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Effect of Hydrogen on the X-Ray Parameter and Structure of Electrolytic Manganese[1]

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The effect of the hydrogen content of electrolytic manganese on the average lattice parameter was determined. The parameter varies approximately linearly with the hydrogen content, the enlargement in parameter being 0.0003 percent per cc of gas per 100 grams of metal. The crystals, composing electrolytic manganese metal, are generally not uniform in parameter but show deviations up to ±0.2 or ±0.3 percent. The deviations in parameter between the unit cells of alpha-manganese in a sample of metal are not proportional to the amount of gas in the metal. The effect of various degassing treatments on the parameter and diffraction patterns was determined. The parameters are not effected unless the metal is heated over 300°C. At 500°C and over, the parameter returns to its normal value and the diffraction lines are sharp. The broadening of the diffraction lines in the patterns for the metal containing gas are attributed to non-uniform lattices in the metal due to non-uniform gas distribution, and the results indicate that manganese may be saturated with hydrogen at about 695 cc per 100 grams of metal or 0.06 percent. Manganese metal with normal lattice parameters and uniform structure may be obtained from electrolytic metal by removing the gas and heating it to 500°C for 1 hour. If the metal is heated to 500°C or more during the degassing treatment, subsequent heating is not necessary.

INTRODUCTION

DURING the rather extensive studies by the Bureau of Mines on electrolytic manganese and its alloys, a question has frequently arisen regarding the correct lattice parameter for alpha-manganese. The average parameter as determined from several samples of electrolytic manganese metal was 8.904A. Moreover, the alpha-manganese phase in the Mn-Cu alloys[4] gave a parameter of 8.906A, so it was concluded that the alpha-manganese phase in the alloys was essentially pure manganese. The published[5] parameter for alpha-manganese was only 8.894A, but since the electrolytic metal was more than 99.9 percent pure and the impurities were distributed among a large number of elements, it was unlikely that the discrepancy could be due to impurities in the metal. There was no satisfactory explanation for the discrepancy until the hydrogen content of the electrolytic manganese was investigated. In this study some vacuum-distilled metal was made, and its parameter was found to be 8.8948A. This result checked the published value quite well, and the lines in the pattern were much sharper than those obtained from electrolytic manganese metal. Obviously, some impurity in the electrolytic metal was causing the enlargement in parameter, but the amount of each of the known impurities was small when considered on a percentage basis. The hydrogen content was quite high on a volume basis, however, being 250 cc per 100 grams of metal,[6] so an investigation was made to determine what effect hydrogen might have on the parameters.

TABLE I. Variation of average parameter with gas content.

Material	Parameter in A	Hydrogen content in cc per 100 grams of Mn
Vacuum-distilled manganese	8.8948±0.001	0
Electrolytic manganese transformed from gamma-manganese to alpha-manganese	8.898 ±0.005	95±13
Regular electrolytic manganese	8.904 ±0.004	250±25
Electrolytic manganese, hydrogen content high	8.910 ±0.005	615±50

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

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[4] R. S. Dean, J. R. Long, T. R. Graham, E. V. Potter, and E. T. Hayes, "The Copper-Manganese Equilibrium System," Trans. A.S.M.E. **34**, 443 (1945).

[5] Ralph W. G. Wyckoff, *The Structure of Crystals*, second edition and second edition supplement; *Handbook of Chemistry and Physics*, twenty-seventh edition, 1943–1944.

[6] E. V. Potter, E. T. Hayes, and H. C. Lukens, "Hydrogen Content of Electrolytic Manganese and Its Removal," Am. Inst. of Mining and Metallurgical Eng.–Metals Technology (June 1945), Technical Publication 1809.

CHANGE IN AVERAGE LATTICE PARAMETER WITH HYDROGEN CONTENT

The parameters of a number of samples of regular electrolytic manganese were determined by the Debye-Scherrer method and the hydrogen content of the material was determined by the method outlined in an earlier publication.[6] Most of these samples had about the same hydrogen content; one sample was found with an unusually high hydrogen content, and some samples of manganese, deposited as flexible gamma-manganese, had unusually low hydrogen content. The gamma-manganese changed gradually at room temperature to alpha-manganese, and the parameters were obtained for the alpha-form. The results of these parameter and hydrogen-content determinations are shown in Table I along with corresponding values for vacuum-distilled manganese.

