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# DIFFERENTIAL THERMAL STUDY OF FeO and $Fe_3O_4$

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Two batches of wüstite were produced from a stoichiometric mixture of Fe and $Fe_2O_3$ by sealing in steel tubes in vacuum and helium, respectively, and igniting the first tube at 1300° for 21 hours and the second one at 1200° for 34 hours. There were two exothermic peaks on the DTA curves of both samples at 345 and 545 to 700° due to surface oxidation of FeO to $Fe_3O_4$ followed by bulk oxidation of FeO to $Fe_3O_4$ and of $Fe_3O_4$ to $\alpha$-$Fe_2O_3$. The last two reactions gave rise to a dual (or twin) peak for coarse material but one peak in the case of fine material, indicating that the two reactions occurred concurrently for fine material. Similar investigations on both fine and coarse magnetites showed only two exothermic peaks which corresponded to surface and bulk oxidation, respectively. This result confirms the previous observations that coarse magnetite converts to $\alpha$-$Fe_2O_3$ by surface oxidation followed by bulk oxidation.

Several attempts have been made to follow the changes in iron to oxygen ratio accompanying the heating of magnetite [1—3], but a survey of the literature reveals very few thorough studies [4, 5] of the changes accompanying the heating of wüstite. This is probably due to the difficulty in the preparation of this material as it decomposes to $\alpha$-Fe and $Fe_3O_4$ below 570° [6]. For this reason it must be prepared above this temperature and rapidly quenched.

Gheith [1] postulated that on heating synthetic magnetite it transformed to $\gamma$-$Fe_2O_3$ and then to $\alpha$-$Fe_2O_3$, whereas Schmidt and Vermaas [2] concluded that the two exothermic peaks observed by them on heating $Fe_3O_4$ could be explained firstly by surface oxidation of the particles to $\alpha$-$Fe_2O_3$ and the oxidation of the remaining $Fe_3O_4$ to $\alpha$-$Fe_2O_3$ with no intermediate $\gamma$-$Fe_2O_3$ phase appearing. However, it has been shown by Egger and Feitknecht [7] that the formation of $\gamma$-$Fe_2O_3$ as an intermediate step only occurs with very fine particle size magnetite.

This investigation was primarily concerned with the oxidation of wüstite, specially prepared for this study. The reactions accompanying heating of wüstite were followed by DTA, TG and X-ray examinations. However, the results of the oxidation of various sized fractions of magnetite were also included and compared with the published data.

## Experimental

### a) *Materials*

Two batches of wüstite were prepared by the following procedures. Batch No. I was prepared by enclosing a proportionate mixture of iron (in the form of iron turnings from 99.9% Armco iron) and $\alpha$-$Fe_2O_3$ powder (Baker's reagent grade) in a vacuum sealed steel tube ($10^{-3}$ mm Hg), heating to 1300° for 21 hours to equilibrate and quenching in water to prevent decomposition of the FeO. Batch No. II was prepared from the same mixture but the tube was first evacuated and then sealed in the presence of a positive helium atmosphere, i.e. about 1.1 atmospheres. It was subsequently heated to 1200° for 34 hours, followed by quenching in water. Both batches of wüstite after removal from the steel tube were fractionated using sieves into several size fractions and analysed by X-ray diffraction. Very coarse fractions (+60 mesh) were found to contain both $\alpha$-Fe and $Fe_3O_4$ in addition to a large concentration of FeO. Both $\alpha$-Fe and $Fe_3O_4$ were removed magnetically so that the final X-ray traces showed no lines other than that of FeO from the powder.

The coarse magnetite, $Fe_3O_4$, which is known as permanite (a purified natural magnetite), was supplied by the Foote Mineral Company, Exton, Pennsylvania. This material has a minimum $Fe_3O_4$ content of 92.5%. However, X-ray diffraction analyses of this material showed only lines corresponding to $Fe_3O_4$. In addition, very fine Baker's reagent grade magnetite (ferrosoferric oxide) was used for comparison.

### b) *Apparatus*

The differential thermal analyses were carried out in a DTA device having a sensitivity of 0.10 mv/inch in $\Delta T$ scale and sensitivities varying from 1.5–5 mv/inch in the temperature scale. The furnace used for the DTA study was programmed to 12°/min heating rate. The specimen holder was made of alumina and temperatures were measured by chromel-alumel thermocouples [8] and the set-up was such that the material could be removed easily and rapidly transferred for X-ray diffractometric study. Thus any structural changes accompanying heating could be detected. Debye–Scherrer X-ray patterns were also obtained for the as-prepared FeO and after heating.

Oxidation of the FeO batches was followed by TG, using a DuPont Thermogravimetric analyzer with a sensitivity of 2 mg/inch and having the temperature-measuring thermocouple about one-tenth of an inch above the sample.

