

An Electron Optical Survey of Iron Oxide Films Produced in H₂O, 1.5% LiOH, and LiOH/EDTA (pH 11) Solutions at 316°C

R. L. JONES

*Electrochemistry Branch
Chemistry Division*

and

M. C. BLOOM

*Consultant
Chemistry Division*

September 29, 1966



NAVAL RESEARCH LABORATORY
Washington, D.C.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Abstract.....	1
INTRODUCTION.....	1
EXPERIMENTAL TECHNIQUES AND EQUIPMENT.....	1
IRON OXIDE FILMS FORMED IN H ₂ O AT 316°C.....	2
IRON OXIDE FILMS FORMED IN 1.5% LiOH AT 316°C.....	7
IRON OXIDE FILMS FORMED IN LiOH/EDTA SOLUTION (pH 11) AT 316°C.....	15
CONCLUSION.....	16
ACKNOWLEDGMENTS.....	18
REFERENCES.....	18

An Electron Optical Survey of Iron Oxide Films Produced in H₂O, 1.5% LiOH, and LiOH/EDTA (pH 11) Solutions at 316°C

R. L. JONES

Electrochemistry Branch

Chemistry Division

and

M. C. BLOOM

Consultant

Chemistry Division

Abstract: In the exploration of steel corrosion mechanisms pertinent to steam power generation, LiOH has been investigated as an alkalizing agent to form protective oxide films on boiler walls. Steel capsules treated in three different ways, (a) with H₂O, (b) with 1.5% LiOH solution, and (c) with LiOH/EDTA (pH 11) at 316°C, formed films which, in the initial stages of development, were shown to be Fe₃O₄. However, the crystallite size, the degree of orientation, and the film uniformity and continuity, determined by electron microscopy and diffraction, varied with the method and length of treatment. The film formed by distilled water showed small (1000 to 2000 Å), oriented crystals with sharply delineated areas of growth. When the LiOH solution was used in the treatment, larger crystals were formed, but flaws were still noticeable after 24 hours. With the LiOH/EDTA solution, the growth of the crystals was very rapid, forming a thick, coherent film on the metal, which should offer excellent protection against corrosion.

INTRODUCTION

In the course of exploration of steel corrosion mechanisms pertinent to steam power generation, attention has recently been given to LiOH as an alkalizing medium for treatment of steel at elevated temperatures (1,2). LiOH cannot be simply substituted for NaOH in the conventional Navy low-phosphate treatment for boiler water primarily because of deposition of Li₃PO₄ on the boiler walls (3). Investigations have been undertaken to evaluate LiOH boiler water treatments where an organic chelating agent, ethylenediaminetetraacetic acid (EDTA), is used instead of phosphate to prevent hard scale formation by the alkaline earth ions which are always present in sea water distillate. Preliminary studies in capsule systems at this laboratory and in model boilers at the Marine Engineering Laboratory have indicated that this type of treatment is preferable from the standpoint of prevention of boiler wall corrosion to the low-phosphate control treatment presently being used by the Navy (3). In the same

series of tests, LiOH was found to be superior to NaOH in corrosion inhibition when these alkalis are used independently in solution with no other additives.

In connection with further studies of corrosion mechanisms in these systems, the techniques of electron microscopy and electron diffraction are being utilized as an aid in the analysis of the structure and of the growth processes of protective films. These techniques have been used to examine the initial processes of oxide film formation in H₂O, 1.5% LiOH solution, and LiOH/EDTA solution at 316°C (conditions related to boiler operation) to ascertain whether the morphology and/or composition of the surface oxide differed systematically with the treatments and whether such differences, if found, could be correlated with the relative degrees of corrosion inhibition previously observed for these additive systems.

EXPERIMENTAL TECHNIQUES AND EQUIPMENT

Three test solutions, prepared from distilled water and reagent grade chemicals, were used in these experiments: (a) distilled water only,

NRL Problem C05-22; Project RR 001-01-43-4758. This is an interim report on one phase of the problem; work is continuing on the problem. Manuscript submitted May 24, 1966.

(b) 1.5% (by weight) LiOH solution, and (c) pH 11 LiOH solution containing 100 ppm EDTA. This last solution was prepared by adding 100 ppm of ethylenediaminetetraacetic acid, neutralizing with LiOH, and then adding sufficient excess LiOH to bring the solution to pH 11.

The oxide films were prepared in a manner previously described (4). Capsules for this investigation were made from cold drawn mild steel tubing having an outside diameter of 0.250 inch and a wall thickness of 0.020 inch. The tubing sections were degreased in trichloroethylene vapor, hydrogen annealed at 875°C for one hour and cooled in the hydrogen atmosphere, then vacuum annealed at 875°C for one hour and cooled in the furnace. They were then quickly removed and placed in closed containers in a desiccator containing anhydrous calcium sulfate for storage until time of usage. Specimen samples were prepared by drawing the solution to be evaluated up into the sections of annealed tubing, which were then pressure sealed into capsules in such a way that no air was trapped within the individual capsule. (The oxygen content of the solutions was less than 8 ppm.) The ends of the capsules were subsequently spot-welded as an additional precaution against leakage. Heat treatment was effected by placing the capsules in a stainless steel beaker which was introduced into a mechanical convection oven maintained at $316 \pm 2^\circ\text{C}$. It was estimated that the capsules came to temperature in less than 5 minutes. To secure oxide films in various states of development, a standardized heating exposure program was adopted in which specimens were taken at the following six time intervals: overnight at room temperature, and overnight at room temperature plus 5 minutes, 15 minutes, 30 minutes, 2 hours, and 24 hours at 316°C. A few specimens were also taken at other heating intervals. After a given exposure, the capsule was withdrawn from the furnace and cooled to room temperature. It was then opened, drained of test solution, and rinsed well in reagent grade methanol. Dried capsules were stored in a vacuum desiccator until they could be examined.

The iron oxide films were then stripped from the base metal in an iodine/methanol solution (5) with concentration 0.1 g iodine/cc methanol. A supporting layer of carbon had to be evaporated on the very thin oxide films formed with 30

minutes or less heating to obtain satisfactory separation. The stripping process was carried out overnight in a vacuum desiccator and, to insure that the solution and vessel were freed of air, the pressure in the desiccator was reduced and the methanol solution "boiled" several minutes just before and after specimens were inserted. The stripped films were washed in methanol, and mounted on 200 mesh molybdenum grids. Buob, Beck, and Cohen (6) have concluded that an oxide film separated by the iodine/methanol technique is not altered if the process is done carefully. No apparent change in the oxide film which could be attributed to oxidation was detected in our experiments.

In the electron diffraction analysis, two modes of diffraction were employed—high resolution diffraction and selected area diffraction, both at 100 kV. In high resolution diffraction, the electron microscope serves only to impinge a beam of electrons on the specimen with the diffracted rays traveling on to the photographic plate without auxiliary magnification by magnetic lenses. Therefore, no lens error intrudes, and the diffraction pattern is inherently more accurate. In selected area diffraction, the instrument functions as a microscope and the diffraction pattern from a selected area of the specimen image is obtained by changing the settings of the lenses. More pertinent to this discussion is that the area contributing to the diffraction pattern is much larger in high resolution diffraction than in selected area diffraction. Oxide film specimens which give polycrystalline patterns by regular diffraction frequently have areas of short range crystal ordering which give predominantly single crystal patterns by selected area diffraction. The selected area mode of diffraction will be so designated, while the term diffraction will be used to mean high resolution diffraction.

IRON OXIDE FILMS FORMED IN H₂O AT 316°C

The oxide layers formed on the capsule walls under this environment are inhomogeneous to the eye, especially those heated for short periods of time, and they remain inhomogeneous when viewed in the electron microscope. If a number of specimens are surveyed, however, the artifacts and inhomogeneities become recognizable, and

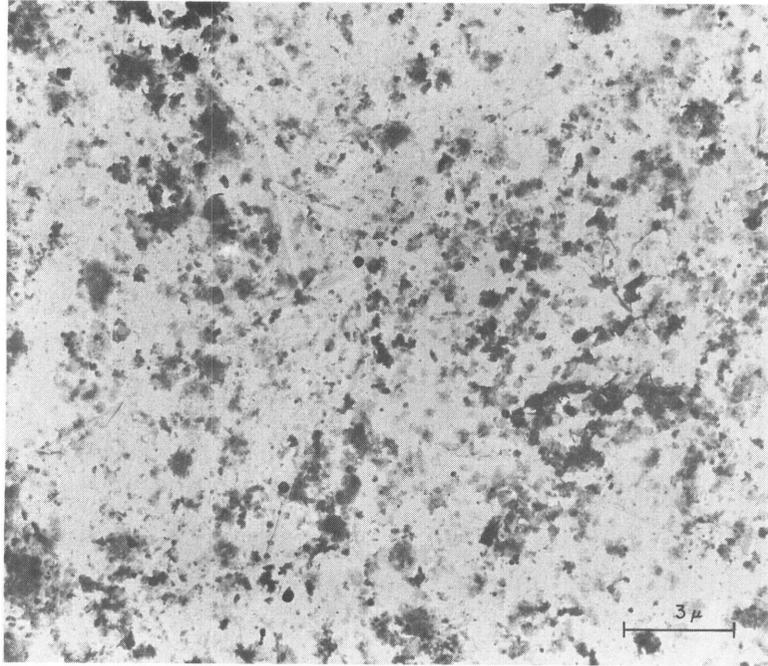
certain trends in the mode of oxide formation are soon apparent. Representative views of the oxide found on iron exposed to water at 316°C temperature for increasing lengths of time are shown in Fig. 1. The oxide film in Fig. 1(a), where the exposure was only overnight at room temperature, is very thin as evidenced by the low contrast of the micrograph; yet even here the oxide growth is far from homogeneous. The stripped oxide layer from a "blank," *i.e.*, a section of tubing that had not been treated with water or heat, is very similar to this one, indicating that little reaction has taken place during the overnight equilibrating period. The diffraction pattern from a film such as this is semiamorphous, but often contains faint lines that can be indexed on the spinel structure of magnetite (Fe_3O_4) which would be expected to form under these conditions.

