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Formation of UHMWPE polymeric transfer films on sliding glass counterfaces: early and steady-state wear studied by transmission electron microscopy

G. C. RUBEN*, T. A. BLANCHET‡§, F. E. KENNEDY‡
Department of Biological Sciences and ‡ Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, USA

At a temperature of 30 °C polymeric transfer films were generated on glass counterfaces during small-amplitude oscillatory sliding contact with an ultra-high molecular weight polyethylene (UHMWPE) pin under a constant load of 6.5 MPa. Early discontinuous and continuous (steady-state) transfer films were studied with vertical platinum–carbon replication and transmission electron microscopy (TEM). Nanometre-scale UHMWPE deposits in these transfer films have been visualized for the first time. Nanometre-scale particles averaging 20.6 ±6.3 nm (5–40 nm) were deposited on glass in the early stages of UHMWPE film transfer. After formation of a continuous transfer film, UHMWPE particles of slightly smaller dimensions, 13.5±6.1 nm (2–41 nm), were deposited on the transfer film surface. In addition, micrometre-scale particles (0.1–6.4 μm) were found at the ends of the wear track. At high magnification, a fraction of the UHMWPE polymer chains observed in particle surfaces and in the transfer film surface nearby were not oriented in the sliding direction. Some crystal- or plate-like particles of UHMWPE were seen in the transfer film. Plate-like and micrometre-scale spherulitic inclusions were also identified on the mostly amorphous UHMWPE pin surface fractured at liquid nitrogen temperatures. The high frequency of nanometre-scale UHMWPE particles in contrast to the less numerous micrometre-scale deposits near the ends of the wear track suggests that the nanometre-scale deposits contribute significantly to transfer film formation and to the wear characteristics of UHMWPE.

1. Introduction

Where traditional fluid-film lubrication techniques are impractical, polymeric materials are frequently substituted as one of the two sliding surfaces, owing to their self-lubricating properties. In orthopaedic prosthesis applications, ultra-high molecular weight polyethylene (UHMWPE) is currently used as an articulating surface in total hip and knee joint implants. UHMWPE implants have superior impact, fracture, creep and wear resistance over other polymer formulations [1]. The conditions of load, temperature and motion used in this investigation are similar to the sliding conditions in implanted artificial hip joints. Polished Ti–V–Al, Co–Cr or stainless steel, usually the femoral head material, was replaced with glass so that early transfer films could be observed on a background of minimal roughness. Since both counterfaces are smoother than a surface roughness of $R_a = 0.1\ \mu m$, a value below which adhesive wear predominates over abrasive wear, UHMWPE wear on stainless steel and on glass should take place by a similar mechanism [2, 3]. Within the tribological system, the mechanism of wear, film transfer and self-lubricity of UHMWPE results from the adhesive transfer to the sliding counterface. The effect of such transferred polymer on the wear and frictional performance of the sliding system is related to the transfer film's mechanical properties, cohesive structure and surface coverage [4–11].

"Films", "fibres", "platelets", "ridges", "bundles", "icicles", "lumps", "anchors", "islands", "patches", "layers", "bands" and "smeared residues" are terms that have been used to describe large micrometre-scale structures of residual polymer adherent to counterfaces following sliding contact with UHMWPE [4, 5, 8–10]. The variety of descriptions indicates the wide range of UHMWPE transfer morphology that has been observed by altering the experimental parameters of the tribosystem sliding speed, counterface roughness, load, temperature, environment and contact kinematics.

When sliding against a hard, smooth counterface (glass), in the absence of a topographically rough surface, adhesion is the dominant source of friction.

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* To whom correspondence should be addressed.

§ Current address: Department of Mechanical Engineering, Rennasler Polytechnic Institute, Troy, NY 12180, USA

Progressive transfer of UHMWPE to the counterface modifies the adhesion and frictional properties of the sliding interface and alters the tribosystem to one of polymer sliding on polymer. Micrometre-scale UHMWPE transfer often is lumpy and roughens the counterface [4, 5, 10], generating an additional deformational contribution to sliding friction.

Similarly, the modification of counterface topography by polymer transfer affects wear. For example, the transient high rate of wear of UHMWPE as sliding begins can be explained by the abrasive action of a rough counterface [3, 7, 11]. The roughness features are progressively masked by UHMWPE transfer, yielding a lower, steady-state rate of wear. Thus the effect of transfer on tribological behaviour depends upon the original topography of the counterface and the morphology of the adherent polymer.

Since we are interested in early and steady-state transfer film formation, vertical platinum–carbon replicas of wear tracks of UHMWPE after a short or long sliding period were observed by transmission electron microscopy (TEM). By observing transfer film formation on glass, it was our desire to link the morphological properties of UHMWPE, the sliding conditions, and UHMWPE transfer behaviour to the mechanism of wear in this tribological system.

2. Experimental procedure

2.1. UHMWPE transfer film generation

Transfer film production was carried out in air on a specially-designed oscillatory pin-on-disc test rig, which had been previously used to study the wear, friction and transfer behaviour of UHMWPE sliding upon glass, oxidized silicon and polished stainless steel counterfaces [3, 8, 10–12]. The large-scale transfer morphology observed on each of these counterfaces has been shown to be quite similar [12], thus glass was used because large surface replicas are easily removed from glass. A No. 2 glass coverslip was ultrasonically bathed in acetone and methanol, air-dried and attached to the disc.

The milled flat end of the polymer pin was dead-weight loaded against the glass disc by a 52.4 N load. This polymer was an injection-moulded, unfilled surgical grade Hoechst RCH 1000 UHMWPE with an average molecular weight of $3.5\text{–}4.0 \times 10^6$. The density was 0.94 g cm^{-3}. The 12.5 mm long pin had a 2 mm × 4 mm cross-section, with the 4 mm dimension oriented along the sliding direction. The resulting normal pressure of 6.5 MPa falls within the broad range of pressures experienced by the polymeric acetabular cup. Randall and Dowson [13] used pressures of approximately 2 and 8 MPa in their UHMWPE–glass investigations. This breadth of pressures results from a dynamic hip force which can vary from near zero to four (or more) times body weight throughout a walking cycle [1].

Two hours of static dead-weight loading established surface conformity and thermal equilibrium of controlled pin and disc bulk temperatures at 30 °C. This temperature is adequately representative of that found in joint replacement, as wear of UHMWPE was found to change little from 30 to 45 °C [3]. The glass disc was then set into oscillatory motion, in ambient air, beneath the stationary UHMWPE pin with an amplitude $A = 0.5$ mm and a frequency $f = 6.7$ Hz (average oscillatory speed $= 4Af$). This small amplitude relative to the 4 mm pin contact length is also representative of the motion found in the hip joint, a contact with extreme mutual overlap of the two sliding bodies, enhancing entrapment of third-body debris [9]. After the desired sliding distance, the UHMWPE pin was raised from the disc and motion was halted. To study the initial deposition of UHMWPE transfer in a discontinuous transfer film, a total sliding distance of 0.2 m (100 oscillation cycles) was used. To study the steady-state nature of UHMWPE transfer, 230 m of oscillatory sliding were performed to produce a continuous film.