These data are plotted in Fig. 1 and show a linear relation between parameter and hydrogen content within the limits of accuracy of the parameter determinations. The lines in the pattern for vacuum-distilled manganese are quite sharp, and the *K*-alpha doublets are resolved for diffraction angles greater than 45°. The parameter could thus be determined to a greater accuracy than for the other samples, where the lines were broader and none of the doublets were resolved.

EFFECT OF DEGASSING TREATMENTS ON LATTICE PARAMETERS AND DIFFRACTION PATTERNS

Several batches of electrolytic manganese were degassed, according to the procedure suggested in a previous publication,[6] to determine the effect of degassing on the parameter. The metal was heated to temperatures from 300° to 925°C at reduced pressure until the pressure again decreased to its initial value before heating. The treatment times were about 1 hour for temperatures up to 700°C and one-half hour at 925°C. This did not remove all the gas, so samples of these batches were tested for gas content by heating them to 500°C in a hydrogen atmosphere at normal atmospheric pressure and determining the amount of gas liberated or absorbed by the sample in reaching equilibrium under these conditions. The solubility of hydrogen in manganese under these conditions is known and the amount of gas that was in the metal originally was either greater or less than this value by the volume liberated or absorbed. All the samples showed less than 10 cc of gas per 100 grams of metal or less than 4 percent of the original amount. X-ray diffraction patterns of each sample were then made, and the parameters were determined. The results are shown in Table II as compared with the parameter for the original metal.

TABLE II. Average parameter for various degassing treatments.

Material	Parameter
Original manganese metal	8.904
Manganese degassed at 300°C	8.902
Manganese degassed at 500°C	8.8944
Manganese degassed at 700°C	8.8948
Manganese degassed at 925°C	8.8935

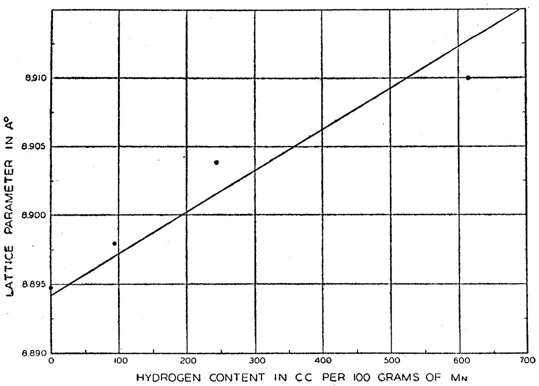

FIG. 1. Variation in average parameter with hydrogen gas content of the metal.

Removing the gas from the metal has little, if any, effect on the parameter at temperatures up to 300°C. At 500°C and over, however, the parameters return nearly to normal value. The parameters listed for these three samples are essentially equal (within experimental error, which is about 0.0005A), and the average value, 8.8942A, agrees well with the published value.

A better comparison can be made from the diffraction pattern shown in Fig. 2; Figs. 2a, 2b, 2c, 2d, and 2e show the patterns for the samples treated at 925°, 700°, 500°, 300°C and the normal untreated metal, respectively. The patterns on the 500°, 700°, and 925°C samples all show sharp lines with the *K*-alpha doublets resolved. The 925°C pattern seems to be the sharpest; the

