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Tribological behavior of nano-undulated surface of diamond-like carbon films

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Abstract

Tribological behavior of nano-undulated diamond-like carbon (DLC) films of the surface roughness ranging from 0.6 to 13.7 nm was investigated in an ambient air of 50% relative humidity. The nano-undulated DLC films were prepared by radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) using nanosized Ni dots on a Si (100) substrate. The friction coefficient between the DLC film and the steel ball was characterized by a ball-on-disk type wear rig. Auger and Raman spectroscopy analysis of the debris revealed that the tribochemical reaction with environment was significantly suppressed as the surface roughness increased. Even if the rough surface increased the wear rate of the steel ball and thus the concentration of Fe in the debris, neither the oxidation of Fe nor the graphitization of the carbon in the debris occurred on the rough surface. However, the frictional behavior was affected by several factors: the composition and the size of debris, plowing effect of the rough surface, and the presence of the transfer layer on the wear scar surface.

Keywords: Diamond-like carbon; Plasma CVD; Tribology; Surface structure

1. Introduction

Although the effect of surface roughness on the friction is still under debate, the surface roughness has been considered as one of the major parameters to affect the tribological behavior [1]. In macro-scale tribology, it was reported that the surface roughness could reduce the friction coefficient by suppressing the wear particle generation, removing the wear particle from sliding interface and/or preventing the wear particle agglomeration [2,3]. Hence, the artificially generated rough surface was investigated to improve the mechanical properties of the artificial hip or knee joint by both reducing the friction coefficient and suppressing the wear particle formation [4,5]. Diamond-like carbon (DLC) films have also been considered as a protective layer for the medical implant materials. However, the surface roughness was not considered in most previous investigations on the tribological behavior of the DLC film. Because the amorphous structure of the DLC film results in an atomically smooth surface [6], it was not simple to exploit the effect of surface roughness in a systematic manner.

Recently, Lee et al. [7] suggested a novel method for nanoscale structural manipulation of tetrahedral amorphous carbon (ta-C) films deposited by filtered vacuum arc (FVA) process. By incorporating the nanosized Ni dots on the substrate surface, they obtained a nanoscale microstructure of nanosized graphitic phases grown from the Ni dots in the ta-C matrix. This method can also be used to control the surface roughness in nanoscale by adjusting the size of the Ni dots. In the present work, nano-undulated surface of DLC film was prepared by using the nanosized Ni dots on a Si substrate. In contrast to the FVA process, radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) method resulted in the carbon coatings of the homogeneous atomic bond structure regardless of the

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substrate materials. The nano-undulated DLC film enabled us to investigate the tribological behaviors of the DLC coating of various surface roughnesses. We investigated the tribological behaviors of the DLC film against steel ball in the range of the surface roughness from 0.6 to 13.7 nm. In addition to the mechanical effect of the rough surface, we focused on the tribochemical reactions since the tribology of the DLC film is considerably affected by the chemical reactions during sliding with the test environments [8,9].

2. Experimental

Nanosized Ni dots on Si substrate were prepared by annealing Ni thin films of thickness ranging from 3 to 14 nm. The Ni thin film was deposited on 600-μm-thick Si (100) wafer by DC magnetron sputtering at room temperature. In order to convert the deposited thin film to nanosized Ni dots, the specimens were annealed in a rapid thermal process (RTP) furnace at 800 °C for 15 min in a pure hydrogen environment. Hydrogen pressure during the annealing was kept at 133 Pa by controlling the flow rate of hydrogen. The diameter of the Ni dots ranged from 15 to 90 nm. The average diameter of the Ni dots monotonically increased with the film thickness. The specimens were then used for the substrate.

DLC films of thickness 100 nm were deposited by a radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) using methane as the precursor gas. Details of the deposition equipment were described elsewhere [10]. The films were deposited at the negative bias voltage of −150 V and the deposition pressure 1.33 Pa. Surface morphology of the specimens were observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Microstructure of the DLC film and the interface were investigated by a cross-sectional transmission electron microscopy (TEM). A micro-Raman spectroscopy was employed to analyze the atomic bond structure of the films.

