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ADHESION AND TRANSFER
OF POLYTETRAFLUOROETHYLENE
TO TUNGSTEN STUDIED
BY FIELD ION MICROSCOPY

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16. Abstract Mechanical contacts between polytetrafluoroethylene (PTFE) and tungsten field ion tips were made in situ in the field ion microscope. Both load and force of adhesion were measured for varying contact times and for clean and contaminated tungsten tips. Strong adhesion between the PTFE and clean tungsten was observed at contact times greater than $2\frac{1}{2}$ min (forces of adhesion were greater than three times the load). For times less than $2\frac{1}{2}$ min, the force of adhesion was immeasurably small. The increase in adhesion with contact time after $2\frac{1}{2}$ min can be attributed to the increase in true contact area by creep of PTFE. No adhesion was measurable at long contact times with contaminated tungsten tips. Neon field ion micrographs taken after the contacts show many linear and branched arrays which appear to represent PTFE that remains adhered to the surface even at the high electric fields required for imaging.			
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ADHESION AND TRANSFER OF POLYTETRAFLUOROETHYLENE TO TUNGSTEN STUDIED BY FIELD ION MICROSCOPY

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SUMMARY

The adhesion between polytetrafluoroethylene (PTFE) and tungsten was studied by utilizing the field ion microscope (FIM). The tungsten FIM tip was contacted with PTFE, and the force of adhesion measured during separation. Following the contacts, the FIM tips were examined by neon field ion microscopy.

It was observed that the adhesion of the PTFE-tungsten contacts at loads of 0.20 to 0.33 milligram were highly time dependent. No adhesion forces were measurable until the contact times reached $2\frac{1}{2}$ minutes. Beyond $2\frac{1}{2}$ minutes, the adhesion force increased markedly to values over three times the load applied. The increase with contact time after $2\frac{1}{2}$ minutes can be explained in terms of the creep behavior of the polymer. With creep of the PTFE occurring, the true area of contact increases with time, and the result is a larger bonded area which must be fractured upon separation and a higher measured adhesion force.

Contacts made with tips which were contaminated with PTFE or which were exposed to air showed no measurable adhesion at long contact times, which indicated the importance of surface cleanliness in the bonding mechanism.

The field ion micrographs taken after the contacts showed heavy arrays of image spots that appeared to be remains of the PTFE that transferred to the metal surface during contact. The observation of these fragments of polymer at the high electric field imposed for neon imaging suggests a strong bonding of PTFE to the metal or a bonding mechanism dependent upon polarization which might be enhanced by the electric field.

INTRODUCTION

The fluorocarbon polymer, polytetrafluoroethylene (PTFE), has been widely studied in friction and wear research (refs. 1 and 2). Efforts have been made in mechanical

systems to utilize the polymer material because of its attractive physical and chemical properties, that is, low friction and chemical inertness. The use of PTFE as a component in a mechanical system is dependent upon the adhesion, friction, and wear behavior. It is thus of significant interest to determine the interaction of PTFE with metals under conditions where adhesion could be expected to occur.

Preliminary work by the authors (ref. 3) indicated that field ion microscopy is an important tool with which the adhesion process can be studied in atomic detail.

Earlier efforts with PTFE-tungsten contacts in the FIM indicated that PTFE adheres to a clean tungsten tip upon touch contact. It was also speculated that postcontact micrographs showed some of the PTFE adhering, as small fragments, to the tungsten surface (ref. 4). Other workers, using Auger emission spectroscopy, confirmed the transfer of PTFE to a clean tungsten surface upon touch contact by the observation of carbon and fluorine in the Auger spectrum (ref. 5).

The objective of this investigation was to study further the PTFE-tungsten contacts by field ion microscopy using a gas of lower ionization potential than helium, that is, neon, to determine if more PTFE can be observed at the lower fields and also to provide a measure of the adhesive forces involved.

APPARATUS

Field Ion Microscope System

A schematic of the FIM system used for these studies is shown in figure 1. The apparatus is basically an ion-pumped ultra-high-vacuum system. The field ion tip is mounted on the end of a cold finger which is insulated from electrical ground by sapphire disks. The cold finger can be filled with suitable cryogenic liquids to obtain the low temperatures required for imaging. Also attached to the electrically insulated end of the cold finger are electrical leads for supplying the high positive potential for imaging (0 to 30 kV) and for heating the FIM tip by resistance heating of the support wire on which the tip is welded.

At the bottom of the chamber is the intensifier and window for viewing the FIM image. The intensifier is the multichannel plate ion-electron converter commonly used in field ion microscopy for image intensification. The channel plate is proximity focused by being placed close to the phosphor coated viewing window underneath. The viewing window has a thin vapor-deposited film of aluminum on it to provide a ground. The intensifier was operated at typical direct-current voltages of 600 to 800 volts across the plate and 2500 volts between the bottom of the plate and the grounded screen. The postcontact imaging was conducted with high-purity neon gas which was bled into the evacuated

chambers to a pressure of 10^{-5} torr. The image was photographed with an oscilloscope camera mounted below the viewing window.

Contactor Apparatus

The device used to make the mechanical contacts of PTFE on tungsten field ion tips is shown schematically in figure 2. The device is basically a stainless-steel beam mounted on a taut band. On the far end of the beam is a small permanent magnet which interacts with two electromagnets, above and below, outside of the glass vacuum tube. The electromagnets are wired so that like magnetic poles face each other. By varying the voltage to these electromagnets, the beam can be made to move either up or down. Also attached to the beam is a flat which serves to intercept some of the light from a lamp. This flat casts a shadow on a photoresistor; thus, any motion of the beam causes an output change in a photoresistor circuit. This photoresistor circuit is used in conjunction with one of the electromagnets to stabilize the beam against sway and vibration.

On the end opposite the bar magnet is the contact sensor platform. The contact sensor platform is moved into a position directly beneath the field emitter tip for contact by the compression of the horizontal bellows (see fig. 1).

The sensor for determining the contact is similar in principle to the photoresistor circuit just described. The PTFE is mounted on a thin foil which is free to move upward or downward when a suitable force is applied. The PTFE was approximately 1 centimeter square and 0.10 millimeter thick and was attached to the foil with a high-vacuum epoxy cement. The foil is bent over at one side so as to cast a shadow on a vacuum bakeable silicon solar cell. When the PTFE-covered foil contacts the tip, the foil is depressed; this depression causes a change in the illumination received by the cell and thereby reduces the cell output voltage. Upon separation, the foil is pulled upward by the adhesive force, and thus the output voltage of the cell is increased.