The sliding situation is shown schematically in Fig. 1, where the UHMWPE pin is in oscillatory motion relative to the glass counterface. Within the wear track, polymer transfers from the pin to the counterface. The length of the wear track is equal to the sum of the length of the pin in the sliding direction and twice the oscillation amplitude.

The molecular weights of the particles were calculated assuming their volume was bracketed with a hemispherical and a spherical shape. Since particle diameters were measured, the following formula was used to calculate the particle molecular weight, assuming a spherical shape:

$$M = \frac{4\pi}{3}\frac{d}{2^3}(0.94\ \mathrm{g\ cm^{-3}})(6.02 \times 10^{23}\ \mathrm{mol^{-1}})$$

Molecular weights of particles of assumed hemispherical shape are also reported, having a value one-half that determined under the spherical assumption.

2.2. Replication of wear tracks on glass and a freeze-fractured UHMWPE pin

UHMWPE transfer surface samples were replicated within a modified Balzers 300 with a 6 in. (152 mm) Lebold-Heraeus cryopump fitted and conflated to the vacuum chamber gate valve. The samples were placed on a Wiltek TSR-1000D rotary cold stage which could be cooled to − 185 °C and which could be shielded from above by a cold finger cooled to the same temperature. A roughing pump brought this chamber to 10^{-3} torr, then a cryopump reduced the vacuum to the low 10^{-8} torr range. The specimen was cooled to

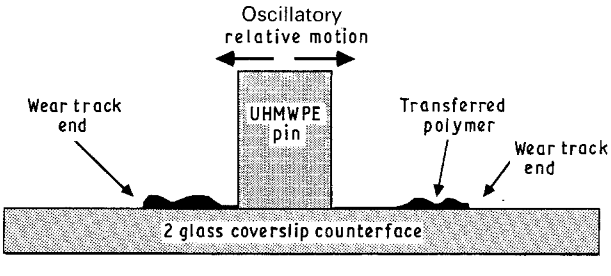


Figure 1 Schematic diagram of the pin-on-disc UHMWPE upon glass oscillatory sliding system, with transfer.

$-185°C$ by flowing liquid nitrogen at a high rate through the stage for a minimum of 10 min. The cold finger cooled to $-185\,°C$ was lowered over the sample (before cooling the stage to $-185\,°C$), reducing the local vacuum around the specimen by up to two orders of magnitude. The cold finger also was used as a shutter after the Pt–C electron beam gun was turned on and running. The cold finger was moved, unshielding the sample and quartz crystal monitor, while the electron beam gun positioned nearly vertically (80°) deposited roughly 1.0 nm of Pt–C on the sample surface. Since the thickness was present on the quartz crystal monitor, the Pt–C gun was turned off by a gun power supply–quartz crystal monitor interlock system. The sample was warmed to about -100 to $-60\,°C$ and the first of two 5–7 nm carbon films was deposited on the sample while it was rotating at about 60 r.p.m. A second carbon film was rotary-deposited on the sample at 10–20 °C. This produced a carbon film support of 10–15 nm thickness. Electron beam gun degassing procedures and the vertical replication technique were employed to provide minimum granularity and the highest resolution replication possible currently [14].

Replicas were removed from surfaces by either digesting the specimen, or stripping the replica from the specimen. For UHMWPE transfer on glass substrates, 49% hydrofluoric acid was used to separate the replica from the glass. Replicas on UHMWPE alone were more difficult to remove. These replicas were stripped from the polymer using a saturated potassium hydroxide solution heated to 50–90 °C. This stripping process can take several days to several weeks. Techniques using solvents to dissolve UHMWPE were ineffective because the polymer first swells before it dissolves and this action can tear the replica to pieces. Separated replicas were then transferred to a 10% salt water solution, and then to distilled water. A 300 mesh grid without a support film was used to pick up the replica after washing for 4–12 h. As water's surface tension can break these thin replicas, a small amount of ethanol was added to the water to reduce its surface tension so that residual water on the grid after replica pick-up could be removed with filter paper without destroying the replica.

2.3. TEM and photographic techniques

Micrographs were taken on a JEM 100CX transmission electron microscope equipped with an LaB_6 source. This microscope has a 5.0 mm focal length and was operated at 80 kV with a 400 µm condenser aperture and 40 µm objective aperture. These TEM operating conditions gave a 262.5 nm depth of field and a resolution of 0.66 nm. Replicas were tilted in the electron beam with an EM-BSR or an EM-SCSH side-entry goniometer ($\pm 60°$). Specimens were tilted 30–45° in the microscope to generate image contrast. Edges orthogonal and opposite to the direction of tilt are low in contrast, whereas orthogonal edges in the direction of tilting overlap the adjacent surface Pt–C film, doubling the film thickness and contrast at this edge. Since metal replicas appear black in direct prints from TEM negatives, the original Kodak 4489 negatives were contact-reversed on 7302 fine-grain positive film so that Pt–C coated areas were white with their structural details modulated in greys and areas without Pt–C appeared black. Processing of the 4489 film, processing of image reversals, and other details have been published [14].

3. Results

The glass surfaces adjacent to the UHMWPE transfer film were imaged along with areas exposed to the sliding contact. The glass surface possessed a complex pattern of shallow, narrow grooves separated by larger flat areas as shown in Fig. 2a. The origin of the fine grooves in the glass is unknown.

Early deposition of UHMWPE in a wear track during the first 100 oscillatory sliding cycles is shown in Figs 2b, 3 and 4. Early transfer has not covered the glass surface with a continuous film since many of the glass grooves are only partially obscured along a series of separate narrow tracks 100–400 nm wide. The UHMWPE transfer appears to be discrete and particulate in nature, with particles falling along "transfer tracks" parallel to the sliding direction. Three such tracks are composed of particles with diameters averaging 20.6 ± 6.3 nm (1.3–2.6×10^6 mol. wt., assuming hemispherical and spherical shape respectively), while a fourth track contained larger irregular particles with sizes from 33.3 to 209.8 nm (Fig. 2b and c). As particles are generally limited to such tracks and not widespread across the counterface, transfer must be occurring from a limited number of asperities on the UHMWPE pin surface.