Friction and wear behaviors were investigated by using a homemade ball-on-disk type wear rig installed in an environment chamber. The 6-mm steel bearing ball (AISI 52100) slid over the surface at the sliding speed of 17.3 cm/s with a normal load of 4 N (average initial Hertzian pressure, 0.53 GPa, assuming that the ball is in direct contact with the Si wafer). The sliding distance per 1 cycle was 4.7 cm. The tangential force was measured by a load cell of 9.8 N in full scale. The tribological tests were performed at room temperature in an ambient air of 50% relative humidity. In order to characterize the tribochemical reactions during sliding, the morphology, the chemical composition and the atomic bond structure of the debris were investigated by employing SEM, Auger spectroscopy and micro-Raman spectroscopy, respectively.

3. Results and discussion

Fig. 1(a) shows the SEM microstructure of the DLC film surface deposited on a bare Si (100) wafer. The inset of the

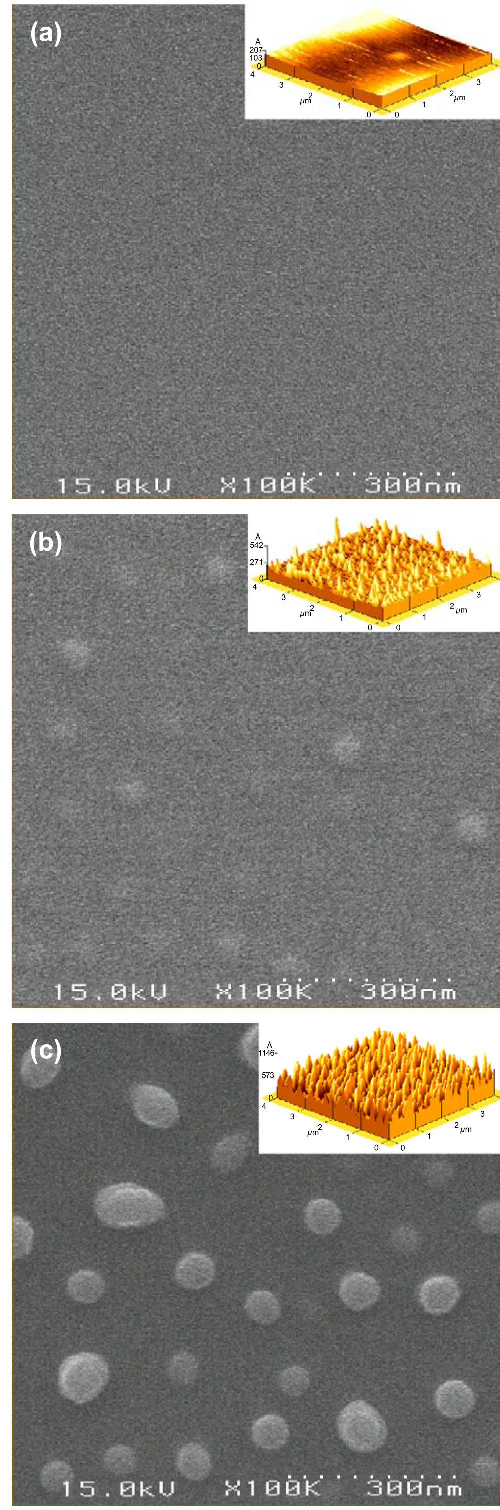

Fig. 1. SEM microstructures and AFM images of the DLC-coated surface for various diameters of the Ni nano-dots. (a) Without Ni dots, (b) with Ni dots of average diameter 15 nm, (c) with Ni dots of average diameter 90 nm.

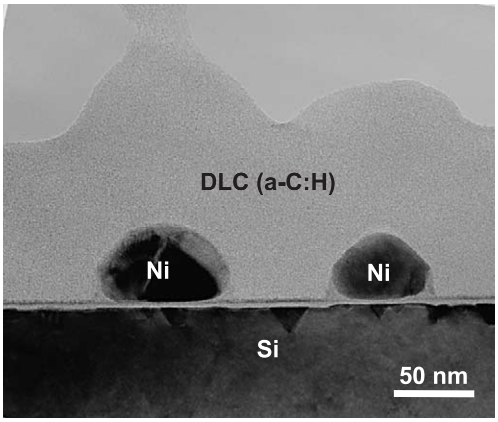

Fig. 2. Typical cross-sectional TEM microstructure of a nano-undulated DLC film.