## Results

### *FeO – Batch No. I*

DTA plots of both the coarse and fine fractions of this material diluted to 50 wt.% with $Al_2O_3$ in air are shown in Fig. 1. A small and a large peak is evident from these plots. For the fine fraction the large peak has shifted from 655° to 545° and may be a twin peak. The reactions which produced these peaks will be considered later. In Fig. 2, the effects of grinding on the peak intensity and peak shift are shown. The DTA plot of the coarse fraction is also included for comparison. As can be seen, the intensity of the low-temperature peak at 345° has

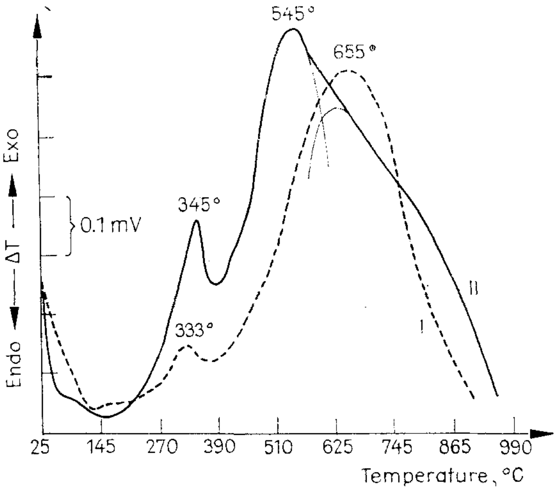

Fig. 1. DTA plots in air of wüstite as produced (Batch I); curve I: coarse (−100 +150 mesh), curve II: fine (−200 mesh) fractions, diluted with $Al_2O_3$

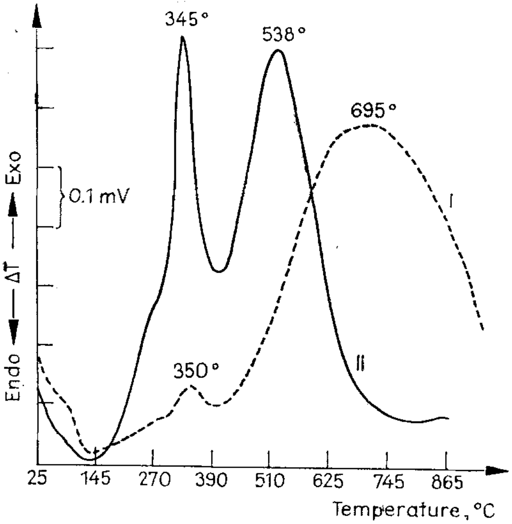

Fig. 2. DTA plots in air of wüstite (Batch I); curve I: coarse as produced (+100 mesh), curve II: mechanically ground (<10 $\mu$), diluted with $Al_2O_3$

been greatly increased and is almost equal to that of the high-temperature peak at about 540°.

In order to identify the reactions which produced these peaks, DTA experiments were terminated at various temperatures; the material was air-quenched and X-rayed for phase identification. The DTA plots of the interrupted experiments are shown in Fig. 3. The structures identified at different stages of heating are shown in Table 1.

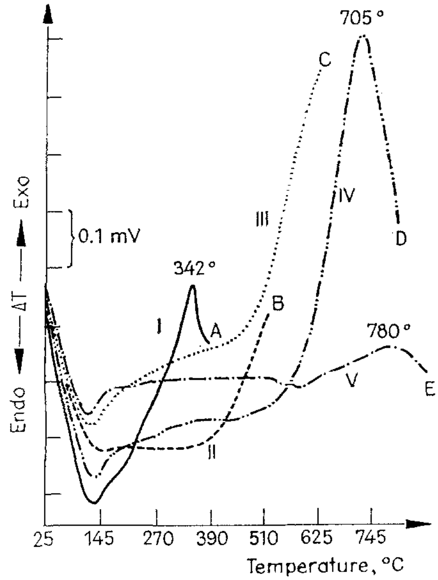

Fig. 3. Interrupted DTA plots in air of mechanically ground wüstite (Batch I), subsequently used for X-ray study; curve I-A: up to 390°, curve II-B: up to 510°, curve III-C: up to 625°, curve IV-D: up to 785°, curve V-E: up to 840°

Table 1

Phases identified by X-ray diffraction at different temperatures

| Maximum temp. °C | Position on Fig. 3 | Oxides present |
|---|---|---|
| 390 | A | FeO + trace $Fe_3O_4$ |
| 510 | B | FeO + $Fe_3O_4$ |
| 625 | C | FeO + $Fe_3O_4$ |
| 785 | D | $\alpha$-$Fe_2O_3$ + trace $Fe_3O_4$ |
| 840 | E | $\alpha$-$Fe_2O_3$ |

When the material that had already been heated to 390° was again run in the DTA, the peak at 342° was not detected, indicating that the reaction was irreversible. An X-ray analysis showed only traces of $Fe_3O_4$ in the system, thus implying that this peak was most probably due to the surface oxidation of FeO. The irreversibility of this reaction indicates that oxidation of FeO proceeds through a surface oxidized boundary layer. To prove this hypothesis, a coarse FeO sample after heating to 390° (which showed the first DTA peak) was reground mechanically. When a DTA run was made with this ground material the first DTA peak at 345° again appeared.