In Fig. 1(b) the capsule had been subjected to 15 minutes heating in the 316°C furnace subsequent to standing overnight. With this treatment the previously amorphous or semiamorphous oxide film has become predominantly crystalline with crystallites in the range 200 to 1000 Å readily visible. The transmission diffraction pattern is now composed of discrete spinel rings; but selected area diffraction often yields patterns consisting of single crystalline arrays of spots, which indicate short range order in the film. There is indication that these crystallites form both within and on top of the original film. As can be seen in Fig. 1(b), what at first appear to be holes in the film occur relatively frequently when examined at high magnification. However, these holes show crystallographic shapes and an underlying base film in which still other crystallites can be discerned, indicating that these are probably sites from which a crystallite has been somehow dislodged. In no instance was a hole of this type found to go completely through the oxide film.

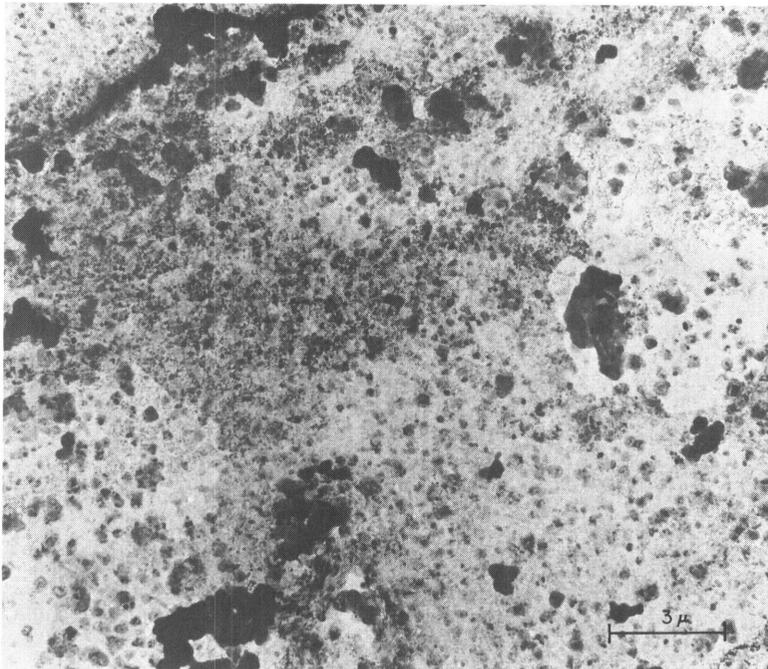
Further heating, as in Fig. 1(c), where the capsule was 30 minutes in the furnace, and in Fig. 1(d), where the heating time was 2 hours, produces very distinct crystals 1000 to 1500 Å in diameter with irregular shapes which sometimes approach hexagonality. The growth areas of these overlying crystals are often well delineated. The reason for this has not been established, but Field and Holmes (7) who have studied the growth of magnetite on pure iron in high-temperature (250

and 316°C) water have observed the same phenomenon and associated it with the presence of grain boundaries in the base metal. The 2-hour specimens frequently exhibited "nucleation sites" (as indicated by the arrow in Fig. 1(d)) which were not apparent in oxide films generated by shorter or longer periods of heating. The tendency with increased heating is to increase the area of the film surface covered by the overlying crystals; however, even after 24 hours at 316°C, although the film was obviously thicker, coverage was not complete, and "thin" local areas as in Fig. 1(d) could still be found. During these extended periods of heating the maximum size of the individual crystal remains relatively small with few crystallites exceeding 2000 Å in diameter. All diffraction patterns from these thicker films showed only spinel, presumably Fe_3O_4 , rings.

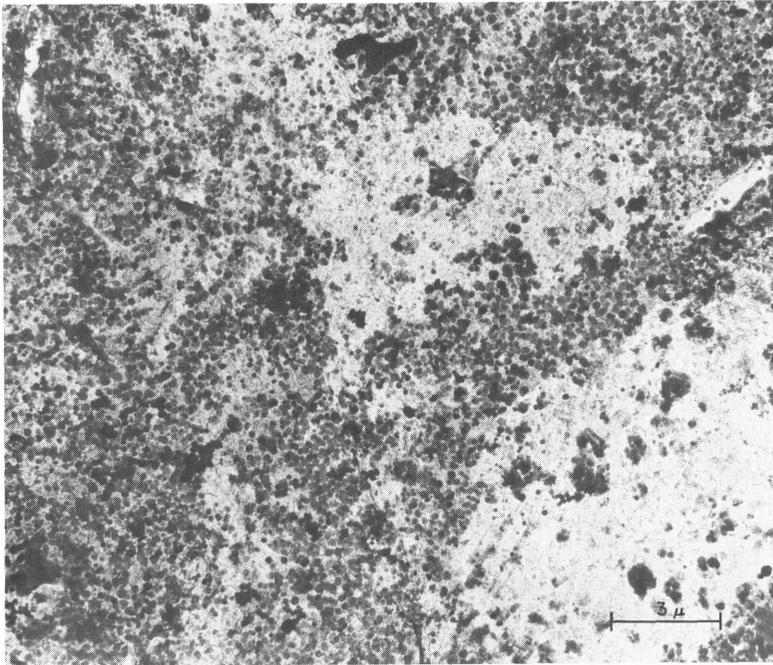
The authors (7) quoted above have published electron micrographs which show pores as large as 300 Å between impinging magnetite grains. From this and other evidence they have concluded that the inner layer of magnetite in their two-layer oxide films is probably porous and that this porosity represents a possible means of access for oxygen to the base metal. With this in mind, the magnetite films prepared in these experiments were examined at high magnification for the presence of pores. In a 15-minute specimen, Fig. 2, spaces between the individual crystals are quite apparent, but there appears to be a coherent oxide layer underlying these spaces such that the bare metal would be protected. A boundary to the growth area of overlying magnetite crystals for a 2-hour oxide film, Fig. 3, allows the observation of pores between the uppermost crystals while showing simultaneously that they are backed by an appreciable and apparently continuous crystalline base film. There are tiny pits (approximately 50 Å in diameter) on the surface of this film which are unexplained, but which appear at higher magnification as if they resulted from some sort of submicroscopic spalling process. Close examination of the original photographic plate of Fig. 3 reveals sites which could be taken as pores between grains in the base film, although it cannot be ascertained that these "pores" do in fact extend through the film body. It can be stated, however, that if pores exist here, they are below 50 Å in diameter.



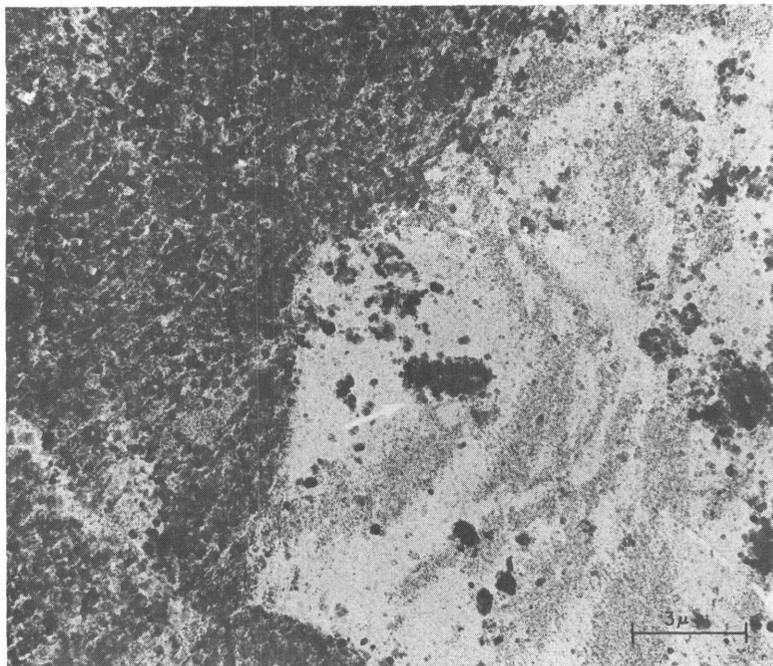
(a) Overnight at room temperature



(b) 15 minutes in 316°C furnace



(c) 30 minutes in 316°C furnace



(d) 2 hours in 316°C furnace

Fig. 1 — Iron oxide films produced by various heating exposures on the interior of capsules containing distilled H₂O. Original magnification 9000X.

