

Oxidation kinetics of fayalite and growth of hematite whiskers

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The oxidation of fayalite to hematite and silica by oxygen and oxygen–nitrogen or oxygen–water vapour mixtures has been studied by TGA, SEM and X-ray diffraction. In the temperature range 690 to 950° C, the isotherms of oxidation are pseudo-parabolic. The Arrhenius plot shows a break near 840° C, related to the quartz–cristobalite transformation, the activation energy being about 230 kJ mol⁻¹. The first stage of oxidation leads to the formation of a covering layer constituted of silica plus iron oxide (mainly hematite). Solid state diffusion of oxygen then takes place through this layer, which progressively evolves with the crystallization of silica and a relaxation of stress due to fracture. After the fracture of the covering layer, whiskers of hematite grow, usually on a silica substrate, and align themselves along linear defects. Under specific conditions, their growth is periodic.

1. Introduction

Fayalite is an important intermediate product in some metallurgical processes. It is a constituent of sintered acid ores [1, 2], is formed in the matte of copper smelting [3] and lead smelting [4], appears as a trace in the oxidation of silicon steel [5], and is formed in the slag of electrical furnaces used for cupro-nickel smelting [6]. Despite the industrial importance of fayalite, few papers deal with its reactions. Some reports on the reduction of fayalite have been published [1, 2, 7–10]. Gaballah *et al.* [7] studied the reduction of fayalite by H₂, CO and H₂ + CO in the temperature range 700 to 1000° C. They observed discontinuities in the Arrhenius plot at 870 and 910° C, which correspond to the polymorphic transitions of silica and iron respectively.

Wones and Gilbert [11] investigated the oxidation of fayalite at a pressure of 2 kbar and temperatures between 600 and 800° C. Such conditions are similar to those found in nature, for fayalite is a constituent of the earth's mantle (and also of the lunar soil).

A better understanding of fayalite oxidation from a kinetic and morphological viewpoint is needed. Thermodynamic data are available and

allow us to predict that, with pure oxygen at atmospheric pressure, oxidation will lead to silica plus hematite at any temperature below that of the dissociation of hematite to magnetite [12]. An interesting point in connection with the oxidation of fayalite is the exact composition and possible non-stoichiometry, which can influence the oxidation process, and of course modify the mass change.

Cirilli [13] has produced some reduction isotherms for CO/CO₂ at 1000° C, from which it appears that the composition of fayalite can vary from Fe₂SiO₄ to Fe_{1.87}SiO₄. Divanach [14] and Ory [15] have estimated the homogeneity range as Fe_{1.93}SiO₄ to Fe_{1.96}SiO₄. Sockel [16] has studied the defect structure and has found iron vacancies and electron holes to be present, but has not determined the limits of this phase for a higher degree of oxidation.

2. Experimental

Five samples were prepared by heating mixtures of hematite and quartz (Fe:Se = 2, 1.96, 1.86, 1.5, and 1) in a controlled atmosphere of H₂:H₂ + H₂O = 0.5 at 1000° C. To ensure good synthesis, each sample was ground and reheated twice. In order to

check non-stoichiometry, each sample was annealed in a sealed silica tube with iron or magnetite at 1050°C for 24 h.

All kinetic experiments were carried out with Sample 2 (Fe:Si = 1.96), which had a specific surface area of 0.5 m² g⁻¹. The oxidation process was performed with samples of 100 mg spread on a gold plateau (area 2 cm²) in a Cahn RG electrobalance. The gas flow (O₂, O₂ + N₂, or O₂ + H₂O) was about 3 cm sec⁻¹ (100 l h⁻¹). The experiments designed to determine the stoichiometry were carried out with a Seteram thermobalance (MTB type). The oxidation products were analysed by X-ray diffractometry, magnetic measurements, and SEM (Cameca type).

3. Results

3.1. Non-stoichiometry of fayalite

The composition of the fayalite was estimated from the weight change during oxidation to hematite. The amount of magnetite present (traces) was determined magnetically. It is possible to calculate the value of *x* in the formula Fe_{2-x}SiO₄ from the weight change, provided the Fe:Si ratio in the mixture of hematite and silica is known. The results from 10 samples give the value of *x* to be 1.98 ± 0.005. Surprisingly, this result appears to be quite independent of oxygen pressure in the range 1.6 × 10⁻¹² to 10⁻¹⁴ bar, corresponding to a large variation in the H₂:H₂ + H₂O ratio from 0.1 to 0.585.

3.2. Kinetics of oxidation

Fig. 1 gives the change of the ratio of O to Fe with time. It is clear that the reaction starts with some acceleration, leading to the pseudo-parabolic shape of the isotherms. Fig. 2 is an Arrhenius plot for

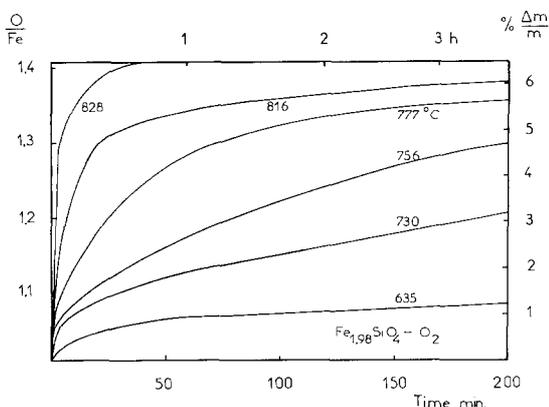


Figure 1 Kinetic isotherms of oxidation.

