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QUANTITATIVE INVESTIGATION OF WEAR PROPERTIES OF SOFT-METAL/DLC NANOCOMPOSITE BY TRANSMISSION ELECTRON MICROSCOPY

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Abstract: The wear properties of soft-metal/diamondlike carbon nanocomposite coatings (SMe-DLC) sliding against bearing steel ball under reciprocating motion have been investigated quantitatively as a function of the metal content by transmission electron microscopy (TEM). The wear amount of thin and hard coatings under macroscopic contact condition is difficult to measure during relatively short frictional test duration because the wear amount is considered to be a trace amount. So, we have employed TEM to measure the wear loss accurately from the cross-section samples. This study revealed that TEM is an effective tool on the quantitative analysis of wear property of thin tribo-coatings showing high wear resistivity such as DLC.

Keywords: DLC, Soft metal, Wear properties, Quantitative evaluation, TEM, Frictional energy.

1. INTRODUCTION

The frictional interface which two bodies are relatively contacting and sliding is considered as a mesoscopic reactor, because the real contact area in nano-meter scale has extreme high pressure and high shear stress [1]. New surface layers being termed "tribofilm" are generated in the mesoscopic interface by many kinds of physical and/or chemical reactions, i.e., tribo-chemical reaction. Temperature is one of the most important parameters in determining the tribo-chemical reaction between many kinds of agents such as oil molecules, additives and elements on frictional interface. The characteristics of tribofilm determine the tribological properties such as friction coefficient and wear volume in machine system. If the direct measurement of the interfacial temperature has realized, further reduction of frictional loss in mechanical system will be possible by optimizing tribo-chemical reaction under the variable operating conditions, which makes a contribution to the reduction of CO_2 and energy saving. However, such direct measurement is not yet achieved, because there is no effective thermo-sensor material that has sufficient anti-wear performance applicable to the frictional interface under such an extreme condition. For now, the thermocouple is embedded beneath the frictional interface deeper than the micro meter scale which is far from the frictional interface that tribo-chemical reaction occurs, to avoid such wear problems during the measurement of interfacial temperature [2]. Thus, the ability of high wear resistance is a key factor necessary to new-create a next-generation type of thermo-sensor material to perform direct measurement of the temperature in the frictional interface.

Diamond-like carbon (DLC) exhibits various kinds of attractive characteristics such as low friction coefficient and high wear resistance, and has been attracting a lot of researchers on the fields such as material science, electric device as well as tribology. The characteristics of DLC coatings vary by adding the other elements [3]. Adding metals to DLC is a powerful method to improve electrical and/or tribological properties. Metal-doped DLC is considered to be a promising candidate for the next-generation type of thermo-sensor material. Previously, we have reported that the nanostructure and tribological properties of soft-metal (SMe)/DLC nano-composite coatings (SMe–DLC) [4–6]. If

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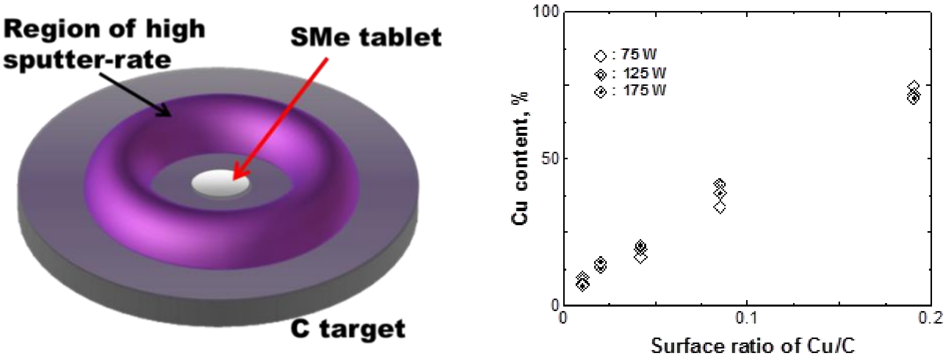
the anti-wear property of DLC is able to combine with the good electrical conductivity by means of adequate structure and compositions, SMe–DLC would be applicable not only to tribo-material but also to thermometer of the frictional interface. In such case, the detailed evaluation of the wear property will be needed.