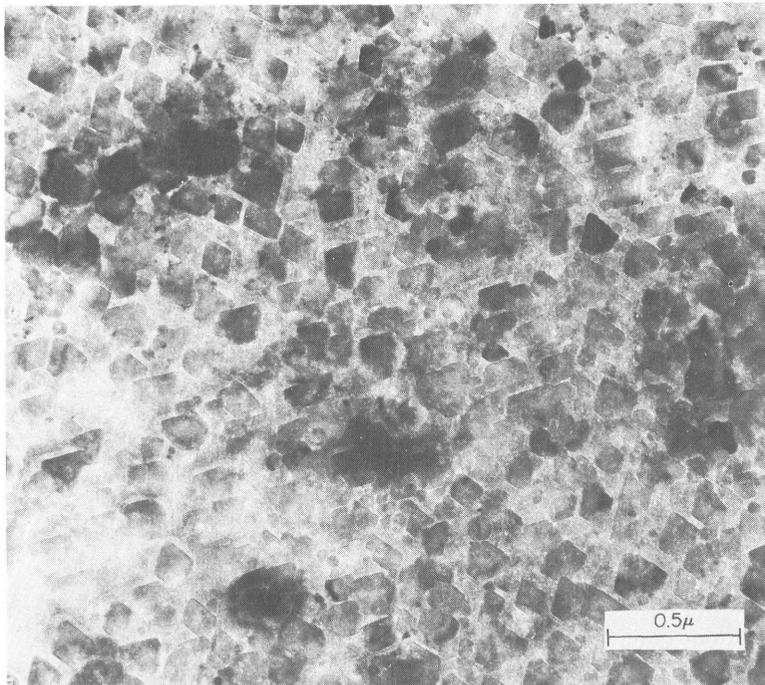


Fig. 2 — Area of good crystal development on H₂O-generated iron oxide film after 15 minutes in 316°C furnace. Original magnification 66,000X.

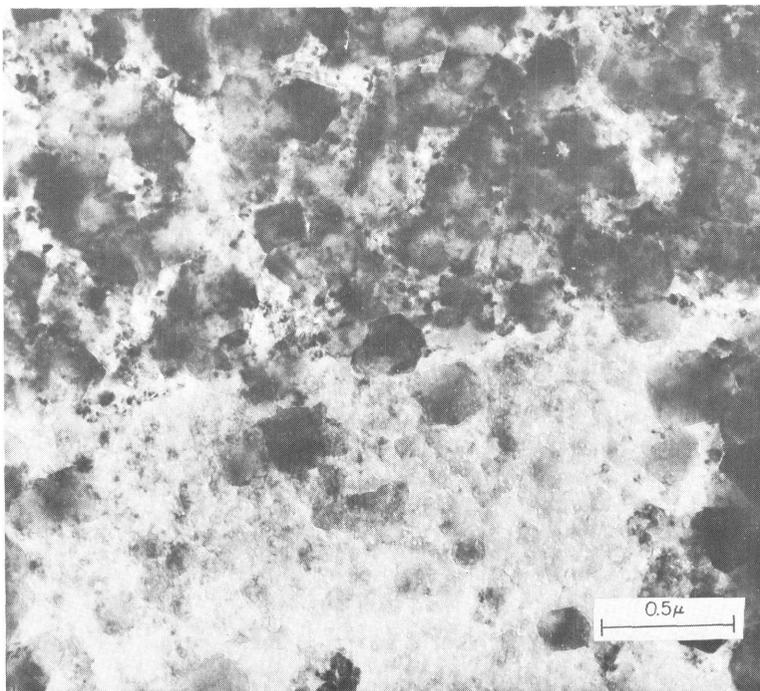


Fig. 3 — Boundary to growth area on H₂O-generated iron oxide film after 2 hours in 316°C furnace. Original magnification 66,000X.

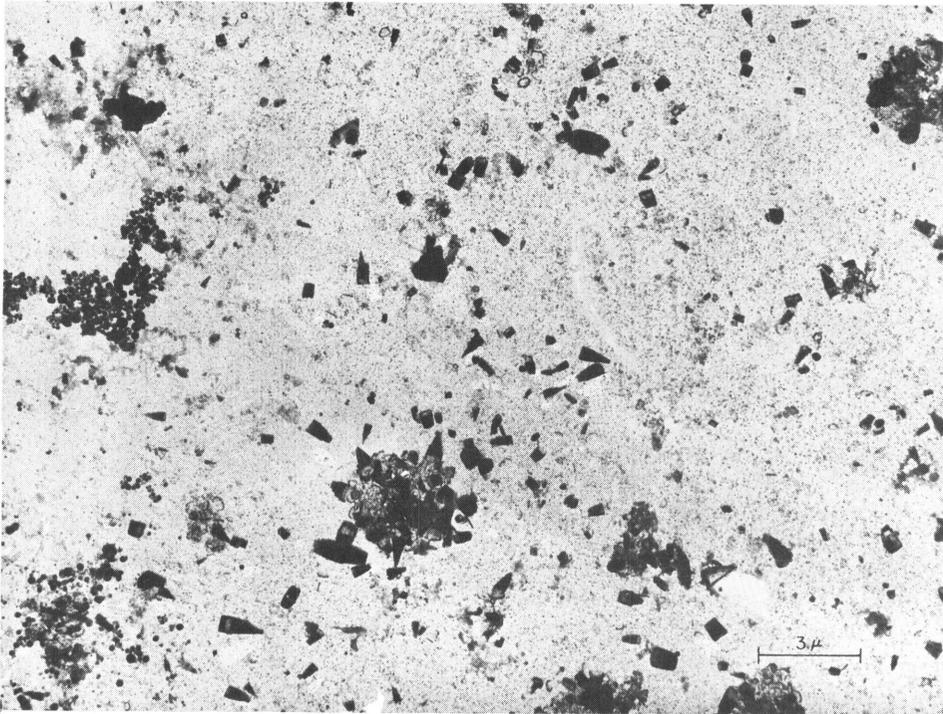
IRON OXIDE FILMS FORMED IN 1.5% LiOH AT 316°C

While macroscopic inhomogeneity of the oxide layer on some specimens was encountered in this series of experiments, a very definite trend in the mode of oxide formation on the microscopic scale with increasing periods of heating was observed. Figure 4 shows stripped oxide films from capsules exposed to 1.5% LiOH at room temperature (Fig. 4(a)) and then heated 15 minutes (Fig. 4(b)), 30 minutes (Fig. 4(c)), or 2 hours (Fig. 4(d)) at 316°C. The oxide film in Fig. 4(a) differs from the one produced with H₂O under the same conditions primarily by the presence of two distinct types of particulate matter, the first being small quasi-rectangular crystals which have very unusual contrast and occur randomly or in "patches," while the second consists of spheroids of uniform contrast which appear in groups arranged in clusters or strings. Platinum-carbon preshadowed replicas of this surface, Fig. 5, show that these are indeed rectangular crystals which rise above the oxide surface and that in each crystal there are sections which, as indicated by the crystal's "shadow," are as thick as the rest of the crystal and yet are quite transparent. The explanation of this phenomenon is not known. It can also be seen from the micrograph that the specimen surface between the crystals in this case is very granular. Selected area diffraction from a sector densely populated with these crystals on another unshadowed film gave diffraction patterns which, although they were obscured by high background intensity, contained the lines listed in Table 1. If it were not for the presence of the 2.21-A line, this pattern could be indexed on the spinel structure of magnetite. Both the lithium substituted spinel, LiFe₅O₈, and *gamma* ferric oxide, γ -Fe₂O₃, give diffraction patterns of the same general "spinel type" as Fe₃O₄ except that extra lines, among them the 2.21-A line, appear. The relative intensity of these reflections compared to the major lines is very low, however, and it is unlikely that they would be visible in a faint diffraction pattern such as this. It was also observed that the crystals in question were never found on oxide films which had been heated to 316°C. This would preclude LiFe₅O₈ and γ -Fe₂O₃, since both are insoluble and stable over these temperature ranges. In a