Subsequent to surface oxidation, the conversion of FeO to $Fe_3O_4$ has been indicated by a large peak below 600° for the coarse material. Oxidation of $Fe_3O_4$, formed from FeO, occurred only above 680°. On further reheating, a sample which already had been heated to 785° (and still showed traces of $Fe_3O_4$), gave a small exothermic reaction, indicating that the remaining $Fe_3O_4$ was being oxidized to $\alpha$-$Fe_2O_3$. $\gamma$-$Fe_2O_3$ has never been detected in this investigation.

### *FeO – Batch No. II*

Although this batch of FeO was prepared in a similar manner to the preceding one, the DTA curves obtained for a mechanically ground material were somewhat

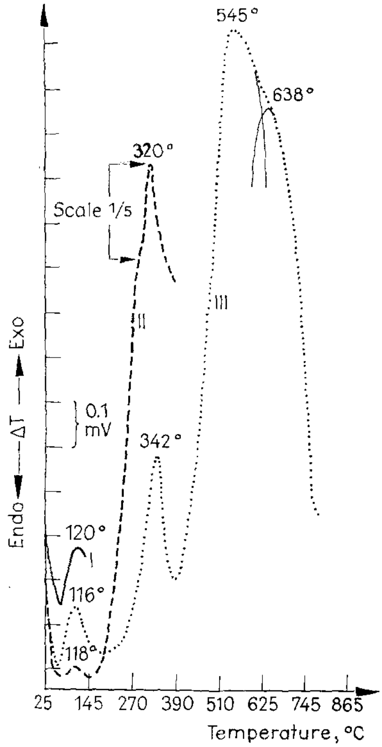

Fig. 4. DTA plots in air of mechanically ground wüstite (Batch II). Interrupted plots indicate that materials from these experiments were used for X-ray study; curve I: up to 145°, FeO + $\alpha$-Fe, curve II: up to 390°, FeO+$Fe_3O_4$, curve III: up to 780°, $\alpha$-$Fe_2O_3$

different, as shown in Fig. 4. First of all, an additional small exothermic peak at about 120° was detected. A diffractometric trace of material heated to 145° showed that the material was still FeO. When this sample was reheated to 390° it showed the peak at 120° but less intense, and also an extremely large peak at about 320° (curve II). This peak is almost similar in size to the corresponding peak of the FeO batch No. I for the same weight of material and instrument sensitivity. (Note: the large peak in Fig. 4 is primarily caused by the fact that the FeO was undiluted.) The phase identification carried out by X-ray diffraction of the material heated to 390° showed that it consisted of FeO and $Fe_3O_4$, confirming the reaction obtained in the previous batch of FeO. A subsequent DTA plot of the same material (previously used for DTA runs up to 145 and 390°) showed four peaks at 116, 342, 545 and 638° (see curve III in Fig. 4).

### *$Fe_3O_4$ – Permanite*

This material was fractionated into three different size fractions, −100 + 150, −150 + 200 and −200 mesh, so that the effect of particle size on the intensity of DTA peaks could be investigated. In addition, this material was mechanically ground for 1 hour, and produced about < 10 μ powder. The DTA curves obtained for the four fractions (diluted to 50 wt.% with $Al_2O_3$) up to 1000° are shown in Fig. 5. A sharp exothermic peak at 330–365°, a very small endothermic peak at 595° and a very large broad peak over 900° were observed. The effect of particle size on the peak intensity (at about 365°) is shown in Fig. 6, when the DTA runs were made up to 430° and each fraction was X-rayed for phase identification.

