

## An Electron Diffraction Study of the Grain Boundaries in Iron

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rapid for accurate measurement, and a slight experimental error in a vapor pressure measurement would be greatly magnified in a calculation of a heat of vaporization. Consequently the only check with the calorimetric data<sup>18</sup> which would have any meaning is in the neighborhood of 350°C. Here Bridgman's data give a value of 19.1 kilojoules per gram atom as the difference in total heats between black (1914) and red phosphorus. This compares favorably with the value of 17.5 which one obtains from Table I. Apparently, this agreement would tend to support the validity of the vapor pressure data for black phosphorus below 560°. At the same time, it would cast some doubt on Smits' hypothesis of the metastability of black phosphorus in this region. This follows from the fact that Smits has placed emphasis on the fact that the data for black phosphorus below 560°C is not good since constant values cannot be obtained. The tendency, he says, is always toward an increase, and presumably toward a value *higher* than that of red phosphorus. Were this the case, there would be no agreement with the calorimetric values like

<sup>18</sup> This comparison of calorimetric data at 20°C with vapor pressure data at 350°C is only justified by the fact that there is no measurable difference in the specific heats of black and of red phosphorus.

that indicated above, since the data for the black phosphorus would admittedly be incorrect.

As a consequence, it seems reasonable to conclude, that black phosphorus below 560°C is the stable form of phosphorus.

Now, glancing again at Table I, one is confronted with a progression of this nature: black, red, white. This is the order of the stabilities, the order of the total heats, and the order of the densities. As far as density and total heats are concerned, black amorphous phosphorus belongs between red phosphorus and white phosphorus. One is tempted to argue by analogy and place black amorphous phosphorus there also in order of stability. Of course, there is no thermodynamical justification for so doing. Quite by accident, however, it was discovered that after prolonged heating at about 125°C black amorphous phosphorus could be transformed into a brilliant violet form of phosphorus, this of course, being a form of red phosphorus. Naturally, now one could positively say that at least at 125°C *red was more stable than black amorphous*, and this would in turn place black crystalline *above* black amorphous in order of stability.

In conclusion, the author gratefully acknowledges the help he has received on this problem from Professor Bridgman.

## An Electron Diffraction Study of the Grain Boundaries in Iron

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Grain boundary membranes, left after the dissolution of iron in ammonium persulphate solution, were studied by means of electron diffraction to determine whether crystalline materials are present in the membranes, and if present to identify the crystals. Samples of untreated and heat-treated transformer iron, and heat-treated electrodeposited iron were used. It was found that heat-treated electrodeposited iron left residues which were suitable for study by electron diffraction when supported by Resoglaz backing films. From the electron diffraction patterns obtained, identification was made of the presence of  $\text{Fe}_3\text{C}$  and of  $\alpha\text{FeOOH}$ . It is suggested that the  $\alpha\text{FeOOH}$  did not exist originally in the grain boundaries, but may have been formed by some chemical reaction either between iron and ammonium persulphate, or between some grain boundary constituent such as an iron oxide and the persulphate solution. The method of studying grain boundary materials does not afford a complete analysis, but it is believed that it makes possible important contributions since the presence of crystalline materials in the residues may be detected.

## INTRODUCTION

THE material present in the space between grains of a metal is commonly designated as grain boundary material, or grain boundaries. Much has been written about its influence on the physical and chemical properties of metals, and in particular, on its effect on the recrystallization and grain growth of metals. Little work has been done, however, to determine the exact nature of the substance.

Rosenhain<sup>1</sup> regarded the material as an amorphous metal, or cement, holding the grains together with very much the same properties as the Beilby amorphous surface layer on polished metals. This hypothesis has been used to explain the alteration of many of the properties of metals when subjected to mechanical and thermal treatment. Sauveur<sup>2</sup> has given an excellent summary of the theory of Rosenhain as well as elaborations upon it by other authors.

