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3 Tribological behavior of tetrahedral amorphous carbon (ta-C) coatings at elevated temperatures

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17 **Highlights**

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19 The tribological behavior of ta-C coatings varies with temperature

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21 ta-C shows lower friction at 200–400 °C than at 23 or 100 °C

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23 Carbon transfer layers are formed on Si₃N₄ balls at 200–400 °C

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25 ta-C is subject to severe delamination at 500 °C

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31 **Abstract**

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33 In this study, tribological behavior of tetrahedral amorphous carbon (ta-C) coatings was investigated
34 at elevated temperatures, from which it was found that it could be broadly defined by three distinct
35 temperature regions: Region I at 23 and 100 °C; Region II at 200, 300, and 400 °C; and Region III at
36 500 °C. A qualitative analysis of the toughness and adhesion of the ta-C coatings within each of
37 these regions was conducted by scratch testing. The formation of a transfer layer on Si₃N₄ balls in
38 Region II was determined as the cause of a reduced friction and higher wear rate when compared
39 with Region I. In Region III, the generation and propagation of cracks in the ta-C coating resulted in
40 severe delamination.
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55 **Key words:** ta-C coating, high temperature tribological behavior, partly graphitization, toughness

Introduction

Diamond-like carbon (DLC) has found widespread application as a protective coating in many fields because of its high hardness, low friction, chemical inertness, and other excellent properties [1]. In some of these applications, the films are subject to high temperatures in which case, both the thermal stability and high-temperature tribological properties are critical for their reliable long-term performance.

The tribological behavior of a DLC coating is strongly dependent on its nature, i.e., whether it is hydrogenated [2,3]. In our previous work, the high temperature tribological behavior of hydrogenated DLC coatings was investigated at 23, 100, 200, and 300 °C [4]. This revealed that a-C:H coatings show a lower coefficient of friction (0.02) at 100 °C than that at 23 °C. However, at higher temperatures (>200 °C), the thermal stability is reduced by the release of hydrogen from the coating surface.

As an alternative DLC coating, non-hydrogenated ta-C coating exhibits outstanding thermal stability and mechanical properties when compared with those of other DLC coatings, thus making it an ideal candidate for high temperature applications [5]. Several techniques have been developed to achieve high-quality and hydrogen-free DLC films, such as pulsed laser deposition (PLD) [6], filtered cathodic vacuum arc (FCVA) [7], and magnetron sputtering [8]. Of these, the FCVA technique is particularly useful for industrial application, as it provides a highly ionized plasma of energetic carbon ions from which dense films can be grown [9]. It is known that the graphitization and oxidation of carbon coatings is inevitable in high temperature environments, with numerous papers [10–14] having reported, on the basis of annealing tests, the thermal stability of ta-C coatings under different atmospheres, such as in N₂, Ar, or vacuum. However, the high-temperature tribological behavior of ta-C coatings in-situ has attracted little attention.

In this paper, the high-temperature tribological behaviors were investigated at temperatures of 23,

100, 200, 300, 400, and 500 °C in ambient air, with the aim of characterizing the relationship between temperature and tribological behavior.

Experimental

The ta-C coatings, as supplied by Nippon ITF Inc. (Japan), were deposited by the FCVA technique onto Inconel alloy plates ($\Phi 20 \times 2$ mm). This so-called super alloy was selected on the basis of its common use in high temperature applications. The thickness of the ta-C DLC coatings produced was in the order of 0.7 μm , providing a hardness of 45 GPa.

A high-temperature ball-on-disk tribometer was used to evaluate the friction between a DLC-coated disk and a Si_3N_4 ball in a high-temperature environment, as shown in Fig.1. These disks were heated to 23, 100, 200, 300, 400, and 500 °C prior to the tribological test, with the temperature being maintained at a set value during the sliding process. The Si_3N_4 ball ($\Phi 8$ mm) was pressed against the rotating disk with a normal load of 1 N. All tests were conducted at a rotation rate of 200 rpm over 10000 total cycles, unless the coating failed sooner. The track radius on the sample was 3 mm, with the resulting wear tracks on the disks and wear scars on the Si_3N_4 ball being observed by optical microscopy. Quantitative wear rates were determined by calculating the volume of the wear tracks removed from the surface profiles.

The coating and wear scars after tribo-test were analyzed by Raman spectroscopy (Jasco NRS-1000, 532 nm laser), the scattering being excited by a wave-number range of 600–2200 cm^{-1} .

The adhesion and toughness of the ta-C coatings was evaluated by an in-situ high-temperature constant-load scratch test. For this, a Vickers diamond indenter used, being orientated such that the corner of the diamond was at the leading edge. The scratching speed was 1 mm/s and the scratch length was 2 mm. A constant normal load of 500 mN was applied for each sample. The resulting scratches and cracks were then observed by scanning electron microscopy (SEM).