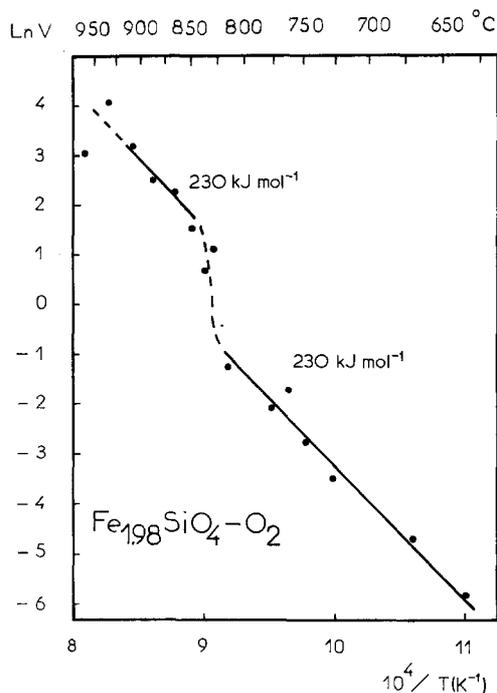


Figure 2 Arrhenius plot.

the temperature coefficient (average rate between 25% and 75% oxidation) which shows a change near 840°C. Table I summarizes the influences of nitrogen and water vapour on the oxidation rate at 777°C.

3.3. Analysis

X-ray diffraction studies show that the oxidized samples contained hematite and silica (quartz plus amorphous silica, and above 840°C quartz plus cristabolite) with minor traces of magnetite (0 to 1%). The amount of magnetite present was better measured by magnetic methods.

Fig. 3 shows the oxidation products as a function of temperature as observed with SEM. Photograph D in Fig. 3 seems to correspond to a maximum of whisker growth. Fig. 4 shows the evolution of the samples as a function of the degree of

TABLE I The influence of nitrogen and water vapour on the oxidation rate at 777°C

Gas composition			ln V
P _{O₂} (Torr)	P _{N₂} (Torr)	P _{H₂O} (Torr)	
765	0		-2.11
161	604		-2.09
760		5.2	-0.81
751		13.6	-0.72