A large deposit of UHMWPE (1–1.5 µm) near the end of a wear track is seen in Fig. 3a. Fine grooves indicative of the glass surface are seen to either side of this track. It is possible that the large deposit was previously part of the asperity that made the track. The ~500 nm wide wear track at higher magnification is shown in Fig. 3b. This track is more continuous than in Fig. 2b, as the glass grooves are covered at the centre of the transfer track but not at its edges. Fine particles with diameters of approximately 25 nm (2.3–4.6×10^6 mol. wt.) are on the continuous transfer surface as well as deposited in the discontinuous transfer areas at the track edges. Several of these particles are shown in Fig. 4a–e. In Fig. 4 the replica was tilted 45° towards the top of the figure. Such tilting overlaps the back of the particle with the Pt–C coated surface making it whiter and reveals the darker, less well Pt–C coated side at the front of the particle. Chain-like filaments with 1.1–1.5 nm diameters are seen in particles and the adjoining surface in Fig. 4a–e. These 1.1–1.5 nm filaments are characteristic of polyethylene and are not observed on the adjacent uncoated glass surfaces shown in Fig. 4f. The 0.7–0.9 nm filaments on the glass are due to a filamentous structure in 1.16 nm Pt-C–films formed at $-185\,°C$. The UHMWPE filaments are not preferentially oriented in the sliding direction, indicated by the arrows which also mark the width of the particles. A replica thickness of 1.16 nm is expected to broaden

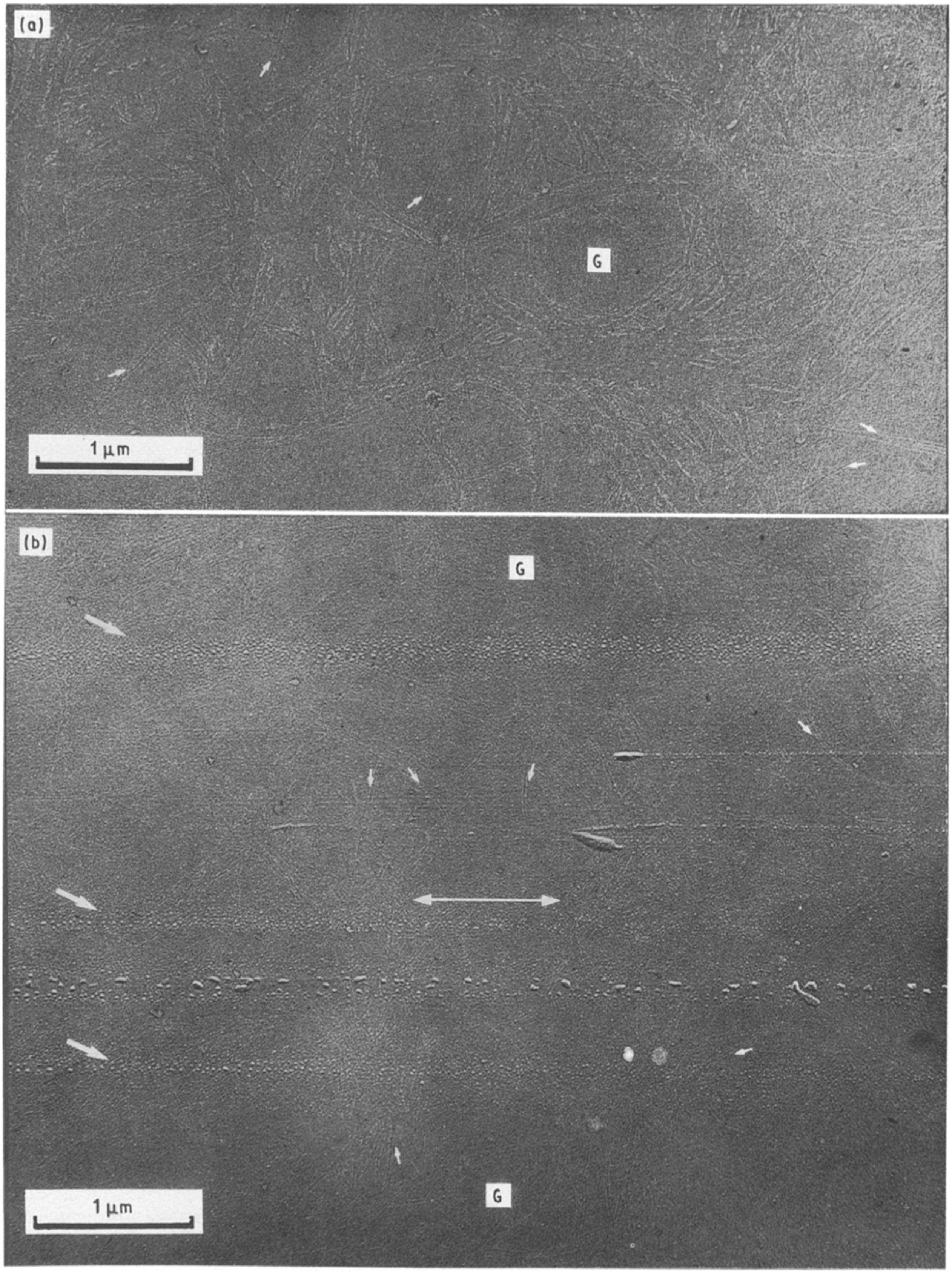
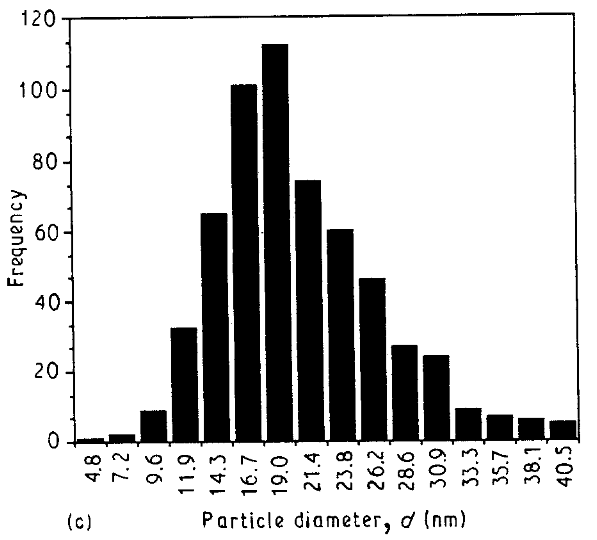


Figure 2 The initial polyethylene transfer on to a No. 2 glass coverslip surface that has been in contact with an ultra-high molecular weight polyethylene (UHMWPE) pin for 100 sliding cycles under a normal load of 52.4 N. (a) This glass surface was cleaned with acetone and methanol and replicated with a 1.16 nm thick Pt–C film at an almost vertical angle (80°) and backed with 13.2 nm carbon film. Unexposed to sliding contact with UHMWPE, the glass surface demonstrates a complex pattern of grooves and flat areas. The replica was tilted 45° towards the top of the figure in the TEM. (b) Initial deposition of polyethylene transfer in areas of glass counterface which were in sliding contact with UHMWPE pin. Replication conditions were the same as in Fig. 2a. The double arrow indicates the direction of oscillatory sliding. The small arrows show grooves in the glass surface (G) that are similar to those in Fig. 2a. Three tracks of transfer labelled by larger arrows are made up of fine polyethylene particles (diameter $d = 20.6 \pm 6.3$ nm, $n = 581$). The fourth, unlabelled track with larger irregular particles ranging from 33.3 to 209.8 nm ($d = 64.7 \pm 31.3$ nm, $n = 35$) also had small particles similar in size to those in the other three transfer tracks. Between the upper two tracks there are fine polyethylene streaks which cross the grooves in the glass surface without filling them. Interspersed between and along these streaks are fine particles ($d = 17.6 \pm 4.5$ nm, $n = 12$). This image was tilted 40° towards the top of the figure.



