Studies on the Oxidation of Pyrite III : The Intermediate Products in the Oxidation of Pyrite

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Studies on the Oxidation of Pyrite. III. The Intermediate Products in the Oxidation of Pyrite

By

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The intermediate products in the oxidation of pyrite were investigated by measurement of the intensity of magnetization, thermomagnetic analysis and X-ray diffraction. In the course of the oxidation, the intensity of magnetization of the sample increases, reaches a maximum, and then decreases. The maximum value of the sample oxidized at low partial pressures of oxygen was found to be much higher than that oxidized at high partial pressures of oxygen. FeS_{1+x} and Fe_3O_4 were the main products of oxidation at low partial pressures of oxygen, and Fe_3O_4 changed into Fe_2O_3 immediately before the end of the oxidation. On the other hand, Fe_2O_3 was formed in addition to Fe_3O_4 from the early stages of the oxidation at high partial pressures of oxygen. The FeS_{1+x} formed in the intermediate stage was ferromagnetic, and its composition was near the upper limit of the solubility of sulphur in FeS_{1+x}.

Samples taken from the roasting hearths of the Herreshoff furnace were investigated by measurement of the intensity of magnetization and thermomagnetic analysis. Pyrite decomposes into FeS_{1+x} in the upper hearths and, in the middle hearths, FeS_{1+x} is oxidized mainly to Fe_3O_4, and finally, Fe_3O_4 changes into Fe_2O_3 in the lower hearths. The intensity of magnetization reaches the maximum in the middle hearths of the furnace. The formation of a large amount of Fe_3O_4 in the middle hearths indicates that the partial pressure of oxygen in the layer of the charge in the furnace was remarkably low.

1. Introduction

In the previous report, it was found that, in the initial stage of the oxidation, the thermal decomposition product of pyrite, FeS_{1+x}, changed into a ferromagnetic one for which the coefficient of the formula was approximately given as 1.14,[1] and that, in the oxidation of pyrite at low partial pressures of oxygen, Fe_3O_4 was formed as an intermediate product, and the rate constant of the oxidation of FeS_{1+x}, k_2, turned out to be not proportional to the partial pressure of oxygen.[2]

Here, we pursued further the study on the composition of the FeS_{1+x} formed in the intermediate stage of the oxidation and on the conditions for formation of Fe_3O_4.

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Studies were also performed on samples taken from the roasting hearths of the Herreshoff furnace to clarify the behavior of pyrite in the roaster.

2. Preparation of the Samples

Pyrite used in this study was described in Part 1,[1] whose particle size was between 200 and 250 mesh. Samples oxidized partially were prepared with the thermobalance.[1] The oxidation temperatures were chosen at 700°, 800° and 900°C. Gas mixtures of O_2, SO_2 and N_2, whose compositions are shown in Table 1, were allowed to flow into the apparatus at the rate of 200 c.c./min.. The change of weight due to the reaction was measured with a cathetometer. After a fixed time from the beginning of the reaction, the flow of the gas mixture was stopped, the furnace was pulled down and the reaction tube was cooled rapidly with a blast of cold air.

Table 1.

O_2 (%)	SO_2 (%)	N_2 (%)
5	12	83*)
3	14	83
1	15	84

*) Measurement was performed at 800°C only.

3. Magnetic Properties of the Intermediate Products of Oxidation

3.1. Measurement of the Intensity of Magnetization

The relative intensity of magnetization of the samples was measured by the method described in Part 1,[1] and the results are shown in Fig. 1. In this figure, the intensity of magnetization is plotted against the oxidation time. Each curve has a maximum in the course of the oxidation. And this maximum value was found to be much higher in the oxidation at 0.01 atm. of partial pressure of oxygen, p_{O_2}, than in the cases of higher values of p_{O_2}.

As shown in Part 2, above 700°C, the reaction occurs in two stages separately, that is, the thermal decomposition of pyrite and the oxidation of the thermal decomposition product, FeS_{1+x}.[2] The progress of the oxidation is considered to be well represented by the ratio of weight decrease, *w*, defined in Part 2, and therefore, in Fig. 2, the intensity of magnetization of the samples was plotted against *w*. In the case of 0.01 atm. of p_{O_2}, it was found that the intensity of magnetization reaches the maximum at $w \doteqdot 0.32$, and that, at $w > 0.32$, it decreases suddenly with incaeasing *w*. This means that there is formation of a product of high intensity of magnetization in the intermediate stage of the oxidation which disappears rapidly in the final stage.

