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FIB and TEM studies of damage mechanisms in DLC coatings sliding against aluminum

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Abstract

Material transfer and adhesion phenomena during sliding contact of non-hydrogenated diamond like carbon (DLC) coatings against an aluminum–silicon (319 Al) counterface tested in vacuum were studied using TEM investigations of the cross-sectional microstructures of the wear tracks. Site-specific focused ion beam (FIB) lift-out method was used to prepare the sections at the precise locations where aluminum pieces were adhered to the DLC surface. The dense amorphous structure of DLC coatings with nanocrystalline graphite platelets is confirmed by the high-resolution transmission electron microscopy. The focused ion channeling contrast images obtained from the cross-sections of the wear track indicated that in some sections of DLC coatings considerable wear was inflicted by aluminum, reducing the coating thickness. The aluminum that was transferred on the DLC coatings' contact surfaces consisted of nanocrystalline grains of less than 100 nm. TEM examination of the contact surface of the 319 Al pin has revealed that the initial aluminum grain size was also reduced to the nanocrystalline scale and this was accompanied with a hardness increase. These observations revealed that local severe plastic deformation accompanied the aluminum adhesion process to DLC coating surfaces.

Keywords: Focused ion beam; DLC coatings; Al–Si alloys; Sliding contact; Adhesion; Material transfer; Wear mechanisms; Nanocrystalline grains

1. Introduction

Substitution of cast iron components in combustion engines with aluminum silicon castings has become an accepted strategy for weight reduction in the automotive industry. Increased use of lightweight aluminum–silicon alloy components leads to fuel economy and improvement in emission standards but also creates new manufacturing challenges. Aluminum chips formed during cutting, shaping and drilling processes tend to adhere to the tool surfaces, especially when these processes are conducted in the absence of metalworking fluids (dry machining). In order to establish dry machining as a viable 'green machining' process, adhesion of the aluminum onto the tool surfaces must be eliminated [1–3]. In this respect, diamond-like carbon (DLC) coatings that are known to have aluminum adhesion mitigating properties have presented themselves as promising tool coatings for aluminum dry machining [4,5].

The bonding of DLC coatings is characterized by a mixture of sp^3 and sp^2 hybridized bonds, and according to TEM studies [6,7] they possess dense, amorphous structure. There is extensive experimental evidence that DLC-coated surfaces when tested against aluminum alloys exhibit better frictional properties than the conventional nitride-based coatings of TiN, CrN, TiAlNi [8–10]. However, frictional characteristics of DLC coatings depend on the atmospheric conditions; tribological tests under various atmospheres including ambient air, dry air and vacuum, have indicated that the hydrogen content of the DLC coatings is one of the main determining factors of adhesion propensity of aluminum to their surfaces [11–14]. The hydrogenated DLC coatings that contain typically 40 at.% hydrogen exhibit extremely low values of coefficient of friction (10^{-2}) when tested in vacuum and under inert atmospheres [15–17]. On the other hand, the non-hydrogenated DLC coatings, with less than 1–2 at.% hydrogen, show coefficient of friction values as high as (5×10^{-1}) in vacuum or when tested in a nitrogen atmosphere [18,19]. Testing of non-hydrogenated

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DLC under inert atmospheres and in vacuum leads to significant aluminum adhesion, which is thought to be associated with the strong bonding formed between aluminum and the 'dangling bonds' of carbon atoms on the DLC surface [8,15]. For hydrogenated coatings this type of interfacial bonding is prevented by hydrogen atoms that bond with the carbon atoms on the surface and hence passivating the reactive surface [20]. Under the ambient conditions, where there is appreciable amount of water vapour in the atmosphere, the non-hydrogenated DLC coatings have been observed to show low coefficients of friction and almost no adhesion to aluminum [21]. Meanwhile, the coefficient of friction and the wear rates of hydrogenated DLC coatings increased when water vapour was introduced into the testing environment [22,23]. The variations in friction and adhesion properties of DLC coatings at different test environments indicate that chemical and physical changes occur at the aluminum/DLC interfaces. Computational models based on first principles calculations have provided significant insight into the interface structures and adhesion properties [24–27]. Recent density functional theory (DFT) calculations performed by Qi et al. [28] have shown quantitatively that the diamond surfaces representing the non-hydrogenated DLC will adsorb H_2 and H_2O molecules that become dissociated as they approach the surface but the dissociation of N_2 is unlikely. DLC coating surface becomes passivated by hydrogen and –OH termination in water but not passivated in nitrogen in agreement with earlier studies [29]. Therefore, DFT calculations successfully explained the atmospheric dependency of the tribological behaviour of non-hydrogenated DLC coatings tested against 319 type Al alloy. However, there is still a need for direct microscopical evidence of the micromechanisms of the material transfer and damage mechanism between aluminum and DLC coating surfaces.

