The mechanism of oxidation in titanomagnetites: a magnetic study

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Summary. A hypothesis for the mechanism of oxidation in titanomagnetites is first put forward on the basis of new oxidation data for pure magnetite and the new model for cation distribution in titanomagnetites. Contrary to previous claims by other workers, it is shown that single-phase spinel oxidation products of titanomagnetites can only be produced under very exacting circumstances. Low-temperature magnetic measurements on such synthetic, oxidized materials were made to show the formation of magnetite by the decomposition of the metastable oxidation products of titanomagnetites on prolonged heating at moderate (~390° C) temperatures. This magnetic method of detection is more sensitive than that of normal X-ray diffraction. It is concluded that previous claims of an increase in magnetization due to the formation of synthetic single-phase, highly oxidized titanomagnetites must be due to the formation of undetected magnetite.

Although very little work has been done on the stability of titanomagnetites, $Fe_{3-x}Ti_xO_4$ $(0 < x < 1)$, to oxidation, and on the possible oxidation mechanisms, a great deal has been done on the oxidation of magnetite, Fe_3O_4, particularly to maghemite, γ-Fe_2O_3, because of its commercial interest. Colombo, Fagherazzi, Gazzarini, Lanzavecchia, and Sironi (1964) studied mechanisms for the first stage of oxidation of magnetite using natural and synthetic samples made both by a high-temperature technique and by precipitation from a solution. The fine-grained precipitated material produces cubic γ-Fe_2O_3, but the natural samples and those synthesized at high temperature, both of which have small specific surface and low degree of crystalline imperfection, were found to produce mainly rhombohedral haematite, α-Fe_2O_3, as a surface layer, and a solid solution of Fe_3O_4 and γ-Fe_2O_3 in the interior of the grains. The effect of hydration is also important, and water may be incorporated in the material in the course of precipitation or be absorbed due to the large specific surface area of fine grain powders. Elder (1965) ground natural magnetite to a submicron grain size both in water and in dry acetone. Both samples oxidized quickly in air at low temperature ($\sim$ 1 hour at 250° C) the former producing a substantial amount of γ-Fe_2O_3 and the latter producing only α-Fe_2O_3. When the sample ground in acetone was oxidized in an atmosphere of water vapour and oxygen, it was partially converted to γ-Fe_2O_3. Samples of grain size $\geqslant 25\ \mu$ did not oxidize quickly and produced only α-Fe_2O_3.

Akimoto, Katsura, and Yoshida (1957) oxidized samples of titanomagnetites of unspecified grain size prepared by grinding together the constituent oxides, firing under vacuum at 1100° C and quenching. The heat treatment was for 2 hours between 400° C and 550° C in air. They claimed that the oxidation products were single-phase and of spinel structure, and that in many cases the oxidation products almost attained the composition of a γ-Fe_2O_3–$FeTiO_3$ solid solution. It is difficult to accept this in view of the absence of water, the probably large grain size and the method of preparation. Havard (1964) found that heating a synthetic titanomagnetite made by the same method (grain size $\sim 100\ \mu$) produced a rhombohedral phase after only a few minutes at 550° C.