G. Tammann has made the most extensive and direct investigations of grain boundaries. He<sup>3</sup> showed that after dissolving certain metals, the material between the grains is left as a residue. This residue is a membrane which has a sponge-like or honey-combed structure—the empty spaces corresponding to the position of the metal grains which have been dissolved. He found that this membrane is so fine and fragile that when the dissolution of metals in acids is accompanied by evolution of gas, the escaping bubbles tear and completely destroy the membrane. When no gas is evolved, as when a lamina of cadmium is dissolved in ammonium nitrate solution, he found that the remaining residue consisted of a very thin, gray, honey-combed film which retains the shape of the original metal lamina. Tammann believed that this film consisted of oxides which form a skin surrounding the individual metal grains. He made similar observations on zinc, but found that the grain boundaries are invisible unless several drops of water saturated with ammonia were added to the ammonium nitrate solution. The ammonia water serves to dissolve

the zinc hydroxide which forms during the dissolution of the metal.

Von Kutzelnigg<sup>4</sup> dissolved pieces of tin foil in a 10 percent iron chloride solution and obtained a small residue in the form of a cohesive, light yellow film, outlining the form of the original foil. He identified the substance as grain boundary material and by a qualitative chemical analysis he deduced that it was a tin compound.

Tammann and his co-workers made further studies of grain boundary residues left after the dissolution of certain metals containing small known quantities of different admixtures. Tammann, Heinzel, and Laass<sup>5</sup> traced with the microscope the distribution of small known admixtures of lead, bismuth, antimony, and tin in the grain boundaries of cadmium. They showed how small quantities up to 0.1 percent of these materials in cadmium can be determined readily by the use of such observations in conjunction with microchemical analysis. They also studied copper and showed how the presence of admixtures of lead, bismuth and antimony can be detected by examining the grain boundary residue. Tammann and Kalge<sup>6</sup> dissolved laminae of electrolytic iron in a solution of ammonium persulphate and by examining the grain boundary residue microscopically were able to detect as little as 0.002 percent ferrous sulphide, less than 0.05 percent aluminum, 0.05 percent antimony, 0.02 percent tin and 0.001 percent silicon. Tammann and Heinzel<sup>7</sup> studied the distribution of admixtures of lead and copper in grain boundary residues of cadmium and thereby determined solubility temperature curves for binary cadmium systems containing lead and copper.

Tammann and Dreyer<sup>8</sup> studied the influence of grain boundaries on the grain size of lead. Thin plates of lead were dissolved in acetic acid-hydrogen peroxide solution. It was concluded that in order to obtain lead of small grain size, about 0.1 percent of copper should be added.

<sup>1</sup> Walter Rosenhain, *Physical Metallurgy* (Constable & Company Ltd., London, 1914), p. 245.

<sup>2</sup> Albert Sauveur, *The Metallography and Heat Treatment of Iron and Steel* (McGraw-Hill, New York, 1935), p. 17.

<sup>3</sup> G. Tammann, *Zeits. f. anorg. allgem. Chemie* **121**, 275 (1921).

<sup>4</sup> Artur Kutzelnigg, *Zeits. f. anorg. allgem. Chemie* **202**, 418 (1931).

<sup>5</sup> G. Tammann, A. Heinzel and F. Laass, *Zeits. f. anorg. allgem. Chemie* **176**, 143 (1928).

<sup>6</sup> G. Tammann and W. Kalge, *Zeits. f. anorg. allgem. Chemie* **176**, 152 (1928).

<sup>7</sup> G. Tammann and A. Heinzel, *Zeits. f. anorg. allgem. Chemie* **176**, 147 (1928).

<sup>8</sup> G. Tammann and K. L. Dreyer, *Zeits. f. anorg. allgem. Chemie* **191**, 65 (1930).

In a paper on recrystallization of metals, Tammann<sup>9</sup> described the changes which take place when metals are cold worked. Each grain is surrounded by a complete skin when it crystallizes out of the melt. He showed that when the metal is cold worked as in rolling, the skin is so torn by the elongation of the grains that after the dissolution of the rolled plate nothing of the original honey-combed structure can be seen in the residue. If the metal is heated subsequently to a sufficiently high temperature, the newly formed grains are surrounded by complete skins and on dissolution the honey-combed structure is again apparent.

The existence of the grain boundary residues in the form of thin films, as described by these workers, suggested an electron diffraction study of the material. Such a study was accordingly undertaken in the case of iron with the hope of determining whether or not crystalline materials are present in the grain boundaries, and if so, to determine what these materials are.

