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EXPERIMENTAL STUDY OF THE COATING FORMED ON NITRIDED-STEEL PISTON RINGS DURING OPERATION IN NITRIDED-STEEL CYLINDERS

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ADVANCE CONFIDENTIAL REPORT

EXPERIMENTAL STUDY OF THE COATING FORMED ON NITRIDED-STEEL PISTON RINGS DURING OPERATION IN NITRIDED-STEEL CYLINDERS

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SUMMARY

Nitrided-steel piston rings that were run in nitrided-steel cylinder barrels showed material of high reflectivity on their running faces. The structure of this material could not be resolved at a magnification of 1500 diameters. No usual strong acid or base was able to attack the outermost skin of the coating and only a few of the reagents tried would attack the subsurface portion of the coating. The Bierbaum microhardness of the coating is 2500, nearly that of the nitrided case. No chemical, electrographic, or spectrographic analysis could be made because of the inertness and the small amount of material present. The coating formed to a thickness of about 0.0001 inch in the surface of the piston rings and was raised above the nominal surface of the rings by 0.00001 to 0.00002 inch. Working was apparent in the ring material directly beneath the coating. The coating was also present in the surface of the cylinder barrel but to a lesser extent. It is believed that (1) the coating was formed by the local melting or softening of the nitrided surface and subsequent sudden cooling; (2) this material is beneficial to the operation of nitrided-steel piston rings; and (3) the coating can be artificially produced on nitrided rings prior to service operation.

INTRODUCTION

The presence of a material formed in the running faces of nitrided-steel piston rings during operation has been observed by the Army Air Forces, Materiel Command, and by the NACA. This material showed high reflectivity when properly illuminated and viewed. Examination at high magnification indicated that the structure of the coating could not be resolved at a magnification of 1500 diameters. The coating was found to be extremely hard, and chemical tests indicated that it was also highly corrosion-resistant.

Material formed on sliding surfaces has been noted by C. Fayette Taylor, J. T. Burwell, Jr., J. Wulff, and H. W. Fox of the Massachusetts Institute of Technology. The material found by these men occurred as eruptions on the surfaces of steel disks that had been run-in against chilled cast-iron disks.

Nitrided-steel piston rings are in the late experimental stage, that is, they are not yet used on combat aircraft, and the question of whether the coating is beneficial immediately becomes important. The answer to this question involves a study of the physical and chemical properties of the coating and a determination of its origin. At the request of the Army Air Forces, Materiel Command, an investigation was therefore conducted at the Aircraft Engine Research Laboratory of the NACA at Cleveland, Ohio, in the summer of 1943.

The primary objects of the investigation were: (1) the determination of the origin of the coating, that is, whether the material was formed from the ring metal or the barrel metal and (2) the determination of the physical and chemical characteristics of the coating. A secondary object was to show whether the coating was detrimental or beneficial to piston-ring and cylinder-barrel operation.

Photomicrographs of piston-ring sections are presented to illustrate the physical structure of the coating material, to show the effects of various etching reagents on the material, and to indicate the probable origin and the process of formation of the material.

APPARATUS

Although the coating in piston rings can be examined with vertical illumination, the setup illustrated in figure 1 was used for visual observation because of the greater ease of viewing. A metallurgical microscope was used for all plan-view photomicrographs at magnifications of from 40 to 70 diameters.

Interference patterns of the coating on the rings were made by placing an optical flat next to the piston-ring face and photographing the face through the flat. Sodium light was used to illuminate the specimen.

A Bierbaum microcharacter (a scratch-hardness tester) using the 9-gram load and a metallurgical microscope with a filar micrometer were used for microhardness determinations.

A grating spectrograph was used for the spectrographic analysis. A sensitive dial gage, on which 3/64 inch was equivalent to 0.00005 inch, was used in an attempt to determine the height of the coatings.

TESTS AND RESULTS

Photomicrographs of nitrided-steel piston rings are presented for convenience of reference. Figure 2 illustrates the cross section of a typical nitrided-steel piston ring. The polished and etched cross section shows the unnitrided core, the thick, dark-appearing nitrided case, and the thin shell of "white" nitrides. The entire ring is covered with white nitrides immediately after nitriding, but the white layer is subsequently removed by machining except at the corners. Figures 3, 4, and 5 are highly magnified details of the core, the case, and the white edge, respectively. The isolated dark spots shown in figure 2 are inclusions in the original unnitrided steel as may be seen from figure 6, which is a photomicrograph of an unetched polished cross section. All specimens intended for cross-sectional observation were plated with nickel before polishing in order to back up the surface profile and prevent rounding of the specimen edges during the polishing operation.

Occurrence of Coating

Observations of nitrided rings after operation indicated that the coating in a piston-ring face may occur in a mottled condition (fig. 7) or a relatively continuous condition (fig. 8). Inspection of many piston rings indicates that the rings which have operated the longest periods show a more nearly continuous appearance of coating than the rings which have operated for shorter periods. The running surface of the barrel appears to contain only small amounts of the coating. (See fig. 9.)

When a ring that contained coating material was sectioned, polished, and etched with the usual metallographic etching reagents for steel, such as 2 percent nital (nitric acid plus ethyl alcohol), the coating was difficult to observe. (See fig. 10.) When the same section was etched with potassium or sodium hydroxide, the coating material was attacked (fig. 11) and was clearly visible. No crystal structure was resolved in the coating layer even at the magnification of 1500 diameters.

Evidence that the formation of the coating material is negligible in the portions of a ring where white nitrides are present is given in figure 12. The nitrided ring shown in this figure was run in a nitrided barrel and it can be seen that the white nitrides have formed little coating material. Figure 13 shows the portion of the ring immediately adjacent to the portion shown in figure 12 and it can be noted that, except for the white edge seen in figure 12, the coating layer is continuous.

No evidence of pitting was found to indicate that the coating material consists of material detached from one sliding surface and deposited on the other.

Thickness of Coating

The thickness of the coating (determined in every case by sectioning) was 0.0001 inch or less. Figure 14 illustrates a magnitude of thickness typical of most coating layers viewed. The chief exception to this thickness measurement is shown in figure 12 where the thickness of the layer has reached 0.00025 inch.

Height of Coating above Nominal Surface

The coating, as a rule, tended to fill hollows in the surface profile of the piston ring. (See fig. 11.) The distortion in a large field of view inherent in photomicrographs made at high magnification made difficult the determination of the relative heights of coating and basis material of the piston ring. The relative heights of the coating and the basis material were determined by light-interference methods. An optical flat placed next to the running face of the piston ring and illuminated by a sodium lamp produced the interference rings shown in figure 15. The distance between adjacent dark bands represents a difference of 0.00001 inch (1/2 wave length of sodium light) in the distances between the surface of the ring and that of the optical flat at the bands. In order to find the height of the material above the basis metal, it is only necessary to count the interference fringes between the top of the coating surface and an adjoining region of basis metal and to multiply by 0.00001. The coating in these tests was from 0.00001 to 0.00002 inch above the nominal surface of the particular specimen.

The photomicrograph of coating material on a cylinder barrel (fig. 9) shows conclusively by light reflection that the coating was raised above the nominal cylinder surface. For convenience, the geometry of light reflection from the coating on a cylinder barrel is shown in figure 16. If the coating were to form as a build-up on the cylinder barrel, the bright sides of the build-up would face the source of illumination. If pits were formed, those parts of the pits away from the direction of illumination would become most brilliant. Figure 7, which is a photomicrograph of a nitrided-steel piston-ring face under oblique illumination, similarly, shows by light reflection that the coating material is slightly raised above the nominal surface of the piston-ring face.

Inconclusive results as to the relative heights of the coating on the cylinder barrel were obtained from tests with a sensitive dial gage. A precision mechanical stage to position the specimen would be necessary in order successfully to use a dial gage.

Chemical Characteristics

The outermost skin of the coating appeared to be extremely corrosion-resistant because none of the customary strong acids (such as hydrochloric, sulfuric, nitric, and aqua regia) nor the strong bases (such as hot concentrated potassium or sodium hydroxide) would attack it. The coating material just below the surface, however, could be attacked, but only by hot concentrated potassium or sodium hydroxide. Typical results of etching are shown in figure 10, where nital was used as the etching reagent, and in figure 11, where hot concentrated potassium hydroxide was used. No reaction occurred using nital, but the hot concentrated potassium hydroxide definitely attacked the coating material. Table 1 lists the etching reagents employed, their purposes (reference 1), and their effects on the coating. It must be concluded that the coating is extremely corrosion-resistant.

It was impracticable to isolate the coating material by dissolving away the basis material because gases that were evolved beneath the coating material fragmented the material from the surface in the form of extremely small flakes.

Physical Characteristics

The values of Bierbaum microhardness obtained were 2500 for the coating and 3200 for the nitrided case. These values correspond

approximately to the value of 2950 given for nitrided steel in reference 2. Conversion tables given in reference 2 list a Bierbaum microhardness of 2950 as being equal to Brinell 750 or Rockwell C-67. The following table compares the microhardness of the coating material and the nitrided-steel case.

Material tested	Bierbaum microhardness	Rockwell hardness	Vickers pyramid hardness
Coating material	[a]2500	--------	----------
Nitrided-steel case	[b]2950, [a]3200	[b]C-67, [b]C-72	[c]950-1000

[a]Test results.
[b]From reference 2.
[c]From reference 3.

The depth of test scratch ranged from 0.000073 to 0.000095 inch. The test diamond, therefore, may well have penetrated through the coating layer into the basis metal for a short distance. In any event, it is probable that the coating material is hard, though not so hard as the nitrided case.

Metallurgical Change

The metallurgical changes observed where coating material had formed in the running faces of nitrided-steel piston rings were twofold; a coating layer was created, and the metal grains just beneath were deformed. A typical cross section of a portion of the running face of a nitrided ring on which no coating has been formed is shown in figure 4. In this ring the grains are undeformed. Figure 14 shows the deformed (worked) grain structure of a portion of a ring face in which a coating has formed. The individual grains apparently retain their identity up to the point of conversion to coating material, even when the elongated grains no longer resemble any part of the original structure. Figures 12 and 13 show another portion of a piston-ring face, but here the grains lose their identity and merge to form a nearly homogeneous layer directly beneath the coating material.