(c) Diameter distribution of fine polyethylene particles measured orthogonal to the tilt direction: $d_{avg} = 20.6$ nm, s.d. = 6.3 nm, $n = 581$.

features by approximately 0.7 to 0.9 nm [20]. The width of the polyethylene filaments is therefore 0.5 ± 0.2 nm, and corresponds approximately with the diameter of straight polyethylene chains (~0.3 nm) [20].

The central zone of a wear track shows characteristic steady-state UHMWPE transfer morphology following 230 m of oscillatory sliding (Fig. 5). Many transfer tracks are seen running along the sliding direction separated by smooth ridges. These tracks are coated with a continuous film of UHMWPE which is also covered with small particles. A few of the tracks deviate from the sliding direction. It is likely that these deviating tracks have not been directly transferred from pin asperities to the surface since asperities travel strictly in the sliding direction. These deviant tracks are likely caused by UHMWPE particles rolling between the pin and the glass surface.

The UHMWPE transfer tracks in Fig. 5 are shown at higher magnification in Fig. 6 to be separated by a

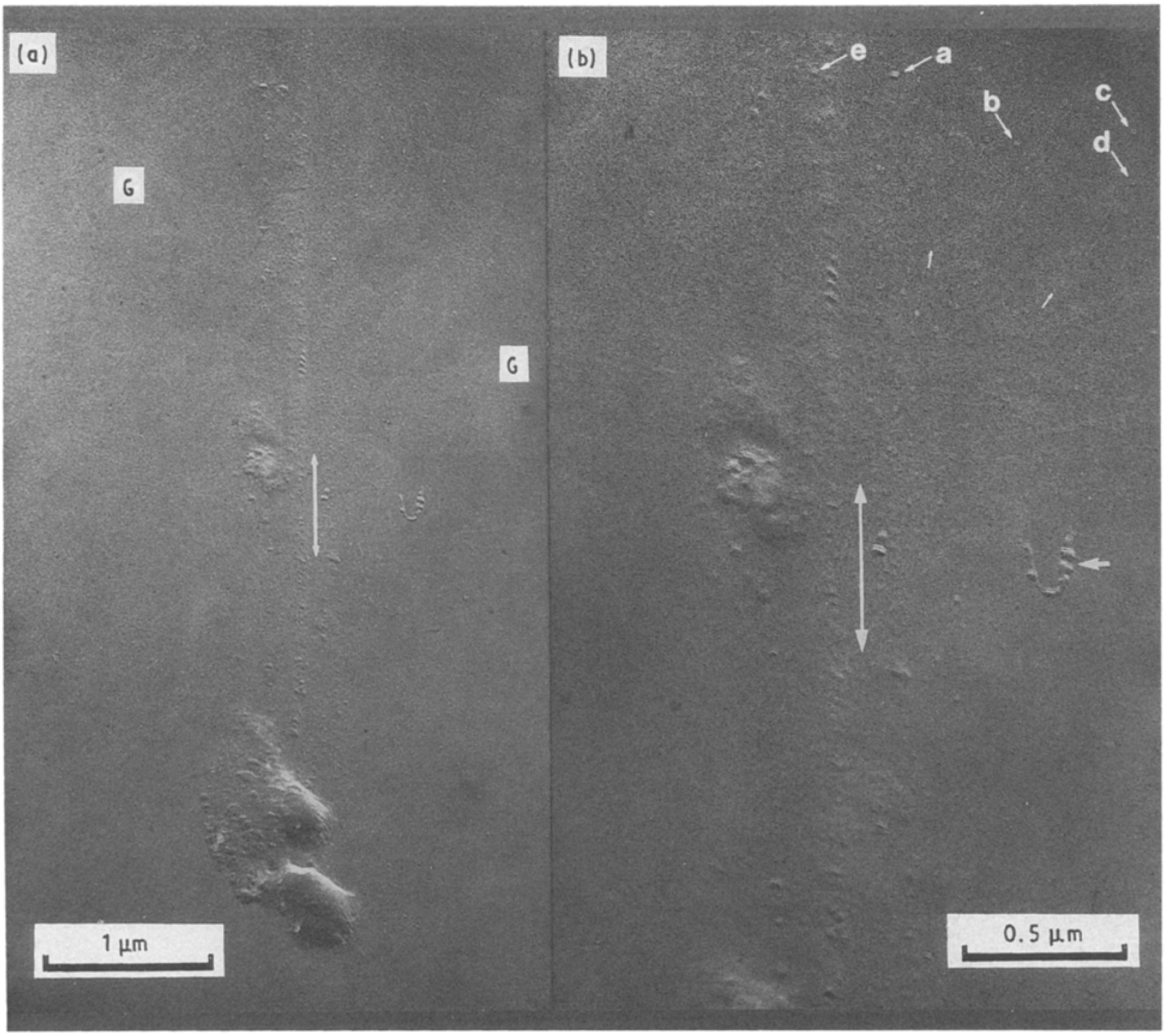


Figure 3 (a) UHMWPE deposition during early stages of wear near the end of a wear track. Small grooves in the glass surface (G) can be seen on both sides of the track of transfer. The replica was tilted 45° towards the top of the figure. Same replica conditions as in Fig. 2. (b) The central area of Fig. 3a has been enlarged, showing a polyethylene film in the direction of the transfer track. The small arrows point to grooves in the glass. To the right of the track the large arrow points to additional material transferred from the UHMWPE pin. The arrows labelled a–d point to even finer particles to the right of the wear track. The arrow labelled e points to a similarly fine particle within the track of transfer. The particles a–e are enlarged in Fig. 4, where they are listed under the same letters.

