Improvement of High-Temperature Performance in Copper-Free NAO Pads

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ABSTRACT: In order to satisfy the copper content regulations in North America, copper-free non-asbestos-organic (NAO) brake pads are being developed with various raw materials to replace copper. Copper fibers are used in brake pads to improve pad wear by reinforcing the friction materials and to stabilize the friction coefficient by spreading frictional interfaces. On the other hand, it is known that copper-free NAO pads have an unstable friction coefficient and excessive pad wear degradation at high temperatures. For these technical issues, the authors conducted research from two viewpoints. The first one is the number of organic components, such as phenolic resins and cashew particles. The second one is the addition of catalysts to evaluate the impact on the decomposition process of organic components. First, a wear test controlled by temperature was performed on brake pads containing a different number of organic components. The authors found that the lower the number of organic components in the pad, the more stable the friction coefficient is, at temperatures above 300 °C, which is the decomposition temperature of organic components. Additionally, the formation of a transfer film was observed on the rotor surface when the number of the organic components was small, but not otherwise. Furthermore, it was also found that the extent of wear at 300 °C or higher depends on whether the transfer film was formed at a temperature exceeding 300 °C. To verify that this phenomenon is caused by the decomposition of organic components, the stability of the friction coefficient in a two-component system, produced from an inorganic catalyst and a phenolic resin, was evaluated. Thus, the authors found that the friction coefficient was stabilized with titanate. Based on this study, wear tests with and without titanate were conducted. It was found that the addition of titanate improved the stability of the friction coefficient and wear resistance. In conclusion, the number of organic components and the addition of the catalyst are strongly related to the formation of the transfer film on the rotor surface, the stability of friction coefficient and the amount of wear. Decreasing the number of organic components or adding the catalyst can improve the wear and friction coefficient stability. This study is an important finding from the viewpoint of environmental conservation, to suppress the emission of brake dust even under high-temperature conditions in which the wear generally increases.

KEY WORDS: friction material, copper-free, high-temperature performance, transfer film, wear

1. Introduction

In order to satisfy the copper content regulations in North America, copper-free non-asbestos-organic (NAO) brake pads are being developed with various raw materials to replace copper. Copper fibers are used in brake pads to improve pad wear by reinforcing the friction materials and to stabilize the friction coefficient by spreading frictional interfaces [1]. On the other hand, it is known that copper-free NAO pads have an unstable friction coefficient and pad wear degradation at high temperatures. In recent years, interest in environmental conservation has raised the importance of low wear and airborne particle emission [2,3]. The stabilization of the friction coefficient and noise, vibration, and harshness (NVH) characteristics were investigated along with the wear resistance as a means of reducing particles released into the air.

It has been reported that a transfer film with the pad component is transferred onto the rotor surface after conducting a friction test, affecting the friction coefficient, wear amount, and noise generation [4–7]. However, there are few reports on how to control the formation of the transfer film in NAO copper-free materials in relation to stabilizing the friction coefficient and improving wear resistance. We believed that there was a strong correlation between the stable formation of the transfer film, the stabilization of the friction coefficient, and the wear resistance in NAO copper-free materials.

We first conducted experiments on the relation between the number of organic components, the formation of the transfer film, the friction coefficient and the amount of wear in NAO copper-free materials. Titanate, known as a decomposition catalyst for organic components, was the focus of this study [8–10]. Experiments were conducted to elucidate the titanate effect on the formation of the transfer film by decomposing organic components, the friction coefficient, and the amount of wear.

2. Materials and Methods

2.1. Friction materials

Friction materials, including phenolic resin, cashew particles, rubber, fiber, titanate, barium sulfate, and other materials were prepared as shown in Table 1. All compounds were combined by a Lödige mixer. Each compound and underlayer was preformed into a tablet at room temperature. After drying, each tablet was molded at 145 °C. The pressure and molding cycles were adjusted so that

Table 1 Formulations of prepared friction materials.