Added visual comprehension of the deformation of the metal grains shown in figure 17 may be obtained from figure 18, which

is a photomicrograph of the same specimen except that oblique illumination was employed. The long slanting grain in the center of figure 17 directly beneath the deformed grains may be seen at the left of the center in figure 18.

Additional Tests

Spectrographic analysis of the coating material was attempted by first striking a spark to the coating layer and second to the basis metal of a ring. The spectrum was identical in both cases, but this result was not unexpected because the thickness of the layer was so small that it permitted the spark to penetrate to the basis metal.

Electrographic tests on the outermost skin of the coating material for nickel and chromium, both of which are present in ring and barrel material, failed to reveal the presence of either element, although the elements were found in the nitrided case. It is believed that the surface of the coating material was too passive to allow usual electrochemical reactions to occur.

DISCUSSION OF RESULTS

It has been shown by experiment (reference 4) that the surface temperature of a metal slider may reach the softening or melting point of the slider. Such high temperatures are not communicated to the bulk of the slider because the heat capacity and dissipation of the bulk mass is great relative to the heat generated at the slider face. Apparently a piston ring in operation may be heated to high local temperatures that cause the metal on the face to soften or melt, flow over the face, and resolidify. Because the heat capacity of basis material is great compared with that of the softened or molten surface layer, it is probable that the topmost layer hardens almost instantaneously. Complete recrystallization would not occur and the material would remain amorphous or small in grain size because the cooling time is short. Such layers may possess chemical and physical properties different from those of ordinary crystalline material (reference 5).

It appears that microscopically high spots on the nitrided-steel piston ring form a coating material, eventually resulting in a continuously coated running face. The same condition apparently manifests itself on the cylinder-barrel surface. This condition may perhaps be accelerated by the high unit wall pressures of the

present design of nitrided-steel piston ring. The coating material should be beneficial in service operation because it is corrosion-resistant, only slightly softer than the nitrided case, and minutely raised above the basis metal of the ring. Because the coating is raised above the basis metal, contact and wear will tend to occur on the coating rather than on the basis metal. Also, steel will not be running on steel with attendant high rate of wear.

The difference in relative heights of the coating material and the basis material is probably a result of the fact that the nitrided case is less corrosion-resistant than the coating material and is corroded until its surface is lowered. In fact, when ring specimens were electrographically attacked by reagents for determination of the presence of nickel and chromium, only the nitrided case was attacked. No evidence has been found that machined nitrided steels are particularly corrosion-resistant; published results of tests appear to have been obtained from unmachined nitrided-steel specimens with the white nitrides intact.

Inasmuch as the coating material has not been identified by the methods indicated in this paper, other means of analysis such as X-ray diffraction and electron diffraction will be attempted.

SUMMARY OF RESULTS

The results of the investigation of coating material found on the faces of nitrided-steel piston rings after operation can be summarized as follows:

1. Coating material was formed in the running faces of nitrided-steel piston rings during service operation.

2. The coating material was extremely corrosion-resistant.

3. The coating material showed a Bierbaum microhardness of 2500, slightly less than that of a nitrided-steel case. This hardness is a preliminary value.

4. The coating material was raised very slightly, 0.00001 inch to 0.000025 inch, above the nominal surface of the piston ring.

5. The thickness of the coating layer on the test specimens examined was approximately 0.0001 inch.

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Cleveland, Ohio.

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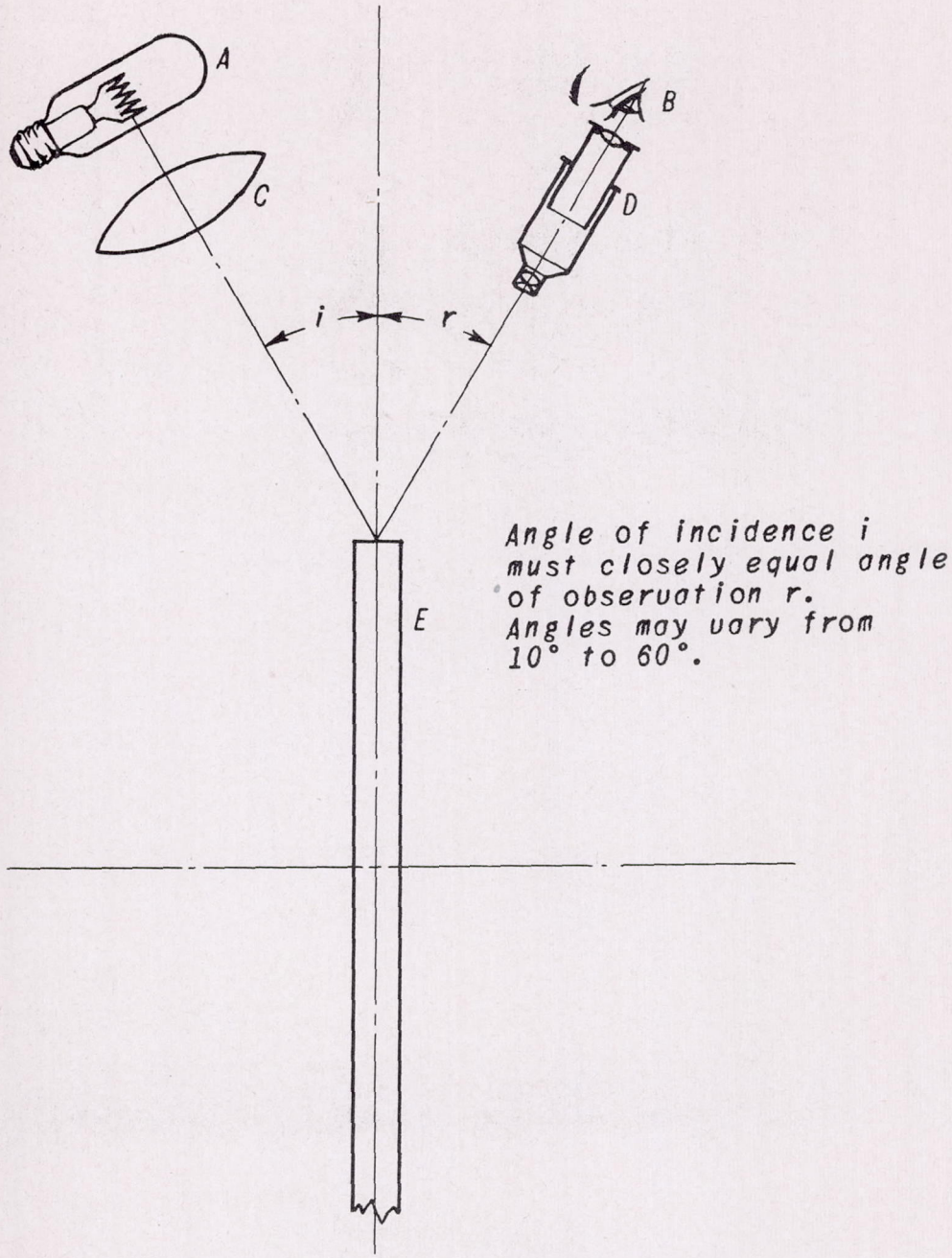
TABLE 1. - EFFECTS OF ETCHING REAGENTS ON COATING

Reagent	Purpose	Effect
Chromic acid[a]	Attacks cementite rapidly	None[b]
Oxalic acid[a]	Reveals precipitated carbides	None[b]
Sodium cyanide[a]	Darkens carbides	None[b]
Glacial acetic acid plus nitric acid	Shows structure of nickel and its alloys	None[b]
Potassium hydroxide, hot, concentrated	General corrosion	Cross section etched[b]
Sodium hydroxide, hot, concentrated	General corrosion	Etched[c]
Ammonium hydroxide, concentrated	General corrosion	None[c]
Acetyl chloride plus aluminum chloride	Reacts with some resonant compounds	Cross section slightly etched[b]
Acetyl chloride	Check on above, should not react	None[b]
Potassium thiocyanate plus hydrochloric acid	Test for passive film of iron oxide	Surface colored[b]
Sodium hydroxide plus hydrogen peroxide	Darkens tungsten carbide	None[c]
Sulfuric acid[a]	General Corrosion	None[b]
Sodium picrate[a]	Colors cementite	Slight color, not reliable[b]
Nitric acid, hot and cold, dilute and concentrated	General corrosion	None[b]
Sulfuric acid, hot and cold, dilute and concentrated	General corrosion	None[b]
Hydrochloric acid, hot and cold, dilute and concentrated	General corrosion	None[b]
Potassium ferricyanide plus potassium hydroxide, hot, concentrated	Nitrides unaffected, carbides blackened	Blackened[c]
Ammonium persulfate	Darkens ferrite	None[c]
Aqua regia	General corrosion	None[d]
Oxidized nitric acid	General corrosion	None[b]
Stead's reagent	Reveals steadite	None[c]
Stannous chloride	Chemical reduction	None[c]

[a]Electrolytic etch.
[b]Reagent applied on cross section and outer skin of coating.
[c]Reagent applied on cross section of coating.
[d]Reagent applied on outer skin of coating.



A Light source
B Observer or camera
C Condensing lens
D Microscope
E Piston-ring specimen

Figure 1. - Geometry of illuminating and viewing coating on a piston ring.

