Nano-Tribological Study on the Smoothness of Writing with a Ball-Point Pen Using Friction Force Microscopy

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The relationship between human sensation experienced in the use of a material and its physical properties was investigated for the case of writing with a ball-point pen containing water-based ink. Friction force microscopy (FFM) and a writing tester were used to measure friction in nano- and macro-scale, respectively, and their results were correlated with the smoothness of the act of writing. FFM allowed the determination of the optimum concentration of a specific lubricant to be incorporated in the ink to minimize the wear of the bearing material, although no significant relationship was observed with the writing tester. The nano-tribological measurements by FFM provide a significant means to understand the relationship between materials and the smoothness of the act of writing.

The five human senses, i.e. sight, hearing, smell, taste, and touch senses, are known as the ultimate sensors, possessing high sensing resolutions. The resolution of those senses have been experimentally confirmed by various studies. Therefore, it is very significant to comprehend sensing ability based on the five senses in relation with the physical quantity affecting those senses. In this paper, we present the relationship between the touch sense and the physical properties of a water-based ball-point (WBP) pen. The concept of the WBP was presented in as early as the 19th century,[1] and the WBP was expected to enable one to write even on a rough surface such as wood. It is empirically explained that the sensation experienced during writing with the WBP pen depends mainly on the friction between the roller ball and the bearing, and the bearing fatigue of the pen determined by the wear of bearing material. On the other hand, the roller ball contacts the bearing under the condition of boundary lubrication, in which direct and indirect contact states are mixed.[2] Because the lubricant added in the ink profoundly affects the friction between the roller ball and the bearing and the wear of the materials on which lines are written, the lubricant is a key element that determines the performance of the WBP pen. Moreover, the friction force is originally exerted due to contact between lubricant molecules and materials such as the roller ball and the bearing; therefore, an extensive investigation is required to find an appropriate lubricant for achieving the best sensation of smoothness of the act of writing. So far, a writing tester with a ball-point pen has been empirically used in order to find the optimum condition of lubricants (hereafter, we define this method as the macro-tribological method, since the contact area between the ball and the bearing is in the order of mm^2, and therefore the measured friction force is averaged). We expected that an intensive investigation of friction in the order of nm^2 area would give deep insight to understand friction that can be related to the human sensation (hereafter, we define this method as the nano-tribological method). To the authors' knowledge, the relationship between the tribology of the WBP pen and writing smoothness has not been quantitatively investigated so far from the viewpoint of nano- and macro-tribological methodologies.

In this work, the effect of ink material on the friction and wear of the bearing of the WBP pen was studied using friction force microscopy (FFM)[3] as a nano-tribological method. Furthermore, a friction coefficient was measured by using a conventional writing tester as a macro-tribological method. The nano-tribological factors of the WBP pen were revealed to be related to the sensation of smoothness of writing.

Experimental

Figure 1a shows SEM image of the top portion of a WBP pen consisting of a roller ball ($\phi = 1.2$ mm) (A), a bearing (B), and a spring (C). As shown in Fig. 1b, several grooves are seen on the bearing surface, which are made intentionally to facilitate wetting of the surface of the roller ball with the ink. Tungsten carbide (WC) alloy (Surface roughness $RMS = 2.3$ nm; Vickers hardness $H_v = 2000\,\mathrm{kgf\,mm^{-2}}$) and ferrite stainless steel ($RMS = 1.1$ nm; $H_v = 240\text{–}270\,\mathrm{kgf\,mm^{-2}}$) were used as materials for the roller ball and the bearing, respectively. Water-based ink was prepared by mixing various concentrations (0–5.0 wt %) of a lubricant, oleic acid, (NOF Corporation, *Nonsoul OK-1*) with a constant concentration (7.5 wt %) of a black dye (Daiwa Dyestuff MFG. Co., Ltd., *Daiwa Black MR*). The oleic acid molecule has a polar terminal group, which causes the molecule to be adsorbed on the metal surface.