Material	A	B	C	D	E	F	G
Phenolic Resin	17.3	19.3	21.3	19.3	19.3	19.3	19.3
Cashew particles & Rubber	21.4	21.4	21.4	17.4	25.4	21.4	21.4
Fibers	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Titanate A	21.0	21.0	21.0	21.0	21.0	21.0	0.0
Titanate B						0.0	0.0
Barium sulfate	6.6	4.6	2.6	8.6	0.6	4.6	25.6
Others	23.7	23.7	23.7	23.7	23.7	23.7	23.7
							vol%

the filling rate was 87% ± 1.5%. After molding, grinding and scorching were performed; then the hardness and compressibility of the pads were measured.

2.2. Wear test with a 1/5 scale dynamometer

The friction coefficient and the amount of wear at each temperature was recorded by using the 1/5 scale dynamometer. The outline of the 1/5 scale dynamometer is shown in Figure 1. Table 2 shows the test conditions of the wear test controlled by temperature. For the wear test, 44 mm × 19 mm test pieces, cut from the finished products, were used. In addition, the scorch layer was removed by grinding 2 mm of the surface of each test piece. The test temperature was monitored by using a thermocouple attached to the inside of the rotor. The appearance of the friction materials and the rotor were observed with a 3D camera. The observation of both the surface and the cross-section of the rotor was performed with scanning electron microscope (SEM) and focused ion beam scanning ion microscope (FIB-SIM).
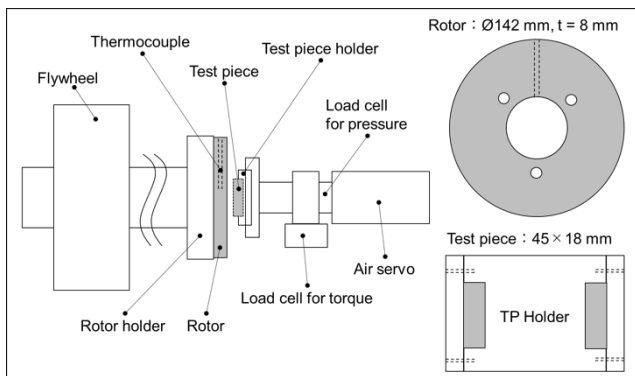

Figure 1 1/5 scale dynamometer outline.

Table 2 List of parameters for 1/5 scale dynamometer wear test.

Step	Moment of Inertia	Initial Velocity	Deceleration	Initial Braking Temperature	Number of braking
	Kg m^2	km/h	m/s^2	ºC	-
Burnish	3	65	2.9	100	50
100 ºC	3	65	2.9	100	200
200 ºC	3	65	2.9	200	200
300 ºC	3	65	2.9	300	200
400 ºC	3	65	2.9	400	200
500 ºC	3	65	2.9	500	200

2.3. Friction test procedure

Straight type phenolic resin containing curing agent and an inorganic additive was uniformly mixed and cured at 200 °C for 1 h. The cured sample was crushed and subjected to TGA (Thermal Gravimetric Analysis) from 25 °C up to 650 °C. The rate of temperature increase was 5 °C/min from 25 °C to 250 °C and 1 °C/min from 250 °C to 650 °C, and the TGA curves in air for titanate and barium sulfate were plotted. The amount of the phenolic resin in the weight loss curve was corrected to 100%.

Straight type phenolic resin containing curing agent and an inorganic additive were uniformly mixed and set in a mold. As inorganic additives, titanate A and barium sulfate were used. The compound was molded with this procedure (1 kN, 125 °C for 3 min, 3 kN, 125 °C for 1 min, 150 °C for 10 min, 175 °C for 20 min, 3 kN, 200 °C for 60 min under vacuum condition). After cooling to room temperature, molded samples were processed into 1 cm × 1 cm × 13 cm test pieces. Holes (1.2 mmØ), for attaching a thermocouple, were made on the top and bottom surfaces. Using a friction test device (EFM-3-F-ADX manufactured by AND Co., Ltd), the friction coefficient was measured on two test pieces at a pressure of 369 N and a rotation speed of 3077 rpm for 1 h. When noise and vibration increased, the test was stopped to protect the tester. The outline of the friction tester is shown in Figure 2. The sample temperature was measured with the thermocouple fixed approximately 1.5 mm from the friction interface. The ambient temperature was appropriately increased from 25 °C to 450 °C so that the sample temperature rose linearly.
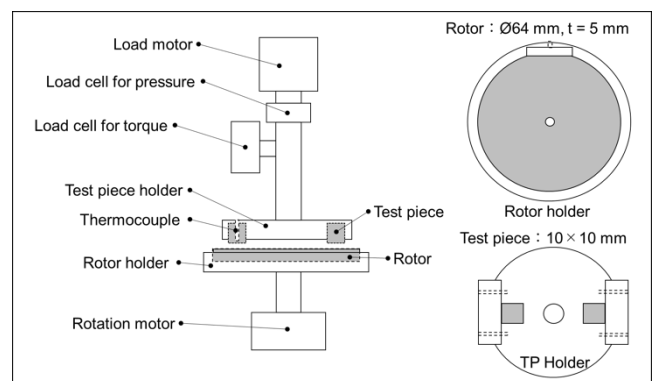