The sensor for determining the contact also serves to give a measure of both the force of contact and the force necessary to separate (force of adhesion). Calibration of the load and breakaway force are accomplished by the use of an electronic balance with a sensitivity of better than 10 micrograms.

A typical recorder trace taken during separation and fracture of the interface is shown in figure 3. The drift of the sensor prior to the start of retraction is due to the temperature change occurring at the silicon solar cell because of the contactor being pushed into the cold finger shroud for the contact. The foil supporting the PTFE is suddenly pulled away from the tip back to the zero load position. When the force applied during separation exceeds the force of adhesion, the junction of the PTFE tungsten tip fractures.

The approach and retraction of the contactor are conducted by a reversible motor-driven potentiometer which controls electromagnet voltage. The motor-driven system ensures a smooth gradual pull during separation.

In order to reduce the effects of ambient vibration on the experiments, the entire FIM system, including pumps, power supplies, gas system, and so forth, are mounted on an air-piston-suspended vibration isolation table with a natural frequency of 1.1 hertz.

PROCEDURE

The procedures for the PTFE-tungsten contacts are similar to those employed in the study of references 3 and 4. The tungsten FIM tips were prepared by appropriate electrochemical etching in dilute sodium hydroxide solution and were mounted in the FIM. Some of the tips were used for more than one contact after having been suitably cleaned by field evaporation. The system was then evacuated and baked for a minimum of 12 hours. After bakeout, the system pressure was 10^{-10} torr.

Following bakeout, the tip was imaged with either helium or neon at 10^{-5} torr and field evaporated to perfect the tip surface crystallographically. A before-contact micrograph was then taken, and the image gas was pumped out. In most cases the tip was kept at cryogenic temperature during the contacts, although the temperature in the contact zone probably approached the temperature of the bulk PTFE rapidly.

When the pressure reached 10^{-10} torr, the field was turned off and the contact procedure was initiated. The time required to make the contact was generally less than 30 minutes. Previously it was shown that no significant interaction with the ambient environment or strain release effects were observed in micrographs taken after equivalent or longer field off times at this pressure (ref. 3).

After contact and retraction, the voltage was turned on, and the after-contact images were obtained by readmitting the image gas.

RESULTS

The PTFE-metal contacts were made in situ in the FIM by utilizing a tungsten FIM tip. Tungsten was used as the tip material because of the ease and reliability of imaging it. A series of contacts was made in which the time the PTFE remained in contact with the tungsten tip varied. Figure 4 shows a before-contact micrograph of the tungsten tip. For reference some of the major planes of the tungsten micrograph are indexed.

Figure 5 presents a neon field ion micrograph taken after PTFE contact with a contact time of slightly less than 1 minute. For all the contacts, the loads were in the range 0.20 to 0.33 milligram and were held constant during the contact time. The contacted

tungsten surface shows many large bright multiatom clusters and some very faint rodlike orientations. Upon separation of the PTFE from the tip, no adhesive force was measurable.

Figure 6 is another micrograph taken prior to contact of the tungsten FIM tip, and figure 7 was taken after a 2-minute PTFE contact. Again numerous clusters and several linear orientations are observed. However, no force of adhesion was measured at separation.

At a contact time of $2\frac{1}{2}$ minutes, the force of adhesion was large enough to measure. With a load of 0.33 milligram applied for $2\frac{1}{2}$ minutes, a force of 0.05 milligram was required to separate the tip from the PTFE. This corresponds to an adhesion coefficient of 0.16 (ratio of force of adhesion to force of load). A second contact was made with a cleaned and field-evaporated tip under a similar load (0.28 mg). Again, the force to separate was measurable (0.05 mg), and the coefficient of adhesion was 0.19.

The contact time was next increased to 3 minutes. Figure 8 is the before-contact micrograph. (Note it is the same tip as was used for the 2-min contact, having been field-evaporated to remove the adhered transferred material.) Figure 9 is the micrograph taken immediately after the 3-minute PTFE contact. The micrograph is similar to those previously discussed, and some of the same features are observed. The force of adhesion at this contact time was very pronounced. At a load of 0.22 milligram, the force of adhesion was 0.37 milligram, and the coefficient of adhesion was 1.7, which is approximately 10 times that obtained at a time of $2\frac{1}{2}$ minutes.

At a contact time of 4 minutes, the adhesive force again increased markedly. Figure 10 is the before-contact micrograph. Two 4-minute PTFE tungsten contacts were made, both with loads of 0.29 milligram; under these conditions separation forces were measured at 0.78 and 0.92 milligram. These values yield adhesion coefficients of 2.7 and 3.15, respectively. Figures 11 to 13 are postcontact micrographs taken at increasing voltages. Figure 12 is taken at 500 volts higher than figure 11, and figure 13 at 750 volts higher than figure 11. Again many clusterlike sets of image points are evident. Some of these, possibly representing linear and branched PTFE chains, remain adhered to the surface.

The 5-minute contact was made at an applied load of 0.39 milligram with the adhesion force measured at 0.93 milligram. Figure 14 shows electron emission patterns taken immediately after PTFE contact and again after a positive potential of 7.0 kilovolts had been applied to the tip. The positive potential produced an electric field of the magnitude necessary for neon imaging of the tip. The emission pattern in figure 14(a) shows the presence of the transferred PTFE on the surface, while the emission pattern in figure 14(b) indicates that the high electric field applied did not return the tungsten surface to the clean state by desorption. This effect further indicates that some of the transferred PTFE may indeed be visible in the neon micrographs. The fact that the emission patterns show very large regions of local brightness does not necessarily indicate that

the transferred PTFE on the surface would be of that size. During emission, molecular patterns can be from 10 to 100 times larger than could be expected from actual dimensions (ref. 6).

A final contact was made with the contact time increased to 6 minutes. Figure 15 is the before-contact micrograph and figures 16 to 18 are postcontact micrographs taken at 6.25, 6.50, and 6.75 kilovolts, respectively. Many of the characteristic features (e.g., linear and branched arrays) are noted. The force of adhesion for an applied load of 0.29 milligram was 1.0 milligram or an adhesion coefficient of 3.5.