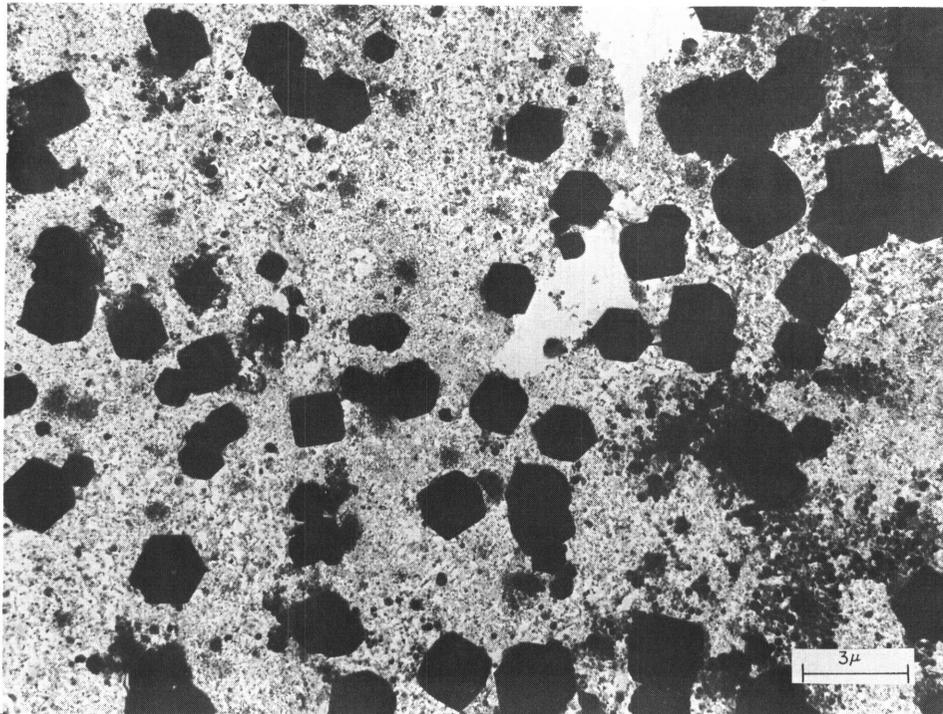
discussion of the oxides found at an iron alkaline electrode, Mee (9) has pointed out that α -FeOOH was a possible source for an unexplained 2.22-A peak observed there. The conditions within our capsule specimen are suitable for the formation of this hydrated oxide. It is also noteworthy that this compound decomposes to Fe₃O₄ on heating, which would explain the disappearance of the surface crystals as the specimen is brought to temperature. The finding that none of the other three strong lines (4.18 Å, 3.36 Å, and 2.69 Å) of α -FeOOH which would be distinguishable from the Fe₃O₄ pattern is disquieting, but with diffraction from very thin films of this sort, it is not uncommon for lines, perhaps because of orientation or crystal shape effects, to be absent. From these considerations it was concluded that the rectangular surface crystals found on oxide films formed in 1.5% LiOH at room temperature were probably α -FeOOH.

Spherical particles of the type seen in Fig. 4(a) have been previously observed to form on iodine-methanol stripped magnetite films after the separated films had been exposed for short intervals to air (10). Figure 6, a platinum-carbon preshadowed replica of the oxide film on an untreated section of tubing which was stripped after the shadowing process had been performed, supports the idea that the particles are produced after (or perhaps during) the stripping step, for while the features of the base film, which still adheres to the replica, are shadowed, the spheres themselves are not. These particles gave poorly defined selected area diffraction patterns which could not be positively identified, although they appeared to be from Fe₃O₄. There is no apparent part taken by the spherical particles in the oxidation processes of the film as a whole.

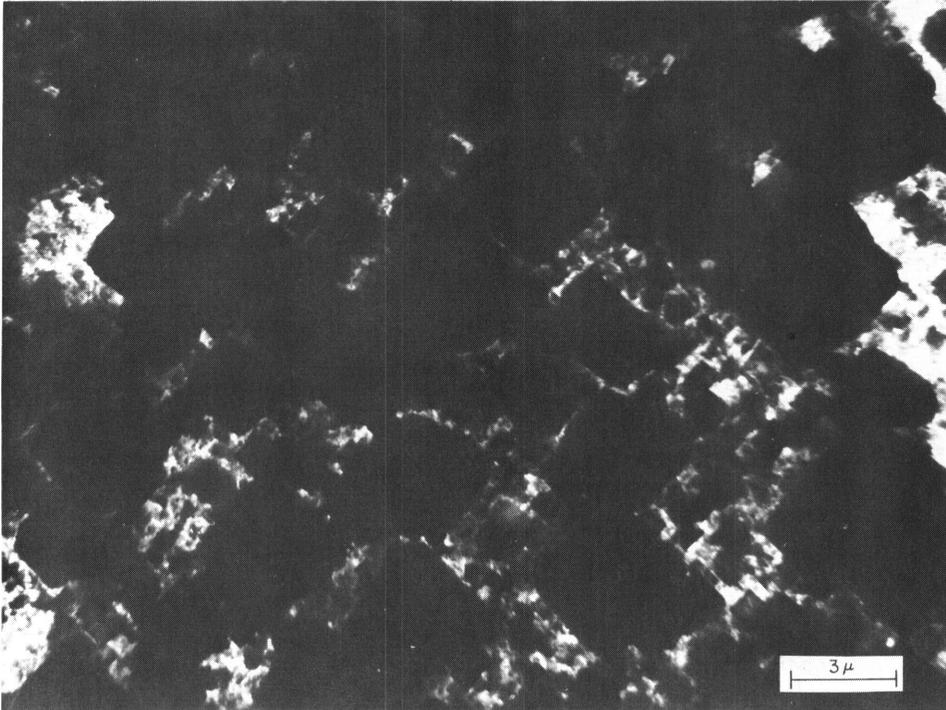
After 15 minutes heating, Fig. 4(b), well-developed, very opaque crystals are found widely dispersed on the oxide surface. Two forms are to be seen, one square and the other hexagonal. Shadowed replicas of this surface indicate that the two forms are of approximately equal thickness (about 1 micron) and that the square-based crystals are about as thick as they are wide, and are presumably cubic. The appearance of the tiny crystallites in the base film here is somewhat altered in comparison to their appearance in films obtained with H₂O under the same conditions (Fig. 1(b)). Nonetheless, selected area diffraction



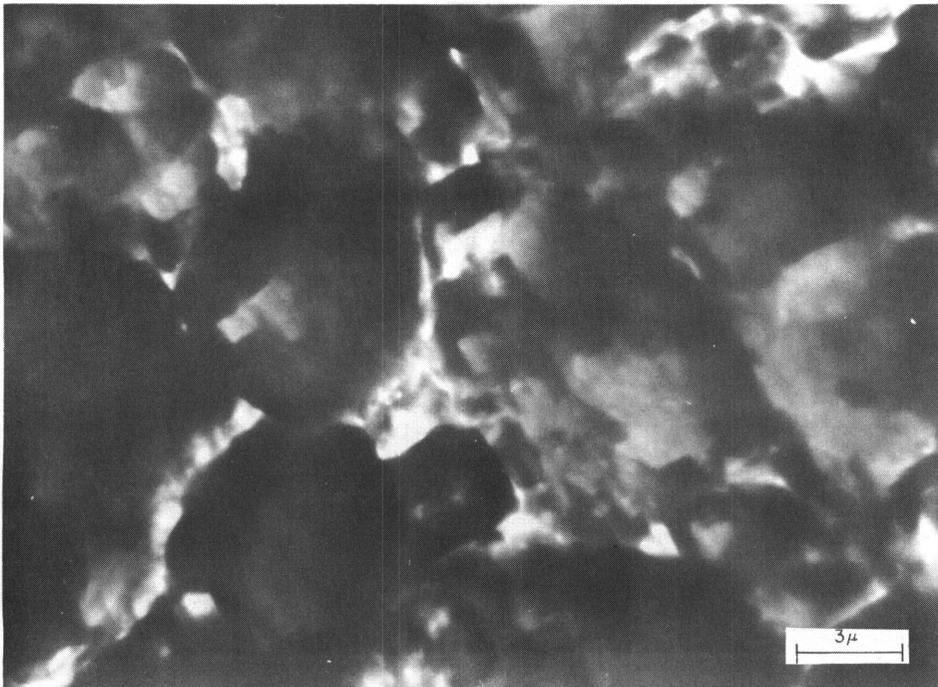
(a) Overnight at room temperature



(b) 15 minutes in 316°C furnace



(c) 30 minutes in 316°C furnace



(d) 2 hours in 316°C furnace

Fig. 4 — Iron oxide films produced by various heating exposures on the interior of capsules containing 1.5% LiOH. Original magnification 9000X.