Figure 2 Friction tester outline.

3. Results

3.1. Effects of organic content

Figure 3 shows the results of the wear test for friction materials with different amounts of phenolic resin. From 100 °C to 200 °C, the wear of pad and rotor was hardly affected by the resin amount. However, at 300 °C and above, the amount of wear tended to increase as the resin amount increased. This tendency was even more significant at 400 °C and 500 °C.

Figure 4 shows the average friction coefficient values at each temperature as well as the maximum and minimum recorded values (μ range) during one braking event. These average values were calculated from the 50th to the 200th values. Sample A with the smallest amount of resin (17.3) had stable μ range values during each braking event from 100 °C to 400 °C, except at 500 °C. In sample B (19.3), the μ range increased at 300 °C. Furthermore, sample C, with the largest amount of resin (21.3), showed an increased μ range during most braking events at 200 °C.

Figure 5 shows the results of the wear tests for samples with different amounts of cashew particles and rubber. At 100 °C and 200 °C, cashew particles and rubber amount had little effect on pad & rotor wear. At 300 °C, as the amount of cashew particles and rubber increased, the amount of wear tended to increase. This trend was even greater at 400 °C and 500 °C.

The average friction coefficient values (μ) as well as their range at each temperature are shown in Figure 6. Sample D with the smallest amount of cashew particles and rubber (17.4) had stable μ and a low wear amount, even at 500 °C. Increased amounts of cashew particles and rubber tend to increase μ at lower temperatures.

The results from samples C and E of these experiments indicate that higher concentrations of organic components tend to increase μ values at lower temperatures and worsen wear.
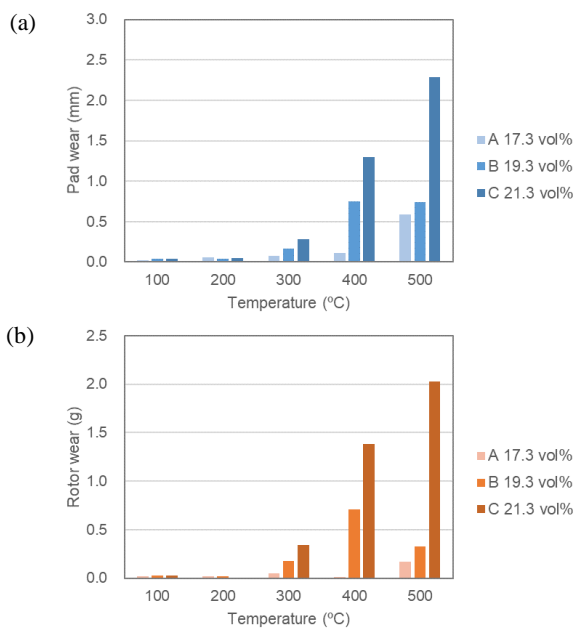
(a)

(b)