In order to determine what effect the cleanliness of the tip had on the adhesion force, experiments were made with tungsten tips that were not clean. A 4-minute contact made with a tip that was still covered with transferred PTFE from a previous contact showed no measurable adhesion during separation. Another contact made at a 5-minute contact time with a previously clean tip exposed to air also showed no measurable adhesion during separation. These results clearly indicate the importance of the state of the metal surfaces for significant polymer bonding to occur. The results of all the contacts are summarized in figure 19.

DISCUSSION

The PTFE-tungsten contacts showed, as suggested in earlier work, that PTFE does adhere to tungsten upon normal contact when the tungsten is in the clean state. The magnitude of the adhesion force is much larger than might have been expected in view of the generally accepted low friction property of PTFE-metal couples. The fact that the adhesion force increased with contact times beyond $2\frac{1}{2}$ minutes indicates that the force of adhesion is significantly affected by time-dependent creep in the polymer. The PTFE and foil during contact is in a region that is cryogenically cooled; thus, the temperature of the PTFE is reduced below room temperature somewhat. Since the creep is highly temperature dependent, the fact that no adhesion was measured during the first 2 minutes might be due to a reduction in the creep rate by the cooling effect of the cryogenic cold finger shroud. Thus, even at the high stress levels the creep rate may be reduced during the initial minutes in contact, and immeasurably small adhesion measurements may result. The bonding of PTFE to clean metal surfaces has been noted to be very strong by investigators studying the friction properties of PTFE. The mechanism for this bonding is, however, not yet known. With the view that PTFE is chemically inert, and thus chemical bonding unlikely, Makinson and Tabor suggest the possibility of Van der Waals bonding (ref. 7).

Other investigators working with polymer-metal adhesion couples suggest an electrostatic contribution to the observed force of adhesion. This occurs as a result of electrons existing external to the metal in the dielectric (ref. 8). Regardless of the bonding

mechanism(s), the bonding would be nearly instantaneous, so the increase in adhesion force with contact time can only be reasonably explained in terms of increasing the total force. This occurs by increasing the area of contact while the force per unit area remains relatively constant. Such an observation is not in conflict with the observed creep behavior of PTFE at significantly lower stress levels than those generated by these contacts (refs. 9 and 10).

During the microscopic study of PTFE-metal sliding couples, Steijn (ref. 11) reports that chains of PTFE are drawn out of the bulk in long highly oriented fibers and are oriented normal to the direction of sliding. This observation is consistent with the requirement that some minimum binding of the polymer to the metal surface occur. Although in these experiments no tangential forces were applied, the forces being as close as possible to strictly normal, the same drawing of the PTFE out of the bulk could be expected. The PTFE linear fiber could be a single chain 5.62×10^{-10} meter (5.62 Å) in diameter, the chain lengths being up to several micrometers long. The chain itself has a zig-zag backbone of gently twisted -CF₂- groups that completely twist 180°, every 13 groups yielding a repeat distance of 16.9×10^{-10} meter (16.9 Å) (ref. 2). Thus, the PTFE that adheres to the tungsten would initially be in the form of linear chains.

As the high electric field is applied for imaging after contact, those chains normal or oblique to the surface may be subject to scission. Those chains lying on the surface might well be undisturbed and yield an image.

Some chains, however, could be subject to effects similar to those occurring in the CASING (cross-linking by active species of inert gases) treatment of polymers or those observed by electron bombardment, specifically further scission and some cross branching of the chains (ref. 12). The postcontact micrographs taken during these experiments show many linear arrays of image spots which could well represent linear chains of PTFE on the surfaces (e.g., fig. 17) as well as arrays which could be the image of branched chains (e.g., fig. 12). If the bonding is polar in nature, it is possible that the applied field might further increase the polarization and thus the bonding. This would result in retaining of the PTFE at field strengths where other organics are known to desorb. This is a system where the application of the atom-probe field ion microscope would be of use.

SUMMARY OF RESULTS

Mechanical contacts between tungsten field ion tips and polytetrafluoroethylene (PTFE) were made in situ in a field ion microscope vacuum system. Contacts were made under similar loads but varying contact times and degrees of tungsten cleanliness. The following results were obtained:

1. Strong adhesion between PTFE and clean tungsten occurred upon normal contact in the load range 0.20 to 0.33 milligram at contact times exceeding $2\frac{1}{2}$ minutes. At contact times less than $2\frac{1}{2}$ minutes, the force of adhesion was too small to measure.

2. The increase in adhesion force with contact time appears to be related to an increase in true contact area by creep (cold flow) occurring in the PTFE.

3. No adhesion was measurable when the tungsten tips were contaminated by either PTFE or air.

4. Field ion micrographs taken after the contacts show many linear and branched arrays of image spots on the tungsten surfaces which appear to be fragments of the PTFE that remain adhered to the tungsten surface even at the high fields required for neon imaging.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 11, 1972,
114-03.