Cation distribution in spinel oxidation products of titanomagnetites

Cation-deficient iron-titanium oxide spinels are found in nature and are considered to be oxidation products of titanomagnetites (Akimoto and Katsura, 1959). The distribution of cations and vacancies between the octahedral and tetrahedral sites of the spinel structure for these oxidation products has not been determined, but by considering the mechanism by which oxidation may take place and the cation distribution in the original unoxidized titanomagnetite it is possible to predict the change in distribution as oxidation proceeds. Extending the oxidation mechanism of Colombo *et al.* (1964) to the titanomagnetites, it is assumed that cations diffusing through the crystalline lattice combine with adsorbed oxygen atoms at the surface, which are ionized by the extra electrons of the Fe^{2+} ions. Octahedrally sited cations have a high diffusion rate, as in the case of Fe^{2+} in magnetite, because chemical bonding in octahedral sites is ionic. However covalent bonding in tetrahedral sites (Goodenough and Loeb, 1955) leads to a very low diffusion rate; this has been verified experimentally for the spinel structure by Lindner and Akerstrom (1956). For this reason oxidation will take place largely at the expense of octahedral Fe^{2+}, the cation population of tetrahedral sites will remain constant, and vacancies will occur largely in octahedral sites. In the unoxidized series, $Fe_{3-x}Ti_xO_4$, tetrahedral and octahedral sites are shared by both Fe^{3+} and Fe^{2+} ions for $x > 0{\cdot}2$ (O'Reilly and Banerjee, 1965). Defining a degree of oxidation z by the reaction $Fe^{2+} + \frac{1}{2}zO \rightarrow zFe^{3+} + (1-z)Fe^{2+} + \frac{1}{2}zO^{2-}$ $(0 < z < 1)$, the cation distribution between tetrahedral and octahedral sites in terms of x, z and δ, where δ is the number of Fe^{2+} in tetrahedral sites, may be calculated. The number of Fe^{3+} in tetrahedral sites in an oxidized titanomagnetite will then be $(1-\delta)$. If there are no Ti^{4+} and vacancies in tetrahedral sites, the number of Fe^{3+} in octahedral sites is $7+\delta-16(3+x)/(8+z+xz)$; the number of Fe^{2+} is $8(9+x)/(8+z+xz)-8-\delta$; the number of Ti^{4+} is $8x/(8+z+xz)$ and the number of vacancies is $3z(1+x)/(8+z+xz)$.

The saturation magnetization, n_B, at 0° K may then be written (Néel, 1948): $n_B = 2\delta-2+48(1-x)/(8+z+xz)$ Bohr magnetons per molecule.

The above premises imply that δ should remain constant and equal to the initial value as oxidation proceeds. Once all octahedral Fe^{2+} has been oxidized, referred to as the first stage of oxidation, further oxidation may be impossible since the higher temperatures necessary to increase tetrahedral Fe^{2+} mobility will probably result in the decomposition of the metastable cation-deficient spinel.

It will be seen that saturation magnetization will decrease with increasing z for all compositions during the first stage of oxidation, but that if further oxidation is possible the magnetic moment of oxidation products of compositions given by $x > 0{\cdot}6$ will decrease to zero and then increase as the magnetic moment of the tetrahedral sublattice becomes greater than that of the octahedral sublattice (see fig. 1).

This is not in accordance with the experimental results of Akimoto *et al.* (1957) who found that the saturation magnetization, measured in a field of 3 kilo-oersteds (kOe) at room temperature, of three samples $(x > 0{\cdot}3)$ increased and that of three samples $(x < 0{\cdot}3)$ decreased.

Because of the lack of agreement between theory and experimental data, which may be suspect first because of the possibility of two-phase samples and secondly because the measurement of saturation magnetization requires a large magnetic field and low temperature, a number of experiments were performed to test the stability of titanomagnetites to oxidation and to make high-field, low-temperature saturation magnetization measurements on the oxidation products.

Oxidation experiments

Oxidation experiments were carried out on titanomagnetite, prepared by the technique of Barth and Posnjak (1932) as extended by

Akimoto *et al.* (1957). The samples were ground under dry conditions to $< 44\ \mu$ and were subjected to various heat treatments in air. Oxidation as a function of temperature was observed using a Stanton 'Mass-flow' thermobalance with a static atmosphere and a heating rate of 5° C/min. Experiments were also made under isothermal conditions mainly at 240° C and 390° C, at which temperatures the reaction rate was found to be slow, as might be expected from the results of Colombo *et al.* (1964) for magnetite. These experiments were made in a separate furnace and the increase in weight measured after cooling down to room temperature.