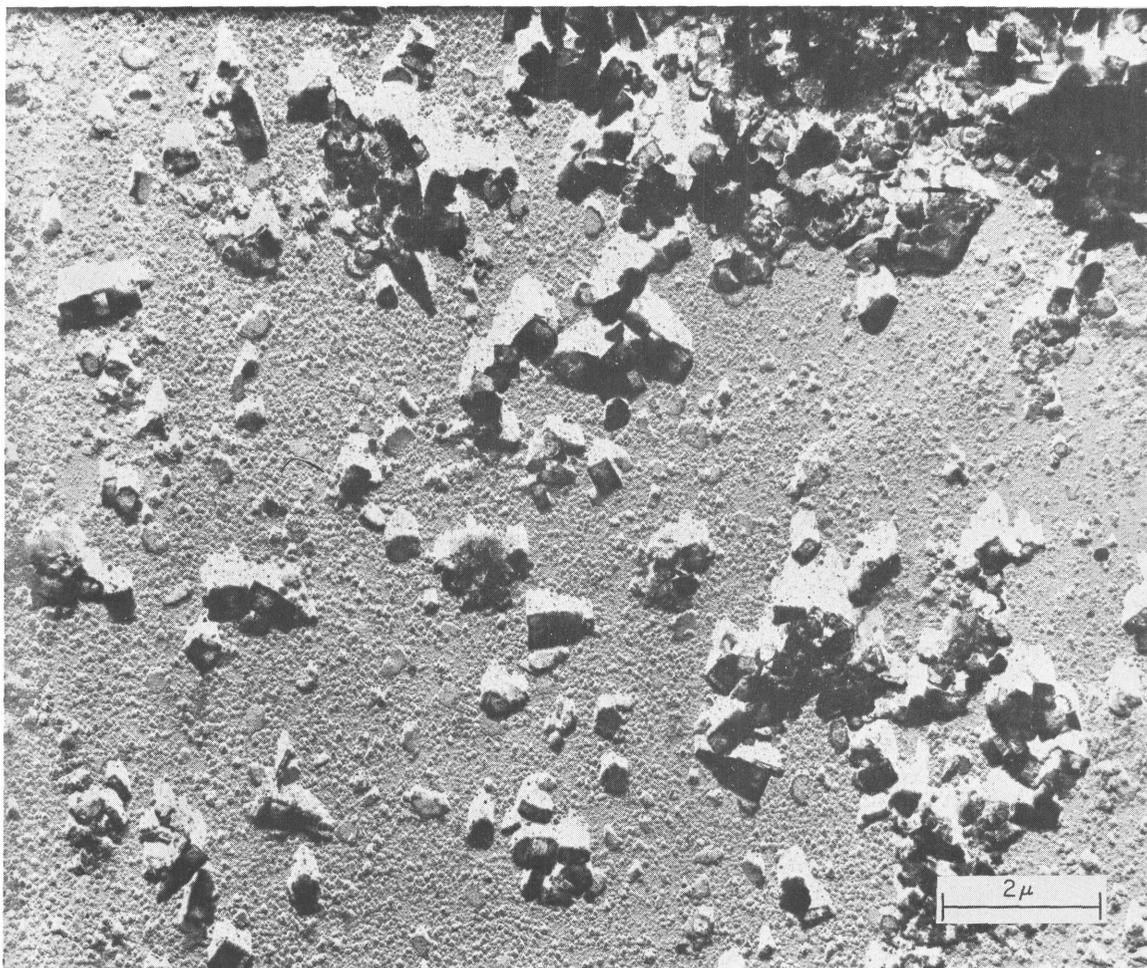


Fig. 5 - Platinum-carbon preshadowed replica of crystals on the surface of an iron oxide film after 24 hours at room temperature in 1.5% LiOH. Original magnification 16,000X.

TABLE I
Comparison of Diffraction Patterns of Anomalous Crystals Found on Oxide After 24 Hours in 1.5% LiOH at Room Temperature and Fe_3O_4

Anomalous Crystals		Fe_3O_4 (ASTM 11-614)	
d (Å)	Est. Int.	d (Å)	I/I°
		4.85	40
2.94	MW	2.966	70
2.50	S (diffuse)	2.530	100
		2.419	10
2.21	MW		
2.09	W	2.096	70
1.70	M	1.712	60
1.61	W	1.614	85
1.47	S (diffuse)	1.483	85

patterns of this oxide film, as well as those exhibited by films produced by more prolonged heat treatments, showed only magnetite reflections. The large surface crystals are too thick for penetration by 100-kV electrons and should contribute little to the pattern.

After 30 minutes at 316°C, Fig. 4(c), surface coverage is more complete, with the overlying crystals starting to form semicontinuous layers. A considerable degree of orientation between neighboring crystals is often noted in these upper layers. Such areas must result from some undefined substrate effect. Gulbransen, *et al.* (11) have reported "lines of growth" for iron oxide crystals produced at low oxygen pressures and have suggested that they are a function of the substructure

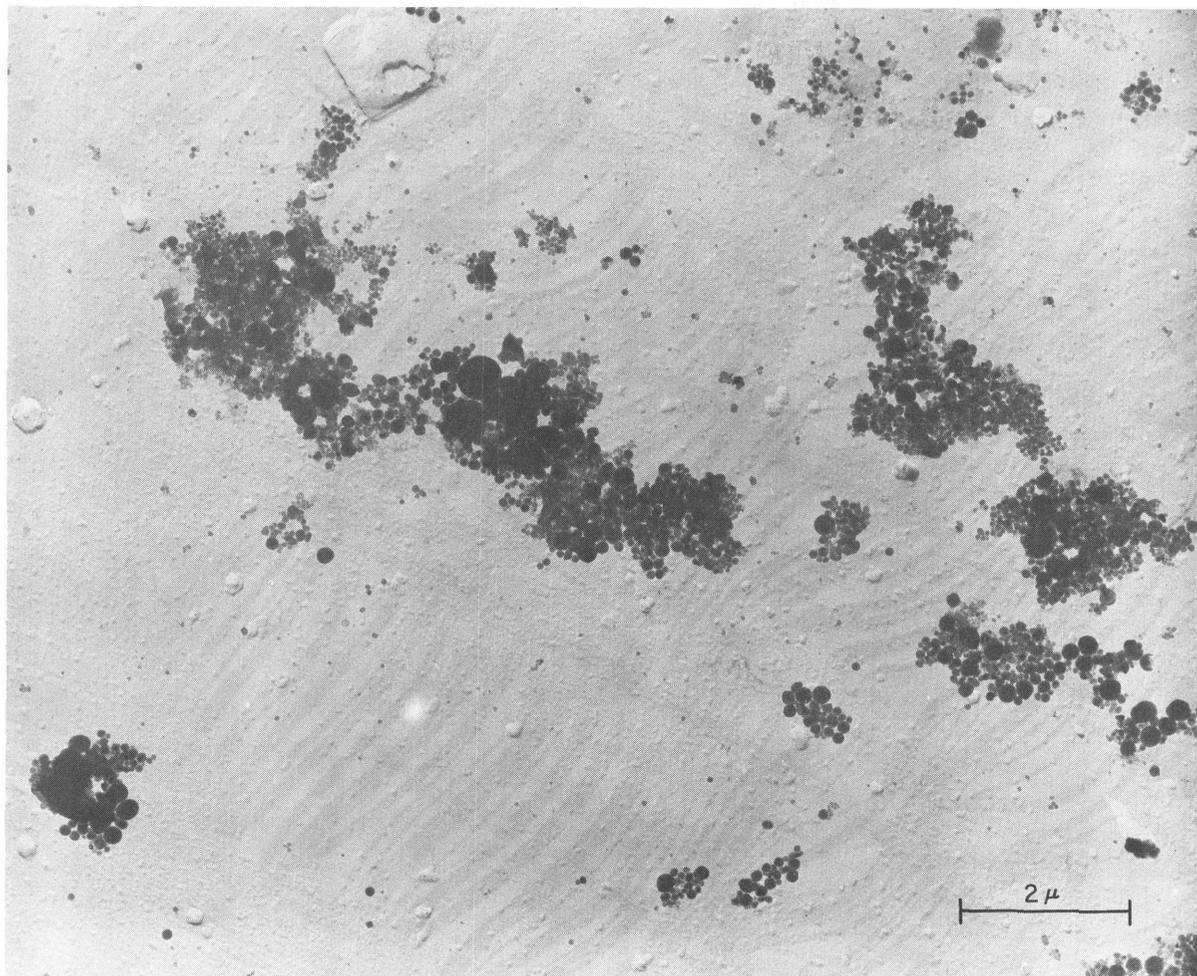


Fig. 6 — Platinum-carbon preshadowed replica of an iron oxide film stripped from an untreated steel tubing "blank." Original Magnification 16,000X.

of the metal grain. Capsules heated 2 hours at 316°C yield oxide films where the degree of coverage by the upper crystals is still greater. The crystals themselves are somewhat larger. As seen in Fig. 4(d), however, cracks and voids do exist between individual crystals. Oxide films from specimens heated much longer than about 2 hours in 1.5% LiOH are too thick for effective study by transmission electron microscopy, but, if films from heating exposures of as much as 24 hours are scanned, fissures and "thin spots" can be found through which the remnants of the base film can be discerned.

The identification of the electron opaque crystals of the upper oxide surface was approached through the technique of extraction replication.

This procedure is depicted schematically in Fig. 7. After a supporting layer of carbon has been evaporated onto the specimen surface, the intervening oxide film is dissolved in approximately 4-N HCl, allowing the carbon film, which retains a certain number of oxide particles, to float to the surface of the acid solution. The extraction replicas were washed in distilled water and then methanol before being mounted on microscopy grids. An electron micrograph of iron oxide grains extracted in this way (Fig. 8), shows that the particles have been diminished and thinned by the dissolution action of the acid. Selected area diffraction patterns can now be obtained from many of these thinned crystals; they show, as in Fig. 9, that the particles are indeed single crystalline.