The wear volume of sliding parts such as a piston ring of a reciprocating engine is measured mainly by the comparison of the surface profile before and after the wear test. However, the wear amount of hard and thin coatings such as DLC with a thickness of less than 1 μm is difficult to measure accurately under macroscopic contact condition, because the wear amount is considered to be infinitesimal compared with the size of contact. In this case, the direct measurement of the cross section of coatings will provide quantitative wear-loss of thickness through wear test by comparison before and after. When both sample preparation of cross-section of hard coatings and observation method of high-precision measurement of coating thickness are possible, a quantitative investigation of wear properties of thin and hard coatings is feasible with high accuracy, under the short test period.

In this study, the wear properties of SMe–DLC have been investigated quantitatively using transmission electron microscopy (TEM), as a function of frictional energy. A focused ion beam (FIB) was employed to prepare the extra-thin cross-section sample of SMe–DLC. This study revealed that TEM is the effective tool on the quantitative analysis of wear property of thin tribo-coatings showing high wear resistivity such as DLC.

2. EXPERIMENTAL

SMe–DLCs were deposited on a Si (100) substrate by RF magnetron sputtering (RF–MS) using a concentric composite target (CCT) [4]. The CCT consisted of C base target and a metal tablet which was located on the center of the base target concentrically, as shown in Fig. 1a. The concentration of metal in SMe–DLC can be controlled widely by changing the area ratio of SMe/C on the CCT (see Fig. 1b). In this study, a Cu was used as additive SMe because of its good electric conductivity as well as a use of journal bearing material. The details were described in previous papers [3–4].



a) CCT configuration

b) Cu/C ratio vs. Cu content in the coatings

Figure 1. SMe–DLC preparation using concentric composite target (CCT): a) schematic diagram of the configuration of CCT; b) surface ratio of Cu/C vs. cu content in the Cu–DLC.

The Cu–DLC was deposited on a Si (100) substrate of the dimension of 20×40×0.5 mm^3. The Cu concentration included in the Cu–DLC was estimated by the composition ratio between Cu and C, which was measured by Energy Dispersive X–ray Spectroscopy (EDS). As a result, the Cu–DLCs with Cu content from 8 to 60 at.% were prepared. The thickness of Cu–DLC was prepared to be 500 nm by deposition rate and measured by surface profiler with a vertical resolution of 1 nm. Both the nano-structure and the thickness of the coatings were observed by TEM from the extra-thin cross-section sample of Cu–DLC which was prepared by FIB as shown in Fig. 2. A protective Carbon-layer 1 was deposited on the sampling area of Cu–DLC with a size of 6×6 μm. Afterwards, the surrounding area of the layer 1 was removed by Ga$^+$ ion beam (see Fig. 2 a). The cut piece was composed of the protective layer, Cu–DLC and Si substrate, and was glued on Mo holder by placing the cross section up. Then, C–protective layer 2 was prepared on the top of the sample piece to prevent sample damages from Ga$^+$ irradiation (Fig. 2 b). Subsequently, the front and back of the side of the sample piece was thinned by a 2nd FIB process under the incidence angle of Ga$^+$ beam smaller than ±3°. As a result, extra sharp-edged thinning-piece of sample was prepared, as shown in Fig. 2 c, d and e. The thickness of the sharp edge side of A is only a few atomic layers therefore, TEM images of high resolution were obtained.