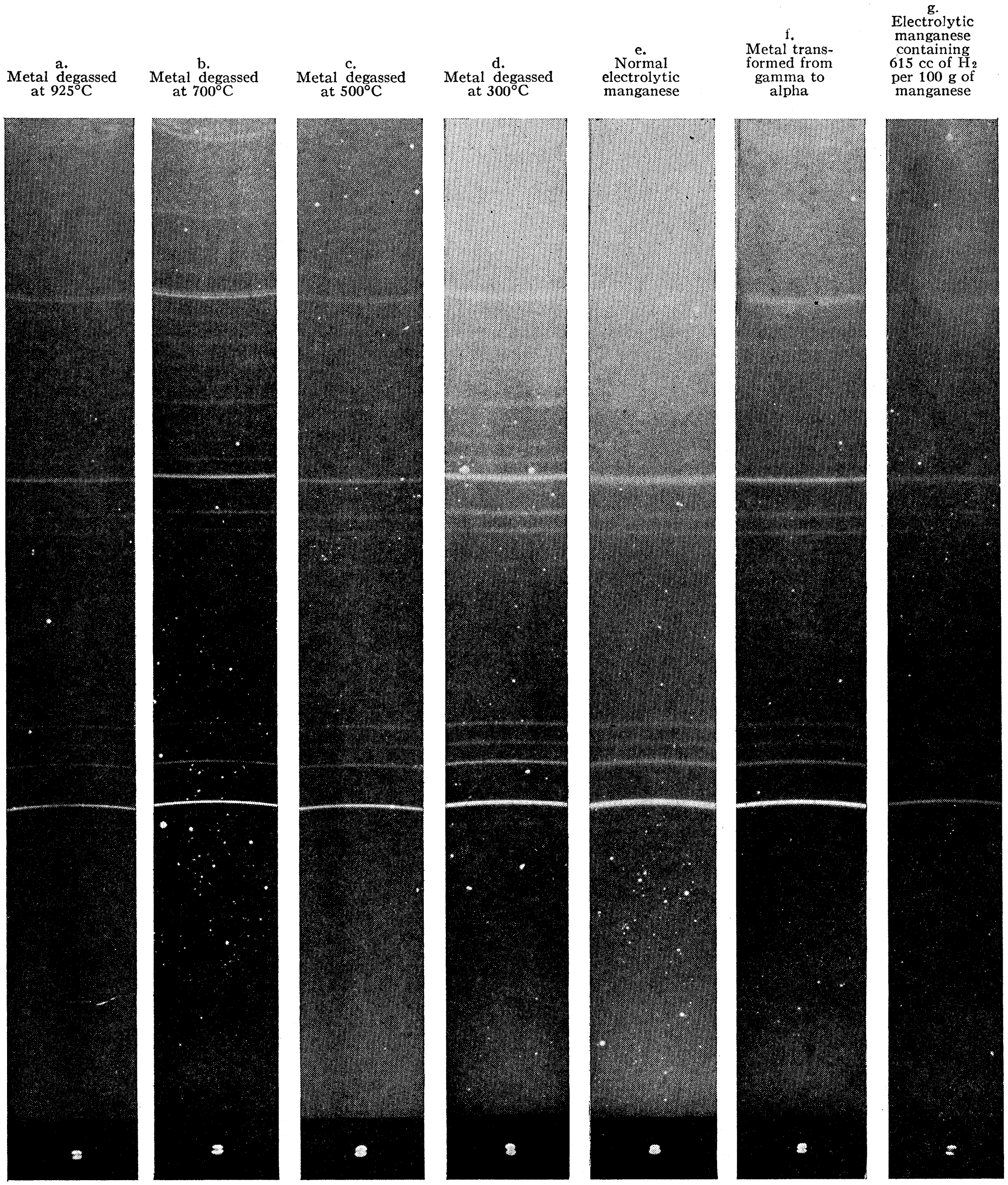

FIG. 2. X-ray diffraction patterns.

500°C pattern is definitely broader. Densitometer measurements shown in Table III show the 925° and 700°C patterns to be essentially the same, though visually the 700°C pattern would seem to be somewhat broader. The 300°C pattern cannot be distinguished from that for the untreated metal, showing that the metal is essentially the same even though the gas has been removed.

The diffraction patterns also indicate other variations in the structure aside from the differences in parameters of the various samples. The patterns shown in Figs. 2a, 2b, and 2c show sharp lines, while those in Figs. 2d and 2e show broad lines. Figure 2f shows the pattern for manganese, which was plated as flexible gamma-manganese and transformed to alpha-manganese, while Fig. 2g shows the pattern for a sample of manganese containing an unusually large amount of gas. Both of these patterns also have broad lines.

Two factors cause lines in a diffraction pattern to be broad: (1) variations in the parameters of the crystals constituting the individual sample or (2) variations in the size of the crystal aggregates in the different samples. Parameter variations in the crystals constituting the sample would obviously cause broad lines because the resulting pattern would be a composite of patterns from the individual crystals, and the lines in the individual patterns would be displaced relative to each other by amounts depending on the variations in the parameter. Measurements made at the densest portion of the lines determine the average parameter, and the width of the lines is a measure of the deviation from the average in the respective crystal units in the specimen.