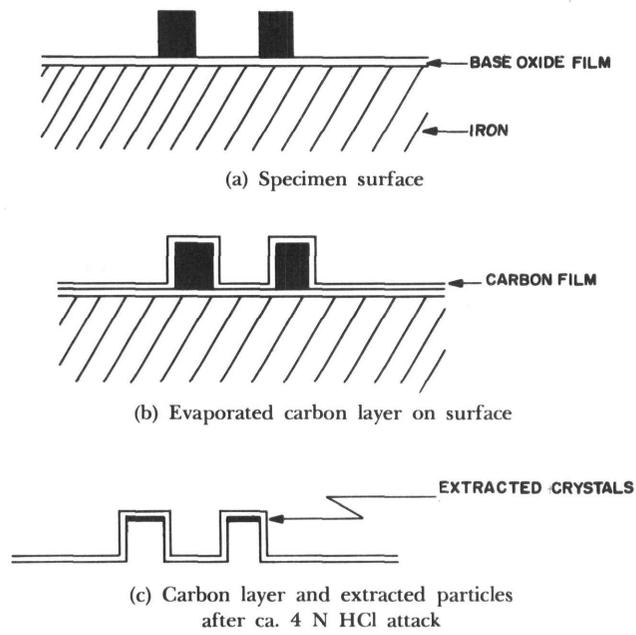


Fig. 7 — Representation of the carbon extraction replica method

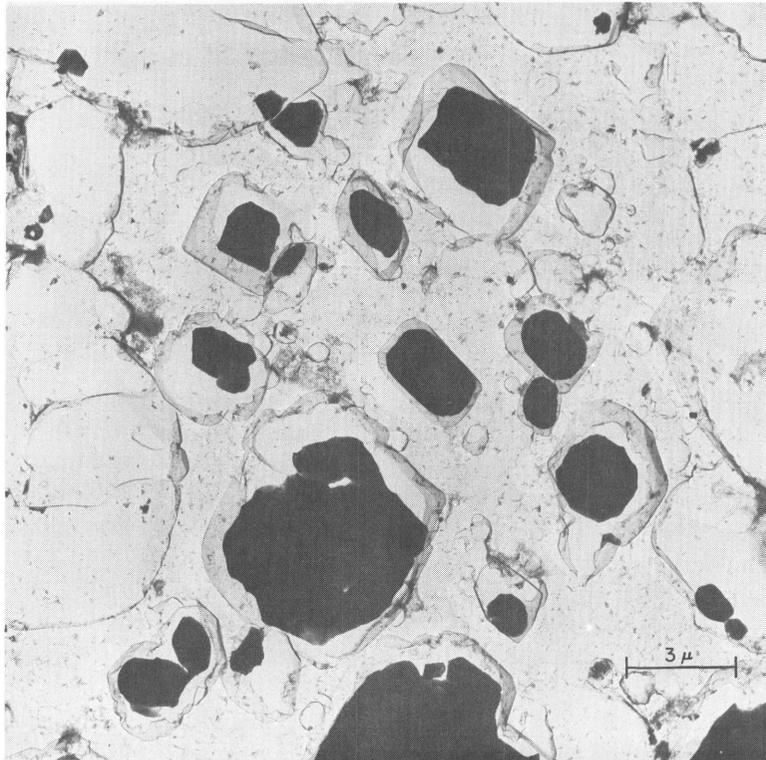


Fig. 8 — Carbon film and extracted surface crystals from a 1.5% LiOH generated iron oxide film after 2 hours in 316°C furnace. Original magnification 9000X.

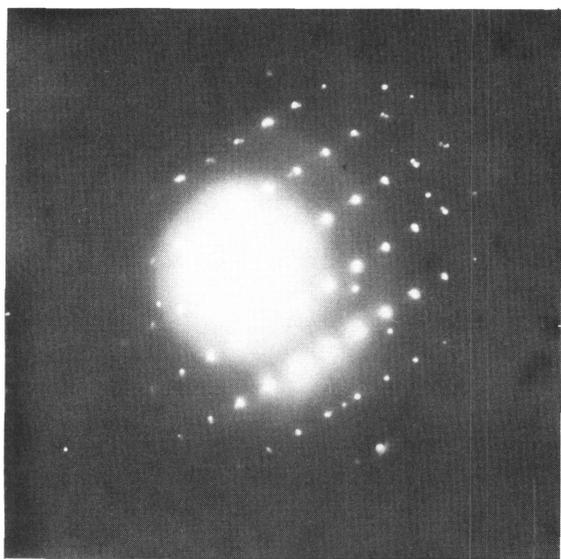


Fig. 9 — Selected area diffraction pattern from extracted surface crystal

TABLE 2
Identification of Surface Crystals Extracted from Iron Oxide Films Produced in 1.5% LiOH at 316°C

Duration of Heat Treatment	Crystal Compound Identified
2 hours	Spinel
24 hours	L. T. LiFeO ₂ plus spinel
2 months	L. T. LiFeO ₂

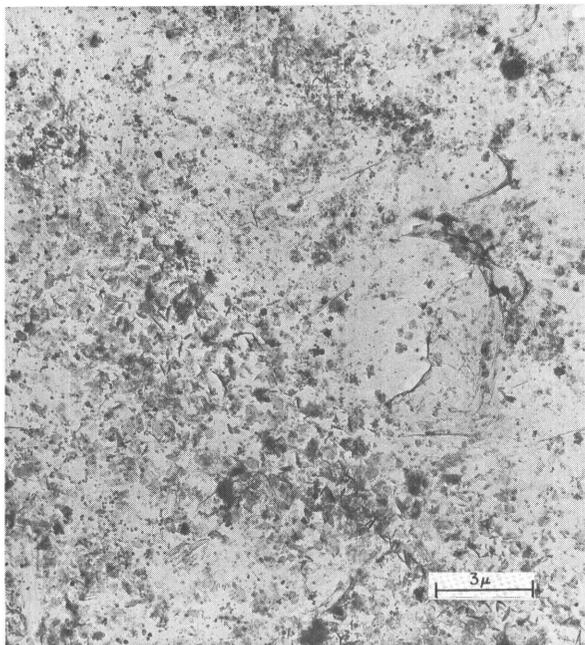
The surface crystals from iron oxide films generated in 1.5% LiOH at 316°C with increasing periods of time were examined in this way. The findings from these experiments are summarized in Table 2. Particles of a distinctively different appearance were also occasionally observed. Their selected area diffraction patterns agreed well with the pattern given for iron carbide, FeC, (ASTM 3-0411), and they were dismissed as artifacts. No particular orientation was shown by either the spinel or low temperature LiFeO₂ crystals, with diffraction patterns from most of the common diffraction planes being found.

To ascertain whether the spinel was the lithium-substituted spinel, LiFe₅O₈, or magnetite, samples of the stripped films were submitted for trace analyses as to the relative amounts of lithium and iron present. These data are given in Table 3. Since the specimen areas from which the oxide films were obtained were approximately equal (certainly within the ratio of 2 to 1), it seems likely that the great increase in the amount of iron detected after 30 minutes heating over that found after 15 minutes heating corresponds to the drastic thickening of the oxide film by the formation of an overlayer of thick crystals as observed in the electron microscope. If so, the bulk of the oxide at 30 minutes consists of the opaque spinel crystals in question, and, if they are indeed LiFe₅O₈, approximately 2μg of lithium should be present. The sensitivity of the lithium test was sufficiently great that this amount of lithium should be easily detected. Since no lithium was

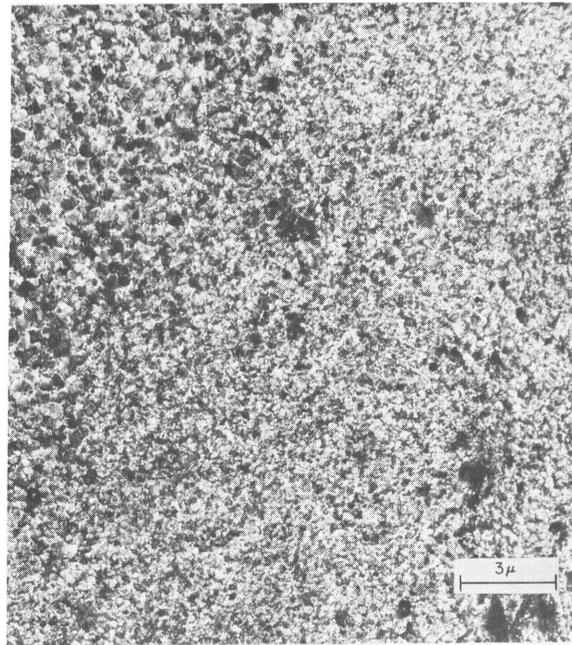
TABLE 3
Analysis for Lithium and Iron Present in Stripped Iron Oxide Films Produced in 1.5% LiOH at 316°C

Duration of Heat Treatment	Lithium (μg)	Iron (μg)	Li/Fe Weight Ratio*
24 hours (at room temp.)	—	—	—
15 minutes	—	1	—
30 minutes	—	79	—
1 hour	—	54	—
2 hours	trace	100	—
4 hours	—	14	—
24 hours	3.5	36	0.097
2 months	12.5	112	0.112

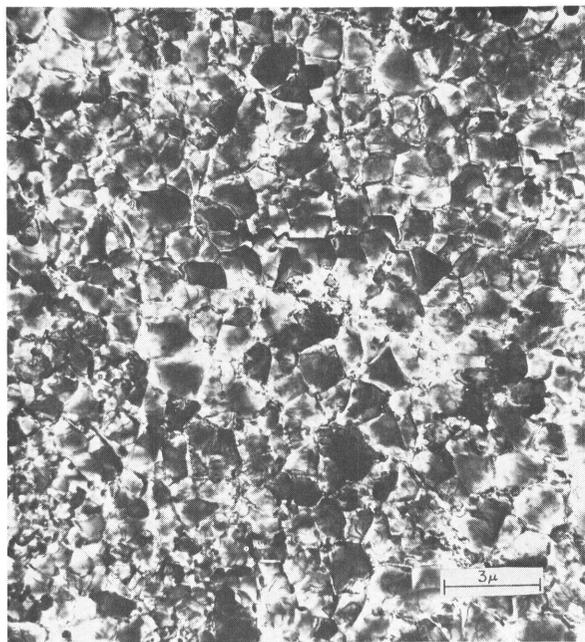
*Weight ratio Li/Fe for L. T. LiFeO₂, 0.124; for LiFe₅O₈, 0.025.