Results and discussions

Figure 2 shows the coefficient of friction for a ta-C coating tested at different temperatures. At 23 and 100 °C, a friction coefficient of about 0.1 is observed after the run-in period. A lower friction coefficient (<0.06) can be seen at 200, 300, and 400 °C, whereas at 500 °C, the friction coefficient increases suddenly at 6000 cycles, and which point the test was stopped. It is also worth noting the run-in period of the ta-C coatings becomes shorter as the temperature is increased.

Figure 3 shows the wear tracks produced on the ta-C coatings tested at different temperatures. At 23 and 100 °C, the wear tracks are only just barely discernible, as shown in Fig. 3 (a) and (b). In contrast, these wear tracks become much more distinct at 200, 300, and 400 °C; however, none of these coatings wore through, nor was any delamination evident, as shown in Fig. 3(c), (d), and (e). When tested at 500 °C, the ta-C coating finally cracked and peeled away from the Inconel alloy substrate (Fig. 3(f)).

The wear rates were subsequently calculated from the cross sections of the wear tracks, with the values presented in Fig. 4. This reveals a low value for the wear rate ($<10^{-8}$ mm³/Nm) at 23 °C and 100 °C, with a sharp increase occurring at 200 °C. Beyond this temperature, the wear rate maintains a value in the range of 10^{-8} mm³/Nm.

Figure 5 shows a summary of the tribological behavior of the ta-C coatings, including the friction coefficient, specific wear rate, and run-in period. From this, the behavior with regards to test temperature can be separated into three distinct regions: Region I at 23 and 100 °C; Region II at 200, 300, and 400 °C; and Region III at 500 °C. In Region I, the ta-C coatings exhibit a low friction (~ 0.1), low specific wear rate ($<10^{-8}$ mm³/Nm) and long run-in period (>1000 cycles). In Region II, however, the ta-C coatings show a lower friction (<0.06), but a much higher specific wear rate ($>4 \times 10^{-8}$ mm³/Nm) and shorter run-in period (<1000 cycles).

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3 In order to explain the difference in tribological behavior between these different temperature
4 regions, the wear scars on the Si_3N_4 balls were observed using optical microscopy, as shown in Fig.
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8 6. At 23 °C (Fig. 6(a)), a black powder can be seen to be attached around the wear scar, with it
9 clearly evident that there was no transfer layer on the Si_3N_4 ball. At 100, 200, 300, and 400 °C (Fig.
10 6(b), (c), (d) and (e)), however, there appears to be a transfer layer formed on the surface of the wear
11 scars. In order to confirm the presence of a carbon transfer layer on the wear scars, their surfaces
12 were analyzed by Raman spectroscopy.
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19 Figure 7 shows the Raman spectra measured at the center of each wear scar (as indicated by the
20 circles in Fig. 6 (b) to (e)). This shows a typical Raman line shape of a DLC transfer layer [15] for
21 the wear scars produced at 200, 300, and 400 °C, whereas these peaks did not appear on the wear
22 scar for 100 °C. It is therefore suggested that a carbon transfer layer forms on the surface of the wear
23 scars at 200, 300, and 400 °C, but that no such transfer layer is formed at 100 °C.
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31 It is known that the tribological behavior of DLC is controlled in all environments by an
32 interfacial transfer layer that is formed during friction [16]; this layer is formed by friction-induced
33 transformation of the top layer of the DLC film into a material with low shear strength. This transfer
34 layer, and its adhesion on sliding surfaces, can therefore be easily affected by the environment,
35 especially temperature [17]. This study reveals that carbon is more readily transferred to a Si_3N_4 ball
36 under the Region II temperature conditions than those of Region I. Furthermore, this transfer layer
37 reduces the friction and the number of run-in cycles. It is also noted that the Raman line shape in Fig.
38 7 is somewhere between that of a ta-C coating and graphite, and therefore likely results from phonon
39 damping that is related to the degree of structural disorder in the graphitic precursors [18].
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53 Figure 8 shows the surface topography of the ta-C coatings tested at different temperatures. From
54 23 to 200 °C (Fig. 8(a)–Fig. 8(c)), each coating exhibits a smooth surface, with few defects which
55 are formed in the deposition process. At 300 and 400 °C (Fig. 8(d), 8(e)), quite a few holes defects
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3 appear on the surface, and some white spots are also observed at 400 °C. At 500 °C(Fig. 8(f)), many
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5 big white spots with a diameter of 2-10 μm are observed.
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7 To confirm structural change during the high temperature tribological testing, the structure of the
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9 coatings was analyzed by Raman spectroscopy. Fig. 9(a) and 9(b) show Raman spectrum measured
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11 on the smooth area and the white spots of the coating, respectively. Fig. 9(a) shows that the Raman
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13 spectrum does not change a lot from 23 to 500 °C on the smooth area. However, in the area of white
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15 spots on DLC coating tested at 400 °C and 500 °C, Raman spectrum shows typical graphitized shape,
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17 as shown in Figure 9(b). It hints that the graphitization partly occurred on the surface, centered on
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19 some point defects and extended with increasing temperature.
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24 Two popular mechanisms of low friction coefficient on DLC coatings, ‘friction-induced
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26 graphitization mechanism’ and ‘passivation mechanism’ were discussed by L. Wang et al. [20] It
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28 remains an open question that whether graphitization phenomenon is the main cause of low-friction
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30 of DLC. In my study, partly graphitization occurred on the DLC at elevated temperature. In this
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32 condition, the wear rate tends to increased with the increasing graphitization rate [21]. The wear rate
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34 can promote the the formation of the transfer layer since the transfer layer forms from the wear
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36 debris [22]. The transfer layer is the main cause of lower friction coefficient in Region II (200, 300,
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38 and 400 °C). And Fig. 5 and Fig. 7 proof the relationship between the existence of transfer layer and
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40 the low friction.
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46 The high temperature adhesion and toughness were investigated by a high-temperature, in-situ
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48 scratch test, with Figure 10 showing SEM images of the scratches produced. At 23 and 100 °C (Fig.
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50 10(a) and (b)), there is no evidence of any cracking on either side of the scratch. Conversely, parallel
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52 cracks along the scratches are observable at 200, 300, 400 °C and 500 °C (Fig. 10(c)–(f)). The
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54 average length of these cracks was subsequently calculated, as summarized in Fig. 11, revealing that
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56 the average length at 200, 300, and 400 °C is almost the same, whereas it is much greater at 500 °C.
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Toughness is defined as a material's ability to resist the crack propagation; however, its measurement in thin films is made quite difficult by the small dimensions involved. Consequently, although a number of methods have been developed to measure the toughness of hard coatings - such as bending tests, tensile tests and scratch tests [20] - there has until now been neither a standard procedure nor a standard methodology. Moreover, the quantitative assessment of toughness is made even more difficult at elevated temperatures. The purpose of the scratch test in this paper was therefore to provide an evaluation of the effect of temperature on the ability of ta-C to resist crack generation and propagation. The appearance of cracks at 200 °C suggests a reduction in the crack resistance of ta-C at this 200 °C, which is coincident with a reduction in the coating toughness. By summarizing the tribological behavior under different temperatures, the ta-C coating clearly undergoes very different wear mechanisms in relation to temperature. In Region I, the high crack resistance and low specific wear rate is indicative of abrasive wear, whereas in Region II, the low crack resistance and much higher specific wear rate suggests that spalling wear is predominant. At higher temperatures, i.e., Region III, the hole defects (as shown in Fig. 9(f)) provide a greater number of crack nucleation sites. This, combined with the low toughness of the coating at high temperatures, results in a greater number of cracks being generated and the coating being more easily peeled away from the substrate. This loss of coating adhesion can be assessed by studying the delamination in the scratches, with the SEM images revealing that there was no significant change in the morphology of this peeling/ delamination. This means that adhesion of the coating is not directly affected by changes in temperature.