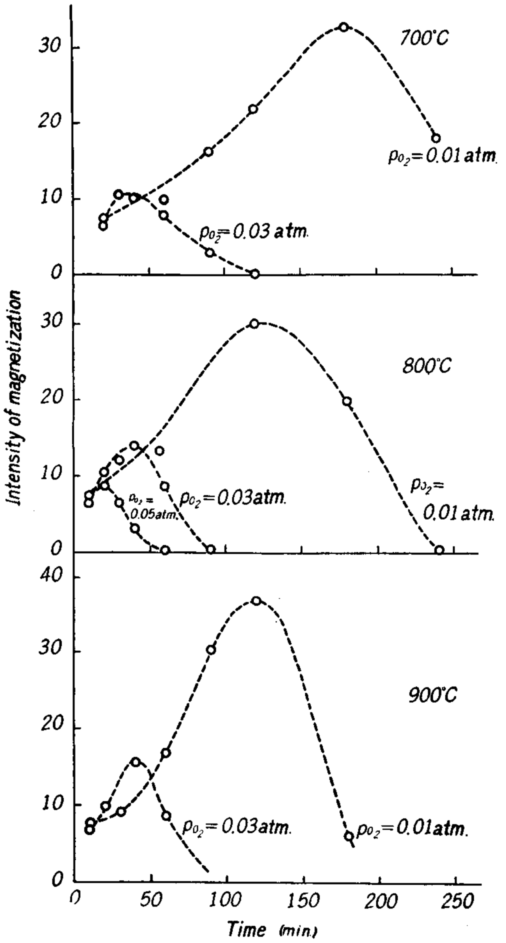


Fig. 1.

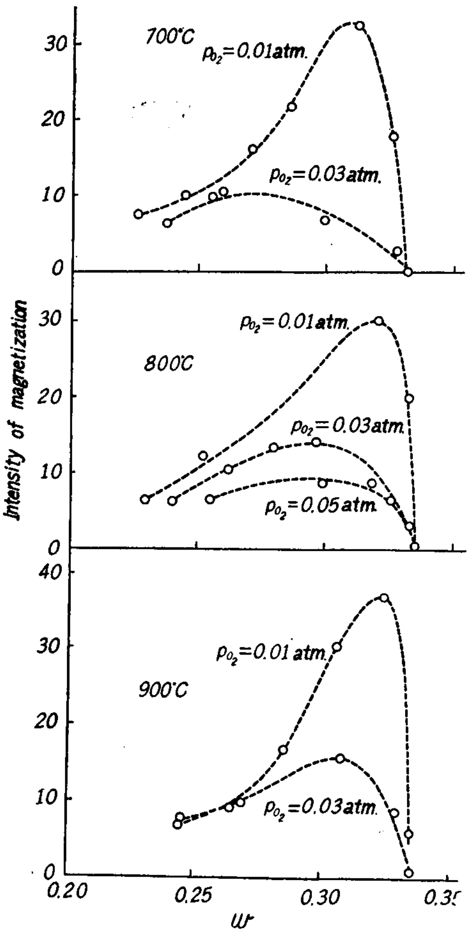


Fig. 2.

3.2. Thermomagnetic Analysis of the Intermediate Products of Oxidation

Thermomagnetic analyses were carried out with the above-mentioned samples which were put in evacuated and sealed quartz glass capsules. As an example, the results obtained with the samples oxidized at 7000°C are shown in Figs. 3 and 4.

Among the intermediate products, Fe_3O_4 is ferromagnetic whose Curie point lies at 575°C, and FeS_{1+x} $(1+x\geqq 1.11)$ is also ferromagnetic and its Curie point was found at 295°C.1),3) α-Fe_2O_3 formed in the oxidation below 600°C shows weak parasitic magnetism but the intensity of magnetization of α-Fe_2O_3 formed above 650°C is very weak, as will be described in the supplementary section. It was found, in the preliminary tests, that Fe_2O_3 dissociated into Fe_3O_4 when heated above 400°C in a vacuum of 10^{-3} mmHg or in the evacuated and sealed quartz glass capsule, and consequently, when a sample contained Fe_2O_3, its intensity of magnetization increased by heating in vacuo, and a hysteresis was observed in the curve of the thermomagnetic analysis.

Fig. 3 shows the results of the thermomagnetic analysis with the samples oxidized at 700°C and 0.03 atm. of p_{O_2}. Measurements were carried out with samples whose oxidation was interrupted at 20, 30, 60 and 90 minutes after the beginning of the reaction, respectively.

In the curve of the thermomagnetic analysis of the sample interrupted at 20 minutes, the hysteresis due to the thermal dissociation of Fe_2O_3 did not appear, and therefore, in this stage of the oxidation, Fe_2O_3 was not yet formed and only Fe_3O_4 was formed as the oxide. The Curie point of FeS_{1+x} was observed at about 300°C when heated, breaks in the curve occurring twice, once below and once above 295°C, and was clearly observed at 295°C during cooling. From this result of the thermomagnetic analysis, in this initial stage of the oxidation, Fe_3O_4 and FeS_{1+x} were present in the sample, and as FeS_{1+x} was ferromagnetic, its composition was near the upper limit of the solubility of sulphur in FeS_{1+x}.

Thereafter, with the progress of the oxidation, FeS_{1+x} disappeared gradually, as shown in the figure. On the other hand, in the curve of the sample interrupted at 30 minutes, the hysteresis due to the thermal dissociation of Fe_2O_3 was observed, indicating the presence of Fe_2O_3 in addition to Fe_3O_4. Because this hysteresis increased with the oxidation, the amount of Fe_2O_3 was found to increase with the progress of the oxidation.

The phenomenon of the separation of the Curie point of FeS_{1+x} into two, one below and one above 295°C in the heating portion of the analysis was also observed in the samples oxidized in an atmosphere of more than 0.03 atm. of p_{O_2} at 800° and 900°C. When these samples were sealed in the evacuated quartz glass capsules and kept at about 330°C for 30 minutes, their Curie points tended to be settled at 295°C.