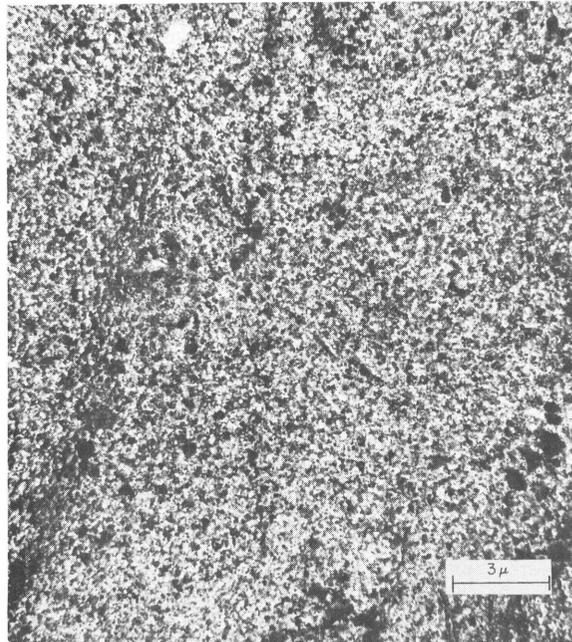
(a) Overnight at room temperature



(b) 15 minutes in 316°C furnace



(c) 30 minutes in 316°C furnace



(d) 2 hours in 316°C furnace

Fig. 10 — Iron oxide films produced by various heating exposures on the interior of capsules containing LiOH/EDTA (pH 11) solution. Original magnification 9000X.

found, it was concluded that the spinel phase could not be LiFe_5O_8 and that it was probably therefore Fe_3O_4 . Although these analytical experiments were cursory in nature, two phenomena were observed which should perhaps be investigated more fully; these being (a) that while the ratio of lithium to iron approaches stoichiometry for L. T. LiFeO_2 , an excess of iron remains in the film even after two months at 316°C , and (b) that there appears to be definite thinning of the oxide film somewhere between 2 and 24 hours heat exposure.

IRON OXIDE FILMS FORMED IN LiOH/EDTA SOLUTION (pH 11) AT 316°C

The macroscopic appearance of the interior walls of the capsules was quite good, with a uniform, well-developed oxide film in evidence after

only 15 minutes heating. This perfection was duplicated at the microscopic level as can be seen in Fig. 10 where the same time sequence of oxide formation as used for the two previous evaluations is shown. The oxide film on a capsule (Fig. 10(a)) allowed to stand overnight in contact with the LiOH/EDTA solution is in general similar to the oxide film found under the same conditions with distilled water or 1.5% LiOH. Once the capsule is subjected to heating, however, this is no longer the case. After just 15 minutes at 316°C the metal surface (Fig. 10(b)) has become extensively covered with a coherent layer of intimately bound crystals. The speed with which this film develops is demonstrated by Fig. 11, which shows an oxide film from a capsule withdrawn after only 5 minutes in the furnace. At 30 minutes heating (Fig. 10(c)) the size of the individual crystals making up the layer has increased to

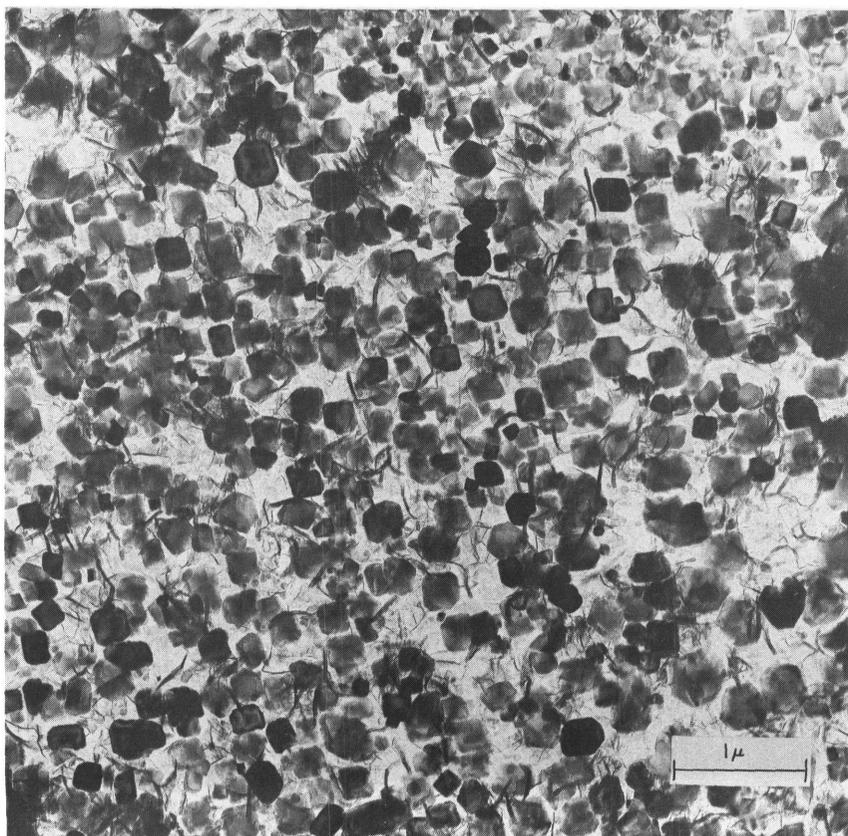


Fig. 11 — Iron oxide film produced by LiOH/EDTA (pH 11) solution after 5 minutes in 316°C furnace. Original magnification 30,000X.

approximately one micron, and the boundaries between crystals are plainly visible. If an aperture that selects a very small area is used, so that the greater part of the field is taken by a single crystal, very good single crystal diffraction patterns which can be indexed on the Fe_3O_4 spinel structure are obtained from the film at this point of development. Figure 10(d) shows the oxide film after 2 hours heating. Note that the oxide grains are once again smaller. At 24 hours, the film is somewhat thicker, but still transparent to 100-kV electrons. Its appearance is virtually the same as at 2 hours heating.

All of the oxide films prepared with LiOH/EDTA solution gave excellent polycrystalline ring patterns (Fig. 12) with sharp, homogeneous lines and no indication of crystal orientation. The interplanar spacings measured from Fig. 12 and

those obtained by Cohen, *et al.* (6), for magnetite films produced by gaseous oxidation of freshly reduced iron are compared in Table 4. In both instances the oxide film was stripped in I_2/MeOH solution. The excellent agreement shown in this comparison indicates that the film produced from the LiOH/EDTA solution under the conditions of these experiments is Fe_3O_4 . Some lines (shown in parentheses in Table 4) which are forbidden by the space group requirements of magnetite do occur; however, these reflections are commonly reported for Fe_3O_4 films and are usually explained as resulting from double diffraction (8).

CONCLUSION

Three distinct trends in surface oxide film growth have been observed for the three different

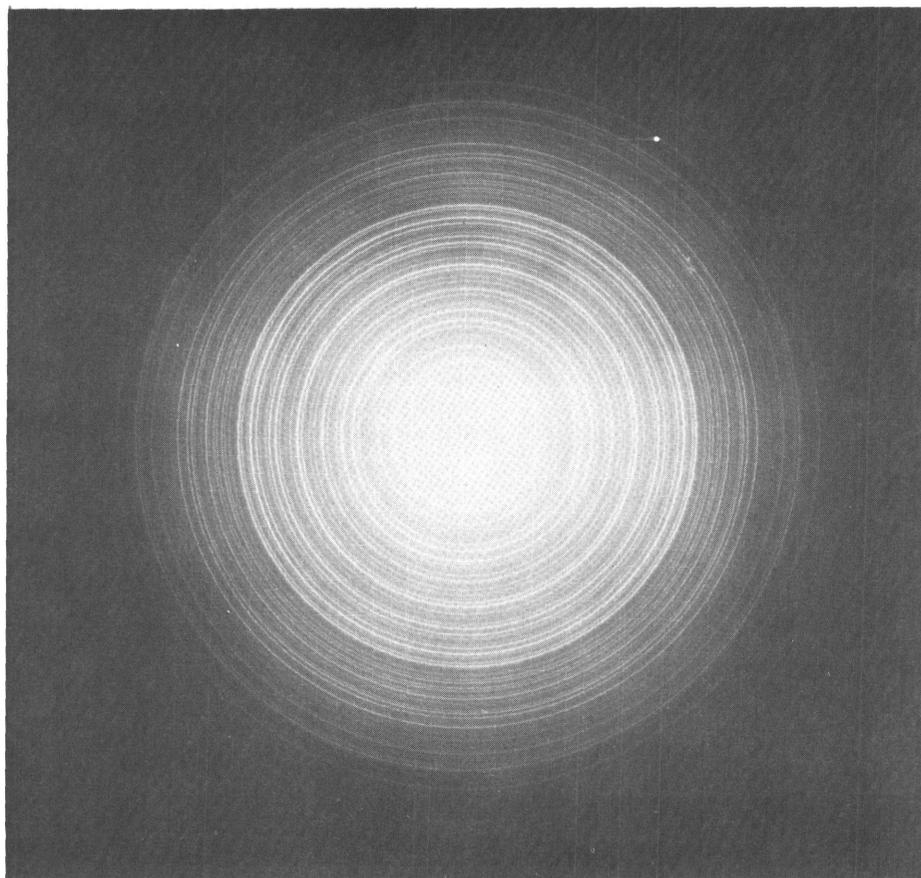


Fig. 12 — Electron diffraction pattern from an iron oxide film produced by LiOH/EDTA (pH 11) solution after 30 minutes in 316°C furnace