Figure 3 Relation between the wear amount and the amount of phenolic resin. (a) Pad wear at each temperature. (b) Rotor wear at each temperature.
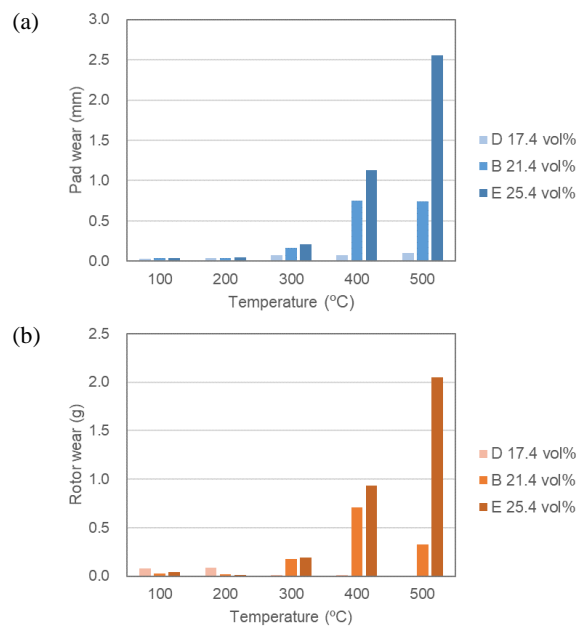
(a)

(b)

Figure 5 Relation between the wear amount and the amount of cashew particles and rubber. (a) Pad wear at each temperature. (b) Rotor wear at each temperature.
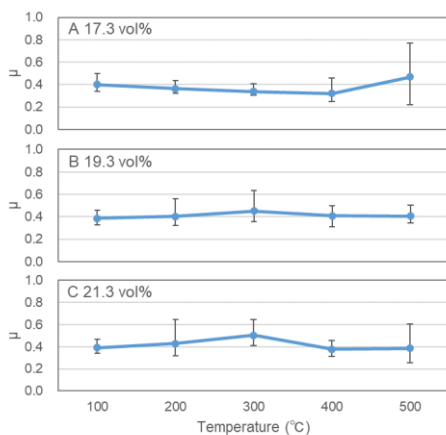

Figure 4 Average friction coefficient (μ) and range during one braking event with different amounts of phenolic resin vs. temperature.
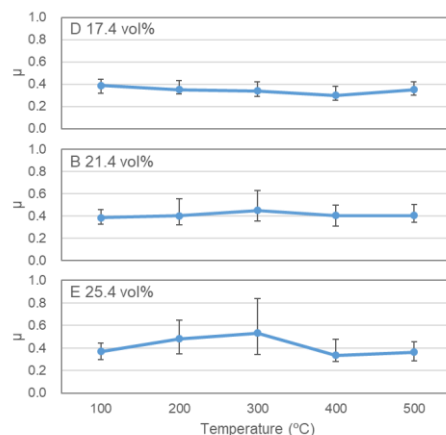

Figure 6 Average friction coefficient (μ) and range during one braking event with different amounts of cashew particles and rubber vs. temperature.

Surface of both the friction materials and rotors with different amounts of phenolic resin and cashew particles and rubber are shown in Figures 7 and 8. On the rotor surface of sample A with the smallest amount of resin, a thin black transfer film was formed from 100 °C to 400 °C, and sample D with the smallest amount of cashew particles and rubber had a thin black transfer film from 100 °C to 500 °C. On the other hand, in sample C containing the largest amount of resin, and sample E containing the largest amount of cashew particles and rubber, the rotor surface was exposed from 300 °C to 500 °C. Figure 9 shows the rotor surface observation
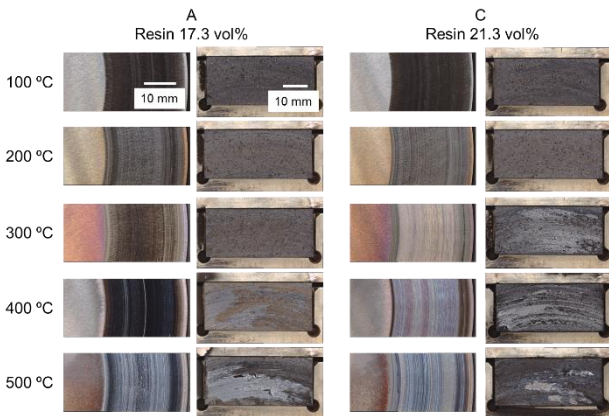

