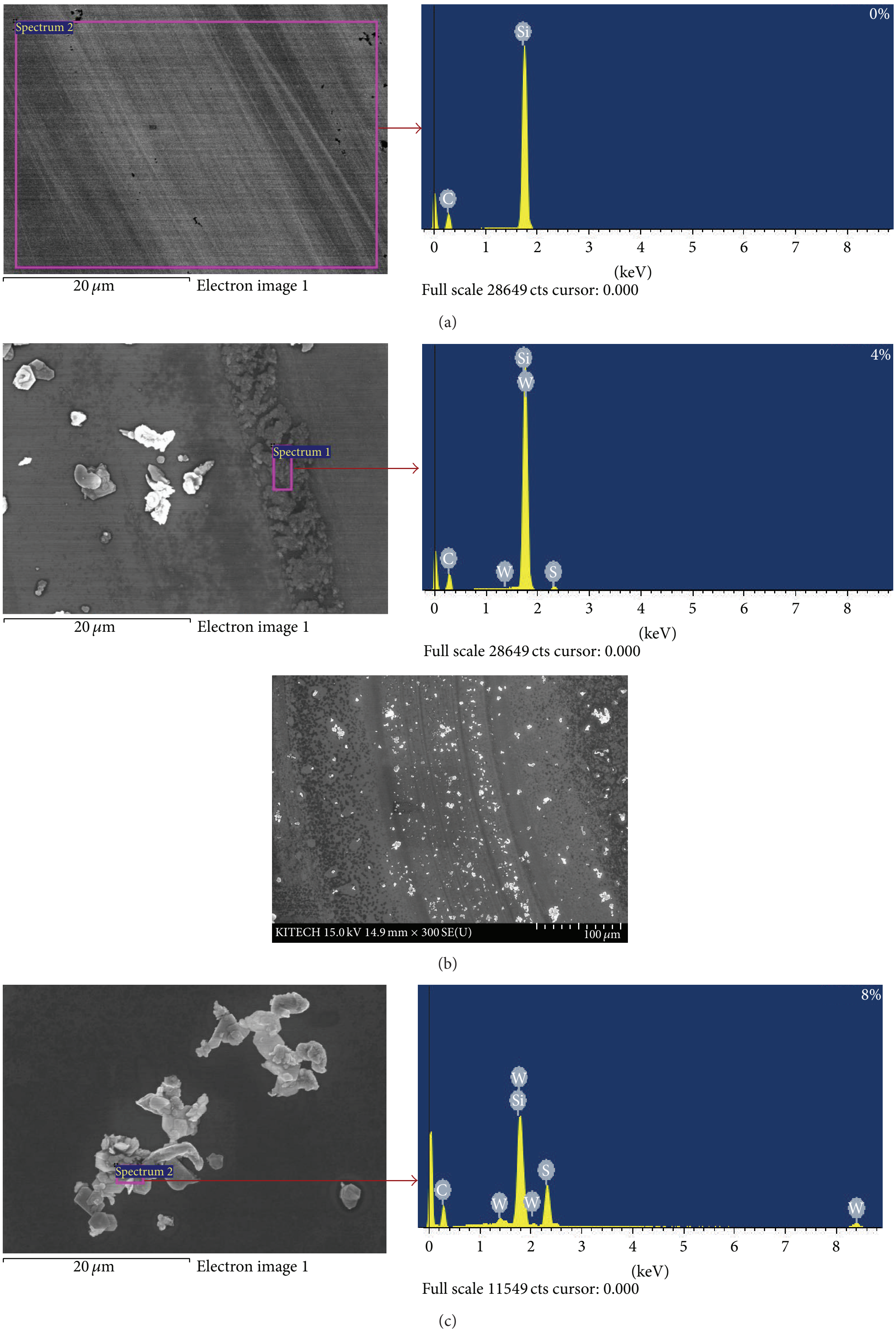


Figure 5: SEM images and EDS analysis of worn ta-C surfaces with (a) 0 wt%, (b) 4 wt%, and (c) 8 wt% of WS_2 powders after tribo-tests.