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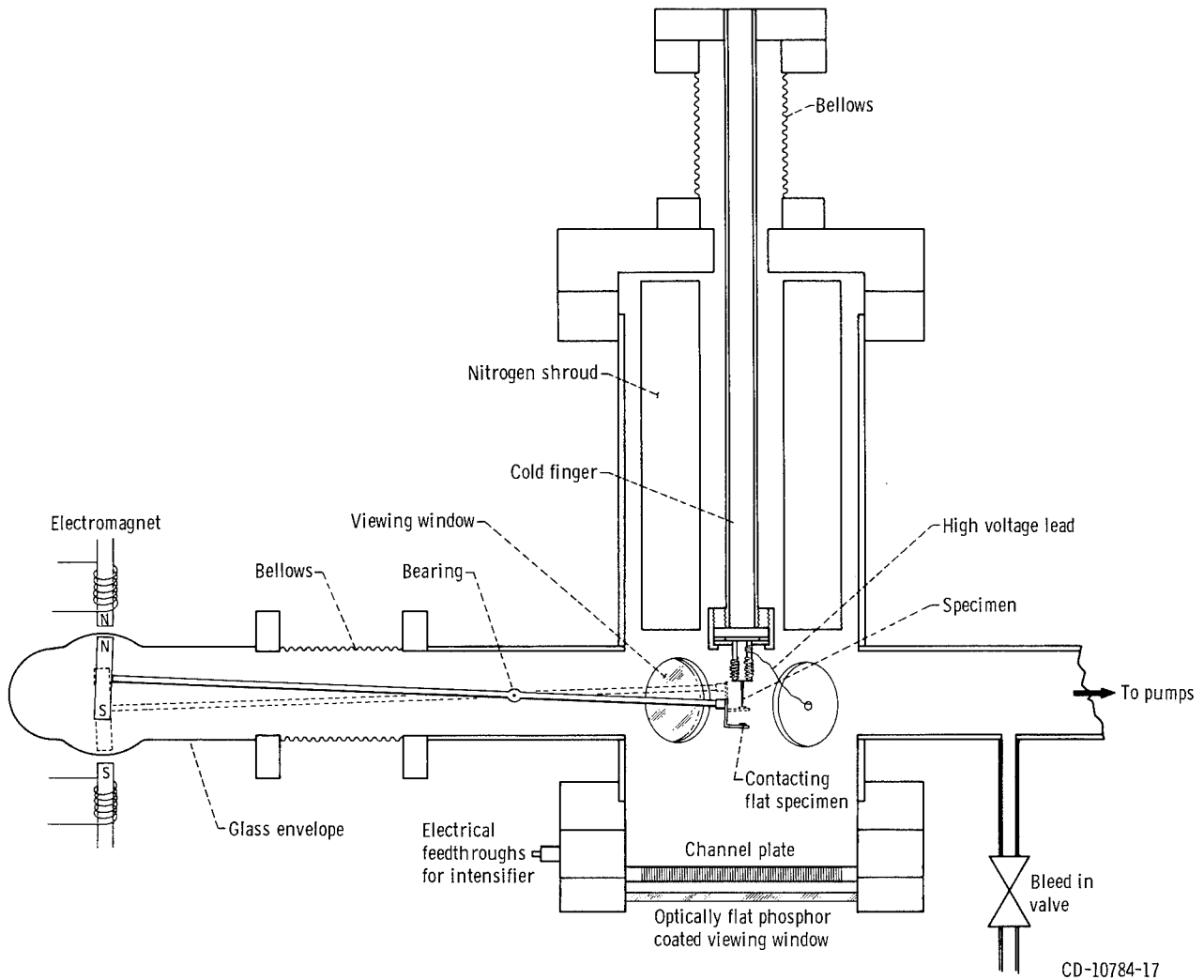
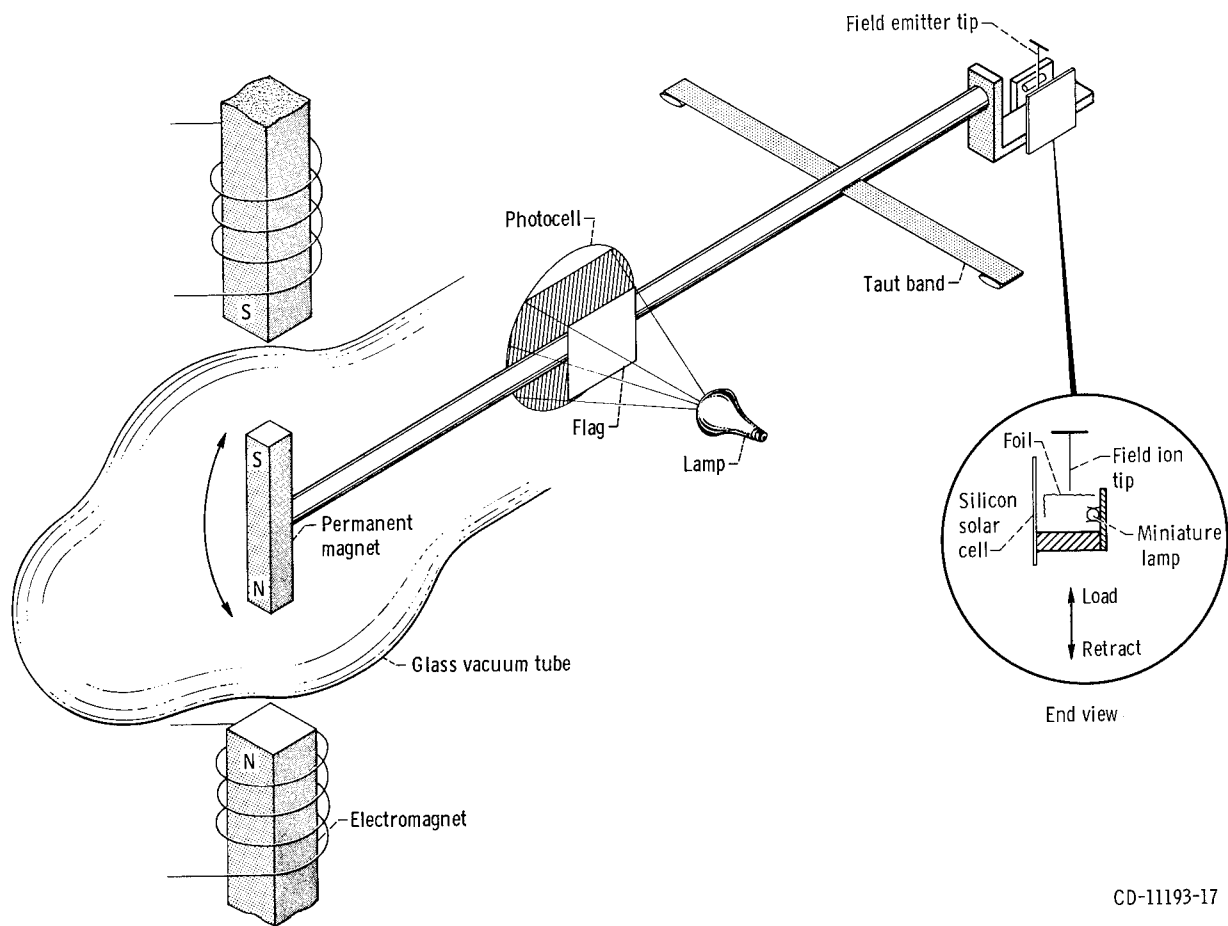


Figure 1. - Schematic of field ion microscope.



