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Effects of Titanate on Brake Wear Particle Emission Using Brake Material Friction Test Dynamometer

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Abstract: We investigated the effect of lepidocrocite-type layered titanate, which we have been using to reduce brake-particle emissions in an environmentally friendly manner. The effect of titanate on reduction was evaluated using a small-scale inertia brake-material-friction-test dynamometer. We suggested that brake-particle emissions are related to the microphysical structure of the pad surface, such as the uniformity of friction film and secondary-plateau formation, and that friction materials containing titanate contribute significantly to the reduction in both particle mass (PM) and particle number (PN) emissions of brake particles for both non-asbestos organic (NAO) and low-steel (LS) pads. In our experiments, the PM- and PN-emission levels of brake particles from LS pads with the addition of titanate were comparable to those of NAO pads.

Keywords: Brake Dust; Friction Additives; Non-tailpipe; Non-Exhaust; Tribometer Test

1. Introduction

Automobile disc brakes typically consist of a cast iron disc and a system of two or more brake pads integrated into calipers [1–3]. During braking, the pistons and calipers press the pads against the disc, generating high contact stresses and dissipating the kinetic energy of the car's travel as heat [1–3]. Optimal brake-pad friction materials require not only mechanical durability but also excellent thermal conductivity and a relatively high and stable coefficient of friction [1,3–5]. Brake pads are manufactured from a blend of 10 to 20 different materials, depending on the specific application and expected life. The most widely applied materials for brake pads are organic resin binders [6]; fillers, such as barium sulfate [7,8]; friction modifiers, such as metal chips or abrasive metal powder [9,10]; organic polymer composites, such as aramid pulp [24] or steel fiber as reinforcement fiber; and solid lubricants [11,12] . Materials of various origins have been tested as friction modifiers and solid lubricants for brake pads [1,3,4], suggesting that the selection of brake-friction materials is still an open research topic and not fully understood [4].

Solid lubricant antimony sulfides [4,5] have been reduced or eliminated by most brake-pad manufacturers due to environmental concerns. As an alternative to antimony sulfide, tin sulfide is often used as a typical metal sulfide component of solid lubricants [13]. Tin-resource reserves, however, are gradually decreasing, posing a challenge to the stability of tin-resource supply. The main causes are deteriorating resource-supply conditions, increasing demand, and heightened geopolitical risks [14]. Reports on the systematic study of metal sulfides other are still scarce [4,5], and a more recent paper showed that good friction properties were achieved with a solid lubricant blend consisting of iron sulfides and titanates [15]. Small amounts of molybdenum disulfide in combination with graphite [16,17] or lepidocrocite-type layered titanate [18–20] used in our study have also been reported as alternatives to the conventionally used whisker-like titanates [21].

Titanate plays an important role in improving friction stability and wear resistance by forming a strong friction film on the friction surface along with the synergistic effects of titanate shape [22] and aramid pulp [23]. In our previous studies, we pointed out the importance of friction-film formation on the pad surface, as the chemical reaction between titanates and phenolic resin produce

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carbides on the pad surface, which improves friction stability [18–20]. Pad-surface contact during braking also consists of two different contact regions: a primary plateau and secondary plateau. A primary contact plateau consists of large, hard components such as metal fibers and coarse abrasives., which are exposed to the friction-material surface until worn away. A secondary contact plateau is formed by the compression of wear particles around the primary plateau, and their size and mechanical properties vary depending on the composition of the wear particles and braking conditions [24,25]. Thus, the formation of the contact plateau and brittleness of the friction film play an important role in the wear resistance of titanates [26,27]. There have been few studies on the role of titanates in the emission of brake particles derived from brake wear into the atmosphere, for which regulations have recently been introduced [28]. It is nearly impossible to predict the effect of a single component on the brake-performance characteristics of friction materials, yet their basic compositions vary widely [4]. Friction-performance properties can be learned from many observations and experiences obtained during material development and dynamometer testing.

Brake pads for basic braking systems are available in a wide range of friction-material compositions, including gray cast iron brake discs. The most important categories are low-steel (LS) pads (also called European performance "ECE"), which are developed and produced primarily for the European market, and non-asbestos organic (NAO) pads designed primarily for the US and Asian markets [41]. These two types of pads can be distinguished by, among other things, the percentage of steel. LS pads contain a significant percentage of steel, while NAO pads are usually free of steel [33,41,42]. Brake-dynamometer experiments have verified that LS pads have higher brake-particle emissions and NAO pads have lower emissions when comparing commercial brake systems [33,42]. Although a reduction in brake-particle emissions with titanate has been suggested for commercial brake systems [33], there is a lack of knowledge on the role of the friction-modulating ability of titanate in brake-particle emissions for NAO and LS pads.