Fig. 4 shows the results of the thermomagnetic analysis of the samples oxidized at 700°C and 0.01 atm. of p_{O_2}. Differences between Fig. 3 and Fig. 4 were as follows.

a) In Fig. 3, the Curie point of FeS_{1+x} in the heating curve of the analysis was found to be separated into two, one below and one above 295°C. On the contrary, in Fig. 4, it was observed clearly at 295°C.

b) Fe_2O_3 was formed during the early stages of the oxidation in Fig. 3. On the other hand, in Fig. 4, Fe_2O_3 was not detected until 90 minutes after the beginning of the reaction, and in this stage of the oxidation, the oxide formed consisted mainly of Fe_3O_4. After 180 minutes, where the oxidation was nearly finished, the amount of Fe_2O_3 increases rapidly.

These features of Figs. 3 and 4 were also observed in the oxidation at 800° and 900°C.

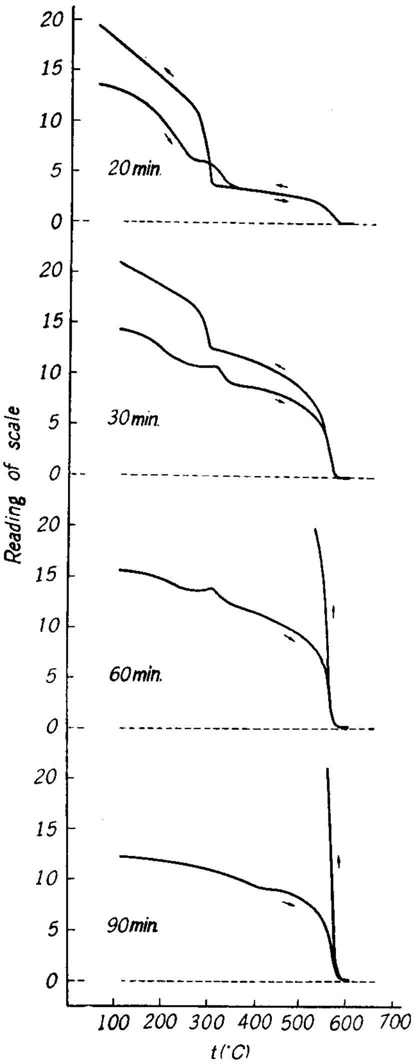


Fig. 3.

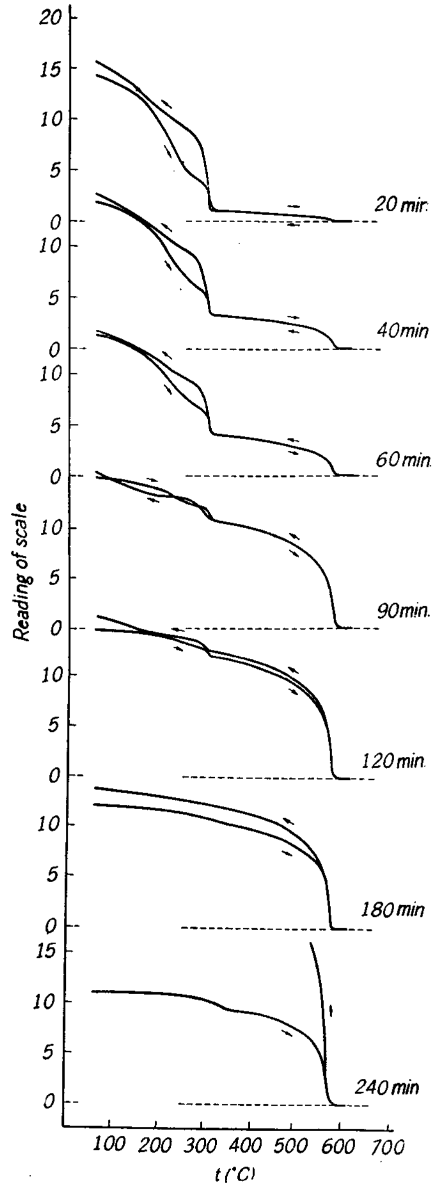
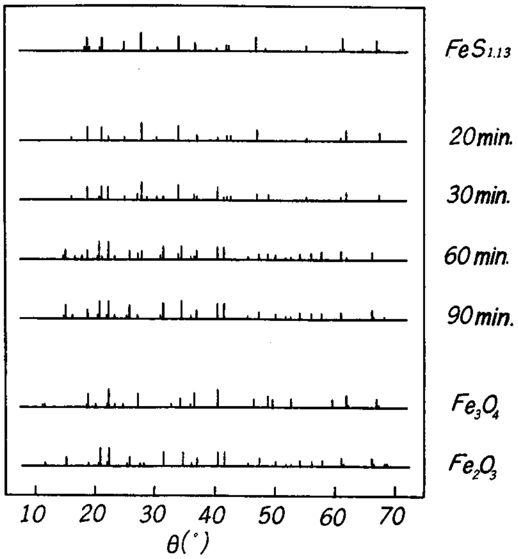


Fig. 4.

