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AN ELECTRON-DIFFRACTION EXAMINATION OF CAST-IRON PISTON RINGS FROM SINGLE-CYLINDER AIRCRAFT-ENGINE TESTS

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AN ELECTRON-DIFFRACTION EXAMINATION OF CAST-IRON PISTON RINGS FROM SINGLE-CYLINDER AIRCRAFT-ENGINE TESTS

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SUMMARY

An electron-diffraction examination of cast-iron piston rings used in a single-cylinder test engine showed the presence of a layer of graphite covering the surface. The wear curves from the rings studied had shown variation from high rates (because of scuffing) to very low rates of wear. In all cases graphite was shown to be present with variations as to quantity and crystalline orientation.

The fact that these piston rings did not have a graphite layer covering the surface before use was shown by a diffraction examination of lapped cast-iron rings. These patterns showed α iron plus graphite, predominately iron, and were similar to the diffraction patterns obtained by mildly abrading both new and used piston rings. A pure graphite pattern was obtained by mildly etching new cast-iron rings.

Graphite was also found on the used cylinder barrel (SAE 4140 steel) used in the tests and, to a lesser extent, on the used top chrome-plated ring of the piston assembly. The source of graphite in all cases was probably the graphite enclosures in the cast-iron rings that had been exposed or extruded by the wearing process and spread by the rubbing of the piston rings against the cylinder barrel.

The formation of a graphite layer was not assumed to be the only surface change that occurs to piston rings and cylinder barrel during engine operation. No other substances were identified by electron diffraction because the graphite layer in the thickness present on the rings and barrel observed is opaque to electrons.

INTRODUCTION

Among the changes that occur during the running-in of piston rings and cylinder barrels are changes in the physical and possibly the chemical nature of the running surfaces. The term "break-in" is used in this report to denote a procedure of preliminary engine operation involving the increase of loads and speeds to normal operating values. The term "run-in surface" is used to designate a surface, certain properties of which have altered resulting in optimum performance characteristics.

The occurrence of a surface change during the polishing of metals was first suggested by Beilby (reference 1). With the development of electron-diffraction techniques, work on the nature of polish was carried out by several investigators in Great Britain, Germany, and in this country. Because a run-in surface need not be a "polished surface", the conclusions drawn in polish investigations are not necessarily applicable to piston rings and cylinder barrels. The only electron-diffraction study of run-in piston-ring or cylinder-barrel surfaces known to the authors was made by Finch, Quarrell, and Wilman (reference 2), who studied used aircraft-engine cylinder sleeves. Neither the chemical composition of the sleeves and the rings run in them nor the conditions of the test, except for the total number of running hours, are specified in reference 2.

An investigation is being conducted at the NACA Cleveland laboratory to determine the nature of a run-in surface. The investigation has two objects: to detect the changes that occur during engine operation and to determine which of the observed changes are necessary to produce a run-in surface. This report describes electron-diffraction experiments conducted during the spring and summer of 1944 to determine the changes that occur to the surface of cast-iron piston rings during operation in a steel barrel. Electron diffraction was used because it permits the detection of a substance on the surface being examined, even if the substance occurs to a depth of only a few molecules. The ring specimens examined varied from scuffed rings to rings that showed a very low rate of wear. The used cylinder barrel and the top chrome-plated ring of the assembly were also examined. Some of the electron-diffraction photographs obtained from the piston rings, as well as standard patterns of α iron and graphite, are presented for comparison.

The results obtained by diffraction methods are limited to detecting the changes that occur. Final determination of whether the observed changes are necessary to the run-in surface will require engine tests.

APPARATUS AND TEST PROCEDURE

The graphite particles of the cast iron in the piston rings examined correspond closely to 60 percent sizes 7 to 8, type A and 40 percent sizes 4 to 5, type B (A.S.T.M. designation A 247-41T for graphite-flake size and type). The structure of this piston-ring cast iron is the same as that shown in figures 1 and 2 of reference 3.