Variations in the size of the crystal aggregates, which act as units to the x-ray beam, influence the width of the diffracted beam and the width of the diffraction lines. This phenomenon has been made the basis of a method for estimating the size of the crystal aggregates which act as units to the x-ray beam.[7] In the present case both of these factors may be contributing to the observed line width, so an attempt was made to determine the actual deviations in parameter. In the following discussion "deviation in parameter" will be used to mean the difference between the parameter of an individual crystal and the average parameter for a sample while "variation in parameter" will mean the difference between the average parameter of a sample and the normal parameter for manganese metal.

X-ray data alone are not sufficient to separate the two effects, so the specimens were examined microscopically to detect any variation in crystal or grain size in the different samples. No difference could be seen between the regular electrolytic manganese metal and the degassed metal for temperatures up to 700°C even though the diffraction patterns showed marked changes. In each case the grains were very small. At 925°C some evidence of larger grains was seen, but the diffraction patterns show little difference between the 925° and the 700° samples. It would seem, therefore, that crystal aggregate or grain size has little influence on the line widths and that the grains are all sufficiently large to produce sharp diffraction lines. We can then attribute the variations in the line widths to deviations of parameter only and estimate the magnitude of this deviation.

The width of the lines in six of the patterns in Fig. 2, measured with a densitometer, are shown in Table III.

The line widths were measured at an intensity equal to one-half the maximum. The sharpest lines were obtained on the samples degassed at 700° and 925°C, the widths being essentially the same. The pattern for vacuum-distilled metal is not shown because it was identical with that for the metal degassed at 900°C. These three materials should be the most uniform, in structure and, since they gave almost identical patterns and line widths, it was assumed that they most nearly represented material with a uniform parameter. The observed line width in the patterns for these samples is then due to the optical characteristics of the x-ray camera, and the size of the crystal aggregates in the specimens. These factors were assumed to be constant, and this minimum line width was used to correct the other

TABLE III. Line widths and parameter deviations in various samples.

Material	Line width in mm	Parameter deviation
Regular electrolytic manganese	0.84	±0.21 percent
Electrolytic manganese degassed		
At 300°C	0.84	±0.21 percent
At 700°C	0.52	0
At 925°C	0.55	0
Electrolytic manganese containing 615 cc per 100 grams of Mn	0.61	±0.06 percent
Electrolytic manganese transformed from gamma-Mn to alpha-Mn	0.99	±0.31 percent

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[7] (a) R. Brill, "X-Ray Determination of Size and Shape of Submicroscopic X'tals," Kolloid Zeits. **55**, 164–169 (1931); (b) G. H. Cameron, and A. L. Patterson, "The X-Ray Determination of Particle Size," Symposium on Radiography and X-Ray Diffraction, A.S.M., p. 324 (1936); (c) H. Mark, "The Determination of Particle Size by the Use of X-Rays," Trans. Faraday Soc. **25** (1929).

values, the increase in width relative to this value being attributed to non-uniformity in the parameters.

The maximum parameter deviation required to explain the broadening of the lines is only 0.3 percent but, in this case, we are not justified in assuming that the crystal aggregates are the same size as in the other samples because the plating conditions required for producing gamma-manganese are different from those used for plating alpha-manganese. In the other samples a deviation of 0.2 percent in parameter value is indicated. It might be expected that the deviations would be greater with the larger amounts of gas, but this does not seem to be the case, since the samples containing the most gas show a deviation of only 0.06 percent in parameter. This observation leads to some possible conclusions regarding the solubility of hydrogen in manganese which will be discussed later.

DISCUSSION OF RESULTS

a. Variation of Average Parameter with Hydrogen Content

The data in Table I and Fig. 1 indicate that the lattices of the manganese crystals are distorted by the hydrogen present in them. This distortion produces an enlargement of the average lattice parameter roughly proportional to the amount of gas in the metal or about 0.0003 percent per cc of gas per 100 grams of metal. The lattices are not necessarily distorted uniformly; any deviations from the average parameter should cause a widening of the lines in the x-ray diffraction pattern, the widening being proportional to the amount of the deviation. The lack of resolution of the *K*-alpha doublets in the patterns obtained from the samples containing gas indicates that such deviations may exist within the lattices of those samples, but the vacuum-distilled metal seems to have rather uniform lattice dimensions.