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Figure 2. - Field ion microscope emitter tip contact apparatus.

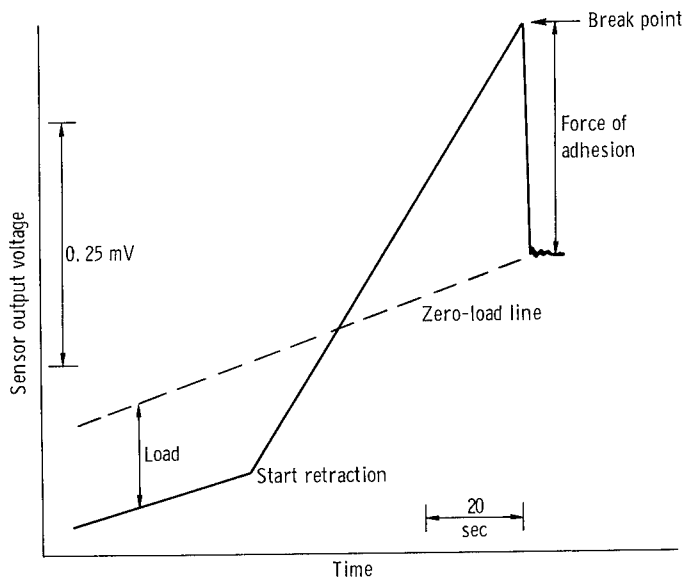


Figure 3. - Sensor output voltage during separation of PTFE-tungsten contact of 4 minutes duration.

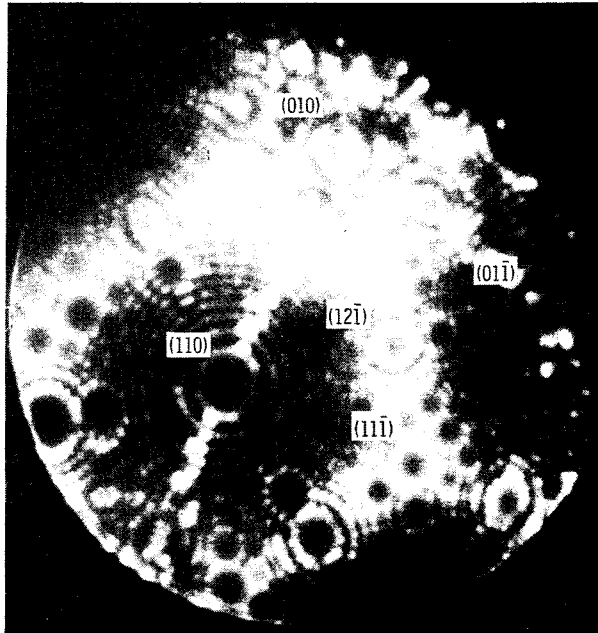


Figure 4. - Tungsten prior to PTFE contact. Applied voltage, 8.25 kilovolts; helium image gas; liquid nitrogen cooling.

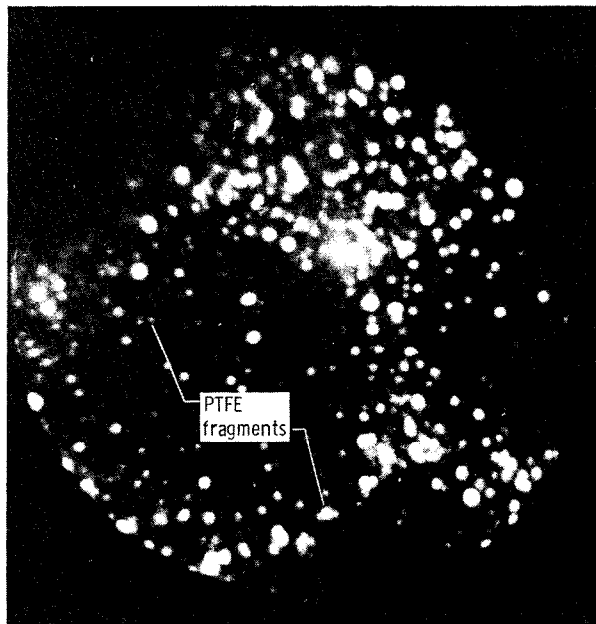


Figure 5. - Tungsten after PTFE contact for 1 minute. Applied voltage, 5.5 kilovolts; neon image gas; liquid nitrogen cooling.

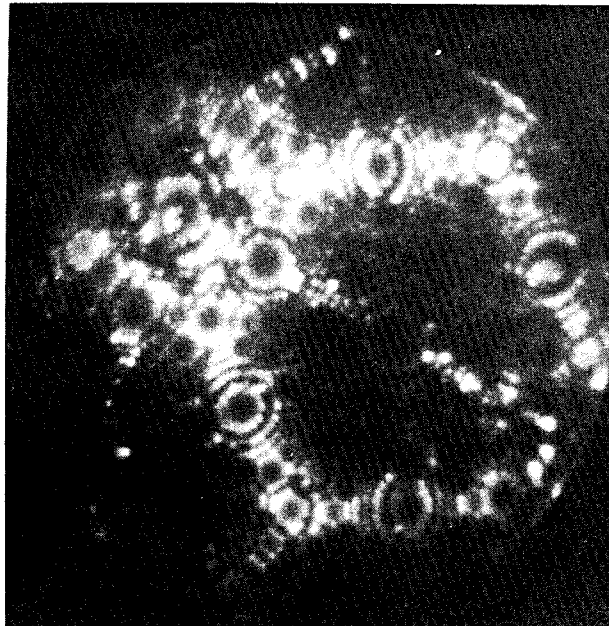


Figure 6. - Tungsten prior to contact. Applied voltage, 8.5 kilovolts; helium image gas; liquid nitrogen cooling.