#### EXPERIMENTAL PROCEDURE

Transformer iron was first chosen because it was believed that the high silicon content would make for strong boundary residues. A series of experiments with the iron, however, indicated that the residues were too thick to obtain satisfactory diffraction patterns. Electrodeposited iron was then used and it was found that when the grain boundary residues were properly supported, satisfactory diffraction pictures could be obtained. It is believed that the experimental work done on the transformer iron is of interest and is accordingly described.

#### TRANSFORMER IRON

The chemical composition of the transformer iron is shown in Table I. Laminae of the metal about  $4 \times 6 \times 0.2$  mm in size were used. The laminae were carefully cleaned and the surfaces polished on fine emery paper to remove all visible oxide films. Immediately after polishing, the specimens were degreased with carbon tetrachloride, and then placed in small petrie dishes containing a 12 percent solution by weight of

ammonium persulphate. These dishes were placed on a large block of ice and allowed to stand until the metal grains were completely dissolved, which required about 16 hours. The low temperature was necessary to prevent rapid evolution of gas.

The first observable reaction of the ammonium persulphate with the laminae was the etching of the surfaces. Then, after several hours, the surfaces usually became black and remained so until all the iron was dissolved, or at least the specimens had become flexible. The black coating now slowly disappeared leaving brown membranes which underwent no further visible changes until they were dried.

After the complete dissolution of the metal grains, the grain boundary residues were washed by a slow stream of distilled water until no acidity could be detected. An excess of alcohol was then added slowly to lower the surface tension as much as possible below that of water. The films could then be mounted readily over the 0.1 mm holes of the specimen holders of the electron diffraction camera.<sup>10</sup> A microscopic examination, however, of the grain boundary specimens while they were still in the water showed that they were nonuniform and torn, brownish in color and possessed large deposits of black material. Since such films are rather unsatisfactory for electron diffraction study, the metallic laminae were treated to see if a recrystallization as described by Tammann<sup>9</sup> would produce a more uniform grain boundary skin.

The laminae were pounded on an anvil until they were reduced to roughly half their thickness, and then heated in an oven to a bright red color and allowed to cool slowly. The surfaces of the specimens were then cleaned and polished as

TABLE I.

	ELECTRODEPOSITED IRON	TRANSFORMER IRON
T. Carbon	0.015%	0.018%
Manganese	None	.078
Phosphorus	None	.008
Sulphur	.005	.030
Silicon	.003	4.373
Slag and Oxide	.700	Trace
Copper	.013	.036
Nitrogen	None	.0014

<sup>9</sup> G. Tammann, *Zeits. f. anorg. allgem. Chemie* **185**, 41 (1929).

<sup>10</sup> R. Morgan and N. Smith, *Rev. Sci. Inst.* **6**, 316 (1935).

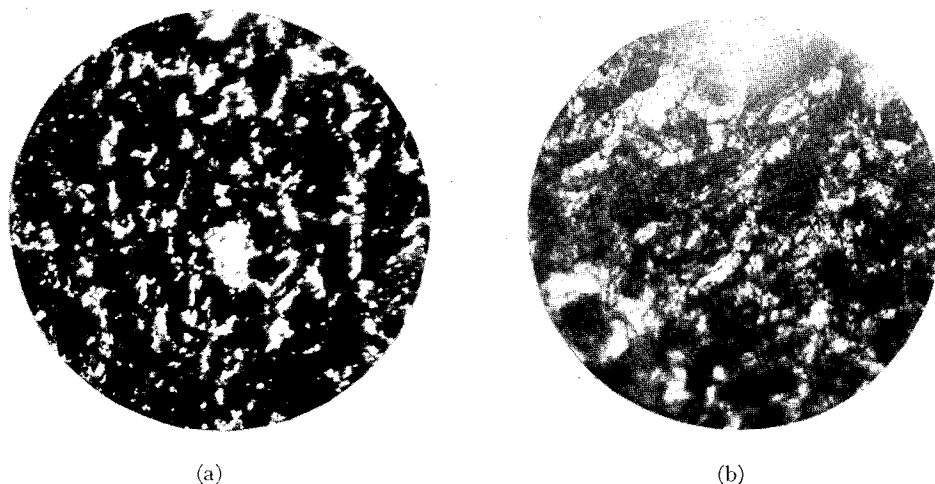


FIG. 1. (a) Not heat treated. (b) Heat treated.

before and the specimens were placed in the persulphate solution for dissolution.