The cast-iron rings examined were new, lapped, and used. The operating conditions for the used rings are listed in table 1. These rings were run in a single-cylinder test engine with Pratt & Whitney R-2800 piston and cylinder assemblies. The ring assembly consisted of cast-iron rings except for a top ring, which was porous chrome-plated. In all tests, the cast-iron rings were lapped previous to operation using an abrasive of silicon-carbide grains (specified grit No. 400) dispersed in an oil binder. After the rings were removed from the engine, they were immersed for 24 hours in a compound that loosened the "carbon" (combustion products of the oil) deposited on the rings. The rings were then washed with an organic solvent and covered with grease to prevent rusting. Several specimens were taken from each piston ring examined. Unless otherwise specified, no other treatment was given to the running faces before diffraction photographs were taken except for a benzene wash to remove the grease.

An RCA electron microscope supplied with a diffraction adapter (reference 4) was used for the electron-diffraction work. The instrument was operated at 60 kilovolts and the specimen-to-plate distance was 31.0 centimeters. The electron-diffraction patterns obtained from the rings were compared with three standard patterns: α iron, graphite that showed preferred orientation, and randomly oriented graphite. The α iron pattern was obtained from a sample of cold-rolled, very low-carbon steel that was abraded with No. 280 grit emery paper. The graphite pattern showing preferred orientation was obtained from powdered graphite rubbed on the steel as a base. The randomly oriented graphite pattern was obtained by putting a little petroleum jelly on the steel surface and touching it to the powdered graphite without rubbing; some larger particles thus adhered to the surface of the steel.

Results of the diffraction examination are given in terms of d, the Bragg interplanar spacing in the crystal, which is inversely proportional to r, the radius of the corresponding diffraction ring for the small angles used in electron-diffraction work. The proportionality constant was determined by photographing zinc oxide as a

calibration pattern. For the specimen-to-plate distance and accelerating voltage used in these experiments, the zinc-oxide pattern gave as the relation between d and r

$$d = \frac{14.0}{r}$$

Precision of the d values was estimated from the uncertainties of ±0.1 millimeter in the measurement of the radii for fairly sharp diffraction rings. The uncertainties of the d values decrease rapidly for the larger rings. In the case of more diffuse or very faint rings, the measurements are more uncertain and the precision correspondingly poorer. The intensities I were visually estimated and graded relative to the strongest ring.

In all the diffraction work, the "reflection" technique (reference 5) was used, except for the zinc oxide. The photographs of the diffraction patterns presented are positive enlargements (X2) and do not show as much detail as the original negatives.

RESULTS AND DISCUSSION

The identification of a diffracting material on the surface of the piston rings was made by comparing the diffraction rings obtained from the specimens with the rings obtained from the standard materials. The data from the patterns of the piston-ring specimens and the standard materials are given in table 2; a comparison was made between all diffraction rings representing the same value of d within the estimated precision listed in column 7 of the table. The number of significant figures given for each value of d was also based upon the estimated precision. The improvement of the precision of d with decreasing values of d is modified by the fact that some rings are stronger and clearer than others. The estimated precision for the (104) and (110) graphite planes is therefore poorer than for planes of higher d value.

The patterns obtained from lapped and used piston rings were poorer than the standard patterns, because surface conditions could not be varied in order to obtain the best results.

Standard Patterns

Standard diffraction patterns of α iron, graphite showing preferred orientation, and randomly oriented graphite are shown in figures 1, 2, and 3, respectively. The Miller indices for the α iron and graphite rings are given in figures 1 and 2 for convenience of reference.