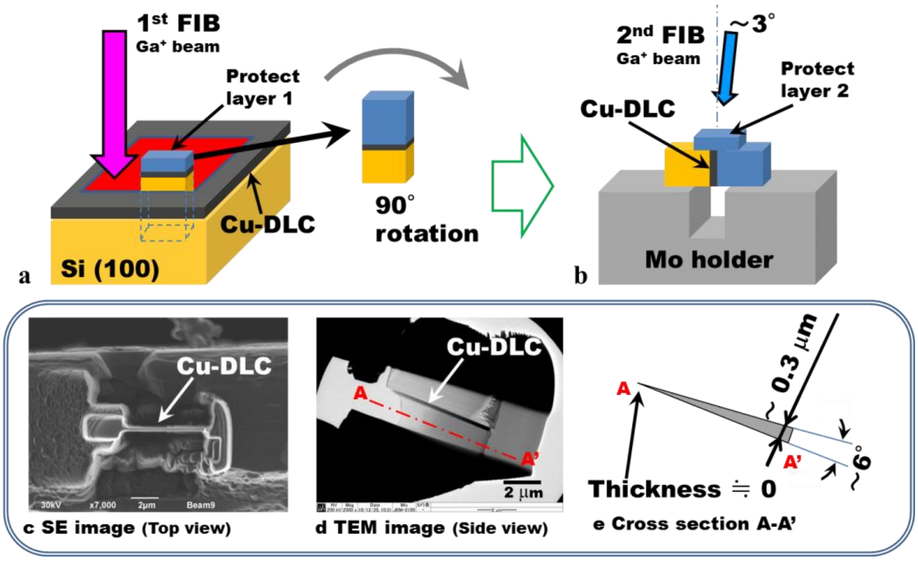
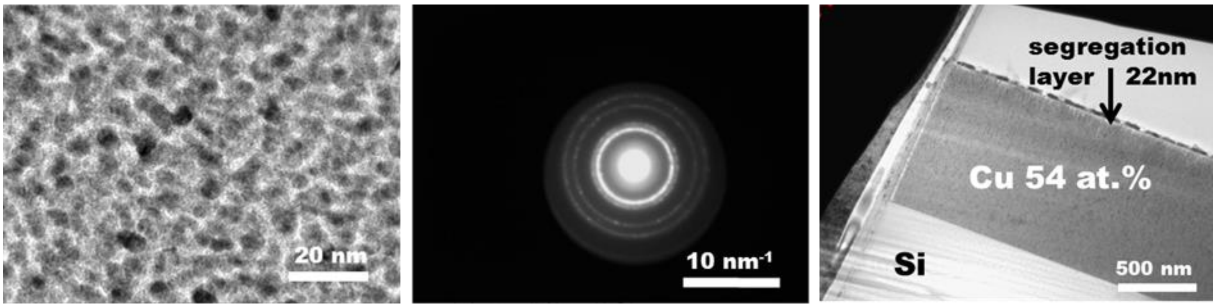


Figure 2. Preparation of thin-cross-section sample of Cu–DLC for TEM: a) 1st FIB process for sample piece processing; b) 2nd FIB process for extra-thin-cross-section sample; c) top view secondary electron (SE) image of prepared sample; d) side view TEM image of prepared sample; e) schematic image of cross section A–A' in d).

The hardness of Cu–DLC was measured by nanoindentation, and the indentation depth of Berkovich indenter maintained 100 nm for all measurements. The resistivity was measured by 4-point probes method. The tribological experiments were performed for 10 hrs using linear reciprocating tribometer under the sliding speed of 20 mm s^{-1} in average. A mirror-polished JIS SUJ2 bearing steel ball with a diameter of 6 mm was used as a counter material. The applied normal load was 1 N. The wear scar was observed by an optical microscope (OM) and a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF Cu–DLC



a) cross-section image; b) electron diffraction pattern; c) segregation layer of Cu.

Figure 3. Cu–DLC structure observed by TEM: a) cross-section image of Cu–DLC; b) diffraction pattern of Fig. 3 a) by transmitted electron beam; c) side view of cross-section of Si substrate/Cu–DLC/Cu segregation layer/C protective layer. *The thickness of this coating is 1 μm.

Figure 3 shows a structure of Cu–DLC observed by TEM. The structure is a granular structure in which the fine crystals of Cu are dispersed homogeneously in an amorphous DLC matrix (see Fig. 3 a and b), and that the average grain size increased as the Cu content increase. A surficial segregation of Cu occurred when the Cu concentration became relatively higher (Fig. 3 c), and the Cu–DLC surface has been covered with a segregation layer having nano-metric thickness. This result indicates that wear amount of Cu–DLC measured by a surface profiler contains two different components; a wear-loss of the Cu–DLC itself and that of the segregation layer on the Cu–DLC. Thus, a direct observation of the cross-section of the coatings is necessary to extract the wear-loss of Cu–DLC from total wear-loss. The TEM observation on the cross-section of Cu–DLC is considered to be the best way to get the actual wear-loss of Cu–DLC, and is able to obtain the wear properties of Cu–DLC quantitatively.