FFM (Digital Instrument Co., Ltd., *Nanoscope IIIa*), a kind of modified atomic force microscopy, enables one to detect the nano-

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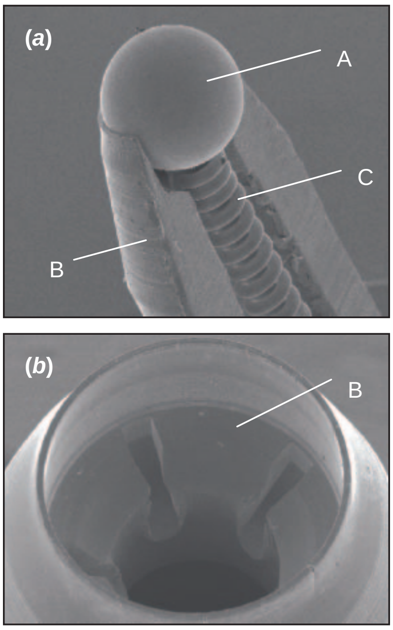

Fig. 1. SEM images of top portion (a) and inner part of bearing (b) of a water-based ball-point pen.

scale torsion angle of the tip caused by friction between the tip and a sample, measuring the nano-scale friction.[4–9] Accurate calibration for the torsion angle was performed based on previous reports,[8–10] which is described in the next section. The torsion elastic (k_x) and normal bending elastic constants (k_z) of a sharpened conical Si_3N_4 tip (OLYMPUS Co., Ltd., *OMCL-TR800CS*, Cantilever length; 100 µm), 447.01 and 0.56 $N\,m^{-1}$, were calculated by using the elastic modulus ($1.46 \times 10^{11}\,N\,m^{-2}$), shear modulus ($0.59 \times 10^{11}\,N\,m^{-2}$) and the dimensions of the cantilever.[11–13] Nanofriction force microscopic images in a $3 \times 3\,\mu m^2$ area of the ink material were obtained by scanning at the scan rate of 73 $\mu m\,s^{-1}$ under an applied force between 19 and 95 nN. The coefficient of friction was obtained by using FFM as the slope of the plot of friction vs applied load calculated from linear least squares fitting. An identical cantilever was used for the FFM measurements of various samples to be compared relatively. The samples for FFM measurements were rinsed with water after having been dipped in the ink for 3 min in order to eliminate the effects of dye component in the ink from the adsorbed layer of oleic acid on the surface of the WC or ferrite stainless steel.

The wear of the bearing and the flow weight of the ink material are obtained from the change in distance between the top of the roller ball and the bottom of the bearing and from that of the weight of the WBP pen, respectively, after writing for a length of 500 m with the WBP pen under an applied load of 980 mN (Writing angle = 60°; writing rate = $4 \pm 0.1\,m\,min^{-1}$; writing character; ϕ36 mm circle). The friction coefficient of the WBP pen on paper was measured with a commercial writing tester equipped on a strain gage (Seiki Kogyo Lab., *PS-5*), under the applied load of 980 mN (writing angle = 60°; writing rate = $4 \pm 0.1\,m\,min^{-1}$; resolution limit = ±10 mN). To determine statistically the lubricant concentration at which the best writing sensation is obtained, a sampling test was performed with the help of a group of 200 persons, consisting of males and females of different age (10–19 years old, 17 persons; 20–29, 47; 30–39, 38; 40–49, 46; 50–59, 37; 60–69, 15). Each person answered as to which WBP pen gave the best feeling after writing with 5 different WBP pens on the same paper. In the test, the same ink with various concentrations of lubricant, the same roller ball, and the same bearing material were used for all individuals.

Results and Discussion

Calibration of Friction by FFM. We should note that experimental parameters that depend on mounted probes must be calibrated precisely in order to estimate an accurate friction with FFM.[7] We calibrated the experimental parameters based on the method proposed by Shindo et al.[8–10] Figure 2 shows an illustration of the optical path of the FFM system. The laser beam deflection observed from cantilever (d_1) is calculated as follows;[10]

$$d_1 = L\sin(b) \times 2\alpha, \tag{1}$$

where α is the torsion angle of the cantilever, b is the angle between the mirror surface and incident laser beam on it, and L is the distance between the cantilever and the mirror. On the other hand, the laser beam deflection observed from mirror (d_2) is calculated as follows;

$$d_2 = L\cos(a) \times 2\delta, \tag{2}$$

where a is the tilted angle of the cantilever and δ is the torsion angle observed from the mirror. Since d_1 equals d_2, the value of α is expressed as follows;