A polycrystalline material is said to show preferred orientation if the normals to any crystallographic plane in the various single crystals do not point in all possible directions. Preferred orientation is detected in the diffraction pattern by the appearance of nonuniform intensity around the diffraction rings representing the oriented planes. In figure 2 the heavy short arcs show that certain planes in the crystal have a preferred orientation. These arcs correspond to successive even orders of reflection from the (001) planes and indicate that these planes, which form the faces of the characteristic cleavage plates of graphite, are oriented parallel to the surface of the backing material within 2° or 3°. The appearance of other rings shows the presence of a smaller number of plates not oriented in this direction because of the method of preparation. Figure 3 indicates a random arrangement of the graphite cleavage plates. The occurrence of the spotted rings is due to the presence of relatively large crystals. Inasmuch as the only essential difference in the preparation of the graphite samples was that they were rubbed in the first case and not in the second, it is clear that rubbing produced the preferred orientation.

A diffraction ring corresponding to $d = 2.5$ to 2.8 A appears in all columns of table 2 including the standard patterns; it represents neither a graphite nor an α iron plane. This ring was found by Nelson (reference 6) on iron at about $d = 2.5$ A and was attributed by that author to oxidation of the iron with the formation of Fe_3O_4 or of γFe_2O_3. In the preparation of the α iron and the graphite specimens, the time between abrasion of the iron and insertion into the camera was not more than 2 or 3 minutes, which explains the low intensity at which the oxide diffraction ring appears in the α iron pattern and in the graphite pattern showing preferred orientation. The ring did not appear in the randomly oriented graphite pattern (fig. 3), probably because the graphite layer in this case was thick enough to prevent penetration of the electrons to the underlying material.

Occurrence of Graphite

Occurrence on new rings. - The diffraction pattern of a new cast-iron piston ring consists of two rather diffuse rings that may be attributed to α iron, graphite, or both. After mild abrasion with No. 600 grit emery paper, however, a sharp ring pattern (fig. 4), identified as α iron plus graphite, predominately iron, was obtained (column 5, table 2). This pattern shows that abrasion of the ring with emery paper results in an increase in the graphite concentration

at the surface inasmuch as its concentration in the bulk material of the cast iron is about 3 percent, which is too low for graphite to appear in the diffraction pattern.

Specimens of new rings were abraded with No. 280 emery paper and then etched in a 2-percent nital solution (2 percent nitric acid in methyl alcohol) for 30 seconds. When the specimens were removed from the nital, they were washed in methyl alcohol and immediately placed in the diffraction chamber. The sharp ring pattern obtained (fig. 5) is shown in column 2 of table 2 to be a graphite pattern. Four graphite rings that could not be seen in the standard graphite pattern appeared here. The occurrence of pure graphite upon etching can be explained by the dissolving of iron at the surface, which left some graphite protruding.

Occurrence on lapped rings. - Examination of lapped cast-iron rings gave a pattern that was poorer, but not greatly different, from the abraded cast iron. (See column 4, table 2 and fig. 6.) The pattern from lapped rings was taken as the control for the examination of the used rings because all rings were lapped previous to running.

Occurrence on used rings. - The diffraction patterns of several specimens from each of the cast-iron rings listed in table 1 were photographed. The patterns obtained in all cases correspond to graphite with varying degrees of orientation. Figure 7 is a highly oriented graphite pattern from test 5 and figure 8 is a randomly oriented graphite pattern from ring 3 of test 3. These figures are, respectively, representative of the types of highly and randomly oriented graphite patterns obtained from the various used piston rings. In no case was the presence of α iron on the surface indicated. Column 3 of table 2 lists the diffraction rings obtained from used piston rings from all the tests of table 1 with the range of relative intensities observed on the various exposures. (The designation $I = 0$ indicates the absence of the ring from some of the negatives.) The greater the orientation, the fewer and heavier the rings appear (see fig. 7); therefore, the more precise measurements were made from patterns showing lesser degrees of orientation.

The general background was very heavy in all patterns from used rings. If the intensity of the diffraction pattern relative to the background is indicative of the quantity of graphite at the surface, ring 2 of test 3 (table 1) shows the greatest amounts of graphite over a large number of photographs of different samples. The other tests varied greatly over different specimens and photographs. Good patterns were not obtained too readily from the scuffed ring of test 5, but the good photographs showed graphite to about the same extent as other tests.