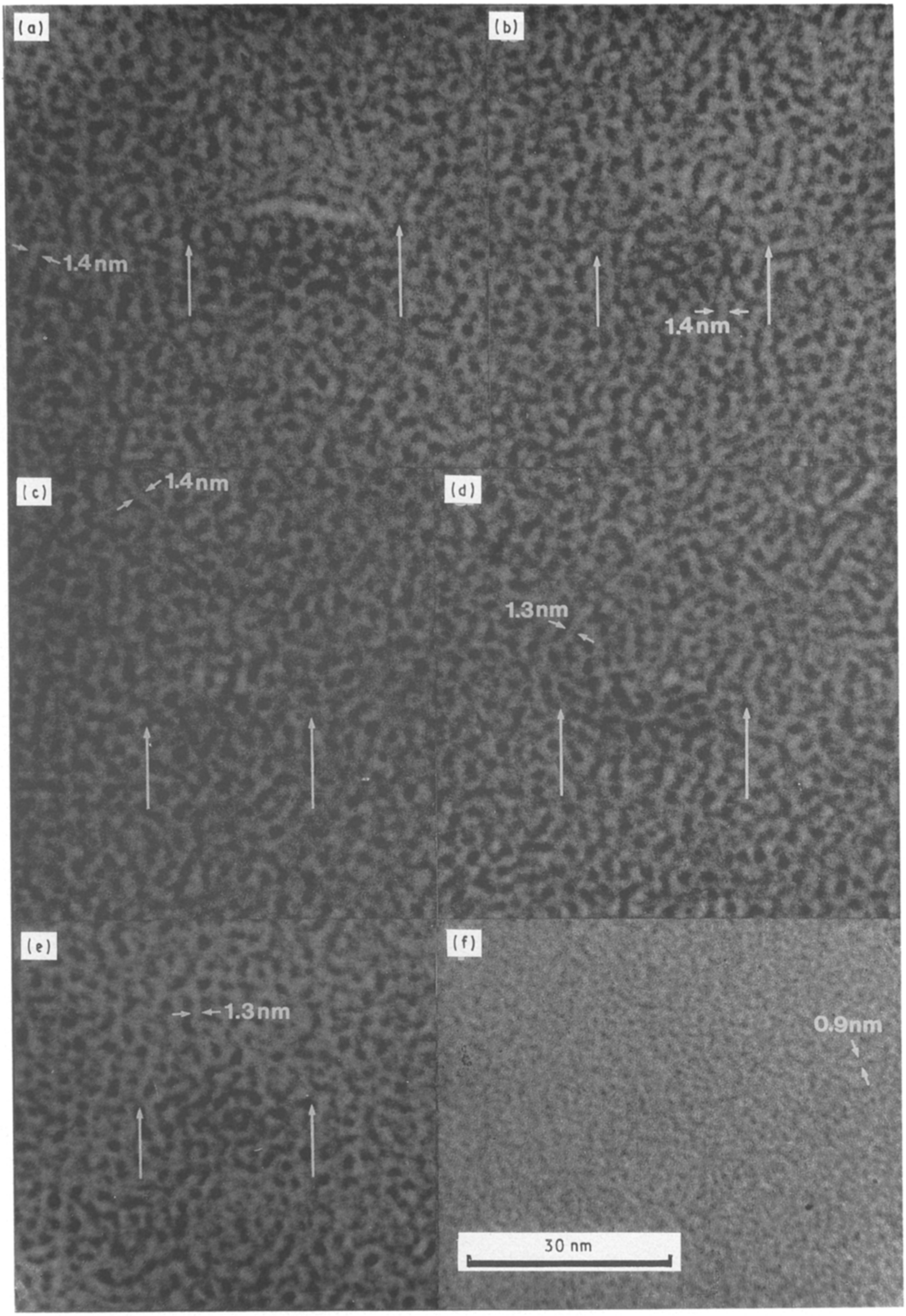


Figure 4 (a–e) UHMWPE particles labelled a–e in Fig. 3b are shown here at high magnification. The polyethylene chains are visible within the particles and on the surrounding surface. The glass surface without polyethylene transfer is shown in (f). Polyethylene chains are 0.3–0.7 nm in diameter depending on whether the single chains are extended or are helical or are double chains. The 1.16 nm Pt–C replica increases the diameter of the polyethylene chains by 0.7–0.9 nm, making the chain diameters 1.1–1.5 nm. Particle diameters: (a) ~25.3 nm, (b) ~25.7 nm, (c) ~25.3 nm, (d) ~28.4 nm, (e) ~26.5 nm. Polyethylene particle images were tilted 45° towards top of the figure. (f) Glass surface far from the tracks of transfer.

Figure 5 UHMWPE transfer film on glass, vertically (80°) replicated with 1.16 nm Pt–C and backed with 13.2 nm of carbon rotary-deposited at 100° angle. The replica is tilted 40° towards the top of the figure. Relatively straight, smooth ridges of polyethylene exist parallel to the sliding direction, although some ridges deviate slightly. Between these ridges are fields of the fine polyethylene particles deposited on wear tracks. These images suggest that the fine particles, 2–41 nm, are the smallest domain of interfacial failure deposited by the UHMWPE pin. The fine particles in this image and in Fig. 6 are deposited directly on the polyethylene transfer films whereas in Fig. 2 they were deposited on the glass.

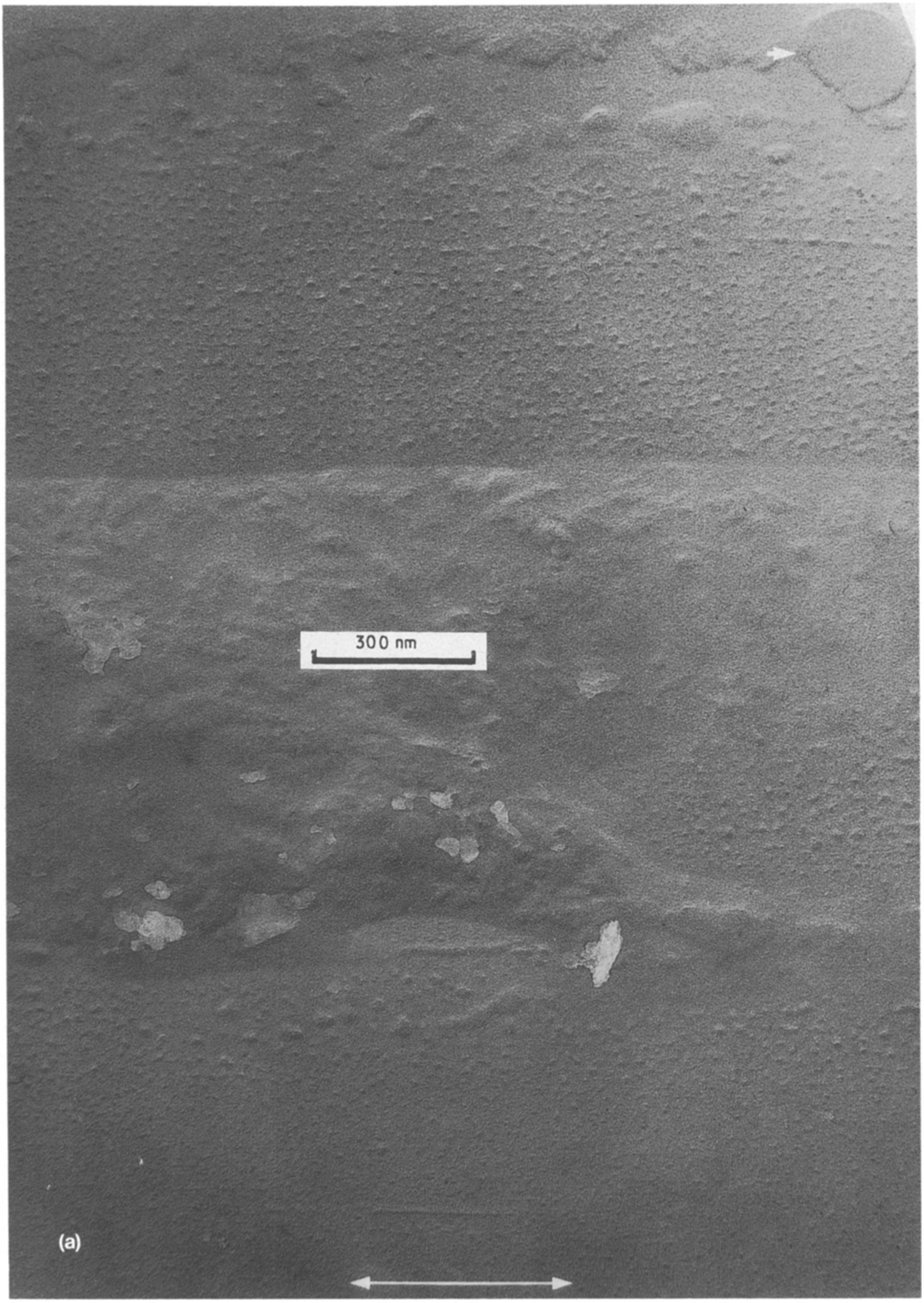
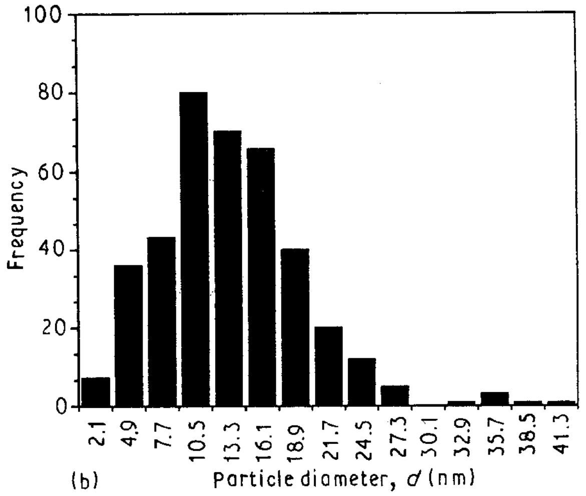