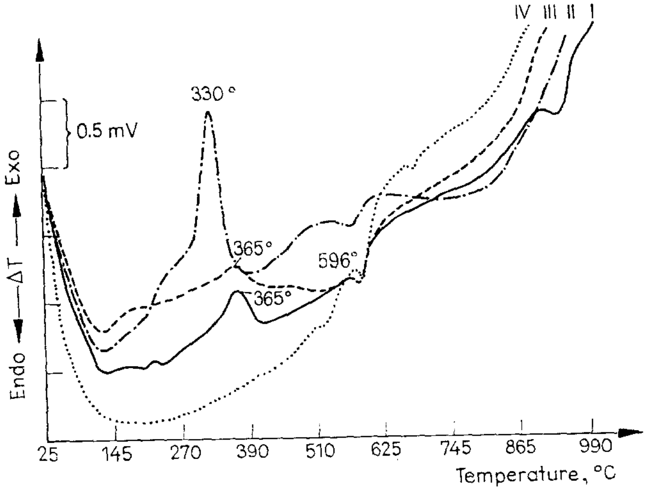

Fig. 5. DTA plots in air of natural magnetite (permanite), coarse and fine fractions; curve I: $Al_2O_3+Fe_3O_4$ (−200 mesh), curve II: $Al_2O_3+Fe_3O_4$ (+200 mesh), curve III: $Al_2O_3+Fe_3O_4$ (+150 mesh), curve IV: $Al_2O_3+Fe_3O_4$ (mechanically ground)

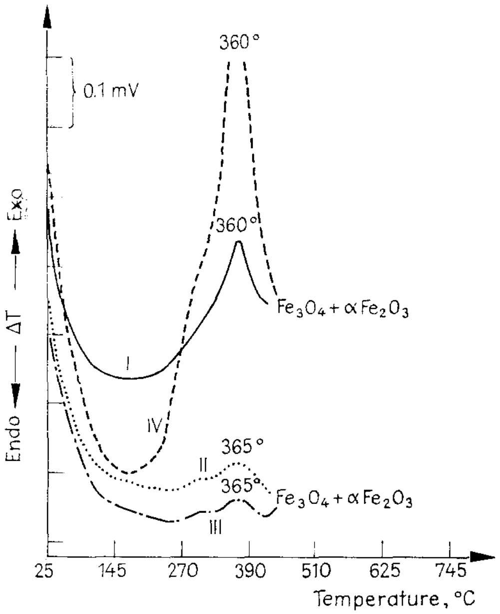

Fig. 6. DTA plots in air of natural magnetite of various size fractions. Peak area and peak intensity depend on the particle size (i.e. surface area); curve I: —200 mesh, curve II: +200 mesh, curve III: +150 mesh, curve IV: 1 hour mechanically ground

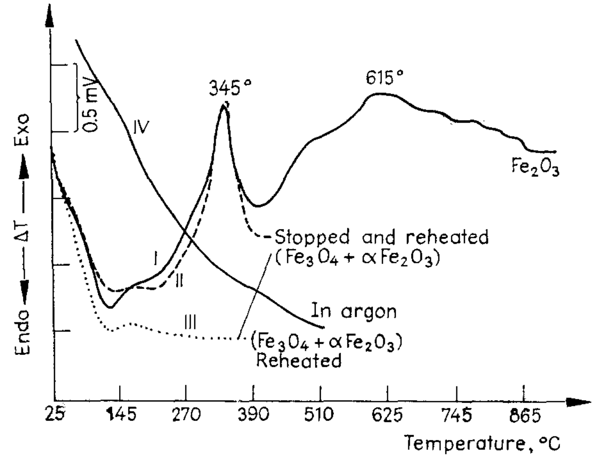

Fig. 7. DTA plots in air (curve I) and in argon (curve IV) of synthetic magnetite. (Baker's, diluted with $Al_2O_3$)

After the first exothermic peak, all fractions contained $Fe_3O_4$ and $\alpha$-$Fe_2O_3$ but no $\gamma$-$Fe_2O_3$. Thus, the two exothermic peaks at 360° and above 900° are considered to be due to surface oxidation and bulk oxidation, respectively. The very small endothermic peak at 595° was probably due to the magnetic transition (ferro- to paramagnetism) which has been reported by several authors [2, 9] to occur at 590°. However, this peak was not detected in the reagent grade magnetite, the DTA plots of which are shown in Fig. 7. In this case the large exothermic peak at 615° completely obscured the small endothermic peak at 595°. Two large peaks were obtained with the pure magnetite at 342 and 615°. The first large exothermic peak at 342° is irreversible, as shown in the same figure. On reheating the material (which had been heated previously to 425°), this exothermic peak was not obtained (compare curve II and curve III). X-ray investigations showed that after the second broad peak, only $\alpha$-$Fe_2O_3$ was present and no $\gamma$-$Fe_2O_3$ was detected at any stage during heating. Curve IV represents a DTA plot of the reagent grade magnetite, heated in argon with a positive pressure of 2 mm Hg. This also shows that the first exothermic peak is due to oxidation, as this peak was not observed during the DTA run in the absence of oxygen.