Mild abrasion of used rings with No. 600 emery paper was always sufficient to give the sharp pattern of α iron plus graphite similar to that from the abraded new ring (fig. 4). An etching treatment similar to the one used for the new rings but without abrasion was given to used rings. The pattern obtained was very similar. The only substance identified on the used ring surfaces was graphite. This fact does not mean that no other surface changes take place during the engine operation of the rings, inasmuch as a relatively thin graphite layer is opaque to electron penetration.

Occurrence on other running surfaces of assembly. - Samples of the used portions of a barrel (SAE 4140 steel) from the Pratt & Whitney R-2800 assembly were examined and found to give a strong graphite pattern very similar to that obtained from the used rings.

Samples of the top chrome-plated ring of the piston assembly from some of the tests listed in table 1 were also examined before and after use. The used chrome-plated rings gave graphite patterns not so intense relative to the background as those from used cast-iron rings, which indicates there was less graphite on the surface.

Orientation of the Graphite

The graphite layer appearing on the used rings exhibited variations from sharp line patterns to those in which heavy arcs appear due to preferred orientation. In figure 7 these arcs are seen to cover about 20° and show that the normals to the characteristic cleavage plates vary in tilt over $\pm 10^\circ$ around the position of the normal to the ring surface.

The degree of preferred orientation shown could not be correlated with the engine tests, because different specimens from the same ring showed great differences in the degree of orientation. In order to determine whether this variation was due to engine operation or to subsequent treatment, a specimen from a used ring that had given a well-defined randomly oriented graphite pattern was rubbed with cloth. This rubbing produced no orientation. It seems probable, therefore, that differences in orientation are due to differences in radial pressure around the ring.

Origin of the Graphite

The graphite layer found on the rings and barrel discussed in this report may be attributed to two factors: it may have come from (1) the "carbon" deposited by combustion of the oil or (2) it may have been caused by the exposing or extruding of graphite from the

cast iron during the wear process with subsequent spreading of the graphite due to rubbing of the cast-iron rings against the cylinder barrel, as suggested by other investigators. (See reference 2.) The first cause was suspected because of the brown coating of so-called "varnish," "lacquer," or both on the surface of the cylinder-barrel specimens examined.

Chrome-plated rings (from a piston assembly in which all rings were chrome-plated) that had been operated in an Allison V-1710 single-cylinder engine using a stock 4620 carburized-steel cylinder barrel mounted on a CUE crankcase showed no traces of graphite. The absence of graphite from this test would seem to eliminate the first cause. Because this test was run in a different engine and under different conditions than the other tests, it cannot be considered as a control.

An X-ray diffraction examination in a powder camera using CuKα radiation of the "carbon" deposited on a piston during operation showed the absence of the graphite pattern. This absence means that not much of the chemically combined carbon has been transformed to graphite in the course of the decomposition of the lubricating oil and that the structure of any graphite present is greatly distorted. It seems improbable, therefore, that a graphite layer can be formed by deposition of combustion products on the rings and barrel even after rubbing. The graphite layer formed during engine operation probably comes from the graphite enclosures in the cast iron that have been exposed or extruded by the wearing of the cast-iron rings.

SUMMARY OF RESULTS

An electron-diffraction examination of new, lapped, and used cast-iron piston rings from single-cylinder-engine tests showed the following results:

1. The diffraction patterns from lapped rings showed the presence of α iron plus graphite, predominately iron. A similar diffraction pattern was obtained by abrading a new ring with emery paper.

2. The examination of the diffraction patterns of used rings whose wear curves varied from high rates (because of scuffing) to very low rates of wear indicated the presence of a layer of graphite covering the surface in all cases. There was some variation in the quantity of graphite present in different samples. Because the graphite layer is opaque to electrons, no substance beneath it could be detected.