Figure 6 (a) UHMWPE transfer upon glass. This surface was replicated as in Fig. 5 and tilted 40° towards the top of the figure. A ridge of polyethylene transfer is shown at the centre of the image. Above and below this ridge are transfer film tracks covered with fine particles. The particles ranged in diameter from 2.8–40.6 nm ($d = 13.5 \pm 6.1$ nm, $n = 385$). The arrow at the upper right points to a thin plate-like deposit of about 216 nm in diameter.



(b) Distribution of fine particle diameters seen in the two wear tracks on either side of the transfer film ridge: $d_{\text{avg}} = 13.5$ nm, s.d. = 6.1 nm, $n = 385$.

transfer film ridge. The transfer tracks in Fig. 6a are covered with fine particulate UHMWPE averaging 13.5 ± 6.1 nm (2–41 nm) (Fig. 6b). The average molecular weight is $0.36–0.73 \times 10^6$, with a range from $0.0012–20.4 \times 10^6$.

The steady-state morphology near the ends of the wear track in an oscillatory contact is considerably different from the morphology observed in the central zone of Fig. 5. Large irregular deposits near the end of a wear track can be seen in Figs 7 and 8. In Fig. 7, the deposits contain plate-like particles in almost all the deposits. The length of the plates in the sliding direction ranged from 112 to 728 nm and averaged 319 ± 162 nm. At the wear track ends in Fig. 8, polymer transfer is heavy and lumpy, with dimensions of 0.1–6.4 μm. This phenomenon, characteristic of oscillatory [6, 10] and reciprocating [6] motion, has been observed extensively with scanning electron microscopy [10, 12].

The surface of liquid nitrogen fractured UHMWPE is presented in Fig. 9a and b. The UHMWPE surface appears to be mostly amorphous, with a few plate-like features similar to those seen in the transfer film in Fig. 7 as well as more organized regions which are thought to be spherulites. The spherulitic domains are similar in shape and size to the lumpy transfer features seen at the wear track ends in Fig. 8. It is likely that the cohesive failure resulting in such transfer would similarly run along the boundaries of these domains. The small UHMWPE transfer particles with diameters of the order of 2–41 nm recorded in Figs 2c and 6b are not features of the fracture surface of UHMWPE.

4. Discussion

Until now, tribological systems have generally been studied with optical microscopy or SEM because these techniques are easy to use and require a small time investment to achieve proficiency. Unfortunately these techniques cannot produce or have not produced high-resolution observations. Because of these deficiencies, we decided to use a new vertical replication technique for TEM which can routinely observe single polymer chains at 100 000 ×. More importantly, it can detect 1.0 nm step heights in mica at more modest magnifications of 20 000–26 000 ×. These unique capabilities are not shared with other replication techniques such as 45° > unidirectional, 20° > rotary, or the more cumbersome two-stage replication methods [5, 14–17]. Vertical Pt–C replicas of UHMWPE early and steady-state transfer films have made it possible for the first time to visualize nanometre-scale UHMWPE deposits and their polyethylene chains in the context of the transfer film.

The micrometre-scale UHMWPE deposits can be visualized easily by light optical or SEM techniques. In consequence, most of our theories of UHMWPE wear are concerned with micrometre-scale features. The zero-velocity condition during motion reversal at the ends of the wear track fosters the development of adhesive interactions while the polymer's viscoelasticity also increases the contact area over which these interactions can develop. Upon resumed motion, cohesive failure along domain boundaries is thought to yield the micrometre-scale transfer. Some of these large transfer particles are trapped between the pin and the counterface. It has been observed that some transfer tracks deviate from the sliding direction, suggesting that a fibril drawing process is occurring between the counterface and large wear particles which are rolling with the contact. In such small-amplitude sliding, the wear properties of the materials are dependent on the ability of third-body debris to escape the contact by having a component of motion perpendicular to the sliding direction [9].

Observation of the liquid nitrogen fractured pin shows the presence of large domains, probably spherulitic domains, within the pin. These domains correspond roughly to the micrometre-scale UHMWPE deposits on the glass counterface. Deposition during sliding probably occurs by cohesive failure along domain boundaries. This explanation would also account for the smaller, less numerous plate-like or crystal-like domains on the pin fracture face that are also similar to wear track deposits. Cohesive failure along nanoscale domain boundaries might also explain the nanometre-scale deposits although such domains are not visible within the amorphous regions of the fractured pin surface. It is highly probable that UHMWPE polymer chains exist in a condensed state since the UHMWPE pin is not drawn out after its formation under high pressure. The average diameter of the nanometre-scale deposits, 20.6 ± 6.3 nm, corresponds to a $1.3–2.6 \times 10^6$ molecular weight, which roughly corresponds to the molecular weight ($3.5–4.0 \times 10^6$) of the original UHMWPE. It is not unreasonable that pin failure occurring during the adhesive regime of wear occurs along boundaries that can separate with a minimum number of polymer chain scissions. This kind of pin failure would be the least energy-expensive. Belyi and Nevzorov [18] have previously reported up to a 50% reduction of average molecular weight for a high-density polyethylene during sliding contact. This was accomplished by first dissolving the wear track in a solvent and measuring molecular weight distributions with light scattering.