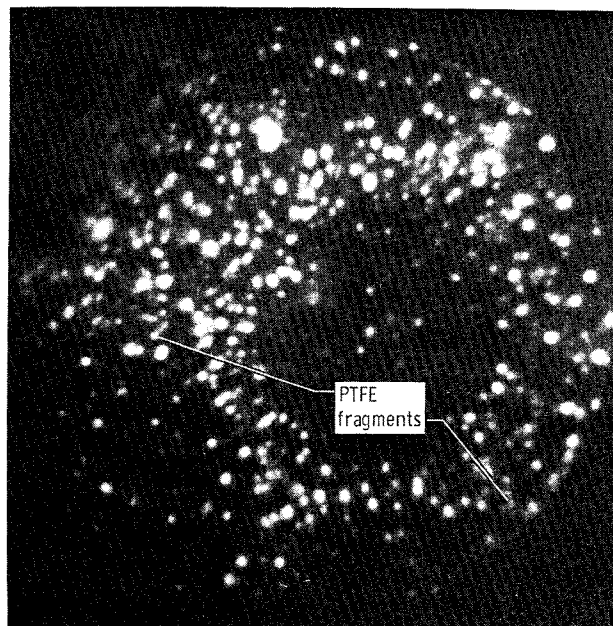


Figure 7. - Tungsten after PTFE contact for 2 minutes. Applied voltage, 6.0 kilovolts; neon image gas; liquid nitrogen cooling.

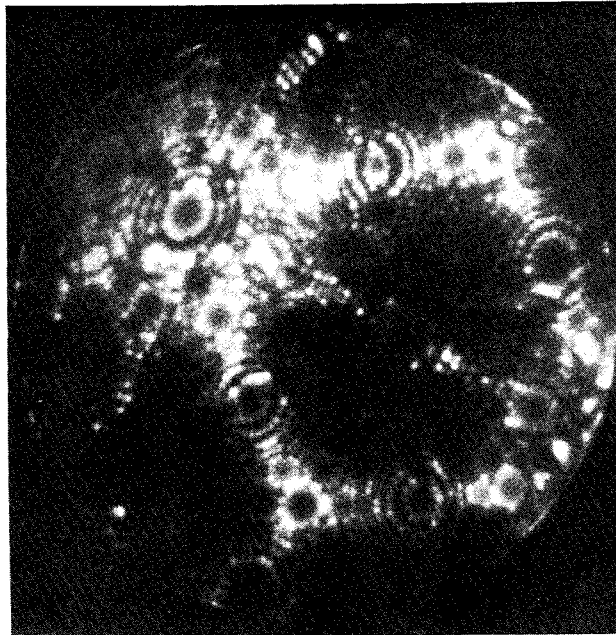


Figure 8. - Tungsten prior to contact. Applied voltage, 7.0 kilovolts; neon image gas; liquid nitrogen cooling.

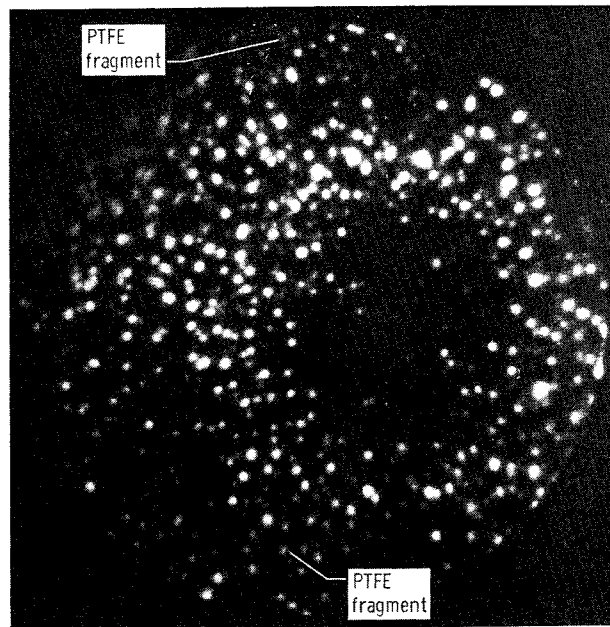


Figure 9. - Tungsten after PTFE contact for 3 minutes. Applied voltage, 6.25 kilovolts; neon image gas; liquid nitrogen cooling.

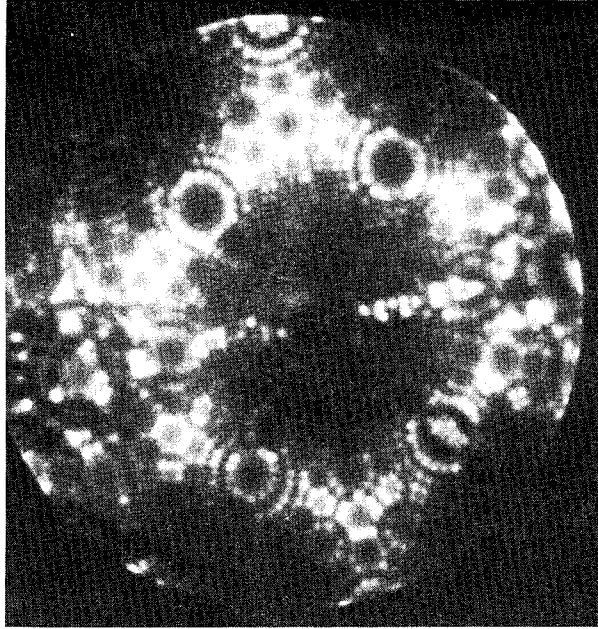


Figure 10. - Tungsten prior to contact. Applied voltage, 6.75 kilovolts; helium image gas; liquid nitrogen cooling.

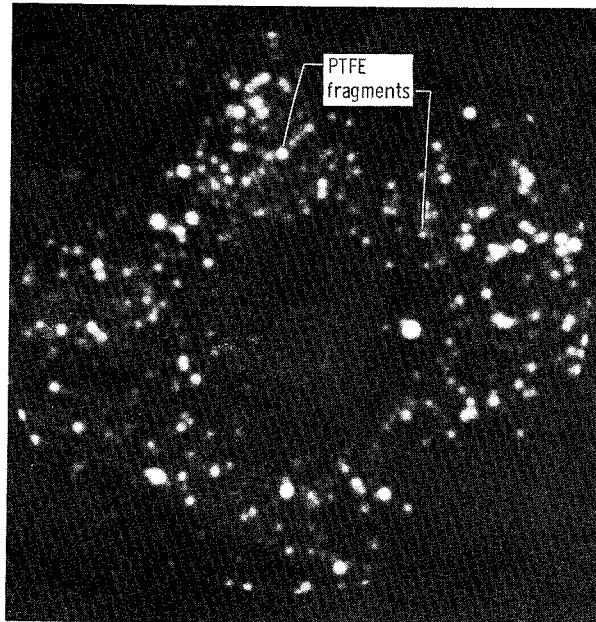


Figure 11. - Tungsten after PTFE contact for 4 minutes. Applied voltage, 4.5 kilovolts; neon image gas; liquid nitrogen cooling.