With consideration from above, we define this new parameter; a relative wear-loss (RWL), which explains the normalized wear-loss of Cu–DLC thickness measured by TEM quantitatively, as equation (1). The "A" indicates the initial-thickness at the as-deposited surface of the coating before frictional test, and the "B" is the thickness at the center of the wear track after the test. The evaluation is shown in Fig. 4. Figure 4 (a) shows the OM image of sampling points on Cu–DLC specimen after frictional experiments. The two sampling pieces, departing from approximately 2.5 mm, are processed by FIB. The difference in initial thicknesses between the tested point and reference point (as-deposited surface) is less than 1 % with respect to the actual coating thickness. Figure 4 (b) and (c) are cross-section TEM images of (b) reference point (as-deposited surface) and (c) the center of wear track.

$$RWL = \frac{A-B}{A} \times 100 \tag{1}$$

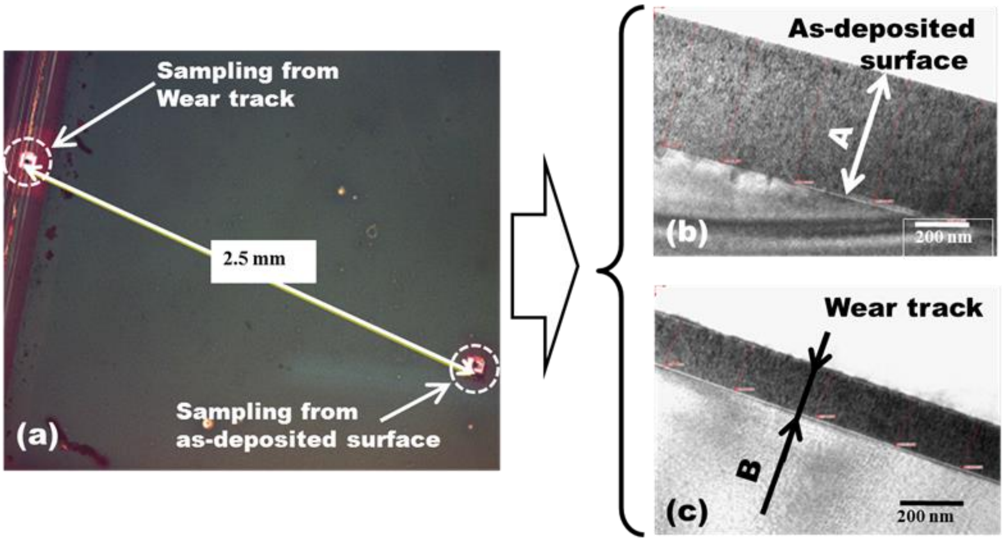
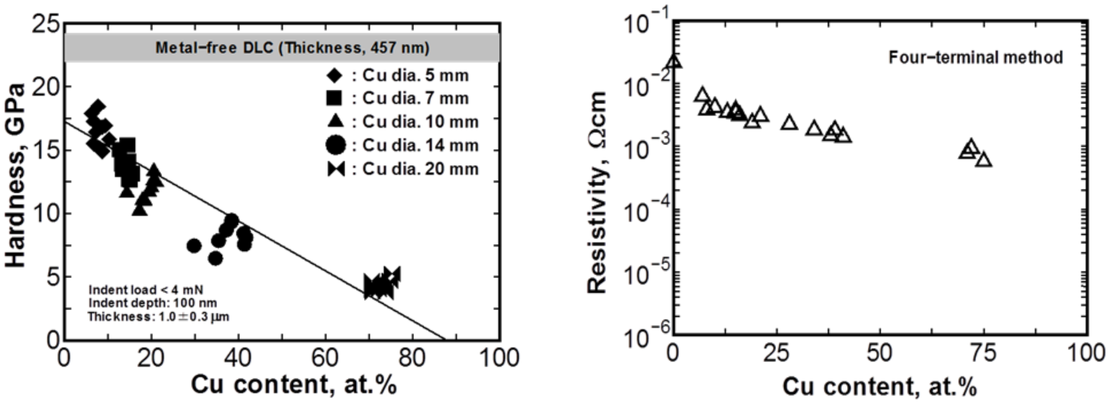


Figure 4. Evaluation of relative wear-loss (RWL) obtained by TEM measurements: a) OM image of sampling points of TEM specimens for; b) cross-section of initial coating (TEM); c) that of the center of wear track (TEM).