## Discussion

### *Wüstite — (a) DTA plots*

The DTA plots of Batch No. 1 (Figs 1 and 2) show that there are two distinct exothermic peaks. The first sharp peak, whose intensity increases with finer particle size of the powder, is at about 345° and is due to the surface oxidation of FeO. This has been confirmed by the interrupted DTA experiments (Fig. 3) and X-ray identification of phases at each stage. The dependence of peak intensity on the particle size (i.e. surface area) also confirms this finding. The second broad peak occurs between 545 and 700°; the peak temperature which was found to vary with the particle size is essentially due to two exothermic reactions, unless the material was very fine ($<10\ \mu$). All these reactions are given below:

$$3FeO_{surface} + \frac{1}{2} O_2 \rightarrow Fe_3O_{4(surface)} \tag{1}$$

$$3FeO_{bulk} + \frac{1}{2} O_2 \rightarrow Fe_3O_{4(bulk)} \tag{2}$$

$$2Fe_3O_4 + \frac{1}{2} O_2 \rightarrow 3Fe_2O_3 \tag{3}$$

This dual peak corresponding to reactions (2) and (3) is partially visible in Fig. 1, for materials of $-200$ mesh particle size. However, for very fine particle size material (i.e. with a very large available surface area), reaction (1) may lead to complete oxidation of FeO to $Fe_3O_4$ at about 345° (see DTA plot of $<10\ \mu$

wüstite in Fig. 2). Under these conditions, the second peak at 545° represents oxidation of $Fe_3O_4$ to $Fe_2O_3$. For a coarser material, however, these three reactions can be easily identified as shown in Fig. 3 and Table 1. Also at point B (510°) and point C(625°) in this figure $Fe_3O_4$ could be detected easily by X-ray diffraction. Only after the peak at 705° (Fig. 3) was all the $Fe_3O_4$ oxidized to $\alpha$-$Fe_2O_3$. This twin peak corresponding to reactions (2) and (3) can also be seen in Fig. 4 for the other batch of wüstite (Batch No. II).

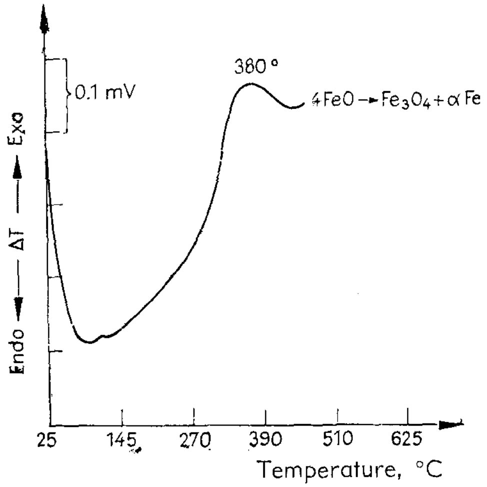

Fig. 8. A DTA plot in argon of wüstite (Batch II). (Diluted with $Al_2O_3$)

For the second wüstite batch, the DTA plot shows four peaks at 120, 320, 545, and at about 638° (see curve III, Fig. 4). The reaction at 120° could not be identified by X-ray techniques. Originally it was thought that this peak may be associated with some form of oxidation of $FeO_{1-x}$ to a higher oxidation state. The reversibility of the peak as shown in curve III, eliminated this possibility. Magnetic transitions – such as Curie or Néel Point of iron or iron oxides – occur at a much higher temperature and thus could not be responsible for this peak. It is possible that under some oxidation states wüstite may have an order-disorder transition, which produces this peak. The next exothermic peak at 320–342° was attributed to the surface oxidation of FeO, but this material represented by curve III had been already used twice before for DTA runs in air up to 145 and 390°. Although the peak at 320° in curve II may be due to the surface oxidation of FeO, the peak at 342° in curve III could not be explained by this argument. To establish if there is any other reaction which may produce this peak at 320°, a fresh sample of FeO (Batch No. II) was used for a DTA run in the presence of oxygen-free argon up to 470°. The plot is shown in Fig. 8. It can be seen that there is an exothermic peak at 380°. An X-ray diffraction analysis of the material quenched from 465° (Fig. 9) showed the presence of FeO, $Fe_3O_4$ and $\alpha$-Fe. On the basis of this evidence, the following reaction responsible for this peak is proposed:

$$4FeO \rightarrow Fe_3O_4 + \alpha\text{-}Fe \qquad (4)$$

This disproportionation reaction below 570° can be predicted by the phase diagram Fe—O (Hansen and Anderko [10]) and has been observed by Aubry and Marion [6].