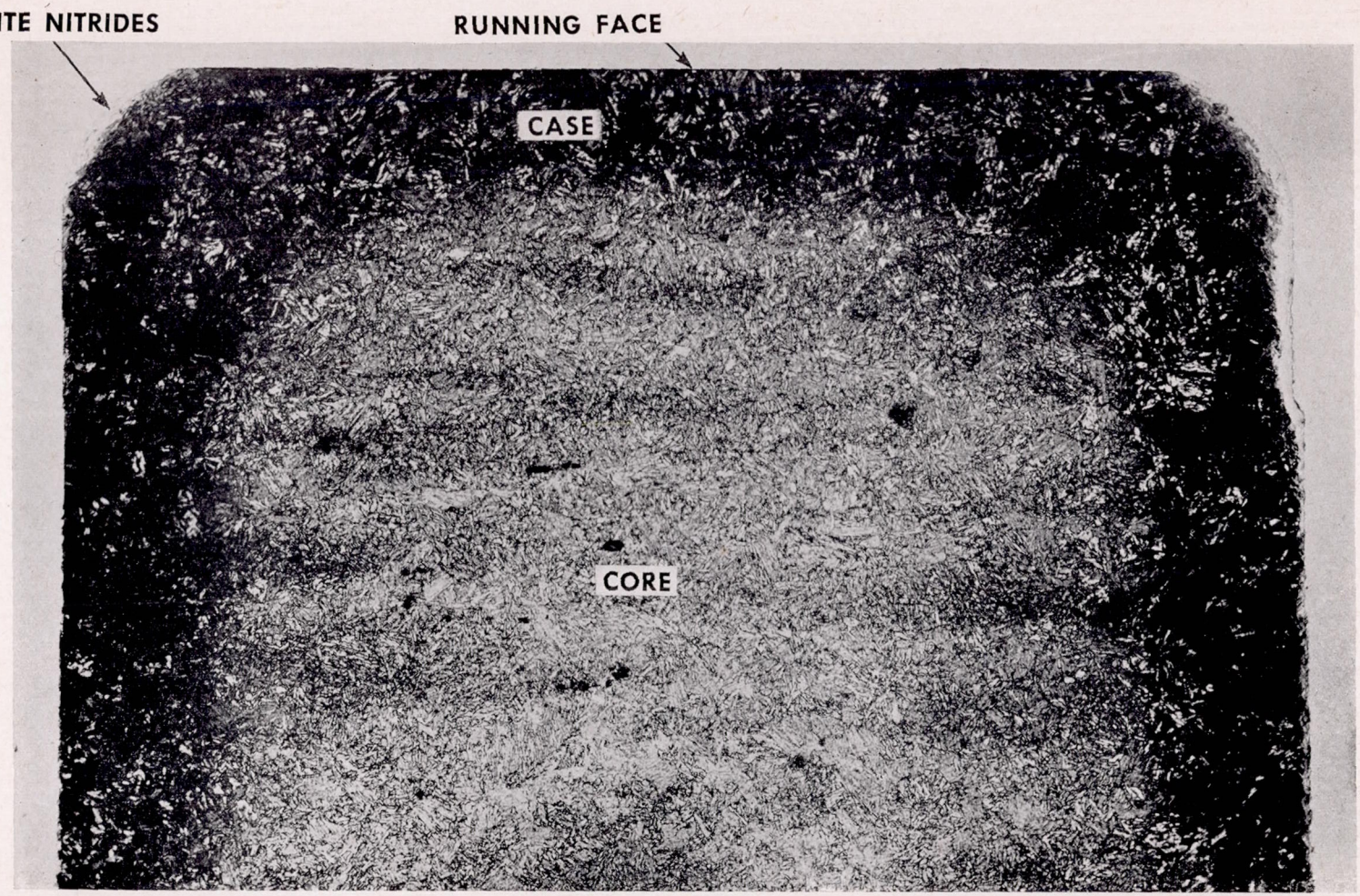


Figure 2.—Transverse section of a typical nitrided-steel piston ring. The black spots in the core are inclusions. (Cf. fig. 6.) The white nitrides are present at the corners of the ring where they have not been removed by machining. Etched in nital. ×100.

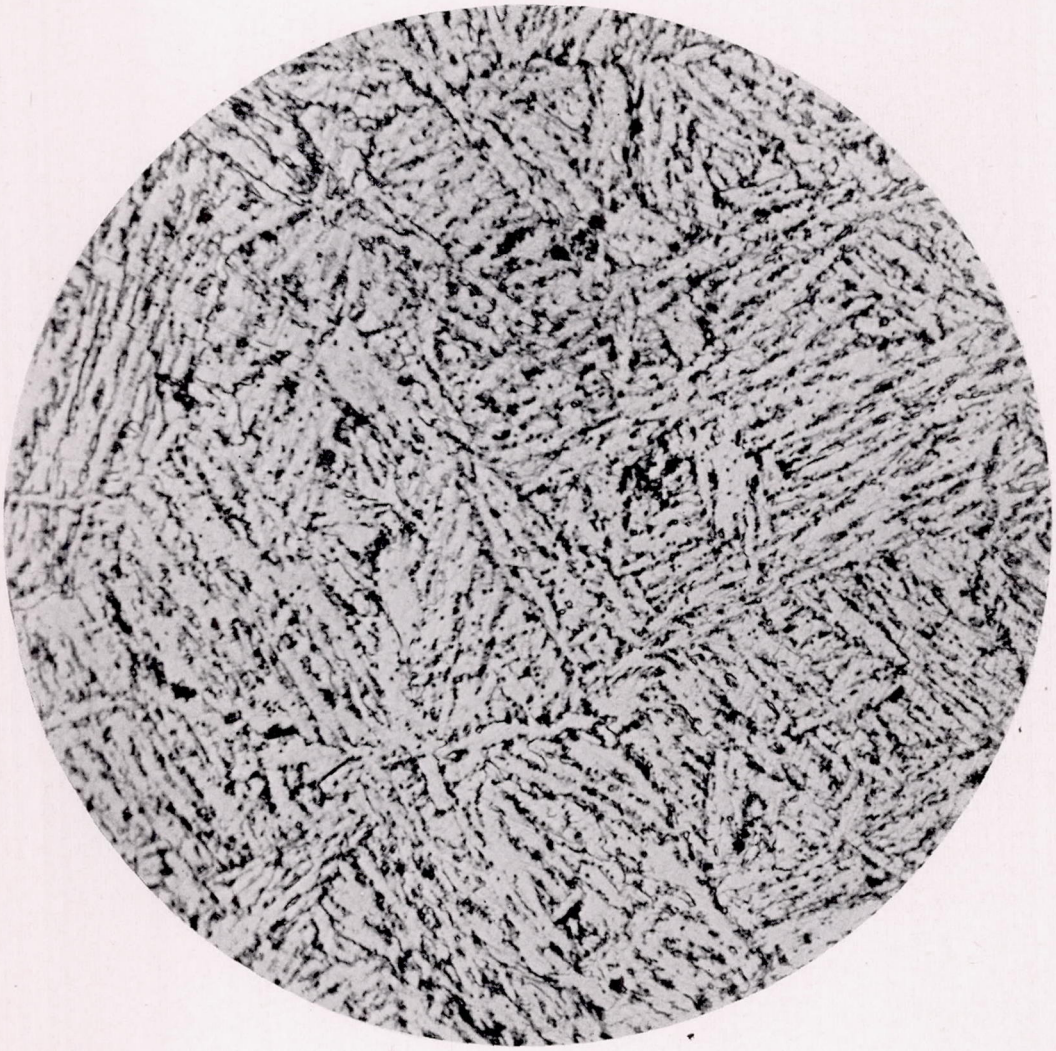


Figure 3.—Core structure of a typical nitrided-steel piston ring. Etched in nital. ×1,500.

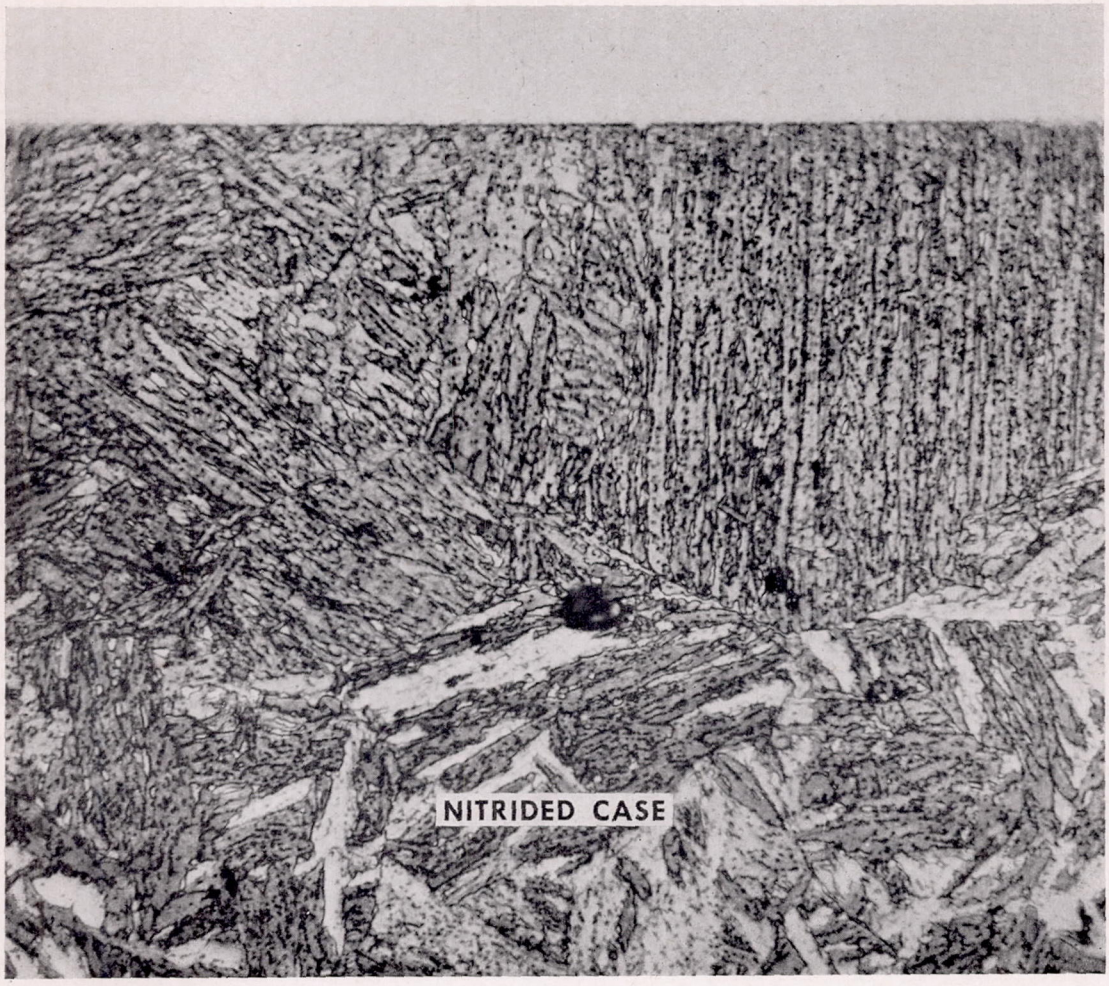


Figure 4.—Transverse section of the running face of a nitrided-steel piston ring after test that has not developed coating material. The grain structure is undeformed up to the surface of the ring. This undeformed material is characteristic of those areas where coating material has not been formed. Etched in nital. ×1,500.