b. Effect of Degassing Treatments on Lattice Parameters

The lattice parameters obtained for the degassed manganese metal (shown in Table II) and the x-ray diffraction patterns for these samples (shown in Fig. 2), show definitely that it is only necessary to remove the gas from the metal and heat it to 500°C or higher to produce a metal with a normal and uniform lattice parameter. Since this treatment cannot affect any of the impurities, other than the amount of hydrogen present in the metal, the enlargement of the lattice parameter in the normal electrolytic metal must be due to the presence of the hydrogen introduced into the metal as atomic hydrogen during the plating process. The amount of hydrogen is about 0.02 percent by weight; it occupies a volume at normal conditions twenty[6] times that of the metal containing it. It is not unreasonable to expect that this highly compressed gas would have some effect on the structure of the metal containing it. Degassing the metal at 300°C has virtually no effect on its lattices, probably because the mobility of the atoms at this temperature is too low to permit any appreciable readjustment of the lattice in the time required for removing the gas.

c. Significance of Broadening of Lines in the Diffraction Patterns

The line widths shown in Table III can be taken as reliable indices of the relative broadness of the lines in the various diffraction patterns, but the calculated deviations in parameter are subject to too much error to be considered as more than rough estimates. It is evident, however, that the broadening of the lines observed in the diffraction patterns might be explained by a slight non-uniformity in the lattice parameters and that the non-uniformity is not proportional to the amount of gas in the metal.

The average parameters for the regular electrolytic manganese, the manganese transformed from the gamma- to the alpha-form, and the manganese with the high hydrogen content were enlarged 0.11, 0.045, and 0.18 percent, respectively (see Table I). The deviations in parameter shown in Table III are larger than this and indicate that some of the crystals in the metal had parameters less than normal. This may be true, in which case the average enlargement must exceed the average compression of the lattice so that a net enlargement in parameter is observed. On the other hand, the calculated deviations may be too large because of improper measurement of the line width or improper correction for the width due to grain or crystal aggregate size. Possible errors from the first source cannot be discussed here because no adequate theory is available for determining the relation between grain size, parameter deviation, and line width. Errors from the second source can produce the effects noted if we assume that there is some grain growth in the manganese during the degassing treatments. The grains would be larger in the samples treated at the higher temperatures, and the lines in their diffraction patterns would be sharper. The correction for grain size, based on the line width of the 700° and 925°C samples, would be too small and we would be attributing too much of the widening effect in the other samples to parameter deviations. A more nearly correct value for the parameter deviation might then be obtained by considering that the deviation above and below the average parameter value is equal to the enlargement of the average parameter relative to that for normal alpha-manganese metal.

The parameter deviations shown in Table III do not vary with gas content in the manner that might be expected. The deviation is zero at zero gas content, high at 95 cc per 100 grams of metal, and decreases with increasing gas content up to the observed maximum gas content of 615 cc per 100 grams of metal. This behavior indicates that the deviation might again be zero at some value of gas content near 615 cc per 100 grams of manganese. In this case each crystal would be enlarged the same amount and would contain the same amount of gas. This would not be likely to occur unless the metal were saturated with gas and, in this case, there should be an integral number of atoms of gas in each unit cell of alpha-manganese. The number of unit cells of alpha-manganese in 1 gram of metal is proportional to the reciprocal of the product of the atomic weight, the number of atoms in a unit cell, and is some constant times 0.31×10^{-3}. On the same basis, 615 ± 50 cc of gas in the metal would provide $(0.55\pm.05)\times10^{-3}$ atom of hydrogen, or nearly two atoms per unit cell of alpha-manganese. If we assume that each unit cell absorbs 2 atoms of hydrogen, then it would require 695 cc of hydrogen per 100 grams of manganese to saturate the metal, and only about 90 percent of the unit cells in the sample containing 6.5 cc of gas per 100 grams of metal would be saturated. The remaining 10 percent of the unit cells would be distorted various amounts and cause the diffraction lines to be wider than if the sample were uniform. The deviation shown in Table III is consistent with this conclusion, and it would be anticipated that slightly higher gas contents would produce sharper diffraction lines.

No samples of manganese were found containing more than 615 cc of hydrogen, so we have no experimental evidence to show whether or not manganese will absorb more than 2 atoms of hydrogen. The fact that the regular electrolytic metal, containing 250 cc of gas per 100 grams, shows definitely fuzzy lines, indicates that the unit cells take 2 rather than 1 atom, however, because if the latter were true, the unit cells could be uniform with about 350 cc of gas per 100 grams of metal, and the observed diffraction patterns show no evidence to support this conclusion.