figure is the AFM image of the surface. The film surface was atomically smooth, and no feature was observed in the SEM microstructure. The surface roughness was measured to be 0.6 nm in RMS scale, which is essentially the same as that of the Si wafer surface. On the substrates with nanosized Ni dots, the coated surface revealed a nanoscale surface undulation as shown in Fig. 1(b) and (c). The surface roughness increased from 5.1 to 13.7 nm as the diameter of the Ni dot increased from 15 to 90 nm. Fig. 2 is the cross-sectional TEM microstructure of the sample with nanosized Ni dots. Amorphous carbon layer was uniformly deposited on both the Si substrate and the Ni dots. Neither the residual stress nor the electrical resistivity was varied with the size of the Ni dots. This deposition behavior is a contrast to the case of the filtered vacuum arc process, where sp^2 rich conducting phase was formed on the Ni dots [7]. Amorphous $NiSi_x$ thin layer between the Ni dots and the Si substrate was formed during thermal annealing to convert the Ni thin film to nanosized Ni dots.

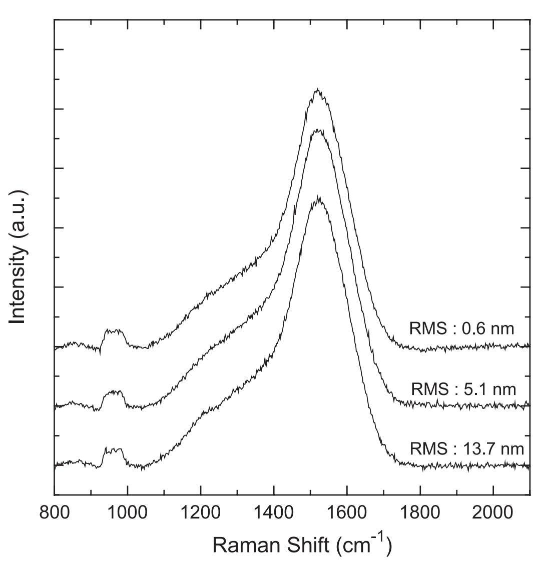

Fig. 3. Raman spectra of the nano-undulated DLC film for various surface roughnesses.

Raman spectra of the samples for various surface roughnesses were summarized in Fig. 3. The intensity of the spectra was normalized to the thickness of the film and shifted upward for comparison. The Raman spectrum has a typical shape of the hydrogenated amorphous carbon film deposited by r.f.-PACVD. The carbon peak is characterized by a large G peak near 1520 cm^{-1} with a broad D peak shoulder near 1300 cm^{-1}. The second-order peak of the Si substrate near 960 cm^{-1} shows optical transparency of the thin DLC film. The Raman spectrum analysis of amorphous carbon includes deconvolution of the spectrum with two Gaussian peaks: the G and D peaks. The atomic bond structure of the film is characterized by the intensity ratio, the full width at half maximum (FWHM) values or the position of each peak [11]. We could not observe any change in these values with the surface roughness. The diameter of the laser used in the Raman spectroscopy (about 5 μm) was much larger