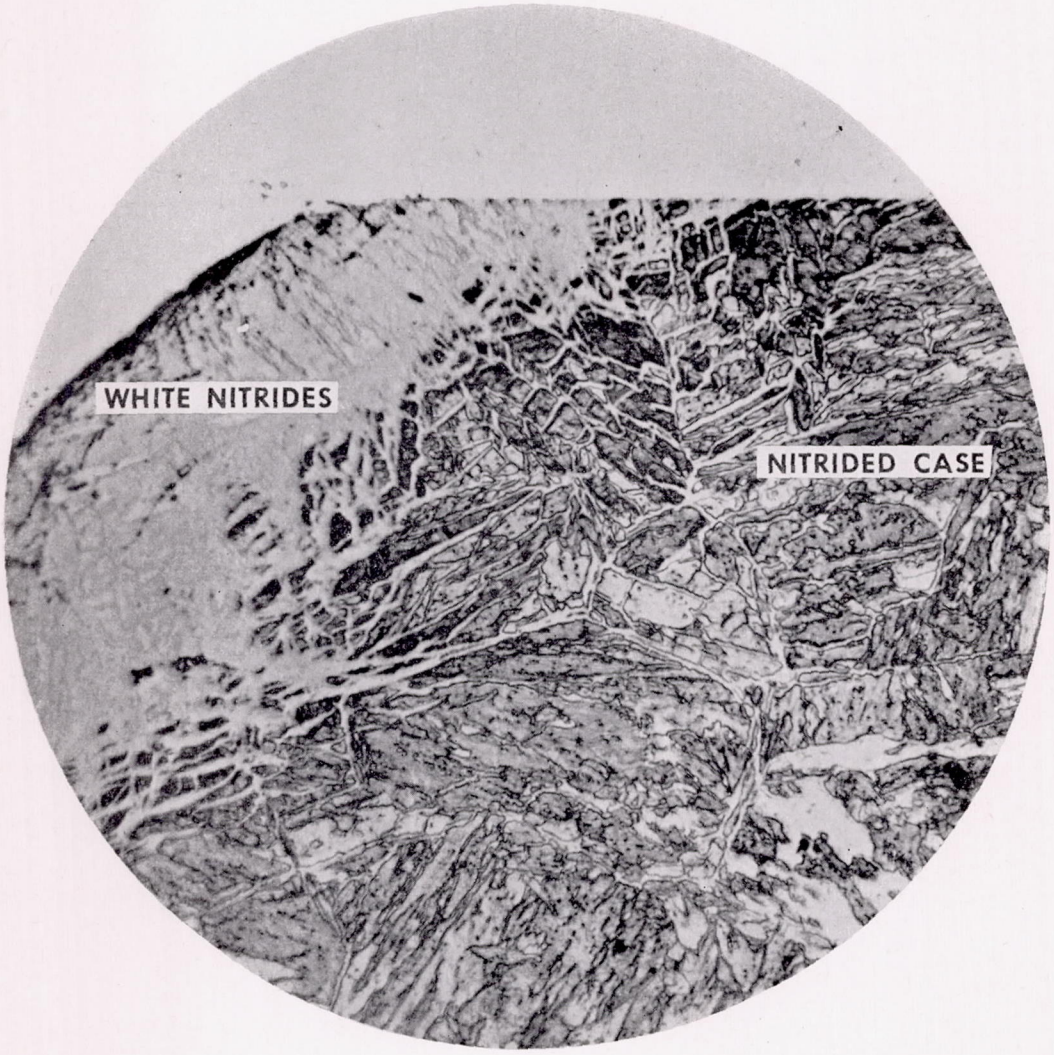


Figure 5.—Transverse section of the upper edge of the running face of a typical nitrided-steel piston ring. The white nitrides are present at the edges of the ring where they have not been machined off. Etched in nital. ×1,500.

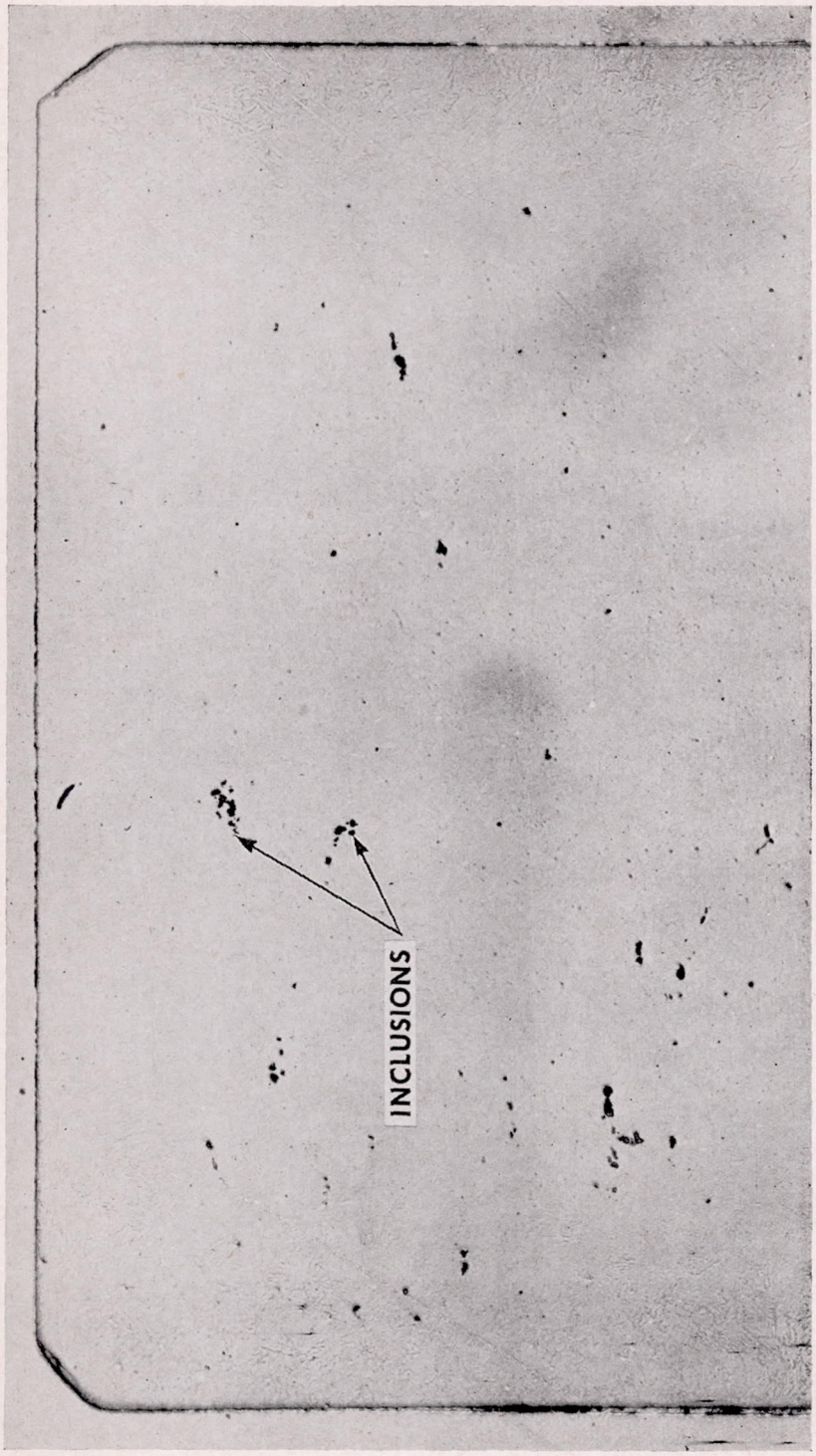


Figure 6.—Transverse section of a typical nitrided-steel piston ring showing inclusions. Unetched. ×100.