A very marked difference was observed between the films prepared from the heat-treated iron and those from the untreated. Figs. 1(a) and 1(b) are microphotographs taken of the films while still in water. Although much of the difference in appearance is lost in the microphotographs, considerable difference can still be seen. A portion of the picture 1(b) shows slight distortion due to the fact that part of the film was not well in focus.

The grain boundary material from the heat-treated iron (Fig. 1(b)) is much more uniform than that from the untreated iron (Fig. 1(a)) and has fewer black inclusions. Moreover, the residue from the heat-treated iron was an untorn network retaining the shape of the original lamina, and was much more transparent than the residue from the untreated iron.

Because of the difference in these two residues, microphotographs were made of etched surfaces of heat-treated and untreated laminae of the iron to compare their grain structures. These photographs are shown in Figs. 2(a) and 2(b). The black inclusions which are rather numerous in the untreated specimens (Fig. 2(a)) are seen to be very much diminished in the heat-treated specimens (Fig. 2(b)).

When the grain boundary specimens from the heat-treated iron were mounted in preparation for making the electron diffraction pictures, it was observed that after drying the films puffed

up, became fairly thick, quite brittle and powdery. They also turned gray in color, although by transmitted light they were still reddish brown. In the great majority of cases no diffraction patterns could be obtained; there was only a general blackening of the photographic plate. Now and then a few rings appeared and in a few cases, portions of Laue patterns were obtained. It was believed that the films were too thick to give good patterns and a great many attempts to get thinner films were unsuccessful.

#### ELECTRODEPOSITED IRON

Electrodeposited iron with the chemical composition shown in Table I was used. This iron was obtained from the National Bureau of Standards.

It was found that the grain boundary residue of electrodeposited iron was a uniform, honey-combed film, brown in color, very much thinner and more fragile than that left in the case of transformer iron. In fact, the slightest disturbance of the solvent so completely destroyed the film that scarcely a trace remained. Accordingly, utmost care had to be used in washing the film and in introducing the alcohol into the petrie dish. Instead of placing the lamina directly in the petrie dish, as was done with transformer iron, it was first placed in a small crystal glass which in turn was placed in the petrie dish. After the lamina was dissolved and the residue washed in the usual way, the water was pipetted out of the petrie dish and alcohol was added to the dish

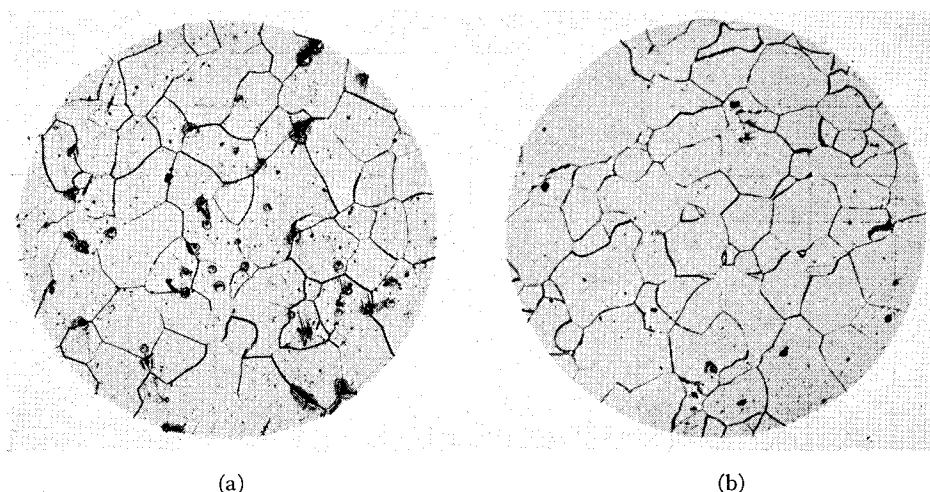


FIG. 2. (a) Not heat treated. (b) Heat treated.

until level with the edge of the crystal glass. This set-up was covered with a bell jar and allowed to stand for several hours. During this time enough alcohol vapor passed into the water in the crystal glass to make possible the addition of alcohol above the level of the crystal glass without setting up convection currents.