3. The degree of orientation of the graphite from used cast-iron piston rings varied over different parts of the same ring.

4. A sharp pattern of α iron plus graphite was obtained from the used cast-iron rings after mild abrasion.

5. A sharp randomly oriented graphite pattern was obtained by mildly etching a new cast-iron ring with nital.

6. Graphite was found to a great extent on the used cylinder barrel (SAE 4140 steel) and to a lesser extent on the top chrome-plated ring of the assembly after it had been used.

CONCLUSION

The graphite layer found on the surface of used piston rings and cylinder barrels is produced by the exposing or extruding of the graphite in the cast-iron rings during the wear process followed by a spreading of the graphite as rubbing between piston rings and cylinder barrel takes place.

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TABLE 1. - TEST CONDITIONS FOR THE USED RINGS

	Test				
	1	2	3	4	5
Compression ring used for diffraction examination	2d	2d	2d and 3d	2d	2d
Fuel additives used during break-in	None	None	None	Organo-silicon compound[a]	Iron carbonyl[a]
Break-in time, hr	$7\frac{3}{4}$	$7\frac{3}{4}$	$7\frac{3}{4}$	2	2
Total running time, hr	$17\frac{3}{4}$	$17\frac{3}{4}$	$17\frac{3}{4}$	12	12
Engine speed at final test conditions, rpm	2400	2400	2400	2400	2400
Brake mean effective pressure at final test conditions, lb/sq in.	225	225	225	225	225
Rate of wear	Normal	Normal	Low	Lowest obtained	High
Remarks on operation	Normal	Normal	Normal	Normal	Rings scuffed

[a]These fuel additives produced abrasive particles of small size during the combustion process.

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TABLE 2. - SPACINGS AND INTENSITIES OF DIFFRACTION PATTERNS FROM STANDARD MATERIALS AND PISTON RINGS

[d, interplanar spacings in Angstrom units A; I, relative intensity with respect to strongest ring, graded in increasing order as follows: O, VVF, VF, F, FM, M, MS, S, VS]

1			2		3		4		5		6			7
[a]Graphite (data from patterns showing preferred orientation; see fig. 2)			Cast-iron ring (etched with 2-percent nital after abrasion with No. 280 emery paper)		Run-in cast-iron rings		Lapped cast-iron rings		New cast-iron rings (abraded with No. 600 emery paper; see fig. 4)		α iron[a] (see fig. 1)			Estimated precision
Indices	d (A)	I	d (A)	I	d (A)	I	d (A)	I	d (A)	I	Indices	d (A)	I	Expected d variation (A)
002	3.4	M	3.4	M	3.4	O-M	3.4	FM	3.5	M	-------	------	----	±0.2
------	2.8	VVF	2.5	VVF	2.5	O-MS	2.6	F	2.7	VF	-------	2.7	F	±.1
100	[b]2.11	------	2.16	VVF	-----	-----	----	----	------	-------	-------	------	----	±.05
101	2.03	VS	2.04	VS	2.03	VS	2.00	VS	2.02	VS	110	2.03	VS	±.03
102	[b]1.81	------	1.87	F	1.87	O-VVF	----	----	------	-------	-------	------	----	±.03
004	1.70	FM	1.71	VVF	1.73	O-M	----	----	------	-------	-------	------	----	±.02
103	1.57	FM	1.54	FM	1.54	FM-M	----	----	1.55	VVF	-------	------	----	±.02
------	-----	------	------	-------	-----	-----	1.42	M	1.40	M	200	1.41	MS	±.02
104	[c]1.33	------	1.35	VVF	-----	-----	----	----	------	-------	-------	------	----	±.05
110	1.23	S	1.23	MS	1.28	O-FM	1.26	VVF	1.21	MS	-------	------	----	±.05
105, 112	1.15	S	1.15	S	1.16	M	1.16	M	1.16	S	211	1.18	VS	±.02
006	1.12	F	1.12	VF	-----	-----	----	----	------	-------	-------	------	----	±.02
200, 201	1.07	F	1.06	VF	-----	-----	----	----	1.05	F	-------	------	----	±.02
106, 114	1.00	FM	1.00	MS	-----	-----	----	----	1.00	M	220	1.01	FM	±.01
------	-----	------	------	-------	-----	-----	----	----	.90	F	310	.90	M	±.01
116	[b].831	------	.828	FM	-----	-----	----	----	.822	F	222	.824	VF	±.005
------	-----	------	------	-------	-----	-----	----	----	.764	FM	321	.766	M	±.005