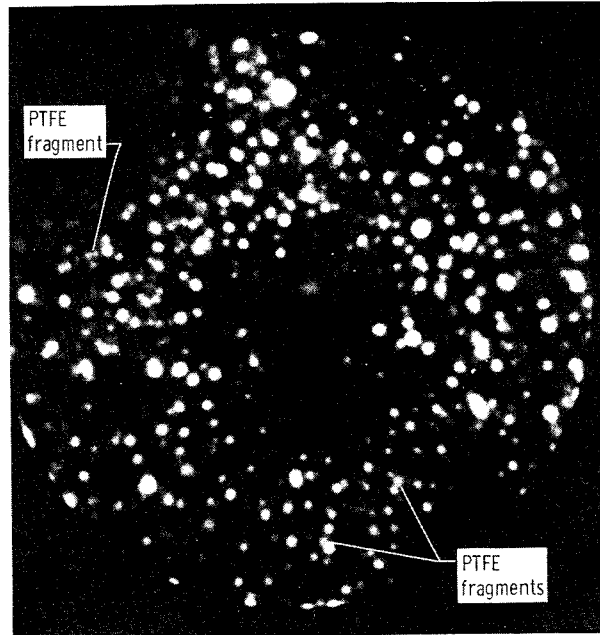


Figure 12. - Tungsten after PTFE contact for 4 minutes. Applied voltage, 5.0 kilovolts; neon image gas; liquid nitrogen cooling.

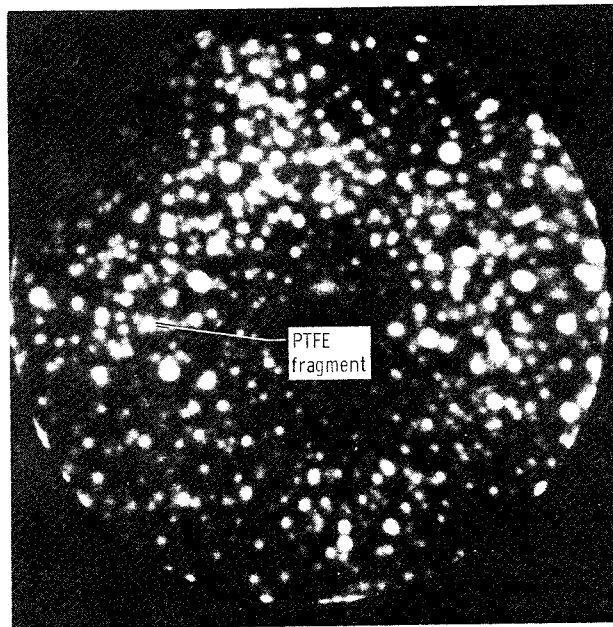
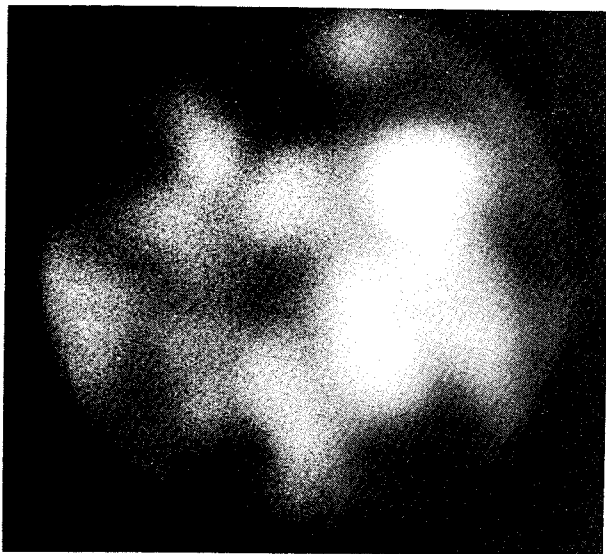
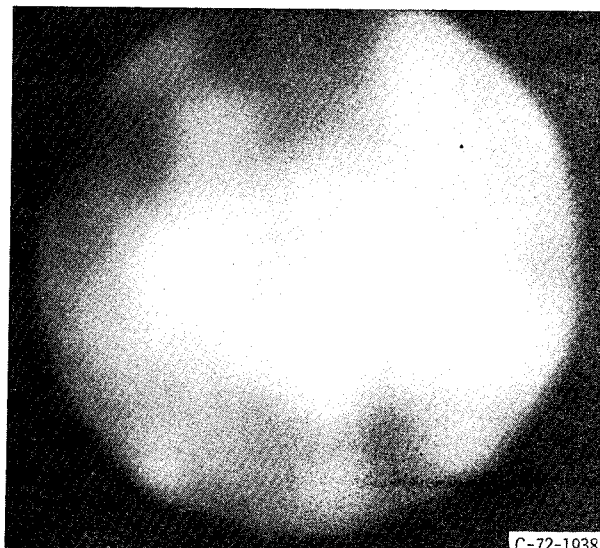


Figure 13. - Tungsten after PTFE contact for 4 minutes. Applied voltage, 5.25 kilovolts; neon image gas; liquid nitrogen cooling.



(a) Tungsten tip emission pattern after 5-minute contact with PTFE.



(b) Emission pattern from tip in (a) after positive 7.0 kilovolts were applied.

Figure 14. - Emission patterns from tungsten tip after PTFE contact before and after neon imaging field was applied (in vacuum).