Figure 7 Surface of the friction materials and rotors after test with each amount of phenolic resin. (samples A, C)
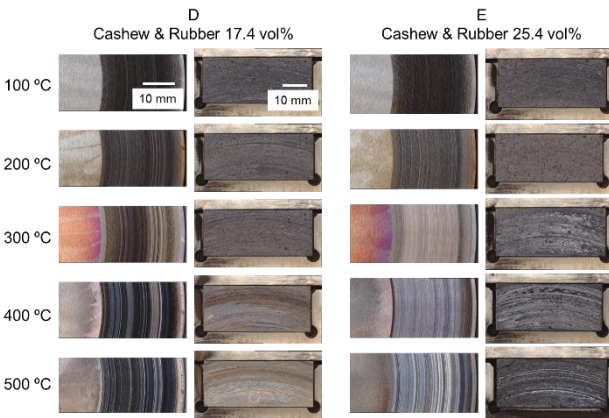

Figure 8 Surface of the friction materials and rotors, after test with each amount of cashew particles and rubber. (samples D, E)
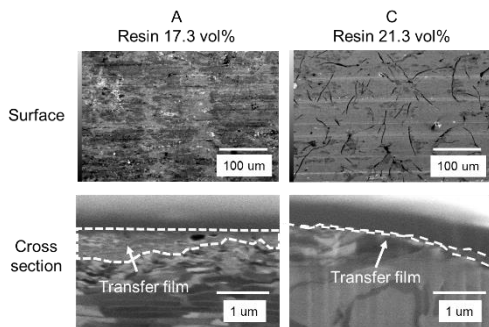

Figure 9 Rotor surface and cross-section analysis after 300 °C test with each amount of phenolic resin.

results with SEM and the cross-section with FIB-SIM after the 300 °C test. In sample A, the formation of the transfer film on the cast-iron structure was confirmed. On the other hand, the transfer film was not present in sample C.

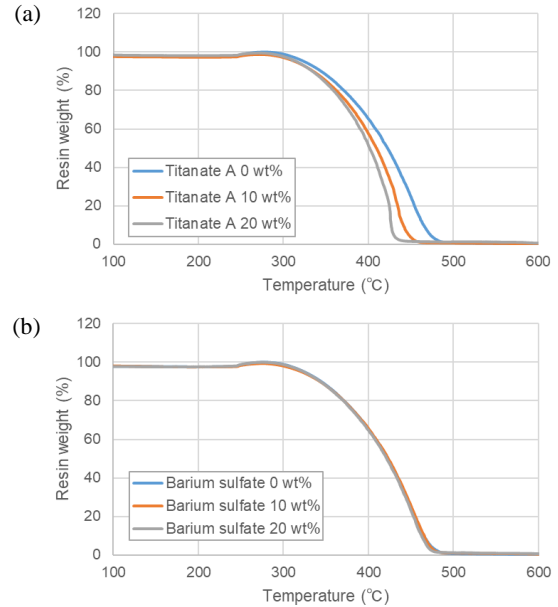## 3.2. Effects of inorganic catalysts

Figure 10 TGA curves with various filler amounts. (a) Phenolic resin with titanate A. (b) Phenolic resin with barium sulfate.

Figure 10 shows the TGA curves for titanate A and barium sulfate in air. In samples with titanate A, decomposition temperature decreased as the filler amount increased. The sample with barium sulfate did not have significant variation.

The results of the friction tester are shown in Figure 11. When the friction test was performed with the resin alone, the friction coefficient became unstable at a sample temperature of around 250 °C. At the same time, friction noise and vibration occurred. The test was stopped to protect the testing machine when the friction noise and vibration increased. Similarly, the sample to which 10 wt% of barium sulfate was added, instability of the friction coefficient and increase in friction noise and vibration were confirmed at around 250 °C. On the other hand, the sample containing 10 wt% of titanate A maintained a stable friction coefficient even when the sample temperature increased to 350 °C. The friction coefficient values of this sample showed an exponential increase at about 370 °C.