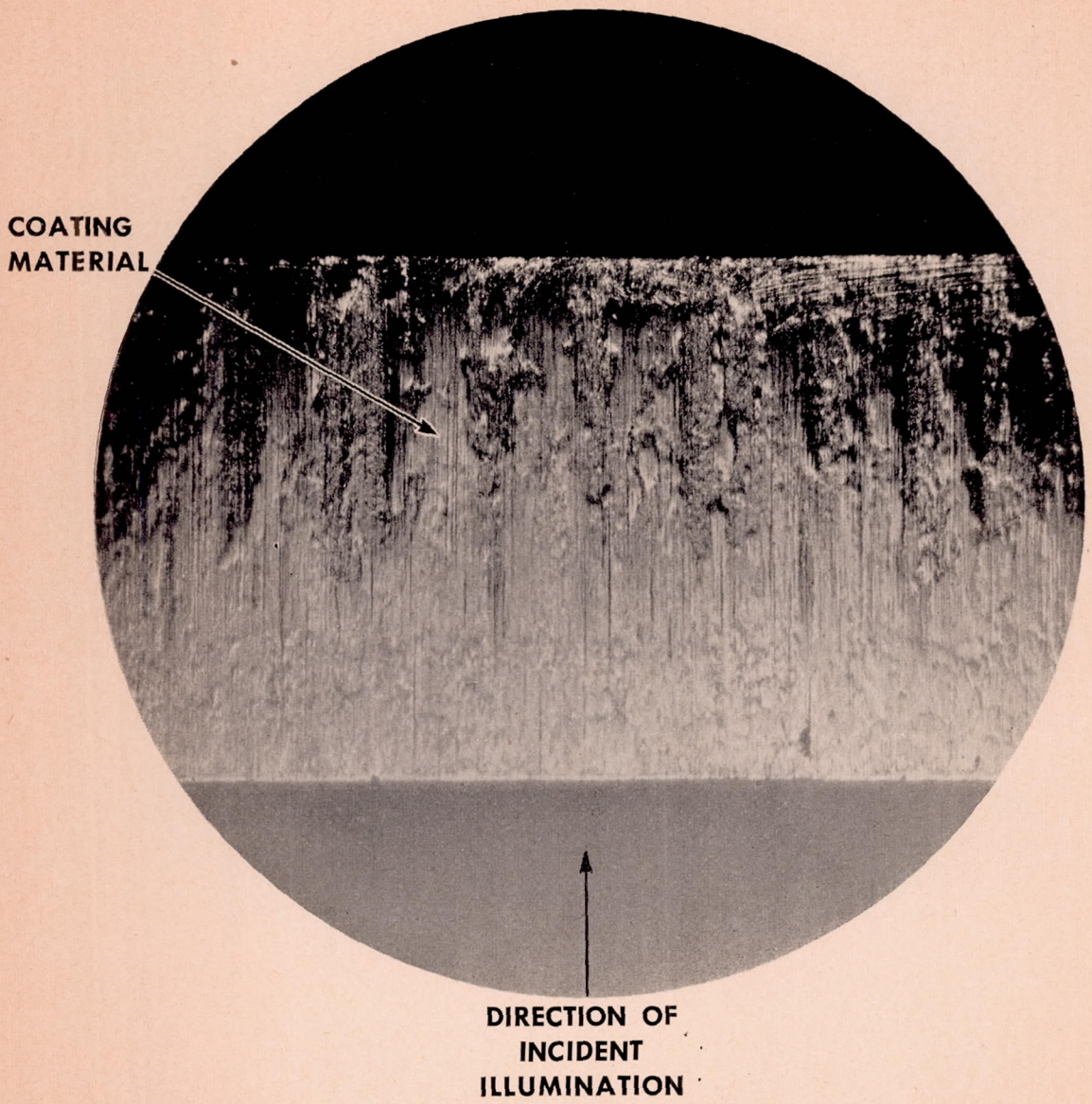


Figure 7.—Running face of a nitrided-steel piston ring after test, showing mottled occurrence of highly reflective material. Oblique illumination. Because the bright side of each area faces the light source, it is apparent that the coating material is elevated above the nominal surface. Same ring as figure 2. Unetched. ×45.

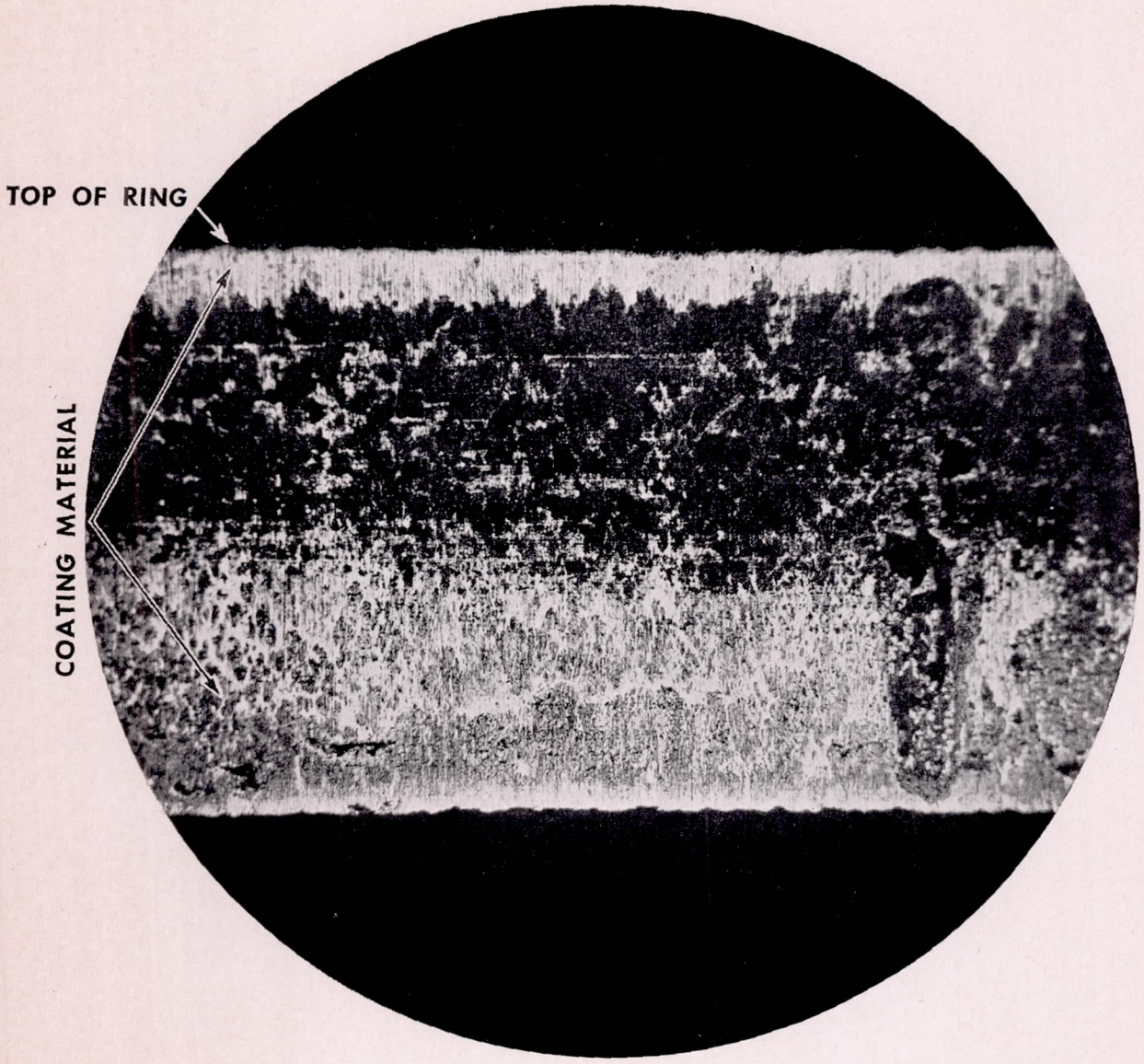
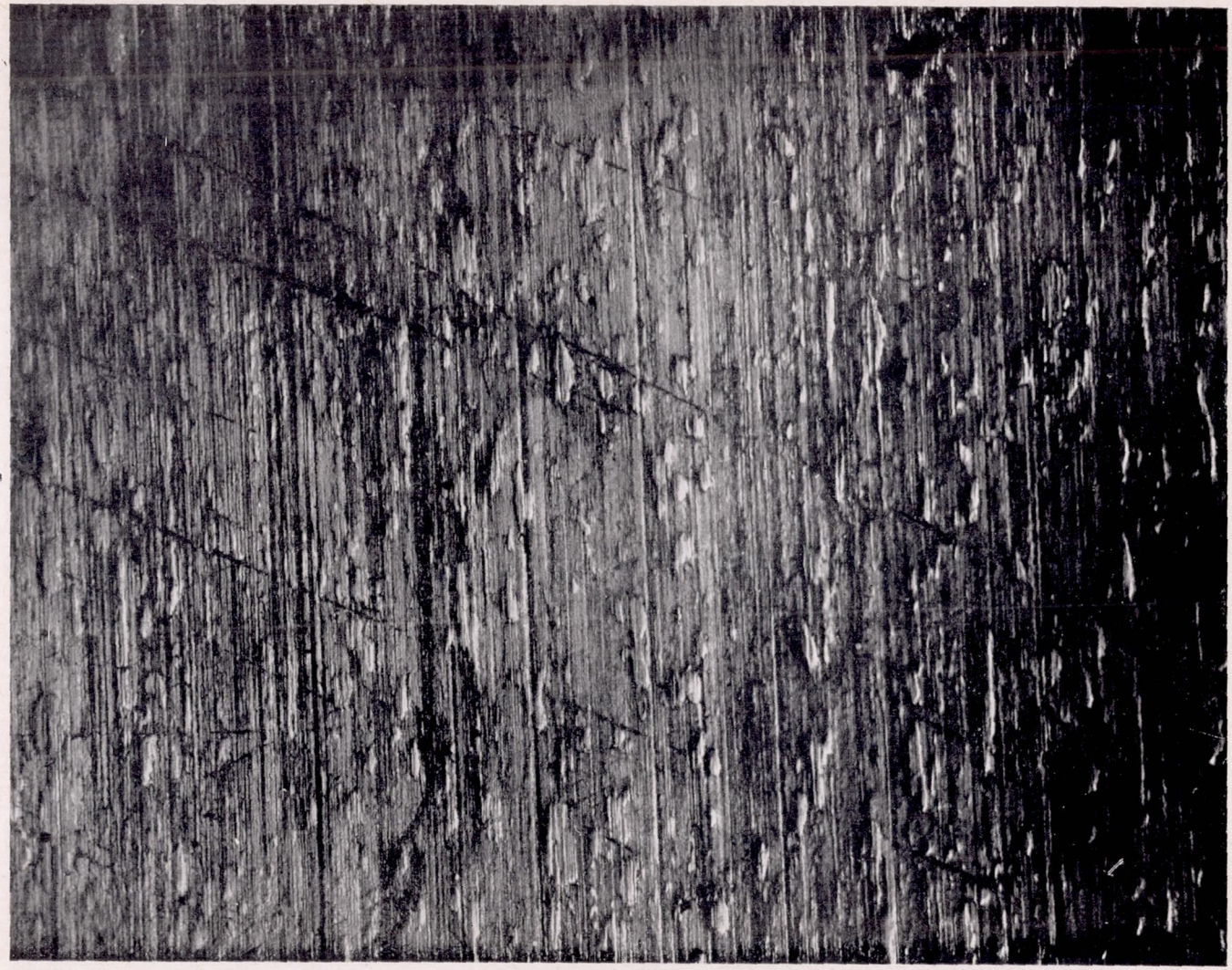


Figure 8.—Running face of a nitrided-steel piston ring after test, showing continuous occurrence of highly reflective material. Vertical illumination. This ring ran for 25 hours at 2,500 r. p. m. and a brake mean effective pressure of 209 pounds per square inch. Etched with dilute nitric acid. ×50.