After the films were mounted over the 0.1 mm holes of the diffraction camera specimen holders, they were placed under a bell jar and allowed to dry slowly in an alcohol atmosphere. When dry, the specimens became gray and puffy as in the case of transformer iron, but were much more transparent. The films proved to be too brittle, however, to remain intact over the 0.1 mm holes. This difficulty was overcome by the use of Resoglaz supporting films as described by Germer<sup>11</sup> and satisfactory diffraction patterns were obtained. Fig. 3 represents one of the patterns taken at 49,200 volts. There are 28 measurable rings on this plate. In most of the plates there were superimposed on the diffraction patterns three broad bands due to the Resoglaz. These made the estimation of the intensities somewhat more difficult.

In view of the interesting results obtained from the polycrystalline material, it was decided to examine the residue left from the dissolution of a single crystal of iron in ammonium persulphate. Accordingly, some laminae of a single crystal of iron were studied. Not the slightest trace of a

grain boundary skin, or membrane, was observed. On the bottom of the petrie dish, however, there was a deposit of black specks resembling the black inclusions noted in the polycrystalline grain boundary membranes.

## RESULTS

In Table II are given the diffraction data obtained from the grain boundary patterns. A comparison was made between these data and the crystal structure data for a number of compounds which were thought might be present in the grain boundary residue. This comparison showed that only two compounds,  $\text{Fe}_3\text{C}$  (iron carbide) and  $\alpha\text{FeOOH}$  (goethite), could be identified. In Table II are given spacings and intensities for iron carbide based on the x-ray data obtained by Westgren<sup>12</sup> and Westgren and Phragmen.<sup>13</sup> The agreement between the grain boundary and the iron carbide data is sufficient to indicate the presence of iron carbide in the grain boundary residues. In the x-ray data of Westgren, the spacing 3.75 for the (101) planes was not ob-



FIG. 3.

<sup>12</sup> A. Westgren, *Jernkontorets Ann.* **116**, 457 (1932).

<sup>13</sup> A. Westgren and G. Phragmen, *J. Iron Steel Inst.* **105**, 241 (1922).

<sup>11</sup> L. H. Germer, private communication.

TABLE II.

Fe <sub>3</sub> C IRON CARBIDE					GRAIN BOUNDARIES		$\alpha$ FeOOH GOETHITE						
hkl	WESTGREN		WESTGREN AND PHRAGMEN		AVERAGE OF 6 PLATES		GOLDSZTAUB		DEJONG		CATES		hkl
	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	
					5.01	vw	5.07	vs	4.85	vw			020
					4.50	vw			4.54	vw			
					4.24	m	4.28	vs	4.19	vs	4.04	m	110
101	3.75	—			3.77	m					3.75	m	
002	3.36	vw			3.30	s	3.41	s	3.31	m	3.30	vw	120
111	3.01	vw			2.98	s			2.96	w	2.95	vw	
					2.73	w	2.73	vs	2.71	vs			130
					2.64	s			2.57	w	2.62	s	021
020	2.54	vw					2.52	vs	2.48	w			040
112	2.38	m	2.39	m	2.39	m			2.44	vs	2.39	s	111
200	2.26	m	2.26	w	2.25	m	2.28	s			2.20	w	121
121	2.10	s	2.11	m	2.14	m	2.20	s	2.18	m	2.12	m	140
210	2.06	s	2.07	m	2.06	w							
022	2.02	s	2.04	s	2.02	m	2.03	s					131
103	2.01	vs											
211	1.97	s	1.98	m	1.96	w			1.92	m			
113	1.87	m	1.87	s	1.89	w			1.88	vw	1.87	w	
122	1.85	s											
212	1.76	m	1.76	w	1.78	w	1.79	s	1.78	w			141
									1.77	w			
004	1.68	w	1.69	w	1.70	w			1.71	vs	1.69	s	221
									1.68	w			240
221	1.61	w	1.64	vw	1.65	m	1.67	s	1.64	w			060
130	1.58	m	1.59	w	1.60	m	1.58	vs	1.60	m	1.58	m	151
131	1.54	w	1.55	vw	1.55	m			1.56	s	1.54	s	
114	1.50	w	1.51	w	1.48	m			1.50	s	1.49	m	
							1.44	s	1.45	m	1.44	s	112
311			1.42	w									
024	1.40	w			1.38	w	1.39	m	1.39	w			122
124	1.34	w											
231			1.34	m	1.36	m							
312	1.32	s			1.33	m					1.34	m	132
							1.29	s			1.29	w	202
232	1.26	w	1.26	vw			1.27	m					212
140	1.22	s	1.23	m			1.26	s					142
313	1.21	s	1.22	m			1.25	w					222
233	1.16	s	1.16	s	1.21	m							
142	1.14	vw	1.16	s	1.15	w	1.14	s			1.12	m	242
400	1.12	w	1.13	s									
006	1.12	m	1.13	s									
331	1.11	w	1.11	s	1.11	w							
314	1.09	m	1.10	w	1.10	vw							
411	1.09	m	1.09	w			1.08	s					252
242	1.05	w	1.06	m									
412	1.04	w	1.05	vw	1.04	w							