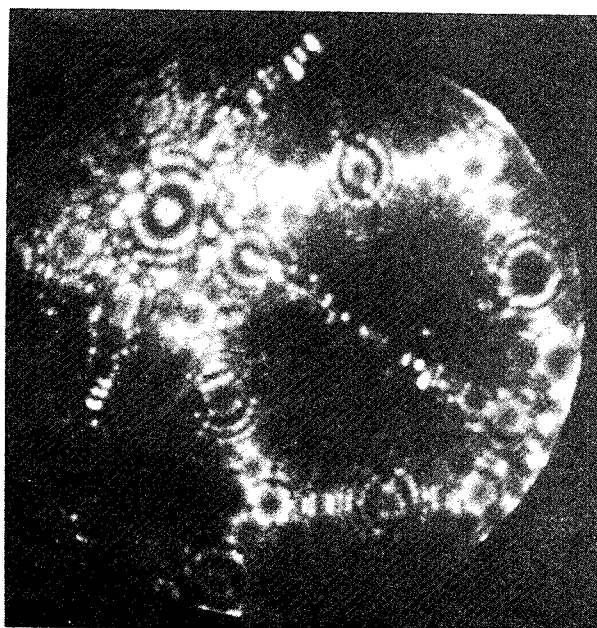


Figure 15. - Tungsten prior to contact. Applied voltage, 7.25 kilovolts; neon image gas; liquid nitrogen cooling.

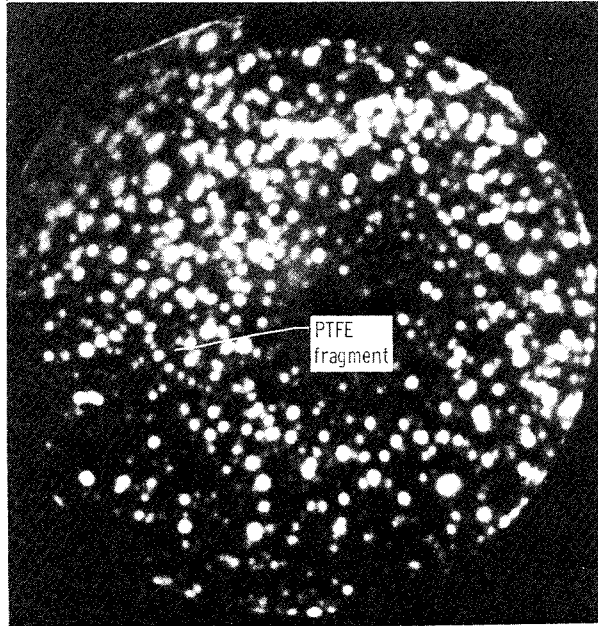


Figure 16. - Tungsten after PTFE contact for 6 minutes. Applied voltage, 6.25 kilovolts; neon image gas; liquid nitrogen cooling.

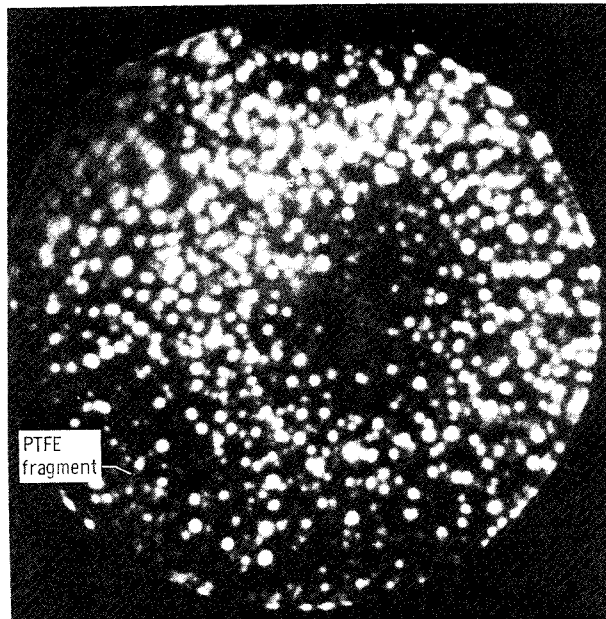


Figure 17. - Tungsten after PTFE contact for 6 minutes. Applied voltage, 6.5 kilovolts; neon image gas; liquid nitrogen cooling.

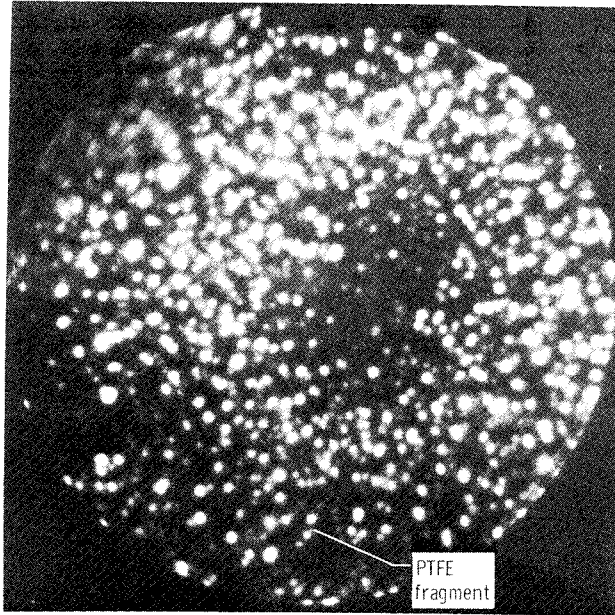


Figure 18. - Tungsten after PTFE contact for 6 minutes. Applied voltage, 6.75 kilovolts; neon image gas; liquid nitrogen cooling.

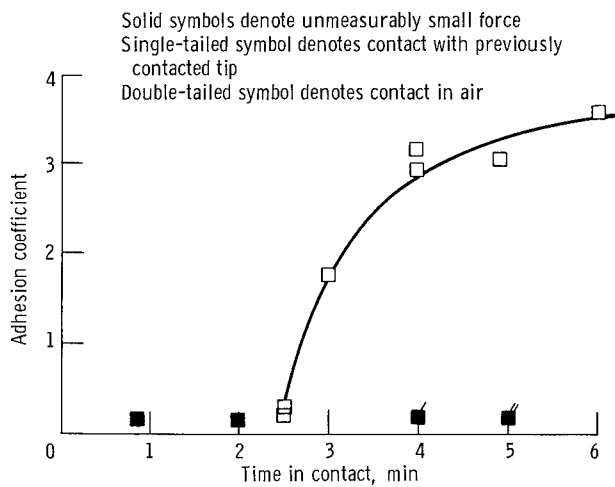


Figure 19. - Adhesion coefficients for PTFE-tungsten contacts.