[a]Diffraction rings of α iron are observed out to the (510) and (431) planes and graphite rings to the (00·10) plane, but d values for rings extending far beyond the range of the unknown patterns are not included in this table.

[b]These diffraction rings appear on the A.S.T.M. X-ray diffraction card for graphite but not in this standard graphite pattern.

[c]This diffraction ring was not listed in the A.S.T.M. graphite card but was calculated from the fact that graphite is hexagonal with a = 2.46 and c = 6.78.

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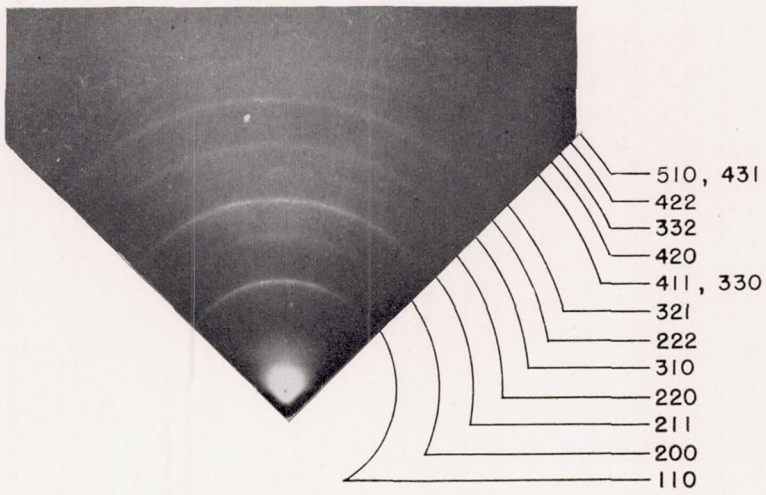

Figure 1.—Electron-diffraction pattern of α-iron. Camera constant, 14.0. ×2.

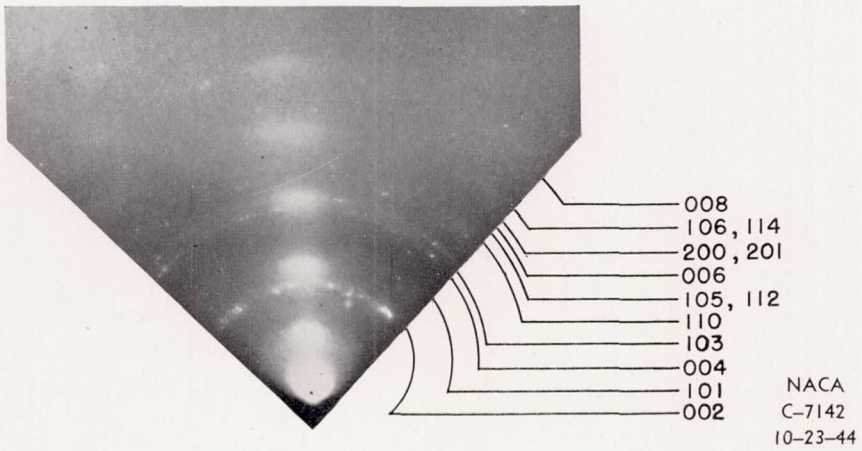

Figure 2.—Electron-diffraction pattern of graphite showing preferred orientation (cleavage planes parallel to the surface). The heavy short arcs are the (002), (004), (006), and (008) planes. Camera constant, 14.0. ×2.