$$\alpha = \delta(\cos(a)/\sin(b)). \tag{3}$$

The displacement of the laser in the horizontal direction (D) that is caused by torsion of the cantilever is expressed as follows;

$$\mathrm{D} = 2\alpha(L + M)\sin(b), \tag{4}$$

where L is the distance between the cantilever and the mirror, and M is the distance between the mirror and the detector. From Eqs. 3 and 4, the value of δ is expressed as follows;

$$\delta = [(\mathrm{S_t} - \mathrm{S_{rt}})/2\mathrm{C}]^{-1} \times [2(L + M)\cos(a)]^{-1}, \tag{5}$$

where C is the torsion sensitivity of a cantilever that changes depending on the mounted probe. The values of S_t and S_{rt} are the output signals of the characteristic voltages obtained along the horizontal line of the detector by scanning the cantilever in one direction, then the other direction, respectively.[7] Figure 3 shows an example of the calibration of C,[14] which turned out to be $47\,V\,mm^{-1}$. Friction can be expressed by the following equation using the tip height (h), torsion elastic constant (k_x), and the torsion angle of the cantilever (δ).

$$\mathrm{F} = h \times \delta \times k_x. \tag{6}$$

Determination of Friction Coefficient by FFM. Figures 4a and 4b show examples of FFM images at the surface of ferrite stainless steel with ink material containing 3.0 and 5.0 wt % lubricant, respectively. Figure 4a shows a nanofriction map in a $3 \times 3\,\mu m^2$ area of the ink material with 3.0 wt % lubricant under the applied force of 95 nN, from which the mean value of the friction was found to be 2.4 nN. On the other hand, from the friction map of Fig. 4b, the mean value of the friction force for the ink material with 5.0 wt % lubricant was found to be 3.3 nN. The friction measured with the ink containing 5.0 wt % lubricant was greater than that for the ink containing

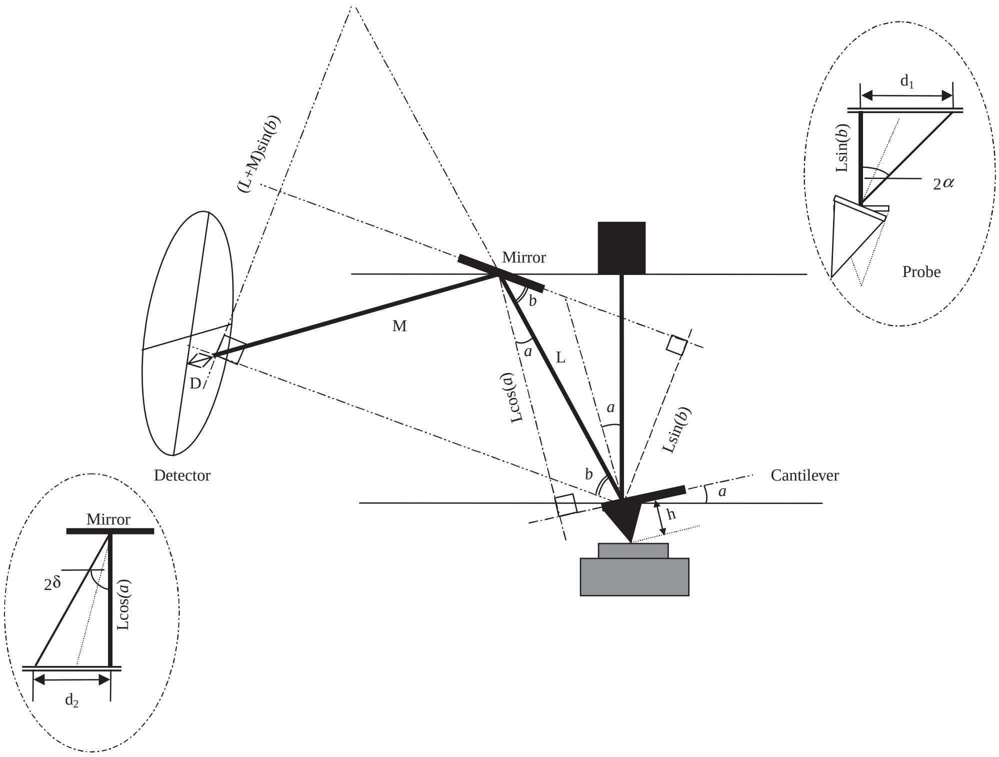

Fig. 2. Schematic diagrams for the calibration of friction force microscopy.