The present work focuses on understanding the microstructural details of adhesion process of aluminum (319 Al) to the non-hydrogenated DLC coatings. 319 Al is a cast Al–6 wt.% Si alloy commonly used in automotive engine components. The non-hydrogenated coatings were tested against 319 Al pins using a pin-on-disc configuration in a vacuum chamber. Testing under a vacuum atmosphere maximized the adhesion of aluminum to the non-hydrogenated DLC surface as shown in Fig. 1 [18]. Detailed cross-sectional analyses of selected areas within the wear track that were covered by adhered pieces of aluminum were carried out first using a FIB microscope and then by investigating the thin sections prepared by a FIB lift-out technique using TEM.

2. Experimental

2.1. Test procedures and selection of site-specific samples

The DLC coatings were deposited using a closed field unbalanced magnetron sputtering system (Teer UDP 550) consisting of two graphite and one Cr targets. Details of the deposition process are described in [10,30]. 25-mm-diameter discs made of M2 type steel with an hardness of 60±2 Rockwell C were used as substrates on which a CrN interlayer

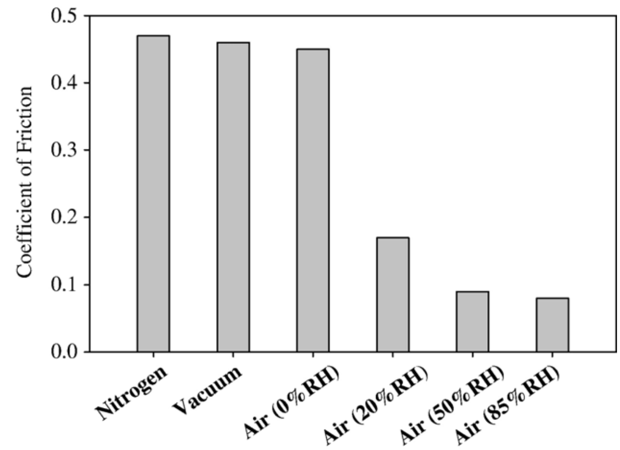

Fig. 1. The coefficients of friction (COF) of the non-hydrogenated DLC coatings measured against 319 Al under various test environments. The applied load and sliding speed were 5 N and 0.12 m/s [18].

was deposited to facilitate bonding of the DLC coating to steel. This was achieved by activating the Cr target and injecting N_2 gas to the system. The DLC sputtering process was carried out in Ar atmosphere without the use of hydrogen gas. The resulting coatings had less than 2 at.% hydrogen in their composition. The Raman spectra of the as-deposited DLC films exhibited an unresolved broad peak between 1000 and 1800 cm^{-1}, which inferred that the film was amorphous with mainly sp^2 type bonding. The hardness of the DLC coating was measured using an instrumented nano-indentation system (NanoXP) with a Berkovich type indenter as 9.5 GPa [19,30].

DLC coatings were subjected to sliding wear tests against 319 type Al–Si alloy pins whose tips were rounded to a diameter of 4 mm. The composition of Al 319 alloy (in wt.%) was 6% Si, 3.5% Cu, 0.26% Fe, 0.01% Zn, <0.01% Ni, <0.01% Mn, 0.08% Mg, 0.08% Ti and the balance Al. The Vickers hardness of the alloy prior to wear tests (in T5 heat-treated condition) was measured using indentations made at 10 gf as 109 ± 14 HV_{10} (equivalent to 1.07 ± 0.14 GPa).

Wear tests were conducted using a pin-on-disc tribometer (CSM vacuum tribometer) operated under a load of 5.0 N and a linear sliding speed of 0.12 m/s. The coefficient of friction (COF) at the beginning of the test was 0.40. It then increased, and after 50 revolutions a relatively constant COF value of 0.46 was maintained. The testing configuration is illustrated in Fig. 2a.

As the main objective of the experiments was to characterize the process of aluminum adhesion to the DLC coatings, the non-hydrogenated DLC coatings from which TEM samples were prepared, were selected from those tested in vacuum environment (8×10^{-3} Pa) that caused large quantities of aluminum to become transferred to DLC surfaces. A typical secondary SEM image of the wear track generated on a DLC sample tested under these conditions is shown in Fig. 2b. The worn surface exhibits a long streak of aluminum, which was transferred from the pin and almost continuously spreading over along one