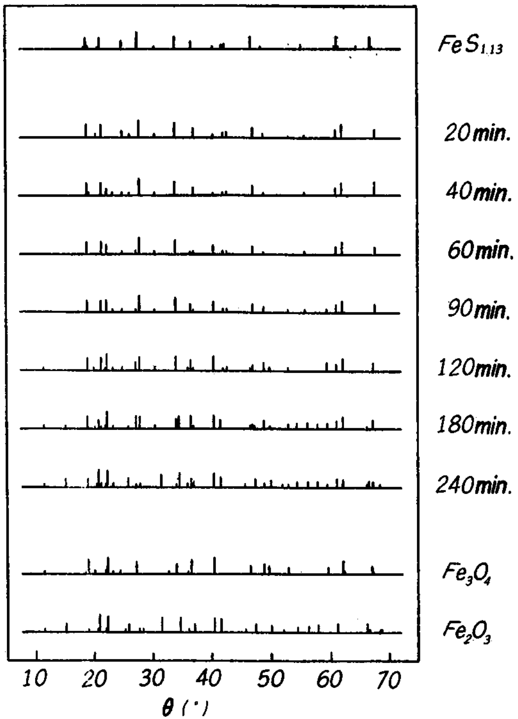
4. X-Ray Measurement of the Intermediate Products of the Oxidation

With the above-mentioned samples, X-ray diffraction patterns were obtained by the powder camera. Patterns obtained with the samples oxidized for different oxidation time at 700°C are illustrated in Figs. 5, and 6, as examples. In these figures, the diffraction patterns of $FeS_{1.13}$ (thermal decomposition temperature[1]: 625°C), Fe_3O_4 and



Condition of oxidation: 700°C, $p_{O_2}=0.03$ atm.

Fig. 5.



Condition of oxidation: 700°C, $p_{O_2}=0.01$ atm.

Fig. 6.

Fe_2O_3 were inserted as the references. In the oxidation at 0.01 atm. of p_{O_2}, the main intermediate products were FeS_{1+x} and Fe_3O_4 which were stable for the greater part of the oxidation, and the diffraction lines of Fe_3O_4 disappeared and those of Fe_2O_3 appeared immediately before the end of the oxidation. In the oxidation at 0.03 atm. of p_{O_2}, the diffraction lines of Fe_2O_3 were observed in addition to those of Fe_3O_4 from the early stages of the oxidation. The intensity of the diffraction lines of Fe_3O_4 was found to be weak in the oxidation at higher partial pressures of oxygen. These results are in good agreement with those mentioned in **3. 2.**

From the X-ray photograms of the samples oxidized at 0.01 atm. of p_{O_2} and 700°, 800° and 900°C for 10 or 20 minutes, the lattice parameters and the axial ratio of FeS_{1+x} were calculated. Values of a, c and c/a were nearly the same for these samples, and their mean values were,

$$a = 3.439\,kX, \quad c = 5.685\,kX \quad \text{and} \quad c/a = 1.654\,.$$

Therefore, the composition of FeS_{1+x} formed in the intermediate stage of the oxidation was found to lie near the upper limit of solubility of sulphur in FeS_{1+x}, independent of the oxidation temperature,

5. Oxidation of Pyrite in the Multiple Hearths Furnace

In order to study the behavior of pyrite in the multiple hearths furnace, the samples taken from the roasting hearths of the nine hearths Herreshoff furnace in which pyrite was roasted were analysed thermomagnetically. The roasting conditions at the time of sampling are shown in Table 2.

Table 2.

Size of charge (mm)	under 6
Charging rate (t/d)	21
Temperature of gas	
at 3rd hearth (°C)	790
at 7th hearth (°C)	520
Temperature of charge at 9th hearth (°C)	135
Lower boundary of red heat zone	1st to 2nd tooth from the center shaft of 9th hearth

Samples were taken from each roasting hearth of the furnace in increments of about 1 kg. Immediately after the sampling, they were put in a covered steel vessel

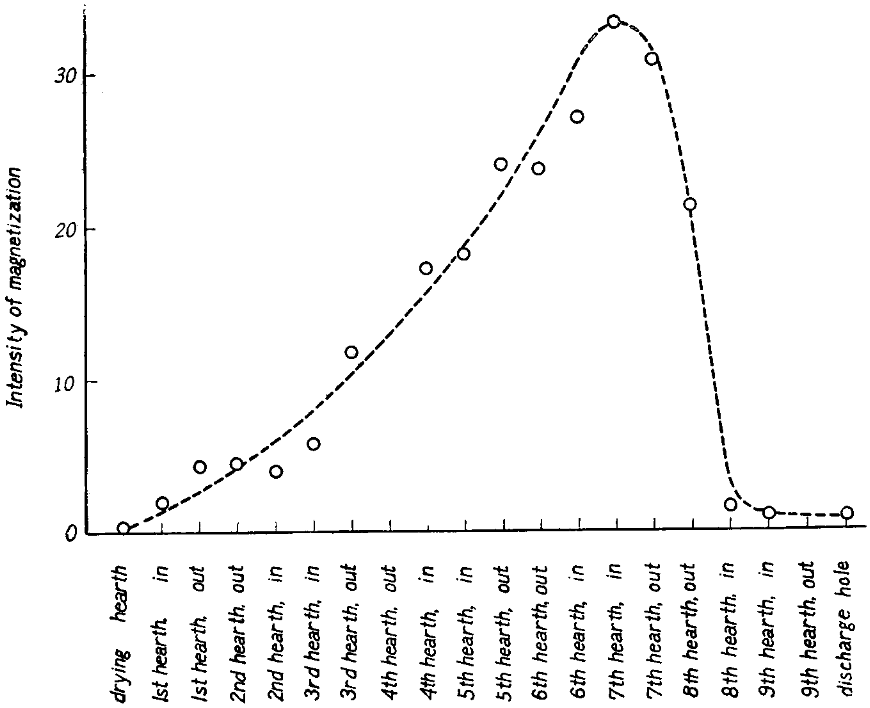


Fig. 7.

and cooled rapidly. Samples were reduced with a riffle-sampler without grinding to about 100 g and then they were ground in an agate mortar to under 150 mesh. Measurement of the relative intensity of magnetization and thermomagnetic analysis were carried out with these samples.