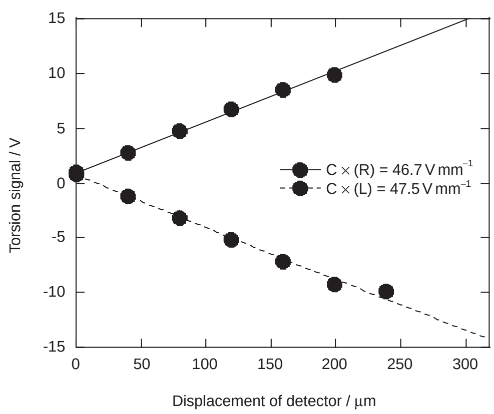

Fig. 3. Estimation of torsion sensitivity of cantilever.

3.0 wt % lubricant. This result suggests that the amount of oleic acid molecules existing on the stainless steel with ink containing 5.0 wt % lubricant is excessive as compared to that with ink containing 3.0 wt % lubricant, and that the presence of the excessive amount of lubricant causes the friction to increase.

Figure 5 shows the dependence of the mean friction on the normal applied load on ferrite stainless steel coated with ink materials containing lubricants at various concentrations. Each data point was obtained from friction images taken in several different regions, each measuring $3 \times 3\,\mu m^2$.

It is seen that the friction for all samples increased linearly with the magnitude of the applied normal load. The fitted lines show certain values of offsets, respectively, although the ob-

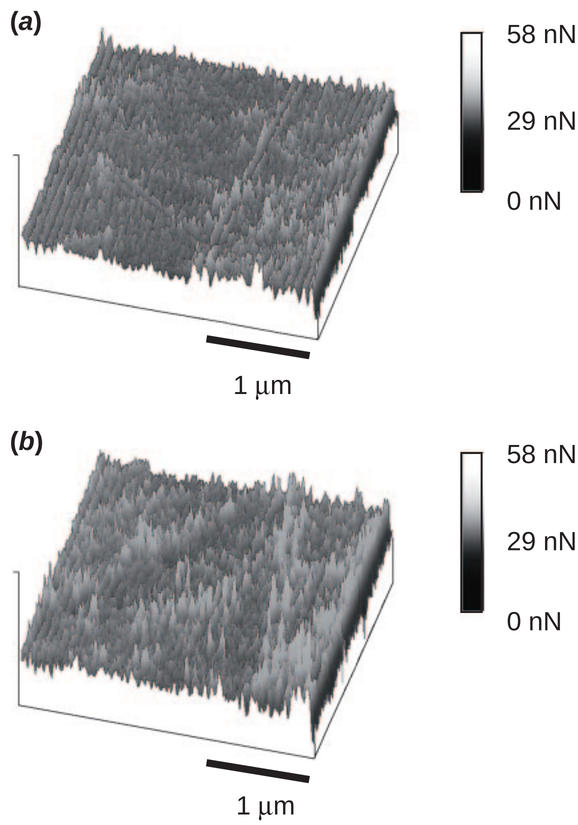

Fig. 4. Friction map of the ink material with 3.0 wt % (a) and (b) 5.0 wt % lubricant on ferrite stainless steel.

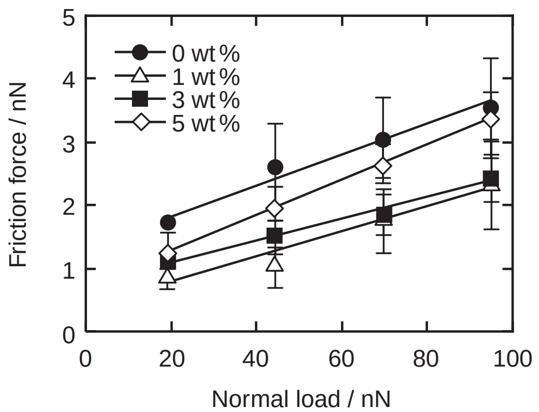

Fig. 5. Dependence of friction on the normal load applied on ferrite stainless steel coated with ink materials containing lubricant at various concentrations.