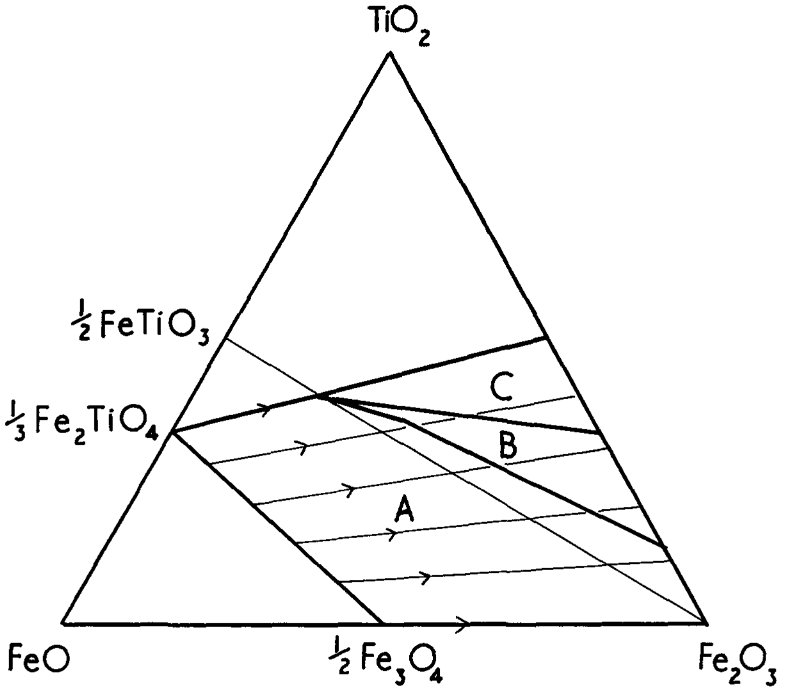

FIG. 1. The FeO–Fe_2O_3–TiO_2 ternary diagram. The arrows indicate the change in composition of titanomagnetites as oxidation proceeds. In region A, oxidation takes place at the expense of octahedral site Fe^{2+} and the net spontaneous magnetization is due to the octahedral sublattice. In region B, oxidation of tetrahedral Fe^{2+} is taking place but magnetization is still due to octahedral sites. In region C, oxidation takes place at the expense of tetrahedral Fe^{2+} but net magnetization is now due to tetrahedral sites.

Isothermal experiments for periods ranging from 3 to 120 hours at

390° C produced degrees of oxidation of $z = 0{\cdot}1$ to $z = 0{\cdot}6$ for all compositions and a rhombohedral phase usually became visible on X-ray powder pictures after less than 10 hours. The degree of oxidation required to produce a composition on the Fe_2O_3–$FeTiO_3$ join of the ternary diagram (fig. 1) is given by the condition $z(1+x) = 1$, i.e. z varies from 1 to 0·5 as x increases from 0 to 1. For $x \leqslant 0{\cdot}4$, 120 hours at 390° C produced a two-phase oxidation product, the bulk composition of which had not reached the Fe_2O_3–$FeTiO_3$ join. For $x \geqslant 0{\cdot}6$, 72 hours at 390° C produced two-phase oxidation products of bulk compositions near the join. Longer periods (195 hours) at 240° C produced only slight degrees of oxidation ($z \sim 0{\cdot}1$). The cell-size of the spinel phase was found to decrease with oxidation.

These results seem to be in agreement with the experiments performed on pure magnetite by other workers who showed that single-phase spinel oxidation products are only obtained for small grain sizes, usually produced by precipitation from an aqueous solution, and that in such cases oxidation proceeds rapidly at low temperatures ($\sim$ 1 hour at less than 300° C) due to large specific surface area, high degree of crystalline imperfection, and possibly adsorbed water. Similar oxidation rates and products are not therefore to be expected for the samples described above and they were not found.

Reaction rates were derived from the thermobalance data by finite difference analysis. A peak in reaction rate was found between 500 and 600° C. The temperature for the peak does not vary systematically with sample composition, and the variation is presumably due to variation in specific area. The height of the peak increased with increasing titanium content but could not be definitely related to the initial cation distribution on the basis of the relative availability of Fe^{2+} in tetrahedral and octahedral sites to oxidation.