Results of the measurement of the intensity of magnetization are shown in Fig. 7. As is clear from the figure, the intensity of magnetization increases as the charge descends in the furnace. The intensity of magnetization reaches a maximum at the 7th hearth or thereabout. After that, it decreases rapidly and shows a considerably

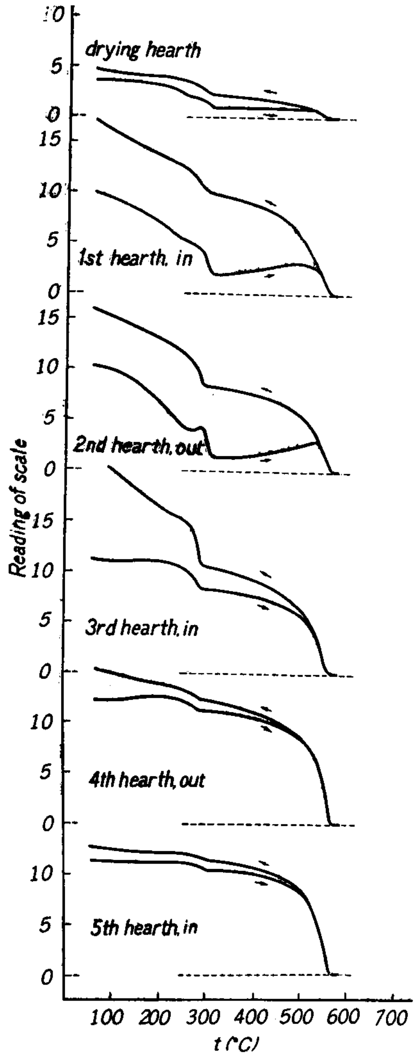


Fig. 8. (1)

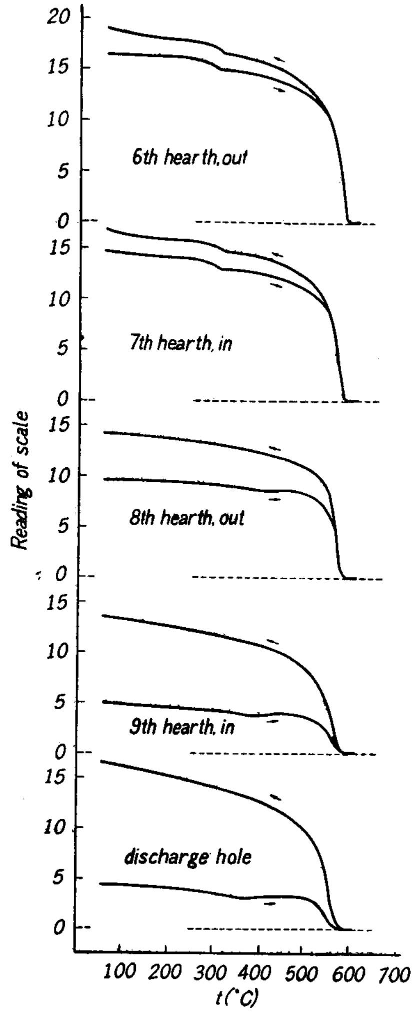


Fig. 8. (2)

low values below the 8th hearth. The samples below that had a tinge of red and showed the formation of hematite.

Results of the thermomagnetic analysis are shown in Fig. 8. Samples were put in evacuated and sealed quartz glass capsules. In the curve of the thermomagnetic analysis of the samples from the drying hearth, breaks in the curve were observed at 295°C and 575°C, and it was found that the pyrite was contaminated with the small amounts of FeS_{1+x} and Fe_3O_4. The curves of the samples of the 1st and 2nd hearths were somewhat complicated, but they showed that the thermal decomposition of pyrite had begun. In the samples between the 3rd and 7th hearths, the Curie point of FeS_{1+x} was observed clearly, and the amount of Fe_3O_4 increased with the progress of the oxidation. Hysteresis was observed in the curve of the analysis, showing the formation of Fe_2O_3 in these roasting hearths. This hysteresis does not increase markedly, and therefore, the amount of Fe_2O_3 increases only slightly in these hearths. In the samples between the 8th hearth and the discharge hole of the cinder, the Curie point of FeS_{1+x} was not observed, and the hysteresis increased with the descent of the charge in the furnace. That is, between the 8th hearth and the discharge hole, FeS_{1+x} was hardly present, the amount of Fe_3O_4 decreased and, in place of it, Fe_2O_3 increased rapidly.