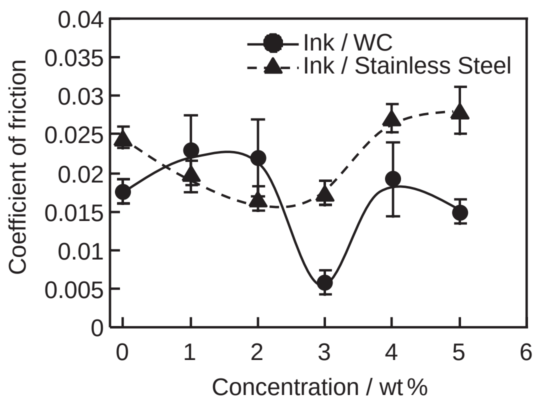

Fig. 6. Friction coefficient of ink materials containing various concentrations of lubricant for WC alloy and ferrite stainless steel.

tained friction force (F) is in proportion to the normal load. Theoretically, a coefficient of friction is defined as a linear coefficient. In this experiment, we expect the pull-off force between a probe and a sample, which depends on the surface condition of measured samples, to give a certain amount of offset. Therefore, in this paper, we defined the slope obtained from the plots as a coefficient of friction and the offset is regarded as a systematic error.

Relationship between the Coefficient of Friction and the Sensation in the Act of Writing. Figure 6 shows the dependence of the friction coefficient on the lubricant concentration in the ink for the WC alloy and ferrite stainless steel. It is seen that the lowest friction coefficient on the WC alloy and stainless steel occurs at around 3.0 and 2.0 wt% in lubricant concentration, respectively. At the lubricant concentration that yields the lowest friction coefficient, we deduce that the most stable and uniform adhesion layer is formed. At lubricant concentrations lower than the concentration yielding the minimum friction coefficient, the ink material shows a high friction coefficient, probably due to insufficient coverage by oleic acid. On the other hand, an excessive amount of oleic acid molecules, which do not absorb on the surface, causes aggregation of oleic acid molecules in the region of high lubricant concentrations. Those aggregated molecules are believed to form a non-uniform layer leading to the high friction coefficient.

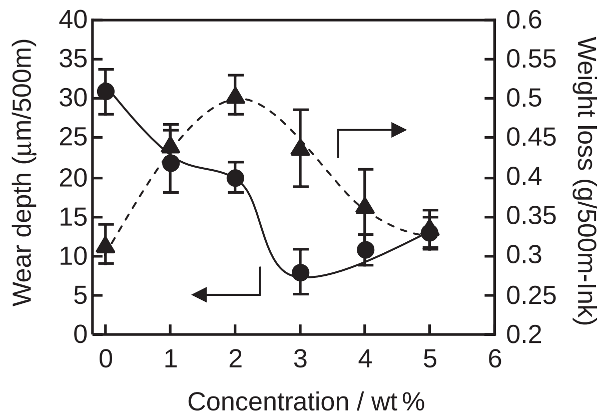

Fig. 7. Dependence of the wear depth of the bearing and the flow weight of the ink material of the water-based ball-point pen on the lubricant concentration.

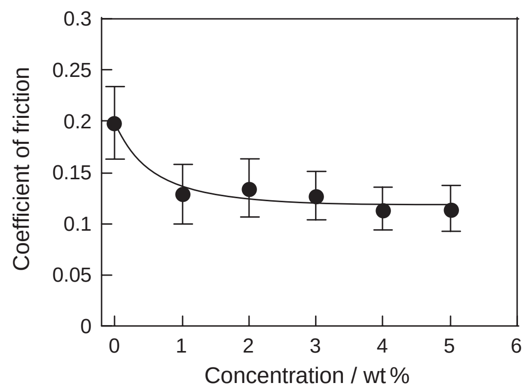

Fig. 8. Friction coefficient of WBP pen with ink materials containing various concentrations of lubricant on paper.