Sample F, including titanate A and sample G in which titanate was replaced with barium sulfate were prepared and subjected to the wear test. Sample G suddenly showed deterioration of the pad and rotor wear after 300 °C, while sample F showed mild deterioration, as shown in Figure 12. Figure 13 describes that sample F showed small μ range during one braking event up to 400 °C, whereas sample G showed large μ range at 300 °C and 400 °C. Both samples F and G showed large μ range at 500 °C. Figure 14 shows the
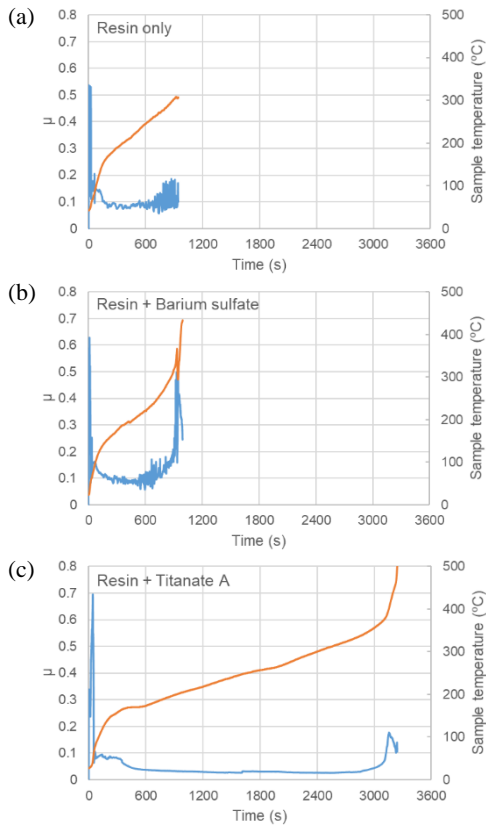
Figure 11 Relation between friction coefficient stability and sample temperature over time. Orange line is sample temperature. Blue line is friction coefficient. (a) Resin only. (b) Resin with barium sulfate. (c) Resin with titanate A.
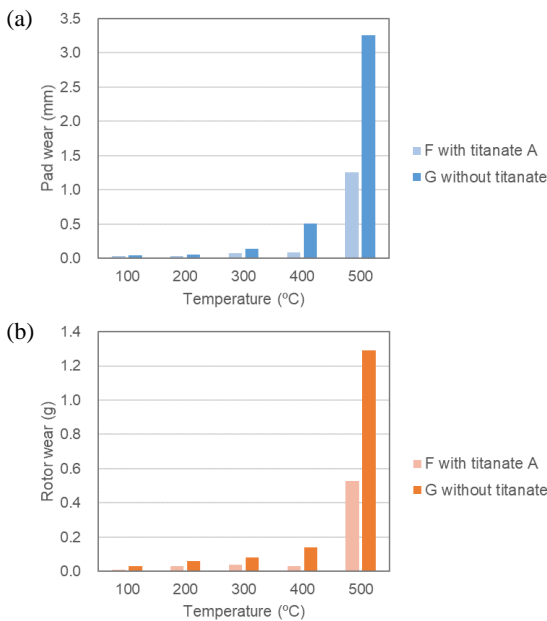

Figure 12 Wear amount with and without titanate. (a) Pad wear at each temperature. (b) Rotor wear at each temperature.

surface of the rotors after each test. Sample F forms a denser transfer film than sample G at 100 °C to 300 °C. Only the rotor surface of sample G was exposed at 400 °C. In both samples F and G, the cast-iron surface was exposed at 500 °C.
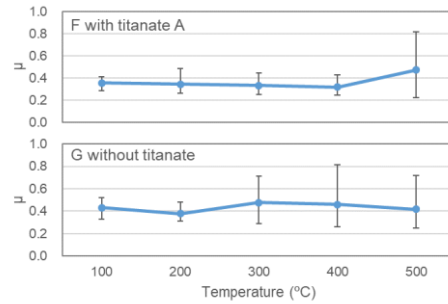