DIRECTION OF INCIDENT ILLUMINATION

Figure 9.—Running face of a nitrided-steel cylinder barrel after test, showing occurrence of highly reflective material. Because the bright sides of the reflective material face the source of illumination, it can be seen that the spots are actually build-ups of coating material. Unetched. ×45.

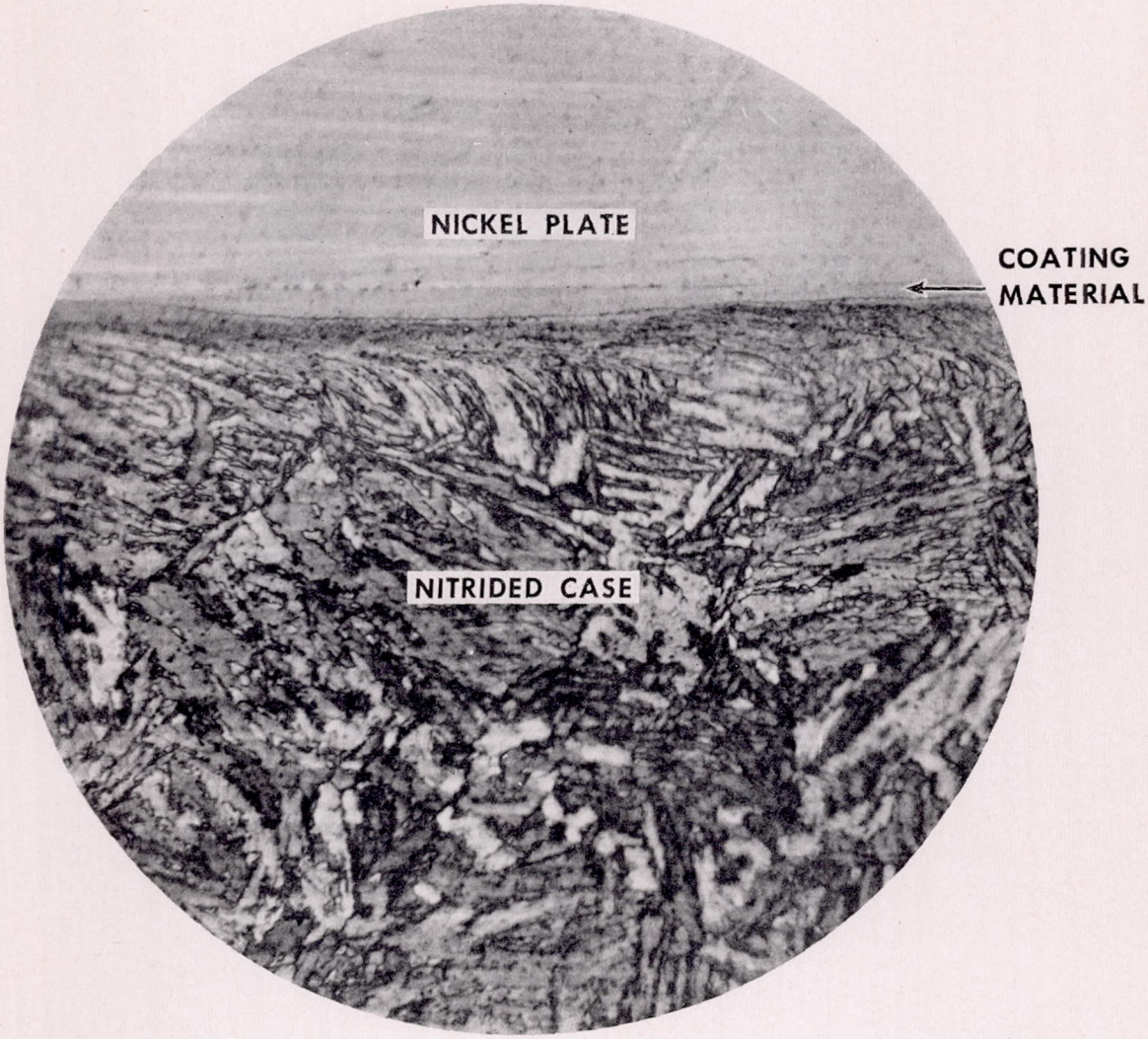


Figure 10.—Transverse section of the running face of a nitrided-steel piston ring after test, showing coating material. The coating material has not been etched and is therefore difficult to distinguish from the nickel layer directly above. Etched in nital. (Cf. fig. 11.) Same ring as figure 7. ×1,500.

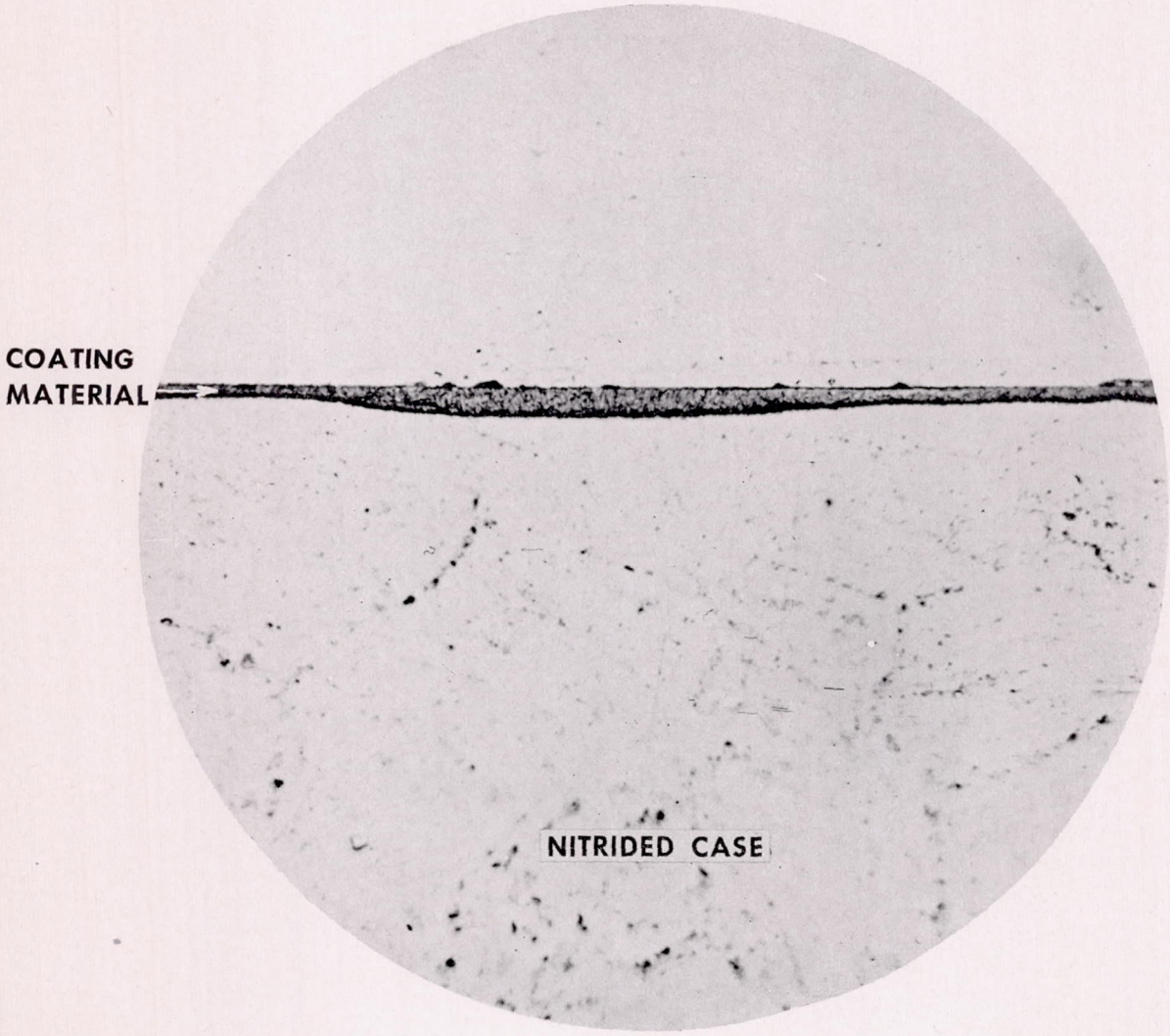


Figure 11.—Transverse section of the running face of a nitrided-steel piston ring after test, showing coating material. Only the coating material has been darkened, thus rendering it easily visible. Same area as figure 10. Etched in hot concentrated potassium hydroxide. ×1,500.