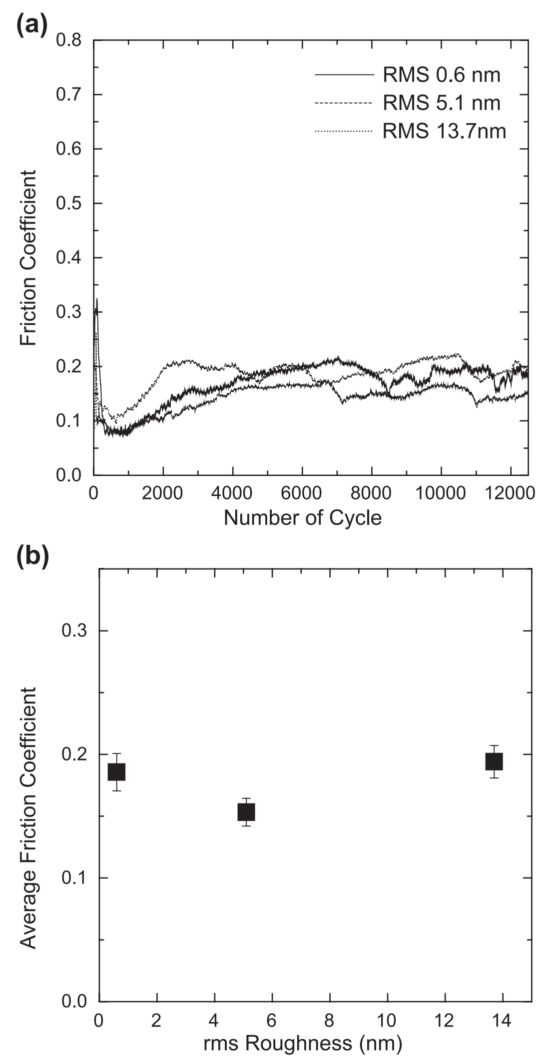

Fig. 4. (a) Evolution of the friction coefficient for various surface roughnesses in ambient air. (b) Dependence of the average friction coefficient on the surface roughness in ambient air.

than the average distance between the Ni dots (less than 100 nm). Hence, the Raman spectra in Fig. 3 represent the atomic bond structure of the film deposited on both the Si substrate and the Ni dots. This result shows that the structure of the film was not affected by the presence of the Ni dot. The homogeneous DLC film with a controllable nanoscale surface roughness enables us to investigate the tribological behavior of the nano-undulated surface of the DLC films.

Fig. 4(a) shows the evolution of the friction coefficients against steel ball in an ambient air of 50% relative humidity. After the initial transient period, steady state of the friction occurred after about 2000 contact cycles. Average friction coefficients shown in Fig. 4(b) were obtained by averaging the measured friction coefficients in the range of the contact cycle from 4000 to 12,000. The average friction coefficients were estimated to be 0.17 ± 0.02 regardless of the surface roughness. Fig. 5(a–c) shows the optical microstructures of the wear scar surface for various surface roughnesses. An arrow in Fig. 5(a) indicates the sliding direction of the ball. Morphology of the debris on the wear scar surface was essentially the same regardless of the film roughness: debris were accumulated in front of the wear scar surface that is covered by a transfer layer. However, the wear rate and the debris formation behavior considerably varied with the surface roughness. Circles in Fig. 5(a–c) indicate the wear scars. The wear rate of the steel ball estimated from the diameter of the wear scar increased from 3.8×10^{-10} to 1.8×10^{-9} mm^3/cycle as the surface roughness increased from 0.6 to 13.7 nm. SEM microstructures of Fig. 5(d–f) show the debris on the wear track. On a smooth surface shown in Fig. 5(d), large debris of diameter ranging from 3 to 5 μm were observed on the wear track. The large debris is formed by an agglomeration of the smaller debris presumably due to the water molecules in the humid environment. As the surface roughness increased, the size of the debris decreased. Submicron-sized debris were scattered on the wear track when the surface roughness was 13.7 nm [Fig. 5(f)]. It is obvious that the debris agglomeration was suppressed on the rough surface, which is in good agreement with the previous observations in the macro-tribology [2,3]. Size of the debris is significant in the frictional behavior. Because the debris in the sliding