Brake-dynamometer experiments typically involve different scales, depending on the purpose of the investigation. An inertial brake dynamometer with a full-scale braking system is used, for example, for measuring brake-particle emissions in the atmosphere, for which emission regulations have recently been established [28]. Following the Global Technical Regulation No. 24, using the adjusting-cooling-flow environment (temperature, humidity, wind speed, etc.) can be controlled, allowing for reliable emission measurements [29–31]. Another possibility method is the use of JASO C470 sampling devices applied to inertial brake dynamometers for small vehicles [32,33]. By adjusting the environment for the adjusting-cooling-flow rate, the quality of brake particles emitted from the test brakes is estimated to have similar brake-particle-emission factors between World Technical Standard No. 24 and JASO C470 [33]. Inertial brake dynamometers are advantageous for measuring brake-particle emissions from brake assemblies with high reliability but have the disadvantage of being time consuming to design and analyze. A pin-on-disk tribometer can be used to investigate material-level contact pairs in a controlled laboratory environment [34–40]. The material-level experiments with a pin-on-disk tribometers are similar to those conducted with inertial brake dynamometers in terms of wear and brake-particle emissions [34–37,40]. Rapid evaluations using pin-on-disk tribometers are advantageous for analyzing friction and wear mechanisms but not for assessing friction-based brake-particle emissions in urban driving.

We therefore aimed to investigate the role of lepidocrocite-type layered titanate used in our previous studies [18–20] in reducing brake-particle emissions, as an additive to NAO and LS friction materials and an alternative to metal sulfides. The effect of titanate on reducing brake-particle emissions in urban driving was also evaluated. A miniaturized inertial brake dynamometer was used to conduct experiments that enabled the evaluation of brake-particle emissions in urban driving for the specimen brakes. The corrosiveness of the specimen brakes due to metal sulfides after friction testing was also investigated.

2. Materials and Methods

2.1. Brake Material Friction Test Dynamometer ; the 1/7-scale Inertia Dynamometer

Brake-friction-material tests were conducted by using the 1/7-scale inertia dynamometer (custom-made 1/7-scale Inertia Dynamometer, Kobelco Machinery Engineering Co., Ltd., Gifu, Japan) [19,20,41–44]. A schematic of the testing apparatus used for our experiment is presented: Two load cells were used to measure the applied load and brake torque. A thermocouple was inserted at a depth of 2.0 ±0.2 mm for the disc surface to monitor the brake temperature. The load and initial speed were obtained from the rotating flywheel (0.5 $kg \cdot m^2$).

2.2. Friction-test Conditions

The inertial mass was adjusted so that the energy per unit area was equal to approximately 2000 $kg \cdot m^2/s^2 \cdot cm^2$ for a typical passenger car when tested at 100 km/h. The experimental conditions were selected as urban driving conditions controllable by using the 1/7-scale dynamometer, first for bedding then for emission measurement. For bedding, braking was repeated 500 times at an initial speed of 65 km/h, deceleration of 3.5 m/s^2, and brake temperature (initial brake temperature) of 120°C at the start of braking. The brake-emission-measurements were conducted on the basis of the simplified driving mode (Otsuka Mode), which minimizes drag by not including cruising, and is referred to "Measurement Method for Particulate Matter Emissions from Passenger Car Braking Wear" JASO C470 [32]. During the brake-emission measurement, ten cycles of the Otsuka Mode were repeated two times ($n = 2$). The average vehicle speed was 22 km/h, maximum speed was 120 km/h, average deceleration was 1 m/s^2, maximum deceleration was 1 m/s^2, and braking frequency was 15 times/cycle. The total distance was 18.3 km.

2.3. Brake Disc and Friction Materials

The brake discs were made of FC-150 grade gray cast iron (carbon content 3.8%, disc outside diameter (O.D.) and inside diameter (I.D) dimensions: 110 and 43 mm, respectively). The brake pads (friction materials) were prepared by Otsuka Chemical Co., Ltd. The brake pads were commonly composed of phenolic resin (powder novolak phenolic resin), aramid pulp (poly-paraphenylene terephthalamide), barium sulphate ($BaSO_4$, ground barite), and Zircon ($ZrSiO_4$, Zirconium (IV) silicate). The content of the lepidocrocite-type layered titanate (Terracess® PM, Otsuka Chemical Co., Ltd., Osaka, Japan) [18–20,41–43], steel fiber (Cut wool BS1V, Bonster, Tokyo, Japan) and tin sulfide were adjusted in accordance with the brake-pad properties.