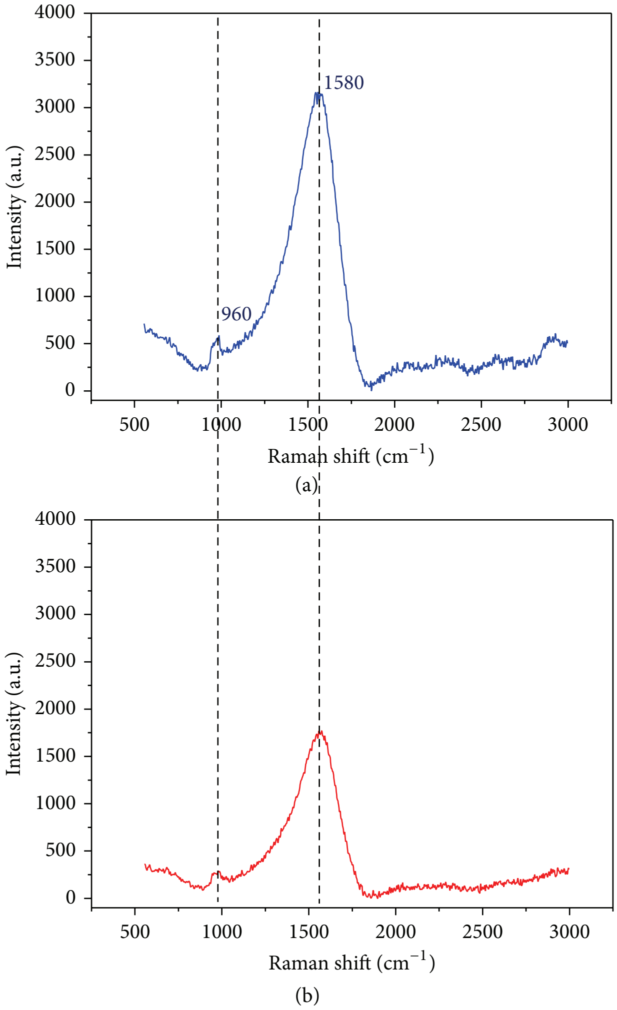


FIGURE 6: Raman spectroscopy analysis of wear trace (a) before and (b) after friction tests on ta-C sample.

It is noted that although we have performed friction test at 80 degree to understand a tribological performance under a real working temperature of lubricant in vehicle industry. However, the tendency of friction coefficient did not show much difference at 80 degree. Another researcher mentioned [13] that tungsten disulfide WS_2 is frequently used as an antifriction additive and showed a stable and similar behavior in friction coefficient at higher temperatures (up to 500°C). However, the average friction coefficients were reduced with the increased nano-size WS_2 powder contents of 6 and 8 wt% in the entire tests performed in this study. These results indicate that the concentration of nano-size WS_2 powders has an important role in reducing and controlling the friction behavior for PAO6. The results demonstrate that the amount of nano-size WS_2 powders can enhance the low frictional characteristics of other lubricants.

3.2. Effects of Load on Friction and Wear. Load variations have been shown to affect the oil film formation between two sliding bodies [14], which in turn affect the development of tribological performance. Figure 4 shows that the friction coefficients increased with the increasing load due to larger contact areas between two bodies during the friction tests. Furthermore, the lubricant entraining through the contact under a high load state may have been interrupted to perform a lubricity or tribofilm of its own WS_2 characteristic. PAO6 without WS_2 powders showed the highest friction coefficient of 0.09 when 8 N was applied in this study. In case of 2 wt% WS_2 powders in PAO6, the variation of friction coefficient behavior showed lower behavior with increasing load compared to only PAO6. Similarly, tests with 6 wt% and 8 wt% WS_2 powders in PAO6 resulted in high friction coefficients as the load increased. However, in case of 4 wt% of WS_2 powders in PAO6, the friction coefficient was relatively stable in the range of 0.043 to 0.048 under the load conditions used in this study. This phenomenon is very important for the industrial application in vehicle, bearing, and engine systems. In other words, although severe wear and friction occur under a high load state during sliding contact states, nano-size WS_2 powder additives can lead to a stable friction behavior and may even improve antifrictional properties due to the absorption of nano-size WS_2 powders on ta-C samples.