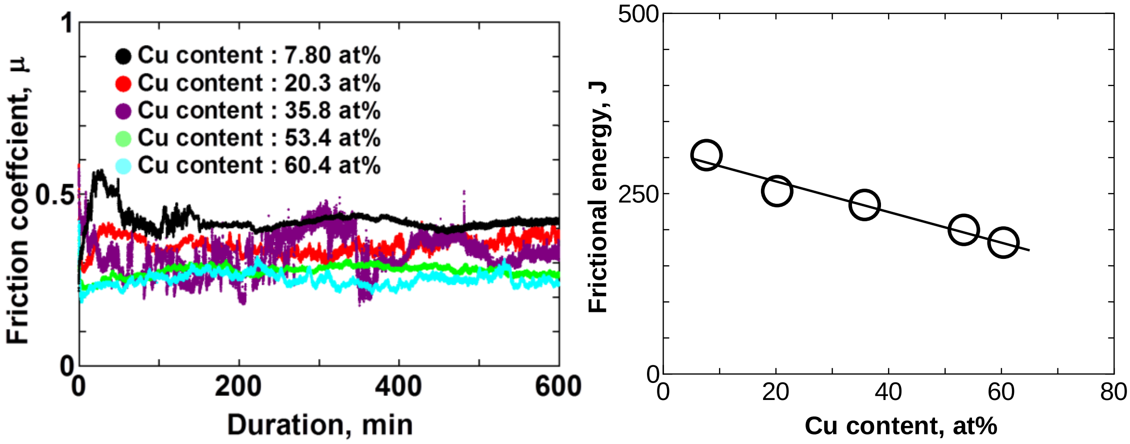
a) hardness vs. Cu content; b) resistivity vs. Cu content.

Figure 5. Mechanical and electrical properties of Cu–DLC: a) nanoindentation hardness of Cu–DLC vs. Cu content; b) electrical resistivity of Cu–DLC measured by four-terminal method.

Since the hardness of coatings affects to the wear properties, nanoindentation hardness was measured as a mechanical property. Figure 5 shows nanoindentation hardness and electrical resistivity of Cu–DLC as a function of Cu content. The electrical resistivity was also measured as shown in Fig. 5. As Cu content increased, both the hardness and the resistivity decreased.

3.2. TRIBOLOGICAL PROPERTY OF Cu–DLC

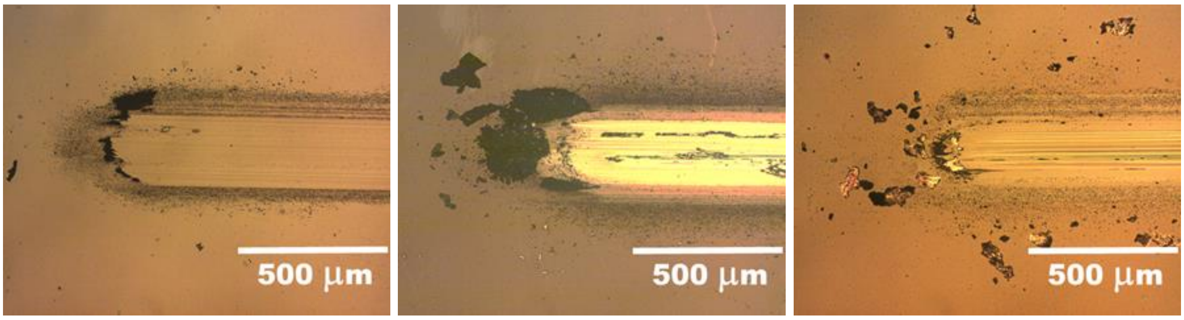
Transitions of friction coefficient of Cu–DLC with various kind of Cu content are shown in Fig. 6 a. The friction coefficient varied depending on the Cu content. Since the strong correlation between the friction coefficient and the wear amount of Cu–DLC is considered, the frictional energies of each tribo-test were obtained as shown in Fig. 6 b. The frictional energy decreased monotonically when there is an increase of Cu content in the coating. This means that the friction loss between Cu–DLC and JIS SUJ2 bearing ball is possible to be reduced by increasing Cu content in the coating.



a) friction coefficient of Cu–DLC; b) Cu content vs. frictional energy.

Figure 6. Result of tribo-test of Cu–DLC for 10 hrs. a) friction coefficient of Cu–DLC with Cu content from 8 to 60 at.%; b) frictional energy of Cu–DLC as a function of Cu content.