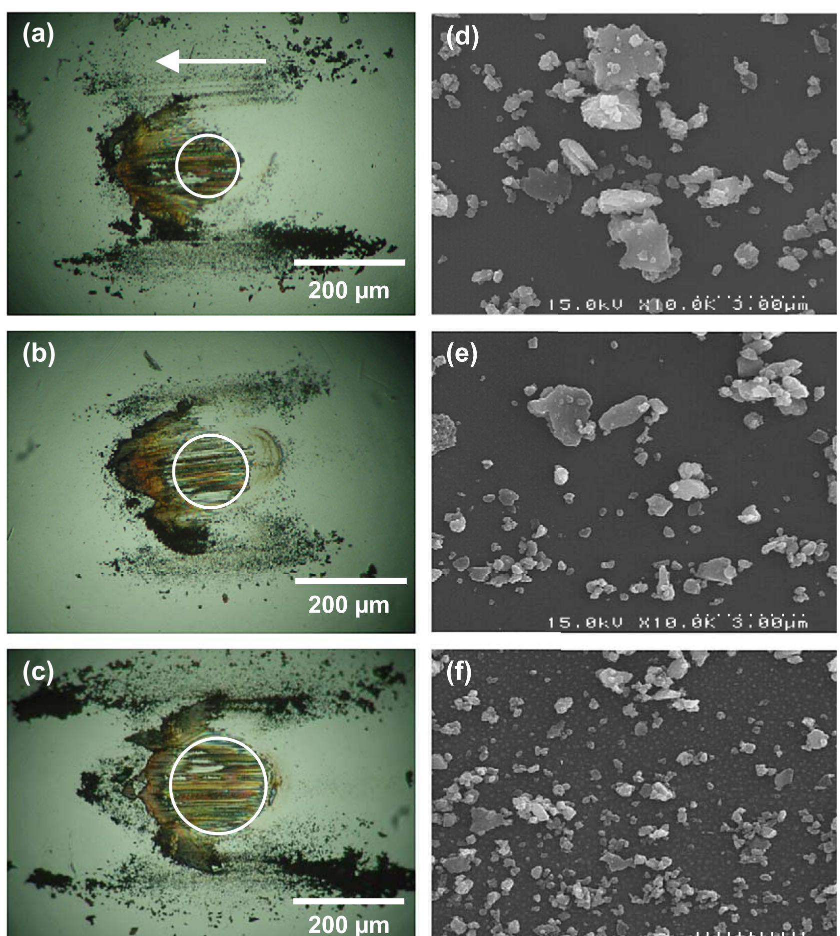

Fig. 5. Microstructure of the wear scar surface (a–c) and SEM microstructure of the debris near wear track (d–f) when the surface roughness was (a,d) 0.6 nm, (b,e) 5.1 nm and (c,f) 13.7 nm.

interface should be continuously deformed during sliding, the energy required to deform the large debris would be higher than that for the small scattered one. Therefore, the decreased debris size with increasing surface roughness would have an effect to reduce the friction coefficient [9]. However, Fig. 4 shows that the friction coefficient was not significantly varied with the surface roughness. This discrepancy will be discussed later.

Fig. 6(a) shows the scanning Auger spectra of the debris. Prior to the analysis, the specimen surface was sputter cleaned by an Ar ion beam in the analysis chamber to remove the surface contaminants. The spectra were normalized with respect to the oxygen peak, and shifted vertically for comparison. (The origin of the Si_{KLL} peak at 1620 eV is uncertain. However, because the DLC film contains no Si, the peak seems to be due to contamination.) The most significant change was observed in the Fe concentration that increased with the surface roughness. High wear rate of the steel ball on the rough surface should increase the Fe concentration in the debris.