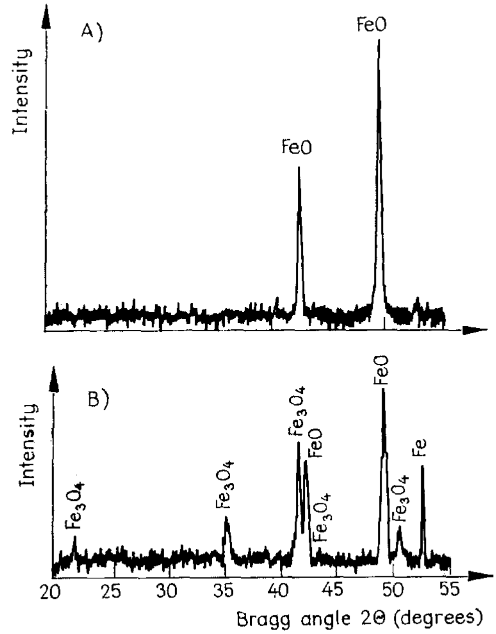

Fig. 9. X-ray diffraction plots showing incomplete decomposition of wüstite to $Fe_3O_4$ and $\alpha$-Fe. A: FeO, as produced, Batch II; B: FeO, after 465° in argon

However, in the previous section, the peak in this temperature region was assigned to reaction (1), i.e. surface oxidation of FeO. It appears that above 300°, wüstite is an unstable oxide. In the presence of oxygen, it oxidized to $Fe_3O_4$, which, because of the slow diffusion rate of oxygen through this layer, prevents further oxidation. On the other hand, in the absence of oxygen, wüstite disproportionates to $Fe_3O_4$ and $\alpha$-Fe. The coexistence of all three phases FeO, $Fe_3O_4$, and $\alpha$-Fe above this peak temperature suggests that reaction (4) occurs only on the surface. Why this transformation should be only on the surface cannot be explained at present.

### (b) *X-ray study*

Both DTA and X-ray diffractometric traces have shown that the two wüstite batches behave differently during heating. As testing conditions were the same, it would tend to indicate that the method of preparation has produced FeO of differing composition, i.e. different Fe/O ratios. Thus the unit cell dimensions of both batches before and after heating to 390° were determined.

Debye-Scherrer X-ray photographs were obtained for both batches of wüstite – as prepared and also after heating to 390°. Thus the variation in unit cell dimensions in the starting materials and any subsequent heat effects on the lattice parameter could be studied. The values of $a$, the lattice parameter, were determined from the intercept of a plot of the lattice parameter vs. the extrapolation function $1/2\,(\cos^2\Theta/\sin\Theta + \cos^2\Theta/\Theta)$, [11]. For this plot the X-ray lines corresponding to the reflecting planes 111, 200, 220, 400, 331 and 420 were used. The results are given in Table 2.

Table 2

Lattice parameters of wüstite

| | As prepared ($a$, Å) | After heating to 390° ($a$, Å) |
|---|---|---|
| Batch I | $4.3050 \pm .0007$ | $4.3080 \pm .0008$ |
| Batch II | $4.3070 \pm .0050$ | $4.3120 \pm .0010$ |

The unit cell dimensions of FeO as a function of the Fe/O ratio have been determined by several workers. Wells [12] quoted two values, 4.2816 Å and 4.3010 Å for Fe/O ratios of 0.912 and 0.944 respectively. Jette and Foote [13] also determined $a$'s as a function of Fe/O ratio, and Willis and Rooksby [14] found the value of $a$ to be 4.3088 Å for the maximum Fe/O ratios within the FeO phase. They also observed that the wüstite produced by quenching a stoichiometric mixture of iron and $\alpha$-$Fe_2O_3$ (or with excess iron) in the range 700° to 1200° had a constant value of 4.305 Å. Finally, Foster and Welch [15] in a detailed investigation showed that gross compositions of 76.13% and 76.82% iron, corresponding to the oxygen- and iron-rich ends of the wüstite phase, have lattice parameters of 4.2915 Å and 4.3080 Å, respectively. In the present investigation Batch I FeO has the unit-cell dimension of the upper limit suggested by Willis and Rooksby, but in the case of Batch II FeO the $a$ value is higher than the upper limit set by them. In addition, the $a$ values of both batches of FeO increased on heating to 365°, Batch I from 4.3050 to 4.3080 Å and Batch II from 4.3070 to 4.3120 Å. The results are summarized in Fig. 10.

It is apparent from this figure that both batches of wüstite used in this investigation belong to the upper limit set by Willis and Rooksby [14] and Foster and Welch [15]. The Fe/O ratios for these batches were 0.952 and 0.956 for as-produced Batch I and Batch II, respectively. The corresponding ratios on heating to 365° were 0.957 and 0.963.