ACKNOWLEDGMENTS

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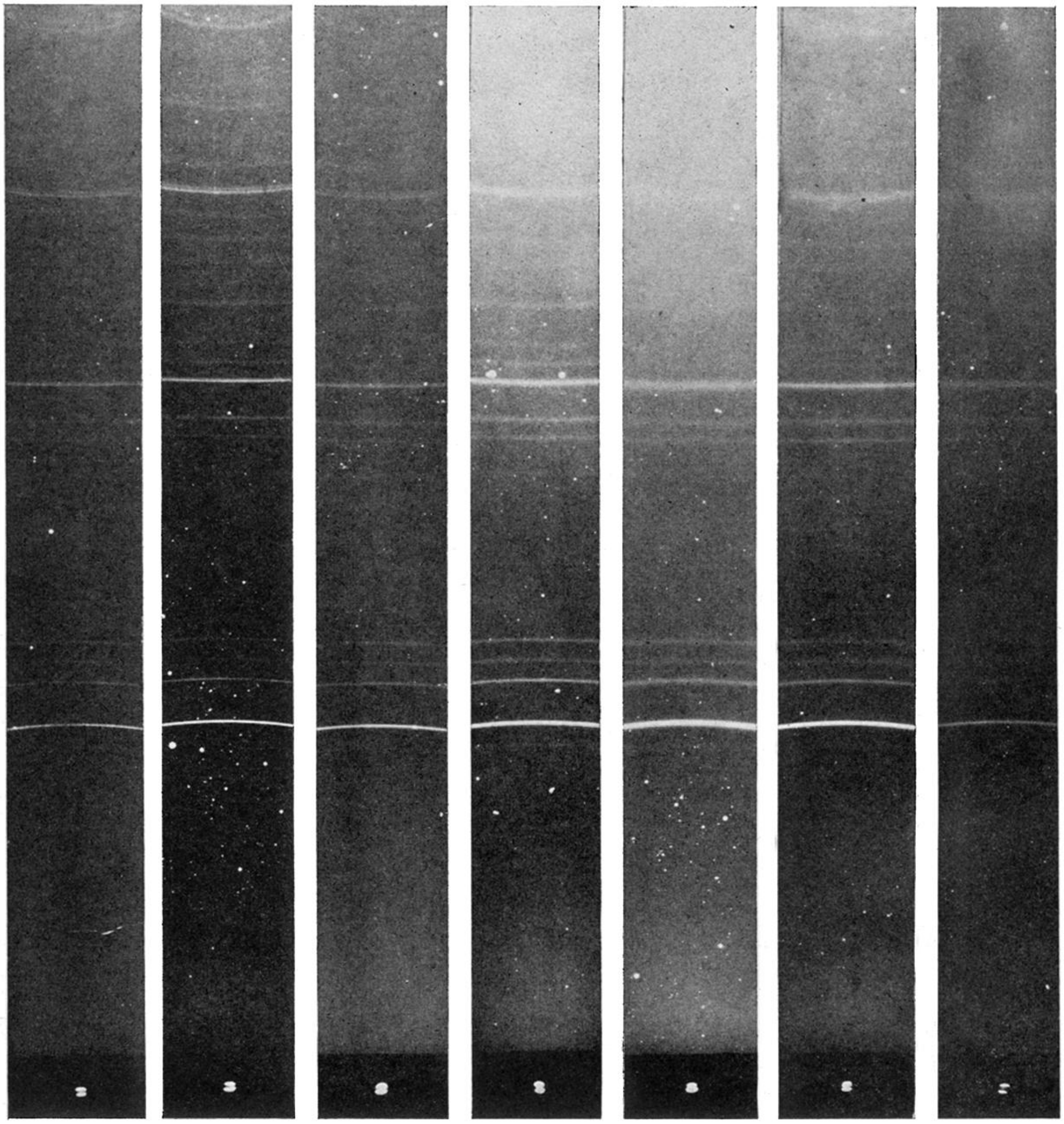

a.
Metal degassed
at 925°C

b.
Metal degassed
at 700°C

c.
Metal degassed
at 500°C

d.
Metal degassed
at 300°C

e.
Normal
electrolytic
manganese

f.
Metal transformed from
gamma to
alpha

g.
Electrolytic
manganese
containing
615 cc of H_2
per 100 g of
manganese

FIG. 2. X-ray diffraction patterns.