The brake pads were prepared as follows. The powders were mixed using an intensive mixer (Model R02, Nippon EIRICH Co., Ltd, Chiba, Japan) at a chopper speed of 3,000 round/min.

We made both NAO and LS formulations. For the NAO formulation, the mixture was temporarily formed at a pressure of 10 MPa for 5 s then hot pressed by heating at 150°C for 300 s with degassing 6 times at a pressure of 20 MPa. The material was then fully cured in an oven at 160 to 200°C for 2 to 6 h and cut into final fan-shaped brake pads (pad area: 5.53 cm^2).

For the LS formulation, the mixture was hot pressed by heating at 150°C for 240 s at a pressure of 15 MPa. The material was then fully cured in an oven at 160 to 210°C for 6 h and cut into final fan-shaped brake pads (pad area: 5.53 cm^2).

A series of brake pads were prepared. The selection of the friction materials was based on the following evaluation parameters, assuming that the pads conformed to copper-free regulations [45,46]:

Brake 1: Cu-free NAO pads, free of potassium titanate.
Brake 2: Cu-free NAO pad, containing potassium titanate.
Brake 3: Cu-free LS pad, containing tin sulfide and free of potassium titanate.
Brake 4: Cu-free LS pad, containing tin sulfide and potassium titanate.
Brake 5: Cu-free LS pad, free of tin sulfide and containing potassium titanate.

2.3. Brake-wear-particle-measurement Instruments

In the sampling system cooling air (temperature 23±3°C, humidity 40±20% relative humidity) through a high-efficiency particle filter (HEPA) flowed from upstream of the enclosure where the test brake was stored, and a constant flow of 2 m^3/min was suctioned in the sampling tunnel downstream

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of the enclosure. Cooling air flowed from bottom to top when the brake disc is viewed from the front with the brake pad at 15 o'clock, and the rotation of the disc was clockwise in this experiment. The same policy as in GTR24 [29] was followed, except for the flow direction of the cooling air, which was from bottom to top.

Brake particles were measured by particle mass (PM) and the total particle number (PN) including volatile particles. PM and PN were aspirated from the isokinetic sampling nozzle. The sampling-tunnel flow rate Q was 2 m^3/min, and the sampling flow rate Q_s was 15 L/min. The sampling nozzle diameter (B: 8.4 mm) was chosen to have an isokinetic ratio of 1, considering the diameter of the sampling tunnel (duct inner diameter A: 97.4 mm. For particle-mass measurement, brake particles were collected as >PM_{10}, $PM_{10\text{-}2.5}$ on a TX40 filter (Emfab TX40HI20-WW, Pall Corp., New York, USA), and $PM_{2.5}$ on a PTFE teflo filter (R2PJ47, Pall Corp., New York, USA) using a multi-cascade impactor (MCI-15, Tokyo Dylec, Tokyo, Japan). The filters that collected brake particles were weighed on an electronic balance (Ultra-Microalance XP6V, METTLER TOLED, Switzerland) using a static electricity eliminator (ionizer PRX U Small set, HAUG, Echterdingen, Germany). PN was measured using a full-flow condensation particle counter (CPC) (model 3772, TSI Inc., Shoreview, MN, USA).

$$PM = PM_{filter} \times Q / Q_s, \tag{1}$$

here,
PM_{filter}: Filter weighing mass for $PM_{10\text{–}2.5}$ or $PM_{2.5}$ (μg).
Q_s: Sampling flow rate, 15 L/min.
Q: Sampling-tunnel flow rate, 2000 L/min.

3. Results

3.1. Friction-surface Conditions

It was compared the non-titanate (Brake 1) and with-titanate (Brake 2) friction surfaces of the NAO pads. The cross-sectional views of the brake pads are shown in backscattered electron (BSE) images obtained using a scanning electron microscope (SEM). To prepare these samples for observation, they were embedded in epoxy resin (Clear epox-2, Sankei, Tokyo, Japan), and the surfaces were smoothed with a rotary polisher (Daiya lap ML-150P, Maruto, Osaka, Japan) and sputtered using an ion milling system (Flat Milling IM-3000, Hitachi-hitec, Tokyo, Japan).

The friction films were formed on the friction surfaces of the non-titanate (Brake 1) and with-titanate (Brake 2) NAO pads. For the non-titanate pads, the friction film was thick but rough and non-uniform, and some were cracked (damaged) or peeling off. For the with-titanate pads, the friction film was found to be thin, widely uniform, and densely formed. We suggest that uniform and dense friction film leads to some of the film not peeling off.