The increase in unit cell dimensions of the wüstite on heating to 365° cannot be attributed to oxidation, as oxidation essentially reduces the lattice parameter, with a corresponding reduction in the Fe/O ratio. However, in the above two cases there is an increase in unit cell dimensions, suggesting that the lattice is expanding due to the loss of oxygen ions or an increase in the Fe concentration giving a more stoichiometric compound. Thermogravimetry could not be used to detect this loss of oxygen as at this temperature (below 365°), the surface of FeO also oxidized to $Fe_3O_4$ [i.e. reaction (1)], as can be seen from the DTA plots (Figs 1 to 4). The reason for this increase in lattice parameter on heating wüstite cannot be determined at present. However, it can be speculated that there was some free iron present in the system, or some α-Fe produced by the disproportionation reaction (4) may subsequently diffuse in the non-stoichiometric wüstite to give a higher iron to oxygen ratio. In addition, it has also been suggested by Owe Berg [16] that the deficit of Fe in FeO may be due to the presence of water or hydroxide in FeO. This loss of $H_2O$ from wüstite during heating to 365° may account for the change in the unit cell dimension. Thermogravimetry of wüstite in air showed that at 365° there was only about 2% increase in weight. If the FeO had been completely converted to $Fe_3O_4$ at this temperature, i.e. to $FeO_{1.33}$, then the increase in weight would be 7.3%. This indicates that only surface oxidation takes place during this period, confirming the X-ray evidence for the formation of $Fe_3O_4$.

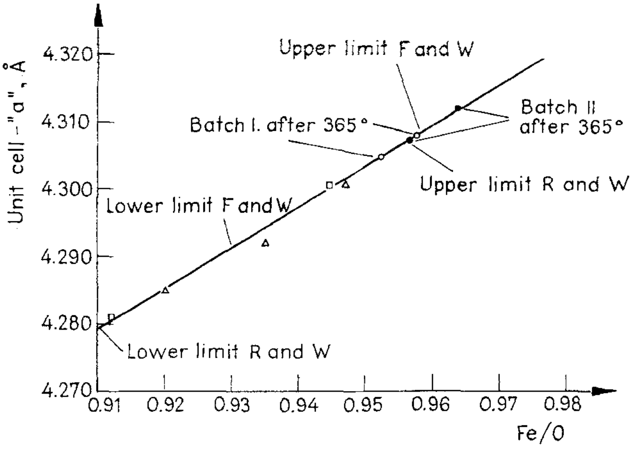

Fig. 10. The change in unit cell dimension of wüstite on heating to 390°. The lattice parameter values of wüstite previously reported are also included for comparison. □: Wells, Δ: Jette and Foote, R and W: Willis and Rooksby, F and W: Foster and Welch, o: Batch I. ●: Batch II

### $Fe_3O_4$ – *Permanite*

The natural magnetite showed two exothermic peaks (Fig. 5). The first exothermic peak is at about 330 – 365°. The variation in the peak temperatures may be attributed to the particle size effect and to the extent of dilution with inert materials. The variation of the peak intensity with particle size (for the same amount of material) is shown in Fig. 6. The second exothermic peak, which is very large and broad, starts at about 580°. The precise peak temperature could not be determined with the existing DTA equipment which had a temperature limitation of 1000°. However, the overall DTA plots supported the observations of Schmidt and Vermaas [2]. These two exothermic peaks can be interpreted as a consequence of surface oxidation (first peak at 360°) and bulk oxidation (peak at over 900°) of magnetite.

The endothermic peak at 595° is most probably due to the magnetic transition, i.e. ferromagnetism to paramagnetism transition at this temperature [2, 9]. This small endothermic peak was suppressed by the large, broad exothermic peak in the case of synthetic magnetite of very fine particle size ($<5\ \mu$), which is shown in Fig. 7. Very fine particle size of the synthetic magnetite has also significantly affected the peak temperature of the second exothermic reaction. For example, the peak temperature of 900° or over for the coarser material was changed to 615° for materials of $<5\ \mu$ particle size. It appears that the large peak at 360° for finer materials is indicative of a large volume fraction oxidized during this period because of the large surface area available. This correspondingly reduces the second exothermic peak associated with the bulk oxidation. In this investigation $\gamma$-$Fe_2O_3$ as an intermediate product during the oxidation of $Fe_3O_4$ to $\alpha$-$Fe_2O_3$ has not been observed. This is primarily due to the fact that the smallest particle size of $Fe_3O_4$ used in this study was always greater than 1 $\mu$. As shown by Egger and Feitknecht [7], $\gamma$-$Fe_2O_3$ as an intermediate step only occurs with particles below 5500 Å, i.e. 0.55 $\mu$. Thus, the consideration of particle size of the magnetite, $Fe_3O_4$, will explain all the observed results in this study as well as the previous observations on $Fe_3O_4$ by Gheith [1] and Schmidt and Vermaas [2]. It has also been suggested by David and Welch [17] that during the oxidation study of synthetic magnetite, $\gamma$-$Fe_2O_3$ only formed in the presence of an appreciable amount of water and not under dry conditions.