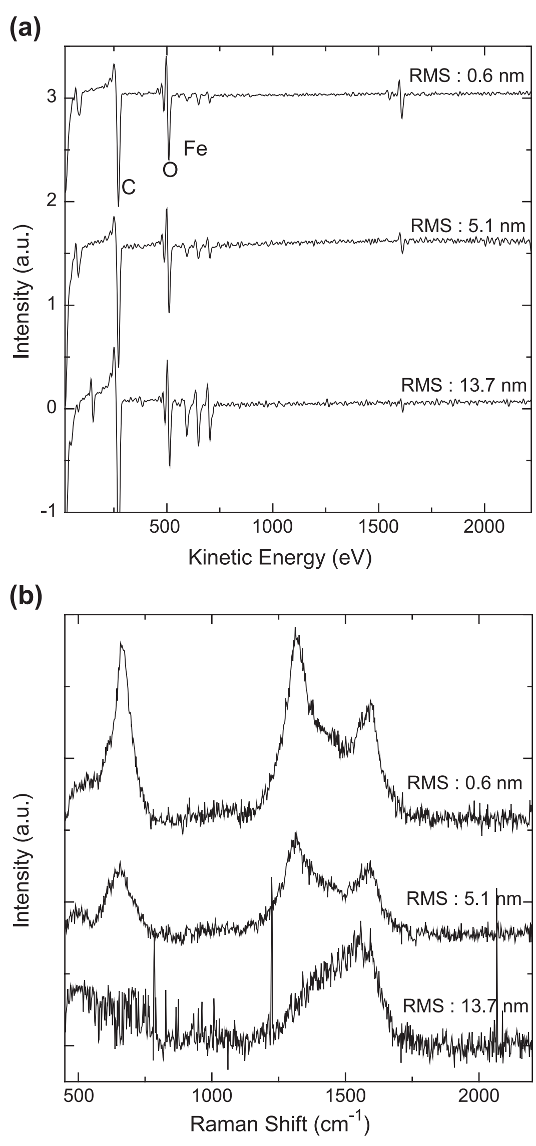

Fig. 6. (a) Scanning Auger spectra of the debris for various surface roughnesses. (b) Raman spectra of the debris on the wear scar surface for various surface roughnesses.

Raman spectra of the debris shown in Fig. 6(b) show that the tribochemical reaction was much suppressed on rough surface. The Raman spectra were obtained from the debris on the wear scar surface. The Raman peak near 700 cm^{-1} is the characteristic line of Fe oxide [12]. D and G peaks, centered at approximately 1300 and 1550 cm^{-1}, respectively, composed the carbon Raman peak. As the surface roughness increased, the intensity of the Fe oxide peak decreased. This result shows that the oxidation of either the ball surface or the Fe in the debris was suppressed on the rough surface. When the surface roughness was 13.7 nm, most of the incorporated Fe in the debris seems to be in the form of elemental Fe. The shape of the carbon peak also changed from that of typical graphitic materials to that of diamond-like phase as the surface roughness increased. In the macro-scale tribology, it was suggested that the smaller debris is mainly due to the topographical effect of the rough surface [2,3]. In addition to the topographical effect, this result also shows that the diamond-like characteristics of the debris can restrain their agglomeration, resulting in the small scattered debris.

This result shows that the tribochemical reaction with environment was suppressed as the surface roughness increased in nanoscale. The tribochemical reaction would occur during severe plastic deformation of the debris that can provide a sufficient thermal or kinetic energy for the reaction with environment. One should note that once the debris was pushed away from the contact area, it would not be deformed any more and the possibility of the tribochemical reaction becomes much smaller. On the rough surface, the debris will spend much shorter time in the contact area, resulting in the suppressed tribochemical reaction.

Even if the size of the debris was much smaller on the rough surface, the frictional behavior was not significantly varied with the surface roughness as shown in Fig. 4. This result is in contrast to both the previous results in the macro-scale tribology [2,3] and the present understanding about the effect of the debris size on the frictional behavior. However, the increased Fe concentration in the debris with surface roughness would provide a possible explanation for this frictional behavior. Large content of Fe in the debris could degrade the lubricating properties between the debris and the transfer layer. It was reported by the present authors that the friction coefficient in a humid air increased with the Fe concentration in the debris [8]. The higher wear rate of the steel ball also implies that a significant plowing occurred during sliding on rough surface. If these effects were balanced with the effect of the smaller debris, the friction behavior could become independent of the surface roughness.

4. Conclusions

Nano-undulated DLC film prepared by the present method made it possible to investigate the frictional behaviors of the DLC film with various surface roughnesses in nanoscale. We investigated the frictional behavior of the nano-undulated DLC film against steel ball in an ambient air. The most significant result of the present work is to show that the tribochemical reaction with environment was suppressed as the surface roughness increased. Even if the rough surface increased the wear of the steel ball and thus the concentration of Fe in the debris, neither the oxidation of Fe nor the graphitization of the carbon in the debris occurred on the rough surface. The agglomeration of the debris was also retarded on the rough surface due to the diamond-like properties of the debris in addition to the topographical effect of the rough surface. However, the friction coefficient of the nano-undulated DLC film was dependent on various factors: the size and the composition of the debris, plowing behavior of the ball and the transfer layer on the wear scar surface affected the frictional behavior. The suppressed tribochemical reaction on the rough surface would have a significant meaning in the tribology of DLC film. It is well known that the frictional behavior of the DLC film is sensitive to the test environment, presumably due to the tribochemical reaction with the environment. Hence, the increasing surface roughness can reduce the environmental sensitivity of the friction coefficient resulting in the stable tribological behavior.

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