It was compared the non-titanate (Brake 3) and with-titanate (Brake 4) friction surfaces of the LS pads. BSE images of the cross sections of the pads are shown respectively. Both samples contained tin sulfide. The non-titanate (Brake 3) friction surface had damaged steel fibers (the primary plateau) and no secondary plateau (no friction film)e. The with-titanate (Brake 4) friction surface had no damaged steel fibers (primary plateau) compared with the non-titanate friction surface. Looking at the friction surface in the sliding direction, wear particles gradually densified, forming the secondary plateau, and eventually the secondary plateau on the steel fibers disappeared, exposing the raw material. We found significant differences in the observed results of steel fibers (the primary plateau) and secondary plateaus for the non-titanate and with-titanate friction surfaces.

The LS pad is Brake 5 with the tin sulfide replaced with titanate from Brake 4, and the formation of a dense friction film was observed as the formation of a secondary plateau. The appearance of Brake 5 shown in the cross-section was similar to the appearance of the widely uniform friction-film formation of the with-titanate NAO pad (Brake 2) shown in the cross-section.

The above results indicate that the microphysical structure of the pad surface differs significantly depending on the friction-material combination.

3.2. Brake-wear-particle Mass Amounts and Number Concentrations

In the JASO C470 testing, the PM and PN are typically represented as emission factors (mg/km or #/km). However, due to the use of a simplified test mode for C470 in this instance, we represent them in µg and #/cm^3 instead of as emission factors. Most of the brake pads had more PM$_{10\text{-}2.5}$, the PM from 10 to 2.5 µm in diameter, detected than PM$_{2.5}$, the PM less than 2.5 µm in diameter; PM$_{10\text{-}2.5}$ is larger in particle size, thus is more likely to be derived from grinding discs and pads and from the PM$_{10\text{-}2.5}$. The PM$_{10\text{-}2.5}$ is considered to originate from abrasive wear, which is the primary particles, or their aggregations generated from grinding of discs and pads because of its larger particle size.

Comparing Brake 1 (the non-titanate) and Brake 2 (the with titanate), PM$_{10\text{-}2.5}$ decreased by 70% with the addition of titanate. Similarly, a 40% reduction in PM$_{10\text{-}2.5}$ was observed from the LS pads, Brake 3 (non-titanate) to Brake 4 (with titanate). The addition of titanate reduced abrasive wear for each of the NAO and LS pads in this study. The PM$_{2.5}$ and PN were also found to have decreased for the NAO pads from Brakes 1 to 2 shown, while PM$_{2.5}$ and PN did not significantly decrease for the LS pads from Brakes 3 to 4 shown. The reduction in PM$_{10\text{-}2.5}$ and the observation of the friction film or secondary plateau suggest that the addition of titanate contributed significantly to the reduction of abrasive wear due to the homogeneous formation of the friction film or secondary plateau.

In Brake 5, which is a blend in place of tin sulfide with titanate, even for the LS pad, both PM and PN measurements were observed to be comparable to the NAO Brake 2 measurement levels.

Comparing Brakes 4 and 5, the LS pads with titanate, we found that both PM and PN measurements decreased in Brake 5. The friction-material blends of these brakes are almost the same in terms of steel and organic resin content. The comparison of the LS pads with titanate, Brake 4 (with tin sulfide) and Brake 5 (non-tin sulfide), also indicates that the addition of titanate contributes to the reduction of both PM and PN.

4. Discussion

Titanate plays an important role in improving friction stability and wear resistance by forming a strong friction film on the friction surface along with the synergistic effects of titanate shape [22,27] and aramid pulp [23]. In our previous studies, we pointed out the importance of friction-film formation on the surface of NAO pads because the chemical reaction between titanate and phenolic resin produces carbides on the pad surface , which improves friction stability [19,20]. The contact of the LS pad surface during braking consists of not only a friction film but also two different contact regions: a primary plateau and secondary plateau. The primary plateau consists of large, hard components such as metal fibers and coarse abrasives, which are exposed to the friction material surface and grind the disc and friction film until worn. A secondary plateau is formed by the compression of wear particles around the primary plateau, and the size and mechanical properties vary depending on the composition of the wear particles and braking conditions [25]. The frictional performance shown in previous studies with lepidocrocite-type layered titanate [19,20] and the frictional properties of the NAO pads support the findings obtained with platelet-like titanates [27].