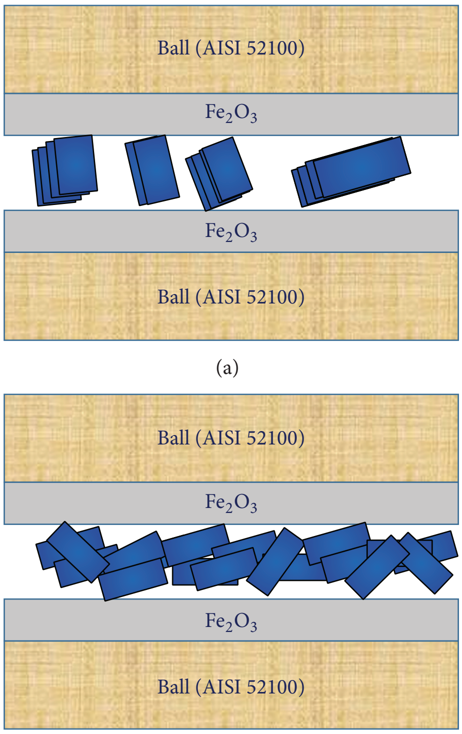
3.3. Morphology, Component, and Structure Analysis of Frictional Surfaces. The morphology and structure of wear debris resulting from nano-size WS_2 and ta-C coating samples during the tribo-test were shown in Figure 5. For the only PAO6 oil, microscopic images of worn surfaces reveal the existence of abrasive wear and plastic deformation of AISI 52100 samples caused by the high hardness difference. In case of 4 wt% WS_2 in PAO6, the presence of WS_2 absorption on ta-C samples is shown in Figure 5(b). And also the absorption of WS_2 powder was clearly observed from the EDS analysis. Furthermore, the worn surface looked very smooth due to WS_2 on ta-C samples. In other words, nano-size WS_2 powders helped reduce the shear strength between AISI 52100 and ta-C bodies. The higher magnification image containing 4 wt% WS_2 in PAO6 as shown in Figure 5(b) revealed uniform and regular WS_2 debris over the ta-C sample. From this result, it can be suggested that a WS_2-rich boundary film has been formed on ta-C during the sliding test that eventually provided a good protection against wear due to its low shear nature.

In case of 8 wt% WS_2 in PAO6, no nano-size WS_2-rich film formed on ta-C was observed. And also strongly agglomerated nano-size WS_2 powders were observed as shown in Figure 5(c). It can be suggested that the agglomerated nano-size WS_2 powders due to the larger WS_2 content induced an irregular tribofilm during the sliding state and reduced the tribological performance.

Raman spectroscopy analysis results from the wear trace (a) before and (b) after friction tests on ta-C sample were shown in Figure 6. In general, Raman spectroscopy method is a relatively simple and nondestructive analysis tool used to characterize the structural changes in carbon materials. ta-C coatings by FCVA method showed that the G-peak position in Raman analysis was shifted from 1520 to 1586 cm^{-1} due to the increased sp^3 content in 156 nm thick samples. Other researchers [15] reported that the bond length of chains is shorter than that of rings, resulting in a higher vibrational frequency for 1586 cm^{-1} peak. These increased sp^3 contents were correlated with hardness and antiwear performance. It can be clearly seen that a strong peak ranging from 1520 to 1586 cm^{-1} was visible after tribo-tests as shown in Figure 6(b). This phenomenon, indicating no wear scar due to high hardness of ta-C, is shown in Figure 5.

Based on our results, the schematic representation of the third body model containing 4 wt% and 8 wt% WS_2 powders in PAO6 is shown in Figure 7. For 8 wt% WS_2 powders in PAO6, a strong agglomeration of WS_2 powders was observed due to the high WS_2 contents in PAO6. And the strongly agglomerated WS_2 powders induced a more inhomogeneous behavior and formed irregular tribofilms between ta-C and AISI5210 steel, indicating no lubricity improvement during the friction tests. In this study, the best tribological performance was obtained with PAO6 with 4 wt% WS_2 powders.

However, further studies of tribofilms using TEM or XPS will be undertaken to obtain more in-depth understanding of the mechanisms involved in improving the friction behaviors of nano-size WS_2 powders.



(a)

(b)

Figure 7: Schematic representation of third body model containing (a) 4 wt% and (b) 8 wt% of nano-size WS_2 powder in PAO6.

4. Conclusions

This paper demonstrates nano-size WS_2 powder on the tribological behavior of ta-C coatings by FCVA method under boundary lubrication conditions; the results reported and discussed in this study are to provide useful penetration on the influence of nano-size WS_2 powders in base oil. In particular, the models of wear and friction induced by the nano-size WS_2 additives and how these change under various loads have been described. Systematic approach which has been reported to extract several analytical data can be useful to optimize vehicle, gear oils, and ta-C coatings by FCVA method for component application. The following conclusions can be drawn from this study:

(1) Average friction coefficient proportionally decreased with the increasing nano-size WS_2 powder concentration up to 4 wt% in PAO6. The lowest friction coefficient measured with 4 wt% WS_2 content in PAO6 showed the optimum tribological performance. This tribological improvement is a result of the synergetic effect of the nano-size WS_2 powder.

(2) In case of 4 wt% WS_2 in PAO6, WS_2 absorption on ta-C samples was clearly observed from the SEM and EDS analysis and uniform and regular WS_2 debris were formed over the ta-C sample. This regular WS_2 debris helped reduce the shear strength between AISI 52100 and ta-C bodies.

(3) In terms of load changes, 4 wt% WS_2 in PAO6 showed relatively stable in the range of 0.043 to 0.048. This phenomenon can be described by the fact that WS_2 powder additives can lead to a stable friction behavior and may even improve antifrictional properties due to the absorption of nano-size WS_2 powders on ta-C samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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