6. Discussion

From the results obtained in **3** and **4**, it may be said that at 0.01 atm. of p_{O_2}, Fe_3O_4 is a stable intermediate product during the greater part of the oxidation, and that immediately before the end of the oxidation, it changes into Fe_2O_3. On the other hand, at higher values of p_{O_2}, Fe_2O_3 is formed from the fairly early stages of the oxidation and the amount of Fe_3O_4 is small.

In the previous report²⁾, it was said that the rate constant of the oxidation of FeS_{1+x}, k_2, was nearly proportional to p_{O_2}, but at lower partial pressures of oxygen, for example at 0.01 atm., this proportionality does not exist and the observed value of k_2 is higher than the value estimated from this linear relationship.

We measured, with the thermobalance, the weight change of the pyrite with the gas mixture whose composition was 16% SO_2 and 84% N_2 at 700°, 800° and 900°C, and from this, the rate constant of the following reaction was calculated.

$$FeS_{1+x}+2/3\ SO_2 = 1/3\ Fe_3O_4+(5/6+x/2)\ S_2(g)\,.$$

As shown in Fig. 9, the value of this rate constant was found to be located at the intercept of the curve of k_2-p_{O_2} (including k_2 at 0.01 atm. of p_{O_2}) at $p_{O_2}=0$ atm. From these results, it may be said that during the greater part of the progress of the oxidation at 0.01 atm. of p_{O_2}, the above-mentioned reaction of FeS_{1+x} with SO_2 is predominant, and immediately before the end of the reaction, Fe_3O_4 changes into Fe_2O_3.

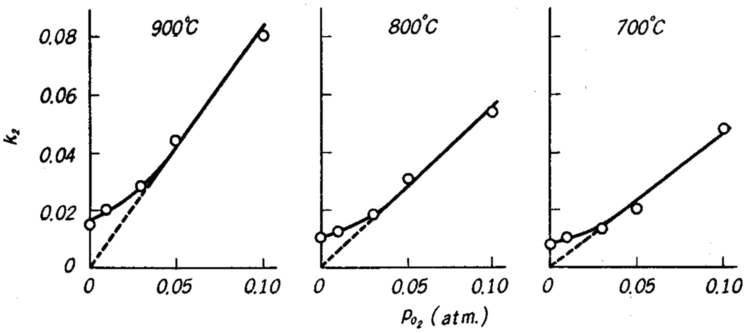


Fig. 9.

It was fonnd, in the previous report, that the rate determining stage in the oxidation of pyrite or pyrrhotite was the diffusion of oxygen. K. Niwa[4) and H. Tohata[5) found, with the thermobalance, that this diffusion of oxygen was vertical to the surface of the layer of the fine sulphide particles, under experimental conditions similar to the present study.[6) Therefore, the oxidation is thought to proceed from the surface downwards into the interior, and the partial pressure of oxygen in the layer also decreases downwards. Because the thermal decomposition proceeds very quickly above 700°C, in the intermediate stage of the oxidation where the thermal decomposition is completed, the intermediate products of the reaction in the layer are thought to be arranged in the following order from the surface to the interior; Fe_2O_3, Fe_3O_4, FeS_{1+x}. From the results of the thermomagnetic analysis and the X-ray measurement, Fe_2O_3 was found to be formed in the fairly early stages of the oxidation at high p_{O_2}, and it was formed immediately before the end of the reaction at low p_{O_2}. Therefore, the progress of the oxidation in fine particles of pyrite above 700°C in the present study may be illustrated schematically as in Fig. 10. The arrows in the figure show the direction of the progress of the oxidation.

From the investigations of the samples taken from the roasting hearths of the Herreshoff furnace, the behavior of pyrite in the roaster may be summarized as follows. Pyrite decomposes into FeS_{1+x} in the upper hearths of the furnace, FeS_{1+x} thus formed is oxidized in the middle hearths where the oxidation proceeds vigorously and a large amount of Fe_3O_4 and a small amount of Fe_2O_3 are formed. In this stage of oxidation, the intensity of magnetization reaches a maximum. Thereafter, in the lower hearths where the oxidation nearly ceases, the amount of Fe_2O_3 increases rapidly, and consequently, the intensity of magnetization decreases.

Because in the intermediate stage of the oxidation in the multiple hearths furnace, a large amount of Fe_3O_4 is formed, the partial pressure of oxygen in the layer of the charge on the roasting hearth is thought to be low.

Therefore, to elevate the roasting capacity of the furnance and to depress the residual sulphur content in the cinder, the following steps should be effective, because by means of them, the partial pressure of oxygen in the layer of the charge will be increased.