## Conclusions

DTA curves of two batches of wüstite in air showed two large exothermic reactions at 345 and 545 – 700°. These peaks are due to surface oxidation and bulk oxidation of wüstite. In the case of fine material ($<10\ \mu$), a third reaction, oxidation of magnetite to $\alpha$-hematite, occurs concurrently with the bulk oxidation of wüstite to magnetite. For a coarse material, the last two reactions resulted in a dual (or twin) peak. In argon, however, wüstite decomposed to $Fe_3O_4$ and $\alpha$-Fe.

All of the reaction sequences have been identified by X-ray diffractions on materials of interrupted DTA experiments. The peak intensity was found to be dependent on the particle size and the high temperature exothermic peak shifted significantly to a lower temperature with finer material. The unit cell dimensions vs. Fe/O ratios showed an increase in Fe/O ratio on heating wüstite to 365°. Both fine and coarse magnetite are characterized by two exothermic peaks, which corresponded to surface and bulk oxidation transforming to $\alpha$-$Fe_2O_3$.

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Résumé — On a préparé deux séries de wüstite à partir d'un mélange stoechiometrique de Fe et $Fe_2O_3$ dans des tubes scellés d'acier sous vide rsp. en hélium. Un tube a été chauffé pendant 21 heures chez 1300° l'autre chez 1200° pendant 34 heures. On observe dans les courbes d'ATD des deux séries d'échantillons deux pics exothermiques chez 345° et de 545° jusqu' à 700° dûs à l'oxydation superficielle de FeO en $Fe_3O_4$ suivie par l'oxydation de la masse de l'échantillon de FeO en $Fe_3O_4$ rsp. de $Fe_3O_4$ en $\alpha$-$Fe_2O_3$. Les deux réactions dernières donnent pour un produit à gros grains, un pic double, et pour un produit à grains fins un pic simple indiquant que dans le dernier cas deux réactions concurrentes eurent lieu. Pareilles investigations avec magnétite grossière et fine n'ont montré que deux pics exothermiques correspondant à l'oxydation superficielle et dans la masse. Ces resultats confirment les observations antérieures de la transformation de magnétite grossière en $\alpha$-$Fe_2O_3$ par oxydation superficielle suivie d'oxydation dans la masse.

Zusammenfassung — Es wurden zwei Serien von Wüstit aus einem stöchiometrischen Gemisch von Fe und $Fe_2O_3$ in versiegelten Stahlröhren unter Vakuum bzw. Helium durch 21 stündiges Erhitzen bei 1300° bzw. 34 Stunden bei 1200° dargestellt. Die DTA-Kurve wies bei beiden Proben zwei exothermische Spitzen auf, bei 345° bzw. bei 545° bis 700° auf, die der oberflächlichen Oxydation von FeO zu $Fe_3O_4$ bzw. der vollständigen Oxydation von

FeO zu $Fe_3O_4$ bzw. $Fe_3O_4$ zu $\alpha$-$Fe_2O_3$ entsprechen. Die beiden letzten Reaktionen verursachten eine Zwillingsspitze im Fall von grobem Material, hingegen eine einzige Spitze bei feinem Material. Diese Reaktionen verlaufen also im letzten Fall gleichzeitig. Ähnliche Versuche mit grobem und feinem Magnetit zeigten nur zwei, der oberflächlichen und massiven Oxydation entsprechenden exothermischen Spitzen. Dieses Ergebnis unterstützt die früheren Beobachtungen, daß grober Magnetit durch oberflächliche und darauffolgende vollständige Oxydation in $\alpha$-$Fe_2O_3$ übergeht.

Резюме — Получены две партии вустита из стехиоме трической смеси Fe и $Fe_2O_3$ в закрытых трубках из нержавеющей стали в вакууме и в атмосфере гелия. Соответственно, первая трубка нагревалась при температуре 1300° в течение 21 ч., а вторая — при 1200° в течение 34 ч. Наблюдалось два экзотермических пика на кривой ДТА обоих образцов при температуре 345° и в области температур 545—700°, в результате поверхностного окисления FeO в $Fe_3O_4$ и $Fe_3O_4$ в $\alpha$-$Fe_2O_3$. Последние две реакции дали двойной пик в случае грубого вещества, и один для тонкоизмельченного вещества. Полученные данные указывают на то, что эти две реакции конкурируют в случае тонкоизмельченного вещества. Исследован как тонкоизмельченный, так и грубый магнетит и получено только два экзотермических пика, соответствующих поверхностному и внутреннему окислению. Этот результат подтверждает предварительное наблюдение, что грубый магнетит переходит в $\alpha$-$Fe_2O_3$ в результате поверхностного окисления, которое сопровождается его внутренним окислением.