After short durations of oscillatory sliding contact, fine particles were found across the width (up to 400 nm) of "transfer tracks" which were generally coincident with the sliding direction. This suggests that they resulted from discrete, near-surface cohesive failures occurring at several points over the area of a contacting polymeric asperity. Ludema [19] suggested that, for some polymeric tribosystems, such mor-

Figure 7 UHMWPE transfer film near the end of an oscillatory wear track. The tracks of transfer can be seen to end in the upper right corner. The accumulations of polyethylene on the surface contain some plate-like particles (see short arrows). The long dimension of these plate-like particles ranged from 112 to 784 nm and had an average length of 319 ± 162 nm ($n = 20$). This surface was replicated as in Fig. 5 and tilted 40° towards the top of the figure. The light regions result from the mass-thickening effect of polymer still adhering to the replica when it was imaged.

phology could actually develop from molten film-like transfer in which surface tensions cause the continuous transfer to transform into discrete spherical forms. There is no evidence in Fig. 4 that the particles were previously liquid because the chains within the particles are not tightly associated. In this particular study, polymer surface melting was unlikely [11] considering the sliding speed selected to generate transfer films. There is also no evidence in this system that a surface film preceded countersurface particle deposition. Finally, the surface polyethylene chains adjacent to the particles in Fig. 4 are not all oriented in the

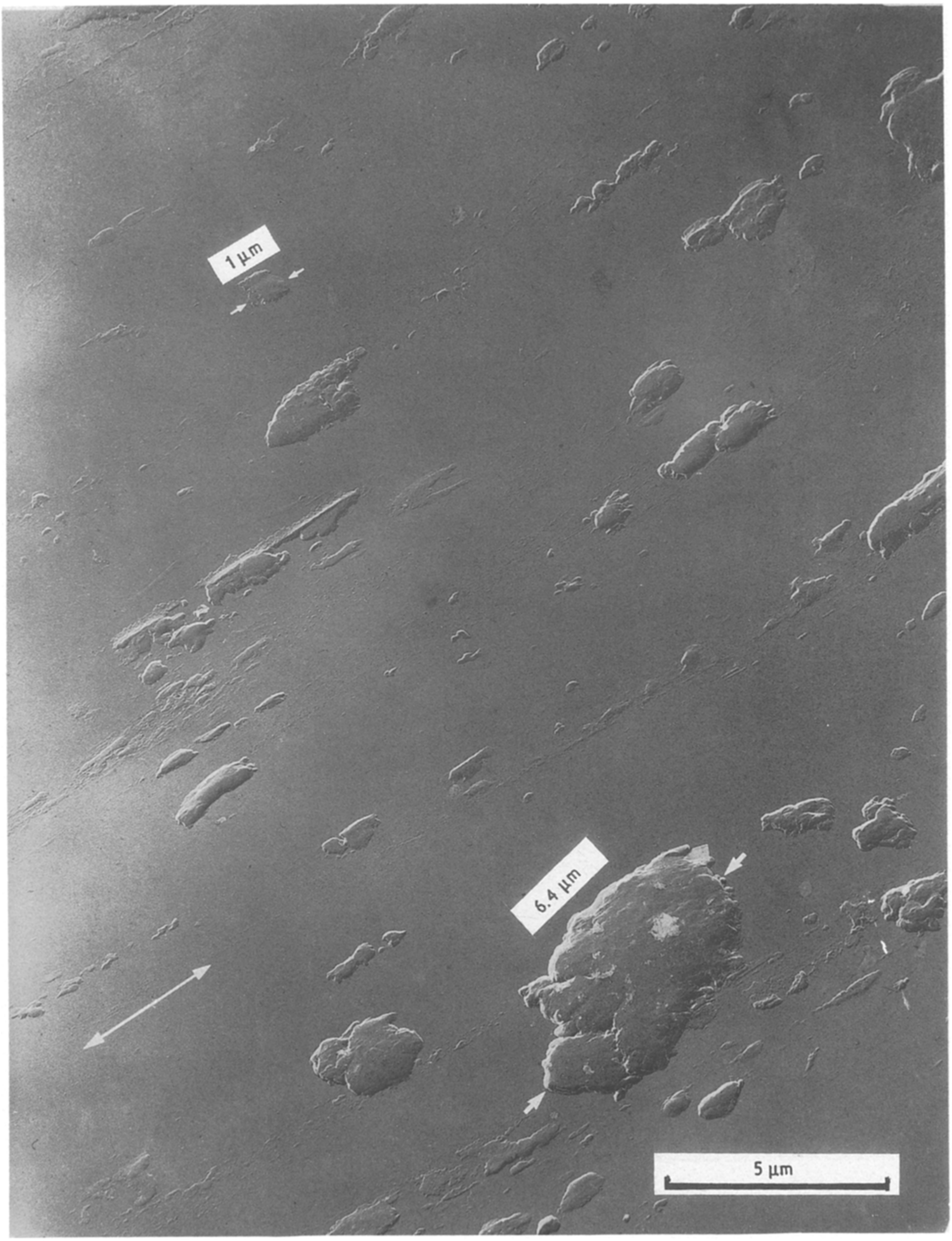


Figure 8 UHMWPE deposition near the end of the wear track on the glass counterface. This surface was replicated as in Fig. 5 and tilted 40° towards the top of the figure. The larger irregular domains which result from cohesive failure within the UHMWPE pin range in length from 0.1 to 6.4 µm in this image.