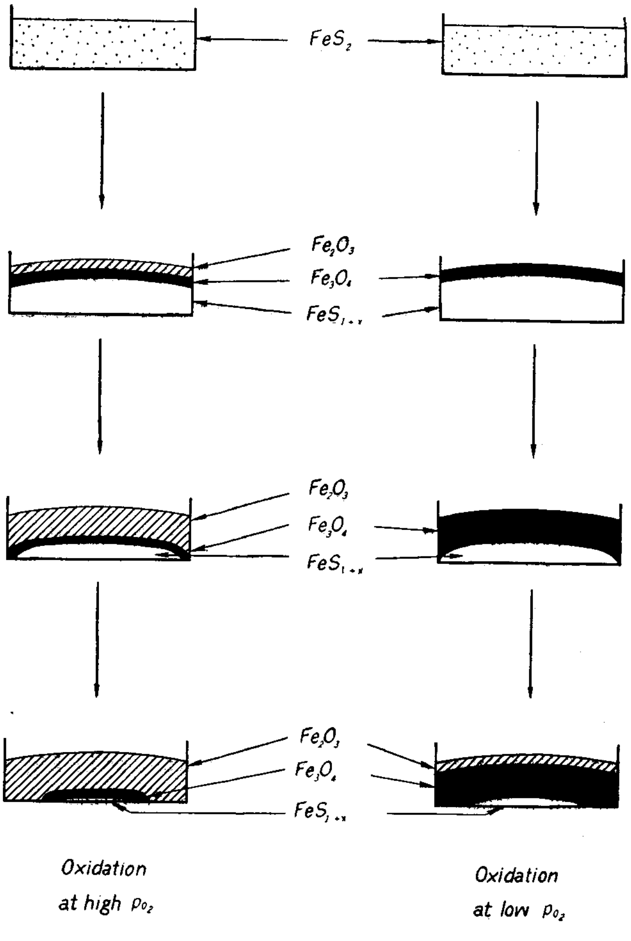


Fig. 10.

a) To reduce the thickness of the layer of the charge.

b) To improve the agitation of the layer on the roasting hearths.

For example, due to these causes, increasing the revolving velocity of the shaft-arm of the furnace proved effective, as shown in the roasting tests of pyrite in the multiple hearths furnace[7].

7. Summary

Measurement of the intensity of magnetization, thermomagnetic analysis and X-ray measurement were carried out with samples of partially oxidized pyrite and samples taken from the roasting hearths of the Herreshoff furnace. The results are summarized as follows:

1. The intensity of magnetization of the sample increases in the early stages of the oxidation, reaches a maximum and decreases finally. This maximum of the intensity of magnetization was much higher in the oxidation at 0.01 atm. of p_{O_2} than at higher values of p_{O_2}.

The intermediate products detected by the thermomagnetic analysis and the X-ray measurement were FeS_{1+x}, Fe_3O_4 and Fe_2O_3. The FeS_{1+x} was found to be ferromagnetic with a composition near the upper limit of solubility of sulphur in FeS_{1+x}. In the oxidation at 0.01 atm. of p_{O_2}, Fe_3O_4 was found to be stable during the greater part of the progress of oxidation, and the amount of Fe_2O_3 was very small in this stage. The amount of Fe_2O_3 increases immediately before the end of the oxidation. In the oxidation at higher partial pressures of oxygen, on the contrary, Fe_3O_4 and Fe_2O_3 were both formed from the fairly early stages of the oxidation.

2. In the multiple hearths furnace, pyrite decomposes initially into FeS_{1+x} and the latter is oxidized in the middle hearths where the oxidation proceeds vigorously. The oxidation products of FeS_{1+x} in this stage are a large amount of Fe_3O_4 and a small amount of Fe_2O_3. In this stage of the oxidation, the intensity of magnetization increases markedly and it reaches a maximum value. Thereafter, in the lower hearths, where the oxidation of FeS_{1+x} ceases, the amount of Fe_2O_3 increases rapidly, and accordingly, the intensity of magnetization decreases. From such an oxidation process of pyrite in the multiple hearths furnace, the partial pressure of oxygen in the layer of the charge on the hearths is thought to be very low.

Supplementary Section

On the Megnetism of Fe_2O_3 Formed in the Oxidation of Pyrite

When pyrite is oxidized in the gas mixture of O_2, SO_2 and N_2 at the temperature between 500°C and 900°C, the final product of the oxidation is Fe_2O_3, as shown by thermodynamic considerations[8] and by measurements with the thermobalance[2]. The X-ray diffraction pattern of the final product was that of α-Fe_2O_3.

K. Honda[9] and H. Forestier[10] studied the magnetic properties of α-Fe_2O_3 and reported that α-Fe_2O_3 was ferromagnetics whose ferromagnetic Curie point lies at 675°C. On the other hand, it is generally known that the Fe_2O_3 formed at low temperatures has parasitic magnetism. With the final products of the oxidation of pyrite roasted at various temperatures, we examined their magnetism with a permanent magnet, and found that the products oxidized below 600°C showed weak magnetism but those oxidized above 650°C did not.

The intensity of magnetization of Fe_2O_3 obtained by the oxidation of pyrite in air was measured and the results are shown in Fig. 11. It was found that the intensity of magnetization increased as the temperature of oxidation was lowered.

As an example, the thermomagnetic analysis of α-Fe_2O_3 obtained by the oxidation of pyrite in air at 500°C is shown in Fig. 12. Measurement was conducted in air. The intensity of magnetization decreases monotonously with heating until it nearly disappears at about 630°C. After cooling, the intensity of magnetization shows a remarkably lower value as compared with that before heating. This shows that the parasitic magnetism disappears with heating. The same behavior was observed with samples oxidized between 480°C and 600°C.