TABLE 4
Comparison of Electron Diffraction Patterns
from Oxide Films from LiOH/EDTA
Solution and from Fe₃O₄ Film
Formed by Gaseous Oxidation of Iron (6)

	Film from LiOH/EDTA	I (est)	Film from Fe ₃ O ₄	I/I°	Spinel Index
1.	4.81 A	S	4.81 A	25	111
2.	4.17	VW	4.20	4	(200)
3.	2.95	S	2.97	40	220
4.	2.52	VS	2.53	100	311
5.	2.41	M	2.43	20	222
6.	2.10	S	2.09	25	400
7.	1.92	W	1.92	8	331
8.	1.87	W	1.87	6	(420)
9.	1.71	MS	1.71	25	422
10.	1.61	S	1.62	40	333, 511
11.	1.48	S	1.48	50	440
12.	1.42	MW	1.42	13	531
13.	1.40	W	—	—	(600)
14.	1.33	M	1.32	13	620
15.	1.28	MS	1.28	20	533
16.	1.26	W	—	—	622
17.	1.21	M	1.21	17	444
18.	1.18	MW	1.17	13	551, 711
19.	1.16	VW	—	—	(640)
20.	1.12	M	1.12	20	642
21.	1.09	MS	1.09	25	553, 731

test solutions. These may be described succinctly in the following manner.

With H₂O, the semiamorphous magnetite film present on the capsule wall after the overnight equilibrating period begins to crystallize when the capsule is lowered into the furnace. The degree of crystallinity and thickness of this film increases with time; however, after about 15 minutes in the furnace, discrete crystals begin to appear, usually in clusters sparsely distributed over the oxide surface. With longer times at 316°C, the "growth areas" for the surface crystals increase in size and number, and the individual crystals themselves in size, so that the thickness of the surface crystal film at a given spot becomes greater. The base film remains relatively unchanged, and the overlying surface crystal film begins to make up the major part of the composite film. Selected area diffraction patterns from fields containing

large numbers of surface crystals frequently are single-crystalline simple arrays, indicating that the crystals grow in an oriented manner. The growth areas for these crystals are localized for short times of heating and are often sharply delineated. Both of these observations are indicative of epitaxial growth of the surface crystals, presumably on the surface oxide film, which may itself be in epitaxial relation with the underlying metal. Even after 24 hours at 316°C, the composite oxide film is not uniform, and many areas consisting primarily of the base film only can be found. The major mass of crystals has a diameter in the 1000-A region, few crystals exceeding 2000 A. All diffraction patterns from films generated in H₂O have shown only spinel reflections, consistent with a magnetite film composition.

When the capsule interiors are exposed to 1.5% LiOH solution, the physical characteristics of the base film are essentially the same as with H₂O, and its chemical composition is once again Fe₃O₄, as evidenced by selected area diffraction, but the surface crystals which appear as the capsule comes to temperature are quite different; here they have very well-defined crystallographic forms—being either cubic or hexagonal—and are as large as 1 micron in diameter even at the 15-minute interval. Selected area diffraction of thinned, extracted surface crystals from capsules given 2 hours heating show that they are spinel single crystals, and, since a Li/Fe analysis shows no lithium in films generated by short heating times, they are taken to be Fe₃O₄. Longer heating produces greater coverage of the specimen surface, but localized growth is observed here also, and the overlying film contains defects and does not give continuous coverage even after 24 hours at 316°C. There is apparently a reaction producing L. T. LiFeO₂ which takes place in the oxide film sometime after approximately 2 hours heating, as evidenced by diffraction patterns from extracted crystals and analytical data concerning the Li/Fe ratio in the total film. No physical change in the stripped film was seen that could be unequivocally related to the change in chemical composition of the film.

A most striking phenomenon is observed in the experiments with LiOH/EDTA additives; in contrast to the situation with H₂O or 1.5% LiOH, a uniform, coherent, and apparently continuous film of oxide crystals is formed on the specimen

surface after 15 minutes in the furnace. Although the individual crystal size decreases somewhat as the oxide thickness increases, the film retains its highly desirable characteristics throughout the heating cycle. Electron diffraction patterns from this oxide film show very good Fe_3O_4 rings with no indication of crystal orientation. Selected area patterns tended to be much more often polycrystalline than was the case with oxide films from the other two treatments. Sites of preferential growth were also absent. These observations were taken as indication that the substrate effect on oxide film formation was somehow reduced by the addition of LiOH/EDTA.

Considered in terms of what specific corrosion inhibitive properties are imparted by LiOH and LiOH/EDTA additives, these investigations of the early stages of oxide film development indicate that the effect of adding 1.5% LiOH is to produce a thicker oxide layer of much larger crystals more quickly than would be the case with H_2O . The additional thickness of the oxide provides greater protection for the steel substrate, and the larger crystallite size would tend to prevent their displacement by water currents as occur in steam boilers. However, oxide films produced in 1.5% LiOH solution show preferential growth sites which hinder the early formation of a continuous oxide layer, and, even in areas where the surface coverage is good, the film is observed to be porous with cracks between the individual crystals extending down to the base film. When LiOH/EDTA additives are used, the film produced does not have either of these faults; it is a continuous, coherent film of intimately bound magnetite crystals which grows quickly to appreciable thick-

ness and which should, from all appearances, provide excellent protection for the base metal. The role of EDTA seems to be to reduce the substrate influence on the mode of oxide film growth, perhaps by some sort of preconditioning. A degree of in-service cleaning was found in the MEL model boiler tests using this additive (3).

Further experiments designed to clarify the function of organic chelating agents in boiler water treatments are underway, and the structural aspects will be followed by techniques analogous to those described in this report.

ACKNOWLEDGMENTS

The authors thank Mr. G. N. Newport who prepared the specimen capsules used here and Mr. O. R. Gates who performed the analyses of the iron oxide films.

REFERENCES

1. Bloom, M. C., Fraser, W. A., and Krulfeld, M., *Corrosion* **18**:401t (1962)
2. Bloom, M. C., Krulfeld, M., and Fraser, W. A., *Corrosion* **19**:327t (1963)
3. Bolander, E. H., MEL Report 209/65, June 1965
4. Bloom, M. C., and Krulfeld, M., *J. Electrochem. Soc.* **104** (No. 5):264 (1957)
5. Vernon, W. H. J., Wormwell, F., and Nurse, T. J., *J. Chem. Soc.* **1939**:621
6. Buob, K. H., Beck, A. F., and Cohen, M., *J. Electrochem. Soc.* **105**:74 (1958)
7. Field, E. M., and Holmes, D. R., *Corr. Sci.* **5**:361 (1965)
8. Haase, O., *Z. Naturforsch.* **11A**:46 (1956)
9. Mee, P. B., *J. Electrochem. Soc.* **112**:646 (1965)
10. Fursey, A., *Nature* **207** (No. 4998):747 (1965)
11. Gulbransen, E. A., *et al*, *J. Metals* **6**:1027 (1954)

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP Unclassified
3. REPORT TITLE AN ELECTRON OPTICAL SURVEY OF IRON OXIDE FILMS PRODUCED IN H ₂ O, 1.5% LiOH, AND LiOH/EDTA (pH 11) SOLUTIONS AT 316°C		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) An interim report on one phase of the problem.		
5. AUTHOR(S) (Last name, first name, initial) Jones, R. L., and Bloom, M. C.		
6. REPORT DATE September 29, 1966	7a. TOTAL NO. OF PAGES 22 pages	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. NRL Problem C05-22	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6442	
b. PROJECT NO. RR 001-01-43-4758	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited. Copies available at CFSTI.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research)	
13. ABSTRACT In the exploration of steel corrosion mechanisms pertinent to steam power generation, LiOH has been investigated as an alkalinizing agent to form protective oxide films on boiler walls. Steel capsules treated in three different ways, (a) with H ₂ O, (b) with 1.5% LiOH solution, and (c) with LiOH/EDTA (pH 11) at 316°C, formed films which, in the initial stages of development, were shown to be Fe ₃ O ₄ . However, the crystallite size, the degree of orientation, and the film uniformity and continuity, determined by electron microscopy and diffraction, varied with the method and length of treatment. The film formed by distilled water showed small (1000 to 2000 Å), oriented crystals with sharply delineated areas of growth. When the LiOH solution was used in the treatment, larger crystals were formed, but flaws were still noticeable after 24 hours. With the LiOH/EDTA solution, the growth of the crystals was very rapid, forming a thick, coherent film on the metal, which should offer excellent protection against corrosion.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Corrosion-inhibition Iron Electron diffraction analysis Boilers						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.