Saturation magnetization

Saturation magnetization of those samples that did not reveal a rhombohedral phase in X-ray powder pictures was measured using a vibrating-sample magnetometer operating at liquid-nitrogen temperature. The saturation magnetization of samples of composition $x < 0{\cdot}4$ decreased with oxidation and those with $x \geqslant 0{\cdot}4$ increased with oxidation. The molecular weight M was calculated from the degree of oxidation and the results converted to Bohr magnetons (μ_B) per molecule in the usual way (Gorter, 1954), multiplying the saturation magnetization by $M/5585$. The value of δ, the number of Fe^{2+} in tetrahedral sites, corresponding to the observed values of n_B and z was then calculated and taking δ for the unoxidized samples from O'Reilly and Banerjee (1965), $\Delta\delta$, the difference in δ for the oxidized and unoxidized samples could be worked out. It was found that even in those cases where the saturation magnetization decreased, the resultant moment required a positive value of $\Delta\delta$, that is, the number of Fe^{2+} in tetrahedral sites must increase with oxidation, which is very difficult to believe. The results for a number of compositions are shown in table I. It is also

TABLE I. Saturation magnetization of oxidized titanomagnetites. Comparison of observed and calculated values leads to cation distribution and in particular the number of Fe^{2+} ions, δ, in tetrahedral sites. As $\Delta\delta$ is positive the oxidation products are shown to be two phase.

	Heat treatment				Saturation magnetization μ_B			
x	°C	Time (hrs.)	z	Molecular weight	calculated	observed	δ	$\Delta\delta$
0	390	5	0·13	229	3·67	3·36		
	240	195	0·11	229	3·92	3·64		
0·25	240	95	0·11	227	$2\delta+1{\cdot}92$	2·65	0·36	+0·31
0·4	390	3	0·10	225	$2\delta+1{\cdot}53$	2·09	0·28	+0·08
	390	5	0·15	224	$2\delta+1{\cdot}52$	2·27	0·37	+0·17
0·6	390	3	0·17	222	$2\delta+0{\cdot}31$	1·28	0·48	+0·08
0·8	310	3	0·13	222	$2\delta-0{\cdot}82$	0·407	0·62	+0·02
1·0	390	3	0·10	220	$2\ -2\delta$	0·168	0·32	−0·58

interesting to note that samples of composition $x = 0$, magnetite, gave values of saturation magnetization that were much too low for a Fe_3O_4–γ-Fe_2O_3 solid solution although the heat treatments in all cases were not severe in the hope of avoiding the decomposition of the metastable maghemite–magnetite oxidation product. The oxidation products of samples of initial composition $x = 0{\cdot}4$ had thermomagnetic curves that were slightly P-type (Néel, 1948), which may indicate that the interaction between octahedral site cations is weakened due to the presence of vacancies. On the arguments given above, the only way the moment of $x = 1$, ulvöspinel, can increase with oxidation is due to the moment of the tetrahedral sublattice becoming predominant over the octahedral sublattice and δ is calculated on this basis. The coercive force of the sample of composition $x = 1$ is 8150 oersteds at liquid nitrogen temperature (Banerjee and O'Reilly, 1966). The high coercivity is thought to be due to Fe^{2+} ions in octahedral sites. Oxidation (3 hours at 390° C) drastically reduces this value to 2000 oersteds. This is consistent with the preferential oxidation of octahedral Fe^{2+} but may more probably be explained by a mechanism outlined below.

Discussion

The clue to this conflict between experiment and theory lies in the low degrees of oxidation produced by fairly long times, that is, the diffusion rates are very low. Colombo *et al.* (1964) have shown that to obtain maghemite a high diffusion rate is necessary and this is produced by a high degree of crystalline imperfection, a large specific surface area (that is, a small grain size), and perhaps adsorbed water. All three are present in samples produced by wet precipitation but from samples made at high temperatures a two-phase oxidation product is obtained.