The results of our previous studies [26,27] supported the finding that titanate plays an important role in the formation of contact plateaus and the fragility of the friction film in wear resistance, whereas wear resistance increases due to platelet-like titanates. The improvement of wear resistance by platelet-like titanates [27] is supported by the reduction in PM and PN emissions of brake particles in the with-titanate NAO pad (Brake 2) and the with-titanate LS pads (Brakes 4 and 5). In the LS pads, contact-plateau formation and friction-film fragility contribute significantly to wear resistance [26,27] and play an important role in terms of brake-particle emissions. Surface roughness, which is a concern with LS pads, is supported by the negatively sloped surface profile of the pad surface, which is a key factor in wear resistance affected by the formation of secondary plateaus near the primary contact plateaus (mainly steel fibers) of the brake pads [24,47].

It is also known that if the contact surface remains undamaged during braking, the pad surface becomes smoother, but if the contact surface is severely damaged, the surface becomes rougher [48]. Iron oxide particles migrating from the gray iron disc prevent the aggregation of wear particles in the friction material and reduce the size of the secondary plateau [25,49]. The size of the secondary plateau is related to wear resistance, suggesting that platelet titanate may increase the friction level and decrease the wear rate when high molecular weight resins are used as binders in the low temperature range [27]. The increased wear resistance of specimens with platelet titanates over whisker titanates at decomposition temperatures lower than the 350°C of organic resins is thought to be due to the accumulation of wear-resistant plate titanates on the surface during the wear process and actively participate to form secondary plateaus [27].

Based on our experimental results and the findings obtained so far, it is possible that the friction film and secondary plateau caused by solid lubricants significantly affect the wear rate of the friction couple and on brake-particle emission, and research on the effect of solid lubricants on brake-particle emission is needed.

While the solid lubricant tin sulfide is often used as an alternative to antimony sulfide, we propose lepidocrocite-type layered titanate as an alternative. Tin sulfide can provide various ribbon-layer structures depending on its oxidation state and is often used as an alternative to antimony sulfides [4,5]. However, the reserves of tin resources are gradually decreasing, and the stable supply of tin resources is a challenge [14]. There is also concern about the formation of corrosive substances from tin sulfide, such as sulfuric acid, a sulfur-oxidizing material and that corrosive substances may lead to disc rust and stiction phenomena. Of particular concern after friction testing of the LS pads used in this study was the stiction phenomenon caused by corrosive substances produced from tin sulfide [50]. Therefore, we evaluated not only environmentally friendly brake emissions as a possible alternative to tin sulfide but also stiction testing as a safety aspect of brake products. From the results of the stiction test shown, the LS pads with tin sulfide showed a suction phenomenon between the pad and disc, while the LS pads without tin sulfide (replaced by the titanate) showed a decrease in the suction phenomenon.

The experimental results suggest that pads with titanate not only have a positive impact on brake-system performance, safety, and reliability but also have a positive impact on the environment by reducing brake-particle emissions due to brake friction.

5. Conclusions

We evaluated the friction stability of NAO pads by using l lepidocrocite-type layered titanate we used in our previous studies. We previously investigated the role of titanate in reducing brake particle emissions as an additive to NAO friction materials, as an additive to LS friction materials, and as a substitute for metal sulfides, which are solid lubricants, with the aim of reducing brake particle emissions in an environmentally friendly manner.

The effect of titanate on reducing brake-particle emissions in urban driving was evaluated using a small inertial brake dynamometer. Images of pad cross-sections showed that the microphysical structures, such as the uniformity of friction film and secondary-plateau formation on the pad surface, differed significantly for NAO and LS pads, depending on the combination of friction materials including titanate. In terms of brake-particle emissions, it was shown that in relation to the microphysical structure of the pad surface, the friction material containing titanate can reduce emissions for both NAO and LS pads. Our experiments found that the addition of titanate contributed to the reduction in both PM and PN measurements for the LS pads in this study and were even comparable to brake-particle emissions from NAO pads with the addition of titanate.

Supplementary Materials: Not applicable.

Author Contributions: Conceptualization, E.D. and Y.I.; methodology, E.D. and Y.I.; validation, E.D. and Y.I.; formal analysis, E.D. and Y.I.; investigation, E.D. and Y.I.; data curation, E.D. and Y.I.; writing—original draft preparation, H.H., E.D. and Y.I.; writing—review and editing, E.D. and Y.I.; visualization, E.D. and Y.I.; supervision, H.H.; project administration, E.D.; funding acquisition, E.D. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are not available to the public due to confidentiality agreements with material providers.

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