Figure 13 Average friction coefficient (μ) and range during one braking event with and without titanate vs. temperature.
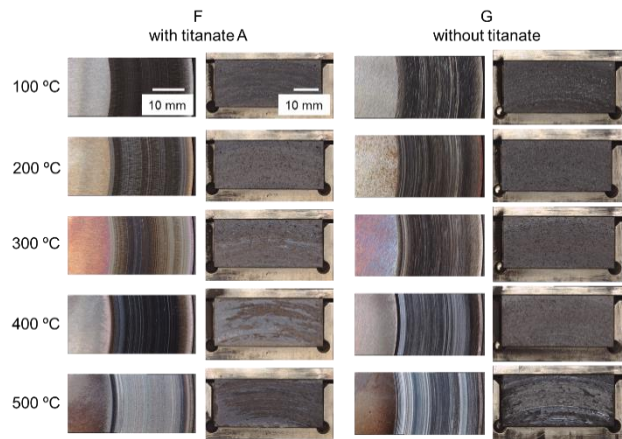

Figure 14 Surface of the friction materials and rotor after test with and without titanate. (samples F, G)

4. Discussion

During the execution of the wear test, μ at 300 °C became unstable as the number of organic components contained in the friction material increased. At the same time, the transfer film peeled off and the wear amount increased. On the other hand, when the number of organic components was small, μ was stable even at 500 °C, and the wear amount was maintained at a low level. Since the decomposition point of the organic component is around 300 °C and the friction surface temperature is higher than the measured disc temperature, it is considered that decomposition products of organic components are generated at the friction interface during the wear test at around 300 °C. In addition, observations of the rotor surface and cross-section were made, after the test described that no transfer film was formed at 300 °C, when the number of organic component was large. These results show that when many decomposed products of organic components are generated at the interface, the friction coefficient is destabilized, the transfer film of the rotor disappears, and the wear increases. It is considered that if

the generation of organic decomposition products can be suppressed, pads with a stable friction coefficient and less wear can be made without changing the number of organic components.

In order to verify the aforementioned hypothesis, TGA and the temperature dependence of the friction coefficient experimented in the simple system consisting of two components (phenolic resin and inorganic fillers) was studied. TGA showed that titanate decomposed phenolic resin effectively in lower temperature. On one hand, in the system composed of only phenolic resin and phenolic resin with barium sulfate, the friction coefficient became unstable at around 250 °C. On the other hand, in the system composed of phenolic resin with titanate, the friction coefficient was stable up to 350 °C. These results are due to the fact that the catalytic action of titanate suppressed the friction destabilizing effect of the resin decomposition products generated at the friction interface.

The results of wear tests performed with and without titanate showed that the friction coefficient was destabilized at a temperature of over 300 °C without titanate but stabilized with titanate. At 500 °C, the friction coefficient became unstable and the wear increased even for materials with titanate. This increase is thought to be because the decomposition of the organic component exceeds the catalytic properties at 500 °C. These observations at 300 °C and 400 °C show the formation of transfer film on the rotor surface, but their friction coefficients and wear tendencies are very different. These facts suggest that not only the formation of transfer film but also its composition and function are essential. Therefore, further study is necessary to elucidate the mechanism and function of the transfer film clearly.

The addition of catalysts provides high flexibility in the formulation design of friction materials since it can be applied without changing the number of organic components, which greatly affects the moldability and pad physical properties.

The findings of this study have to be seen in light of some limitations. The first is the friction material formulation. One particular type of formulation is used as the base material in this study. In the future, it is necessary to verify whether the findings are universal for other formulations. The second is the test method. In this study, a 1/5 scale tester is used to perform wear tests. Verification should be performed by a full-scale dyno or actual vehicle life test. Nevertheless, the findings will be important to designing the friction material formulation.

5. Conclusion

In this study, we concluded that the destabilization of the friction coefficient at around 300 °C was related to organic component decomposition products. The influence of the number of organic components and titanate as a decomposition catalyst was confirmed.

In order to achieve stable μ and wear resistance up to 500 °C, we found it effective to maintain the transfer film by reducing the number of organic components. It was also found that the transfer film was maintained up to 400 °C by adding a decomposition catalyst to stabilize the friction coefficient and reduce the amount of wear.

We plan further study to elucidate the mechanism and function of transfer film formation clearly and investigate other decomposition catalysts.

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