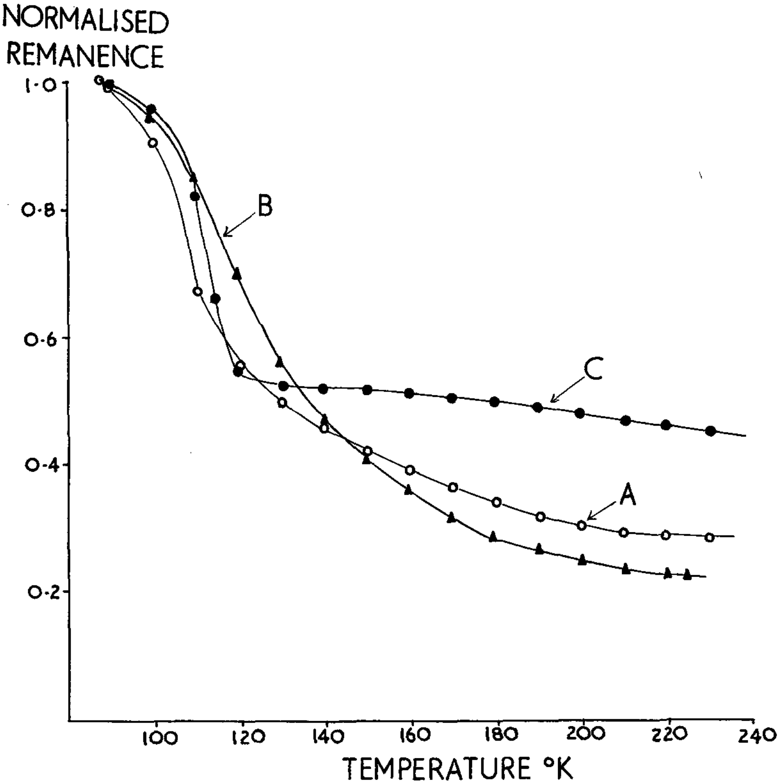

Fig. 2. Decay of low temperature remanent magnetization, normalized to the low temperature value. Curve A shows the result for an unoxidized titanomagnetite of composition $x = 0{\cdot}4$. Curve B shows the result for the same sample oxidized in air for 5 hours at 390° C. Curve C shows the result after heating for 120 hours at 390° C.

Similarly in the present oxidation experiments two-phase oxidation products will result, and small amounts of exsolved magnetite, presumably accompanied by ilmenite, $FeTiO_3$, can cause the apparent increase in saturation magnetization. This would be difficult to detect by X-ray powder pictures but one way in which it can be demonstrated is by cooling the sample down to liquid nitrogen temperature, magnetizing it and observing the decay in remanence as the sample is warmed up. If magnetite is present the remanence should fall sharply at 120° K (Nagata, Kobayashi, and Fuller, 1964). Fig. 2 shows the result of this experiment on a sample of $x = 0{\cdot}4$. As oxidation proceeds the characteristic magnetite curve evolves.

Our observations show that the strict requirements necessary for producing single-phase oxidized magnetites also hold for titanomagnetites. Extremely careful oxidation experiments carried out at as low a temperature as 240° C resulted in a two-phase product of magnetite and ilmenite. The 'exsolved' magnetite can be so small in amount as to evade detection by normal X-ray diffraction techniques, but contributes to the observed increase in magnetization by virtue of its high saturation magnetization. This is no doubt the reason for the mistaken conclusion of Akimoto *et al.* (1957) that they had been able to produce a new synthetic single-phase highly oxidized form of titanomagnetite. If our purpose is to simulate the highly oxidized single-phase oxidation products of titanomagnetites found in basalts, the starting material must be titanomagnetite produced by precipitation from an aqueous solution. Such experiments are now in progress in our laboratory.

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