Optical images of wear scar at the turning point of wear track are shown in Fig. 7. The wear scar on the coating with Cu content of 8 at.%, which yields relatively high hardness, appeared to be a mild wear regime at the turning point of reciprocating, as shown in Fig. 7 a. In this Cu content regime, a C based tribofilm is formed on the counterface [5]. Contrary, the tribofilm becomes a metal-rich composition, when the SMe content becomes relatively higher [5–6]. Such tribofilms are peeled off from the slider sometimes, and remain around the wear scar. The metallic debris around the wear scar in Fig. 7 c is the fragments of the peeled tribofilm from the counterface of SUJ2 slider [5–6]. However, the peeling of coating was observed at the coating that contains 36 at.% of Cu, as shown in Fig. 7 b. Around the center region of wear track where the maximum Hertz contact pressure was generated, the coating is peeling off considerably along the wear track.

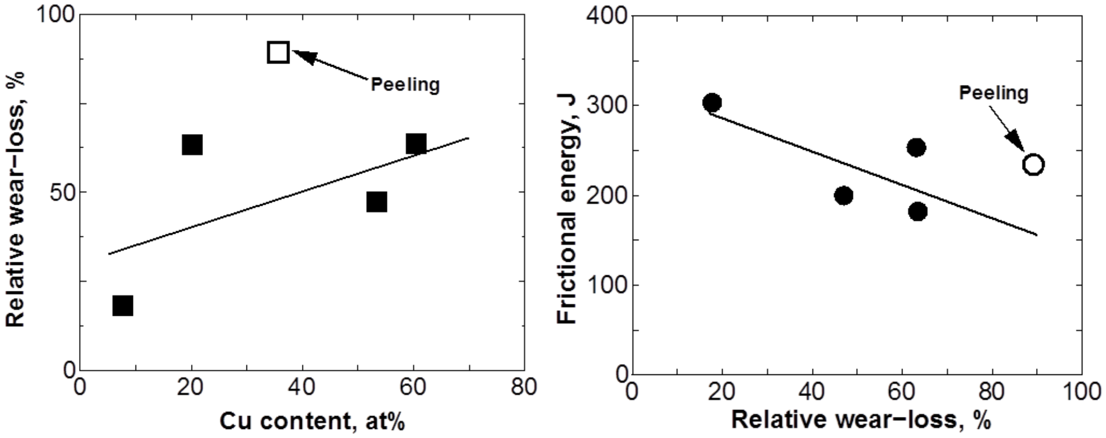


a) 8 at.% of Cu; b) 36 at.% of Cu; c) 60 at.% of Cu.

Figure 7. Optical images of wear scar at center part: a) wear scar on Cu–DLC with Cu content of 8 at.%; b) wear scar on Cu–DLC with Cu content of 36 at.%; bc) wear scar on Cu–DLC with Cu content of 60 at.%.

3.3. FRICTIONAL ENERGY VS. RELATIVE WEAR-LOSS OF Cu–DLC

After tribo-test, the RWL of each coating tested in Fig. 6 were measured by TEM quantitatively, as described in section 3.1. The RWL of the coatings at the center of each wear track is shown in Fig. 8 a, as a function of Cu content in the coatings. The wear property of Cu-DLC is possible to evaluate quantitatively by TEM analysis. The RWL having large fluctuation increased with the increase of Cu content. The decrease of coating hardness is associated with the increase of the wear volume of coatings (see Fig. 5 a), because wear volume at real contact point is considered to increase under the normalized conditions. However, the large variation may include not only the wear amount per unit phenomenon but also the wear mode of coatings. The RWL from the wear scar shown in Fig. 7 b that exhibited peeling mode seems to have different tendency from other coatings exhibiting relatively mild wear mode. Similar tendency can be seen in the correlation between the frictional energy of coatings and the RWL, as shown in Fig. 8 b. Further investigation is necessary to understand the wear properties of SMe–DLC in detail.



a) RWL vs. Cu content; b) RWL vs. frictional energy.

Figure 8. Correlation between RWL and: a) Cu content in the coatings; b) frictional energy of the coatings.

4. CONCLUSIONS

In this study, Cu was selected as a typical SMe for SMe–DLC, and the wear properties of Cu–DLC have been investigated quantitatively by TEM analysis after tribo-test. The frictional energy of Cu–DLC decreased monotonically as Cu content increases. The RWL of Cu–DLC increased as Cu content increases. The frictional energy tended to decrease as RWL increased. The origin of the data variation of RWL is considered to reflect a wear mode of the coatings. The effectivity of combination of FIB and TEM techniques is demonstrated to investigate the wear properties of thin-hard coatings quantitatively under relatively short test period.

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