Generally, a good WBP pen should provide a desirable sensation of smoothness for writing that remains unchanged with use, and the bearing should not wear to any significant extent during the lifetime of the pen. The durability of writing sensation is often speculated to be based on the wear of the bearing materials. Figure 7 shows the dependencies of the wear depth of the bearing and the flow weight of the ink on lubricant concentration, both of which were measured after continuous writing under 980 mN for a distance of 500 m. It is seen that the wear of the bearing materials decreased with increasing lubricant concentration up to 3.0 wt%, beyond which it increased slightly. The lubricant concentration at which the wear depth was a minimum was equal to 3.0 wt%, which is identical to the concentration at which the lowest friction coefficient was observed with the WC alloy (Fig. 6). Therefore, we can predict the minimum wear of the bearing materials from the measurement of the friction coefficient on the nanoscale by using FFM.

Figure 8 shows a coefficient of friction for the WBP pen on conventional paper evaluated with the writing tester under an applied load of 980 mN. In contrast to the result shown in Fig. 7, the coefficient of friction was almost independent of the concentration of lubricant between 1.0 and 5.0 wt%. Apparently, the nano- and macro-tribological method show quite different behaviors of friction coefficients depending on the

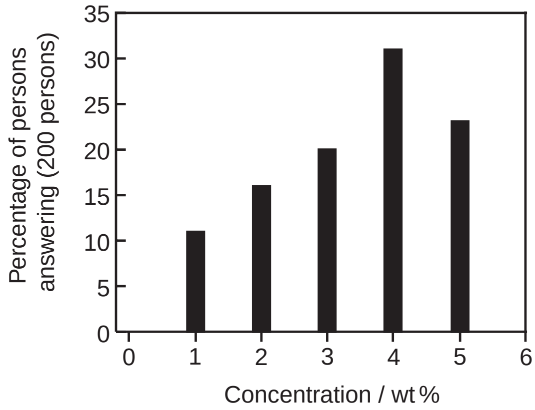

Fig. 9. Dependence of the ratio of the people who answered to obtain the best feeling on writing.

lubricant concentration. The characteristic drop in friction coefficient shown in Fig. 6 was observed only by the nanoscale friction experiment performed by the FFM.

Figure 9 shows the percentage of individuals who stated at which concentration they experienced the smoothest writing sensation for each lubricant concentration. With increasing lubricant concentration, the relative number of individuals who experienced the smoothest writing sensation increased, reaching a maximum value of 31% at the lubricant concentration of 4.0 wt %. It is widely believed that the weight loss of ink during the act of writing functions as an empirical index representing the performance of a pen; i.e., the writing sensation is better when the weight loss of ink is greater. According to the traditional empirical evaluation method mentioned above, this result predicts that the smoothest writing should be realized at the lubricant concentration yielding the highest weight loss of ink. However, the ink flow rate shown in Fig. 7 reaches a maximum value at the lubricant concentration of 2.0 wt %, which disagrees with the concentration of lubricant giving the smoothest feeling when writing. We have considered that the smoothness of writing can be related with a weak vibration, which is caused by the friction, traveling through the ball-point pen to fingers in the act of writing. Therefore, it is reasonable that the coefficient of friction obtained by macro scale measurements (Fig. 8) cannot be merely correlated with such a subtle sense, i.e. smoothness of writing. Since a clear drop in the coefficient of friction was obtained with FFM measurements (Fig. 6) around the value where persons experienced the smoothest feeling of writing (Fig. 9), it is likely that the nano-tribological factors can be correlated with the smoothness of writing. A quantitative measurement of weak vibration, which is caused by friction, is important for the further understanding of human sensation during writing.

The lubricant concentration of 4.0 wt %, which gave the persons the smoothest feeling of writing, is greater by 1.0 and 2.0 wt % than the concentrations at which the lowest friction coefficient in the nanoscale measurement were observed on WC and stainless steel, respectively (Fig. 6). It is considered that the condition of adsorbed layers in the region of an excess amount of lubricants might affect the feeling of smoothness of the act of writing. However, the differences between those values are not clear yet. The FFM is a significant tool to observe nano-tribological behavior that can be related with the smoothness of the act of writing, i.e. the human sense of touch.

Conclusion

This study demonstrates quantitatively that precise nanotribological measurements using FFM is a powerful way for evaluating not only the lifetime of water-based ball-point pens, but also the smoothness of writing. Thus, it is claimed that we have succeeded for the first time in relating human sensation in the use of a material to its physical properties measured on the nano scale.

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