Letters used in describing the intensities are:

vs—very strong  
s—strong  
m—medium  
w—weak  
vw—very weak.

served, but his computation for the intensity showed that there was a faint reflection from these planes. It is, therefore, possible that the 3.79 spacing of the grain boundary data may be due in part to the reflection from the (101) planes of iron carbide.

The spacings and reflection intensities for

$\alpha$  FeOOH, based on the x-ray data of Goldsztaub,<sup>14</sup> deJong<sup>15</sup> and Cates<sup>16</sup> are given in Table II. By comparing the combined findings of these three authors with the spacings obtained for the

<sup>14</sup> M. S. Goldsztaub, *Bul. Soc. Fran. Mineral* **58**, 6 (1935).

<sup>15</sup> W. F. deJong, *Natuurw. Tijdschrift*, **12**, 69 (1930).

<sup>16</sup> J. Cates, *Trans. Faraday Soc.* **29**, 817 (1933).

grain boundary residue it is seen that the agreement is such as to indicate the presence of  $\alpha\text{FeOOH}$ . It is somewhat surprising that there was no spacing in the grain boundary data to correspond with the 2.52 spacing reported by Goldsztaub and the 2.48 spacing by deJong for  $\alpha\text{FeOOH}$ , and with the 2.54 spacing for iron carbide. There is, however, lack of agreement in the literature with regard to the reflections from the (040) planes of  $\alpha\text{FeOOH}$  since Goldsztaub finds that the reflection is strong, deJong that it is weak, and Cates gives nothing.

#### DISCUSSION AND CONCLUSIONS

An examination of the data in Table II shows that practically all the spacings found in the grain boundary data may be accounted for either by the presence of iron carbide, or by the presence of  $\alpha\text{FeOOH}$ . It is therefore impossible to determine whether one of these materials exists by itself or whether both are present. Further analysis, either by the combination of electron and x-ray diffraction, or by some other method, will be necessary to make this determination.

The presence of iron carbide in the grain boundary residues would be expected. It is insoluble in ammonium persulphate, and the initial heat treatment of the iron laminae was such as to cause the iron carbide to gather at the grain boundaries.

The presence of  $\alpha\text{FeOOH}$  in the grain boundary residue would raise the question as to whether the hydrated ferric oxide is present originally in the grain boundaries, or whether it is formed by a chemical reaction accompanying the dissolution of the iron laminae in the persulphate solution. Our knowledge of the impurities in iron leads one to suspect that  $\alpha\text{FeOOH}$  does not occur in the grain boundaries but is formed by some chemical reaction during the process of dissolution of the iron and of washing the residue. Two ways in which it might be formed are: (1) as a result of a chemical reaction of the dissolved iron with

ammonium persulphate, or (2) as a result of a chemical reaction of some grain boundary constituent, such as an oxide of iron, with ammonium persulphate, oxygen and water. This is a problem for a special investigation and work on it is now in progress.

The method of investigation of grain boundary materials which involves the dissolution of the metal grains, does not afford a complete analysis. Materials in the grain boundaries may be changed chemically, or be completely dissolved by the solvent. For example, free copper, present in the grain boundaries of iron, could not be detected by this method due to its dissolution in the persulphate solution. Moreover amorphous material would not be detected by electron diffraction. The method, nevertheless, makes possible important contributions to the study of grain boundaries since the presence of crystalline materials in the residues may be detected.

The authors hope to continue the work by supplementing electron diffraction with x-ray diffraction methods, particularly in the case of heavier films as found in transformer iron. It is proposed to study other metals in addition to iron and if possible to pretreat some of the metal specimens in a hydrogen furnace for purification.

#### ACKNOWLEDGMENTS

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