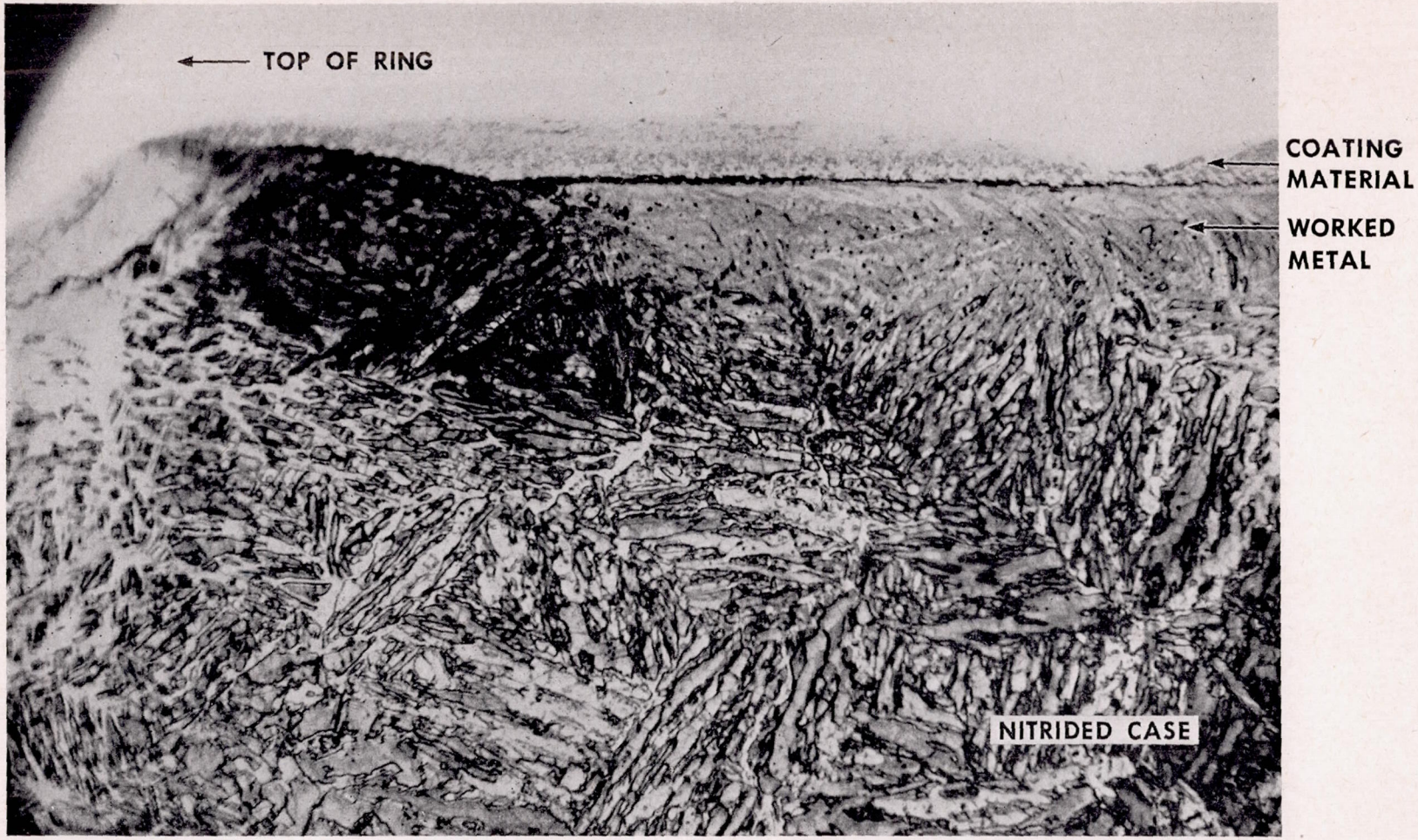


Figure 12.—Transverse section of the running face of a nitrided-steel piston ring after test. The coating material has formed a heavy layer over those parts of the face where no white nitride exists. This ring was used for two tests and then lapped. It was then run in for 1 hour and operated for 25 hours at 2,500 r. p. m. and a brake mean effective pressure of 209 pounds per square inch. Etched in nital. ×1,500.

Figure 13.—Transverse section of the running face of a nitrided-steel piston ring after test, showing coating material. Same ring as figure 12. Etched in nital. ×1,500.

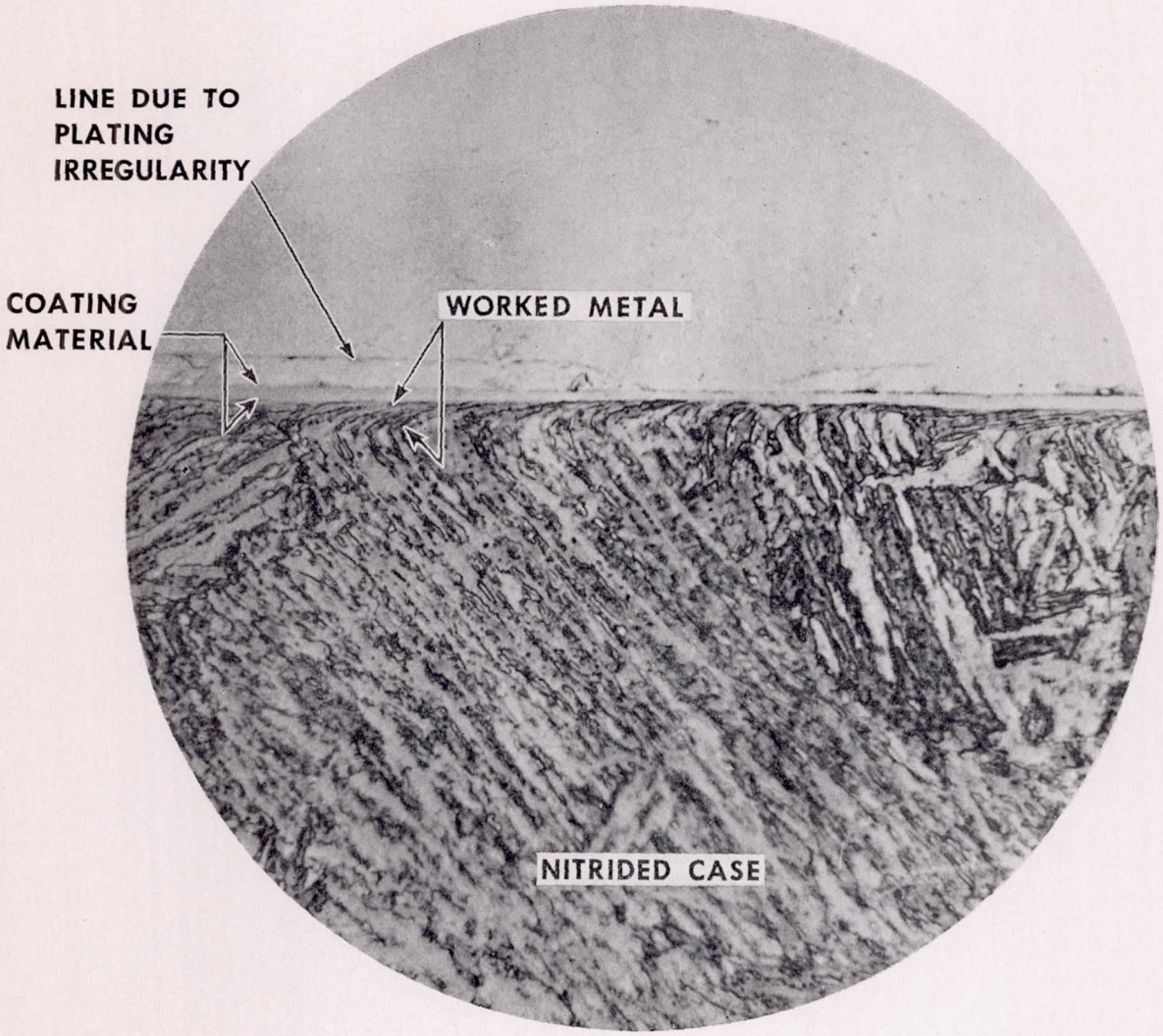


Figure 14.—Transverse section of the running face of a nitrided-steel piston ring after test that has developed coating material. The grains directly below the coating material have been severely deformed by working, but they retain their identity. (Cf. fig. 17.) Etched in nital. ×1,500.