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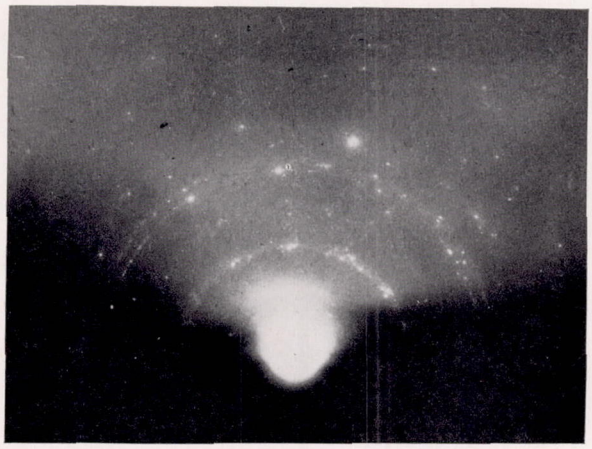

Figure 3.—Electron-diffraction pattern from randomly oriented graphite showing spots due to large crystals. Camera constant, 14.0. ×2.

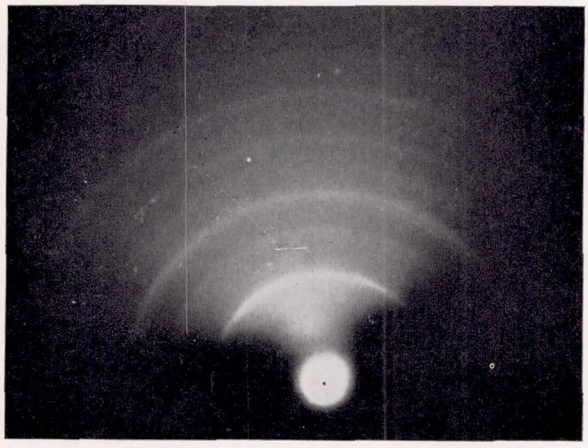

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Figure 4.—Electron-diffraction pattern of α-iron plus graphite from a new cast-iron ring abraded with No. 600 emery paper. Camera constant, 14.0. ×2.

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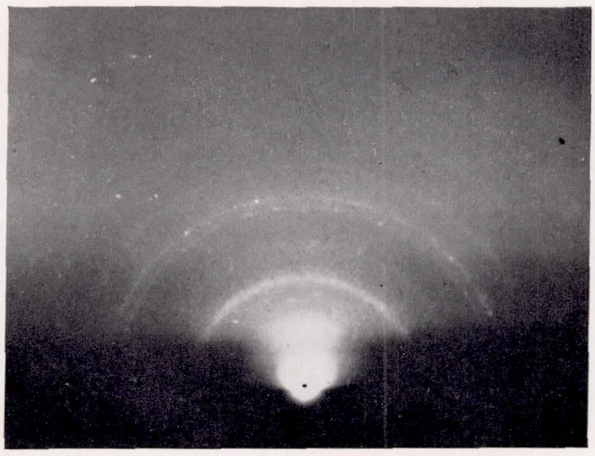

Figure 5.—Electron-diffraction pattern of graphite from a new cast-iron ring abraded then etched with 2-percent nital. Camera constant, 14.0. ×2.

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Figure 6.—Electron-diffraction pattern from a lopped cast-iron ring showing α-iron plus graphite. Camera constant, 14.0. ×2.

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Figure 7.—Representative electron-diffraction pattern of highly oriented graphite from cast-iron ring. Test 5; camera constant, 14.0. ×2.

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Figure 8.—Representative electron-diffraction pattern of randomly oriented graphite from cast-iron ring. Ring 3; test 3; camera constant, 14.0. ×2.

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