Conclusions

An investigation of the tribological behavior of ta-C coatings at elevated temperature revealed

three distinct regions. In Region I (23 and 100 °C), a friction coefficient of 0.1 and specific wear rate of $<10^{-8}$ mm³/Nm were observed. In Region II (200, 300, and 400 °C), the friction coefficient (<0.06) was reduced, however, the specific wear rate ($>4 \times 10^{-8}$ mm³/Nm) was increased. Finally, in Region III (500 °C), the ta-C coating cracked and peeled off after 6000 cycles. Partly graphitization at high temperature is the reason of high wear rate. This resulted in the formation of a transfer layer under the conditions of Region II, which explains its reduced friction coefficient and higher specific wear rate. Moreover, a deterioration of toughness at elevated temperatures also leads to an increase in the specific wear rate. At 500 °C, an increase in crack nucleation sites and propagation results in severe delamination of the ta-C coatings.

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Figure Captions

Fig. 1 Schematic of a high temperature ball-on-disk tribometer

Fig. 2 Friction coefficient of ta-C coatings as a function of the number of sliding cycles at different temperatures

Fig. 3 Optical microscopy images of the wear tracks on ta-C coatings tested at different temperatures

(a) 23 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C

Fig. 4 The specific wear rates of ta-C coatings at different temperatures

Fig. 5 The specific wear rate, friction coefficient and run-in cycles of ta-C coatings for temperature regions I and II

Fig. 6 Optical microscopy images of the wear scars produced on Si₃N₄ balls after tribological testing at different temperature (a) 23 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C. The circles indicate the area used for Raman analysis

Fig. 7 Raman spectra, as measured at the center of the wear scars

Fig. 8 SEM photos of the ta-C coating after high-temperature tribological testing (a) 23 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C

Fig. 9 Raman spectrum measured on the (a) smooth area and (b) white spots

Fig. 10 SEM images of scratches and cracks on ta-C coatings at different temperature

(a) 23 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C

Fig. 11 The average length of cracks as a function of temperature

Figure(s)

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