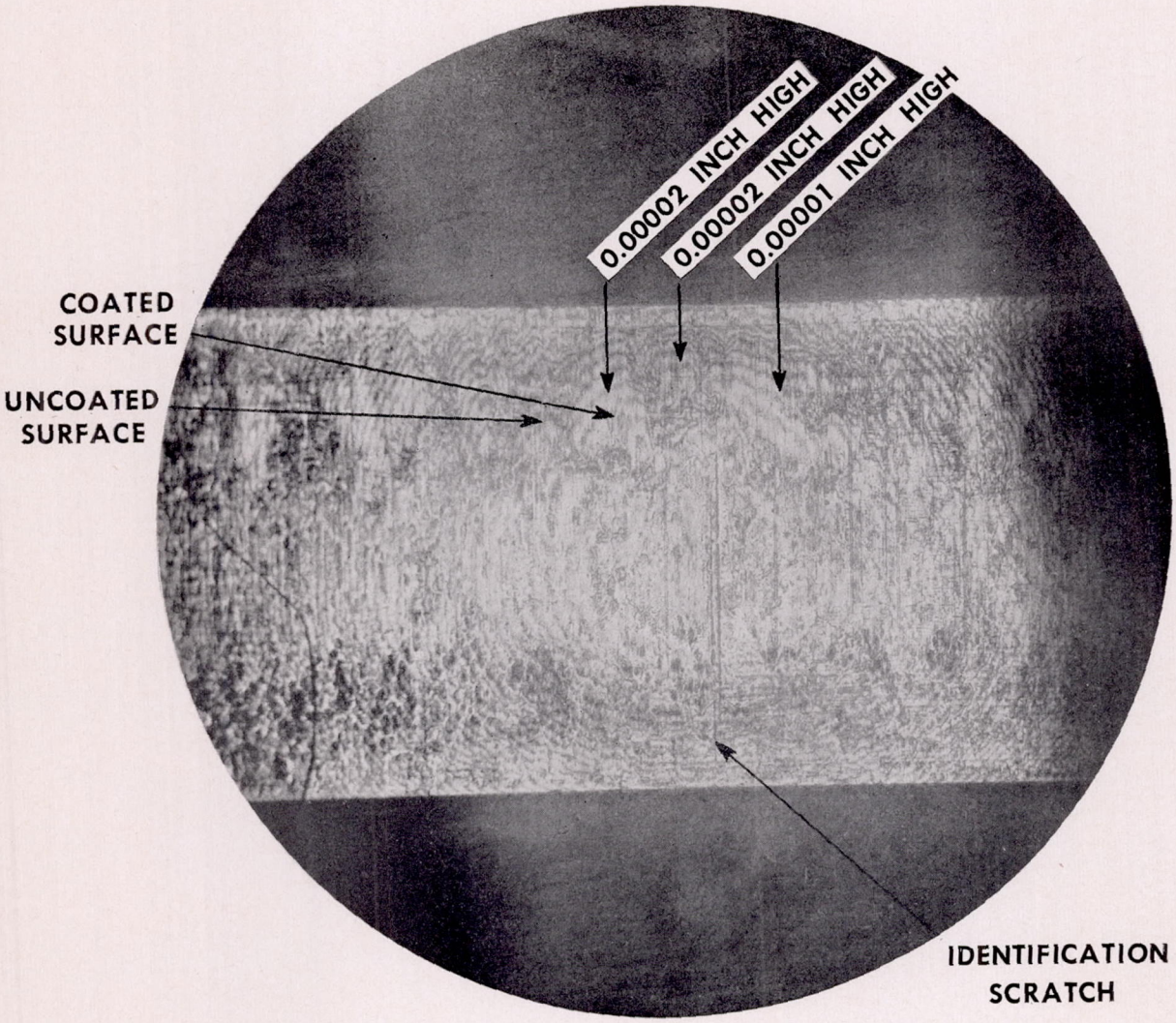
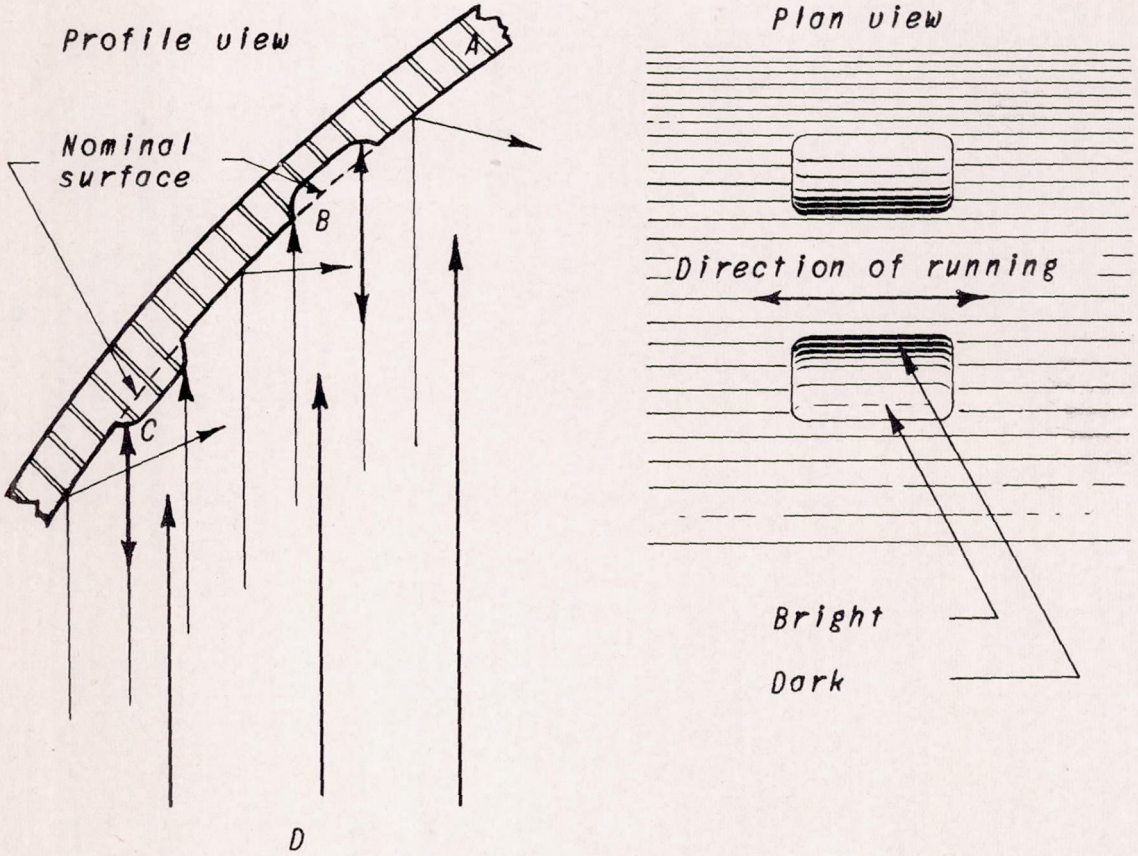


Figure 15.—Interference fringes on the running face of a nitrided-steel piston ring, showing relative heights of coating material and nitrided case. The heights of the coating patches are found by counting the bands between the top of the area and an adjacent area of the bare case. Each band corresponds to a 0.00001-inch difference in height. Unetched. ×40.



A Cylinder-barrel specimen
B Pit (Note that brightest reflection is on far side of light source.)
C Build-up (Note that brightest reflection is on near side of light source.)
D Light source and observer

Figure 16. - Geometry of light reflection.

Figure 17.—Transverse section of the running face of a nitrided-steel piston ring after test that has developed coating material. In this case the working has been so severe that the grain structure has been destroyed for a small depth, and a layer of homogeneous material exists directly below the coating material. There is still a sharp dividing line between the coating material and the homogeneous layer because the homogeneous layer was attacked by the etching reagent. (Cf. figs. 17 and 18.) Etched in nital. ×1,500.

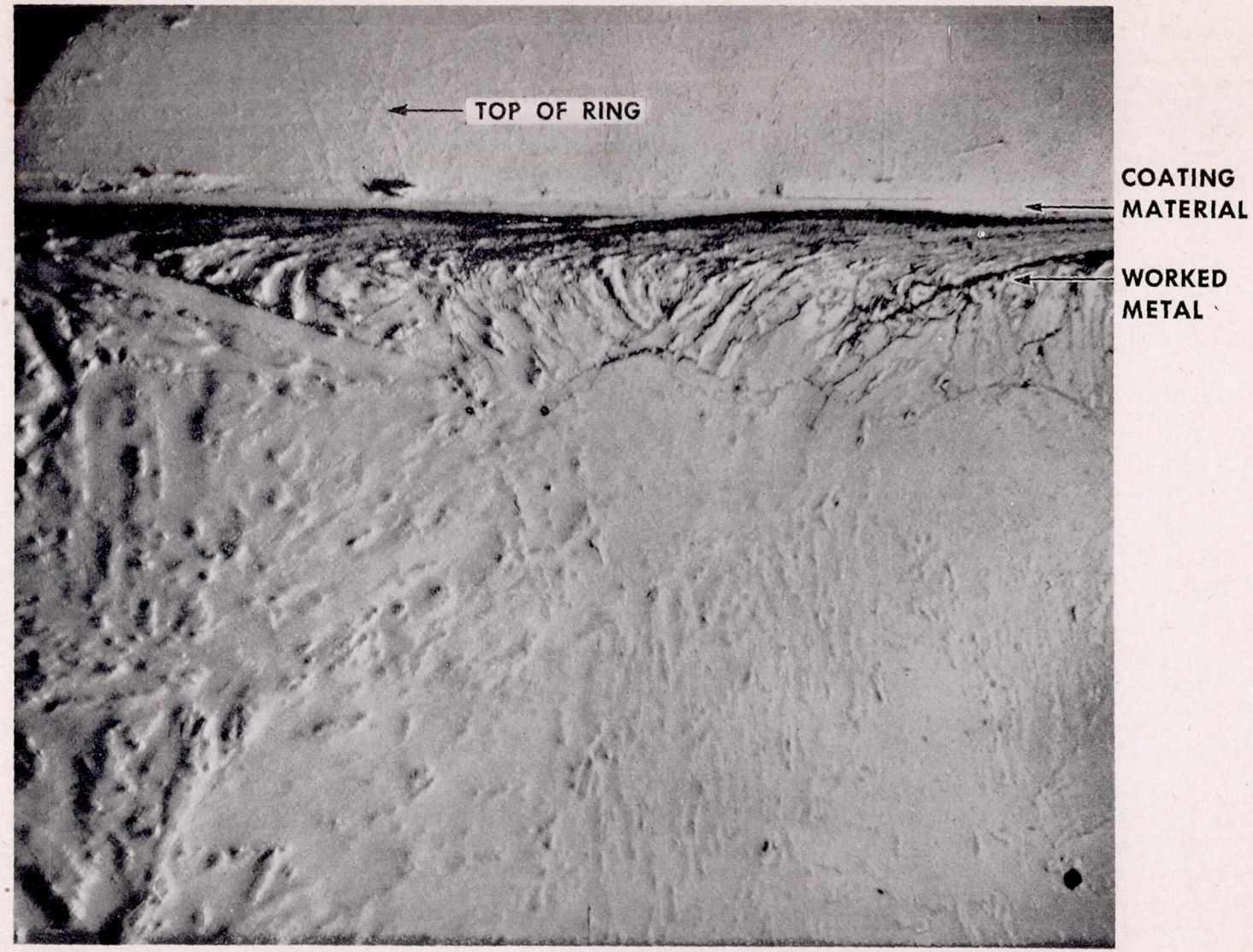


Figure 18.—Transverse section of the running face of a nitrided-steel piston ring after test that has developed coating material and a homogeneous layer. This is the same area as figure 17, but the illumination is oblique. The long slanting grain at the left of the figure appears in the center of figure 17. Etched in nital. ×1,500.