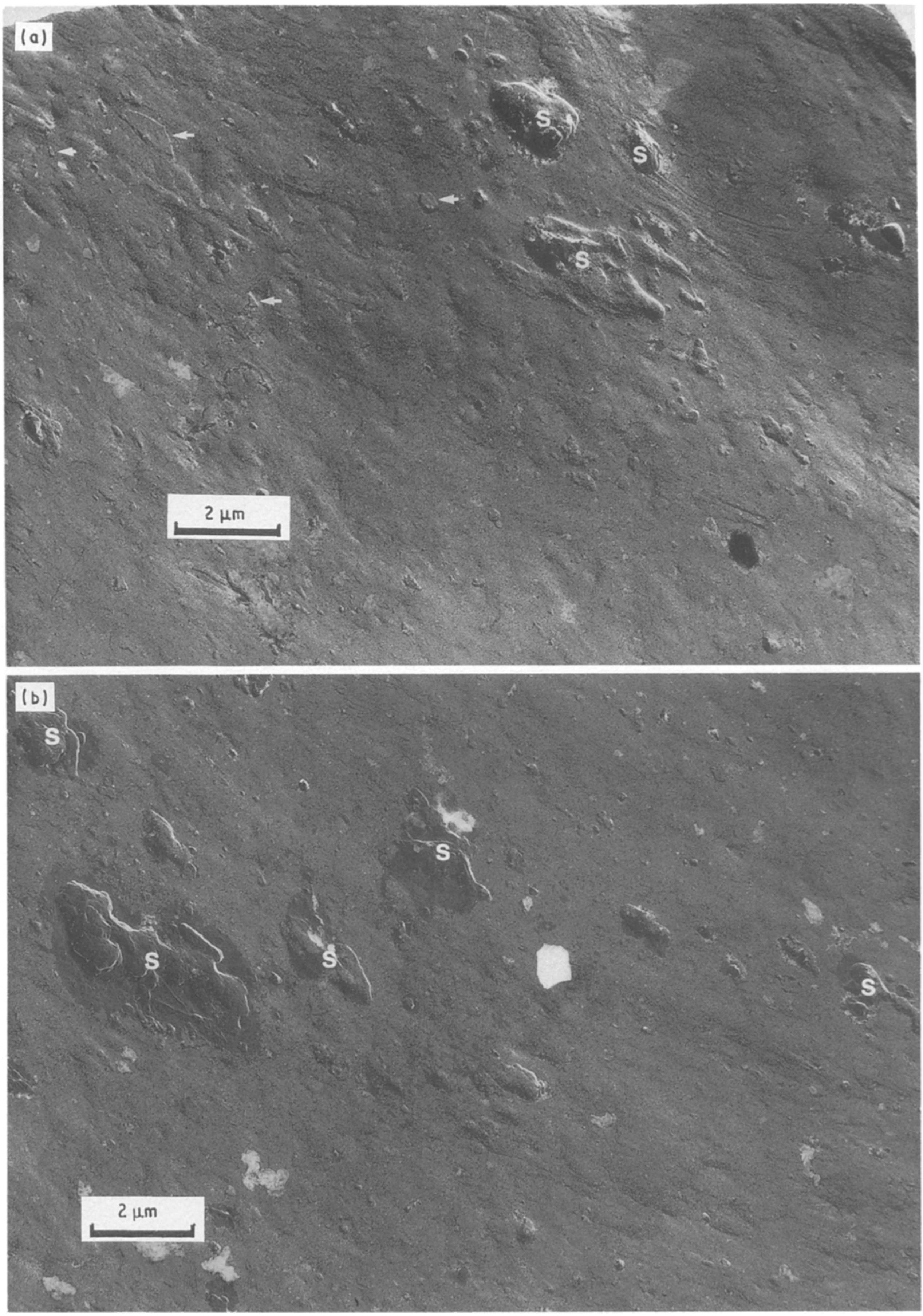


Figure 9 UHMWPE pin fractured under liquid nitrogen and vertically replicated with 1.04 nm Pt–C and backed with 13.6 nm of rotary-deposited carbon at 100° angle. The replica was tilted 45° towards the top of the figure. (a) This fracture surface suggests that the UHMWPE fractures generally like a glassy material under liquid nitrogen with some plate-like inclusions (see arrows) and with larger domains which are probably spherulites (S). The lengths of the plate-like inclusions were found to be 224, 261, 448 and 1419 nm. These lengths correspond with the lengths of the plate-like features seen in the transfer surface in Fig. 7. The larger domains marked S had lengths of 0.97, 1.87 and 3.36 µm. (b) Fracture surface like that in Fig. 9a contains large domains marked S with lengths of 1.79, 2.47, 2.76 and 4.56 µm. These domain lengths as well as those in Fig. 9a are equivalent to the lengths of the large irregular polyethylene domains seen in Fig. 8. In both Fig. 9a and b there are some smaller irregular particles, similar to the irregular transfer particles seen in Fig. 2b, having an average diameter of approximately 65 nm.

direction of sliding. This observation is consistent with the deposition of condensed polymer chain domains from the UHMWPE pin surface which would be very difficult to fully orient in the sliding direction.

5. Conclusions

Discontinuous and continuous transfer films formed during oscillatory UHMWPE pin contact with smooth glass counterfaces were replicated with 1.0–1.16 nm vertically deposited Pt–C film backed with 10–15 nm of carbon and were observed with TEM at 0.66 nm resolution roughly equivalent to the replica resolution of 0.6–0.76 nm [14]. This method provided very detailed images of the transfer films and allowed the following conclusions to be drawn:

1. The fracture surface of a UHMWPE pin, fractured at about − 190 °C, is mostly amorphous with a few plate-like inclusions, 224–1420 nm long, as well as some micrometre-scale inclusions which could be spherulitic domains (Fig. 9).
2. On the glass counterfaces after sliding contact with UHMWPE, large discrete lumps of transfer, 0.1–6.4 μm long (Fig. 8), about the size of spherulitic domains, were observed near the wear track ends where the UHMWPE pin reversed its sliding direction.
3. Within the continuous transfer films near the track ends were also found crystal- or plate-like particles with lengths ranging from 112 to 728 nm and averaging 319 ± 162 nm (Fig. 7). These plate-like particles have the same shape and length characteristics as the plate-like inclusions in the UHMWPE pin. The spherulitic domains and the plate-like inclusions in UHMWPE are probably separated by cohesive failure along their boundaries.
4. During the formation of discontinuous UHMWPE transfer films on glass, we have observed nanometre-scale deposits averaging 20.6 ± 6.3 nm (5–40 nm) in diameter (Fig. 2b and c). These particles are present during the earliest stages of film formation on the glass counterface. Average-size particles based on a hemispherical or spherical shape calculation have a 1.3 or 2.6×10^6 molecular weight, respectively, which would be a slight reduction in molecular weight ($3.5–4 \times 10^6$) if each particle were composed of a single polyethylene chain. The smallest 5 nm particles have a molecular weight of $0.0185–0.037 \times 10^6$ (~1/200–1/100 of a UHMWPE chain) whereas the 40 nm particles have a molecular weight of $9.5–19 \times 10^6$ and could contain 2–5 UHMWPE chains.
5. Nanometre-scale particles averaging 13.5 ± 6.1 nm (2–41 nm) in diameter were found in high frequency on continuous steady-state transfer films (Figs 5, 6a and b). Particles this size have a $0.36–0.73 \times 10^6$ molecular weight (1/5–1/10 of a UHMWPE chain), with a range of molecular weights from 0.0012 to 20.4×10^6. These nanometre-scale particles have no morphological counterpart on the fracture face of the UHMWPE pin. The nanometre-scale particulate deposits appear to be the result of near-surface cohesive failure of the amorphous UHMWPE surface.
6. We believe that the nanometre-scale particles make a more significant contribution to transfer film formation than the crystal- or plate-like particles and the micrometre-scale particles for two reasons: (a) the amorphous regions occupy a larger area on a UHMWPE pin fracture face than the plate-like or spherulitic inclusions (Fig. 9); and (b) the nanometre-scale deposits in discontinuous (Fig. 2a) and continuous transfer films (Figs 2b, 5 and 6) occur at very high frequency in contrast to the crystal or plate-like (Fig. 7) and micrometre-scale deposits (Fig. 8) near wear track ends which occur at much lower frequency.
7. Particle back-transfer on to the UHMWPE pin has not been detected since we have not found any holes in the transfer film. At high magnification we have observed polyethylene chains in the surface of particles and in the surface of the transfer film (Fig. 6). A fraction of these chains are not oriented in the direction of sliding. The interwoven mixture of polyethylene chain directions probably contributes to the cohesive properties of the UHMWPE transfer film.
8. High-resolution vertical Pt–C replication in conjunction with TEM has provided new high-resolution information at low magnification (7640 ×) and at high magnification (1 270 000 ×). This new method is able to observe the important tribological features in context at low magnification and then reveal molecular details at higher magnification. This unique feature is not readily duplicated by any other single microscopy technique.

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