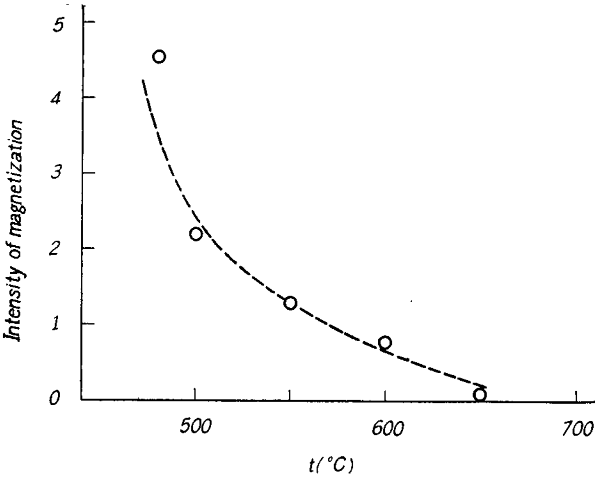


Fig. 11.

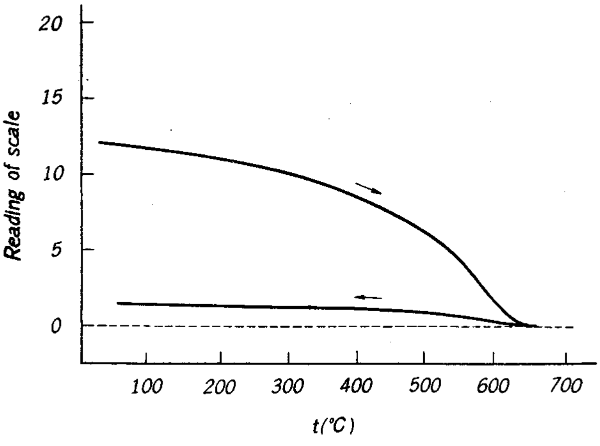


Fig. 12.

As shown in Fig. 12, the greater part of the intensity of magnetization disappears at about 630°C, but above this temperature, it does not decrease to zero but retains a small value. To study this magnetism above 630°C, samples of α-Fe_2O_3 obtained by the oxidation of pyrite between 480° and 900°C were analyzed thermomagnetically. The amount of the sample in these analyses was about 20 mg which was about five times that in Fig. 12. As shown in Fig. 13, the α-Fe_2O_3 formed in the oxidation

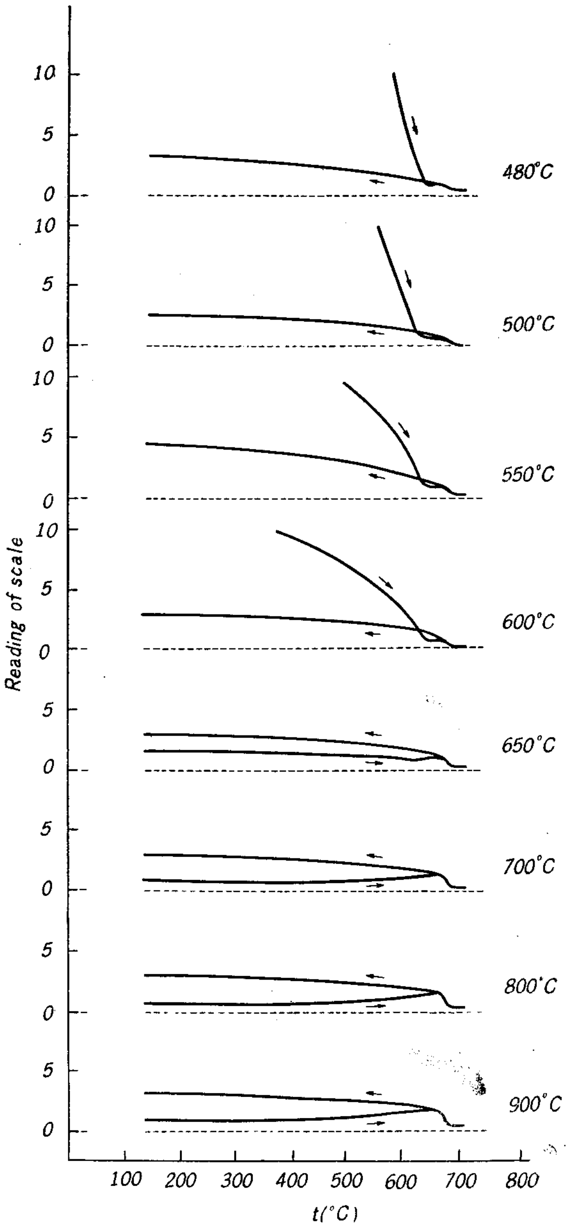


Fig. 13.

between 480° and 600°C has a parasitic magnetism, which disappears at about 630°C. Above this temperature, a small intensity of magnetization is retained which disappears at 685°C. On the other hand, the Fe_2O_3 formed in the oxidation above 650°C shows a small intensity of magnetization which is of paramagnetic magnitude. This magnetism also disappears at 685°C. When the thermomagnetic analyses were repeated with the same sample, a curve without hysteresis was obtained after the second repetition, whose shape was almost the same as the cooling curve of the first run.

The above-mentioned results may be summarized as follows:

a) α-Fe_2O_3 obtained by the oxidation of pyrite below 600°C shows parasitic magnetism which disappears at about 630°C.

b) α-Fe_2O_3 shows ferromagnetism whose Curie point lies at about 685°C. The intensity of magnetization of this ferromagnetism is very small, and it is of paramagnetic magnitude.

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