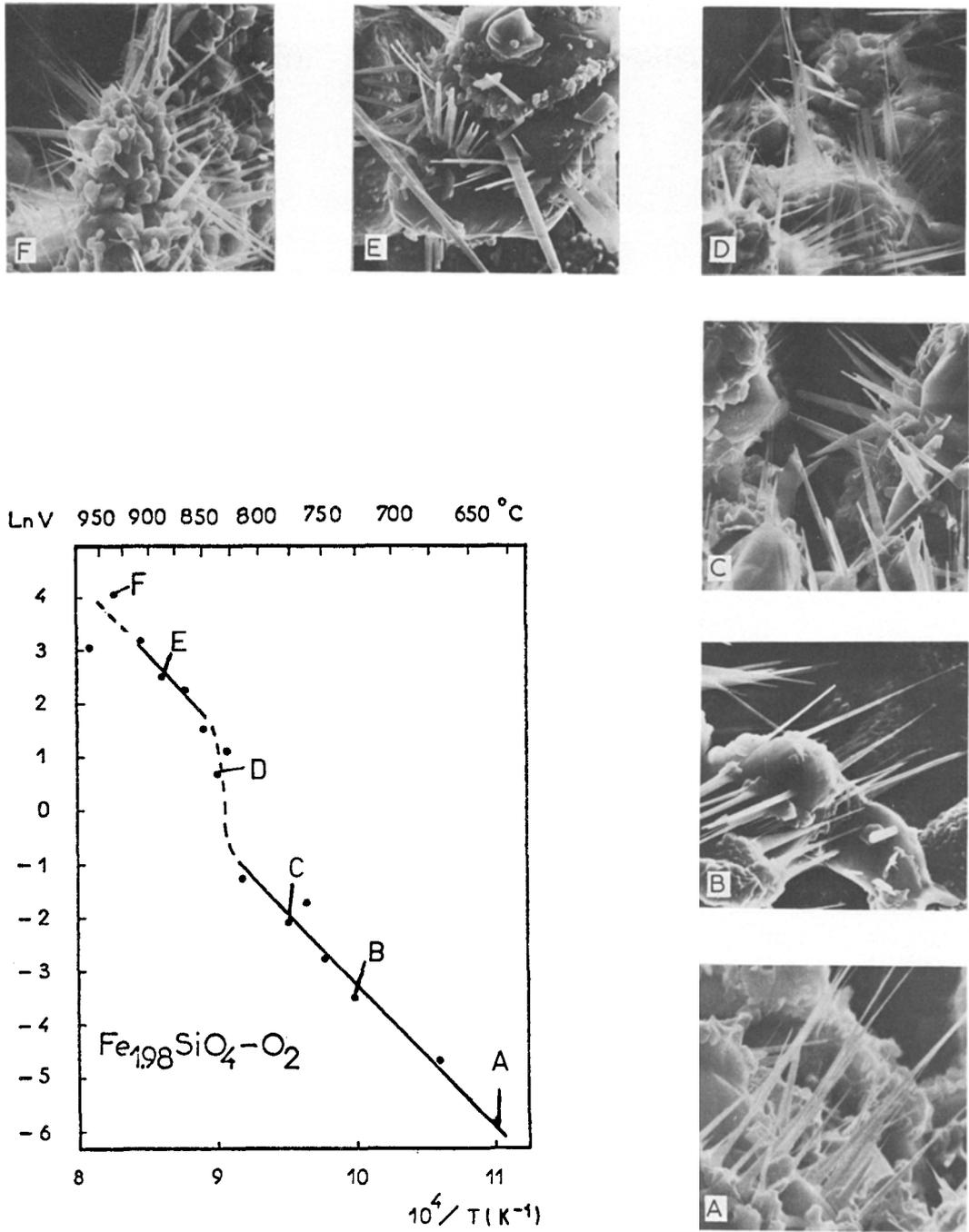


Figure 3 Morphological evolution of oxidation products as function of temperature ($\times 3200$).

oxidation. It is clear that the first stage corresponds to the formation of a granular layer which then breaks before whisker formation. There are no whiskers formed previously. As seen in photograph C, the whiskers begin to grow along lines. They then associate, leading to the formation of

plates (photographs D and I) which are sometimes hexagonal in shape (photographs J, K and L).

Microprobe analysis shows that the whiskers are made of iron oxide growing on a silica substrate. It is noticeable that water vapour favours the growth of whiskers as much as the oxidation.

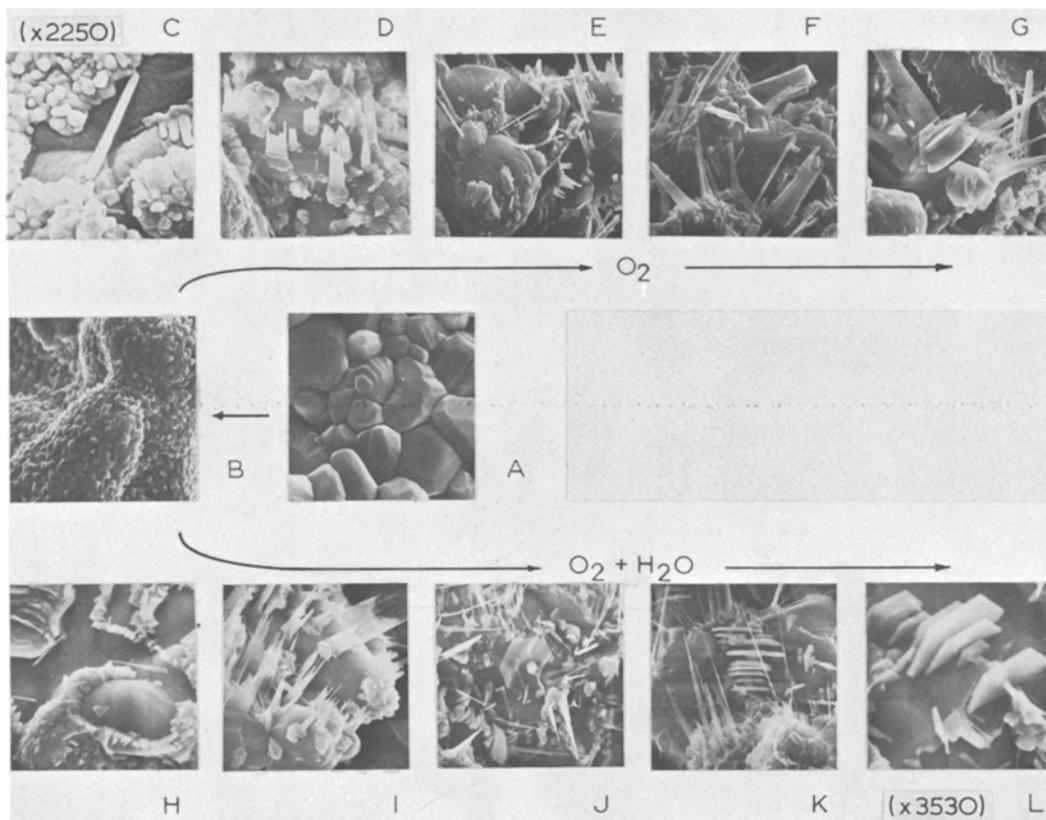


Figure 4 Formation of whiskers of Fe_2O_3 by oxidation of fayalite by O_2 or $\text{O}_2 + \text{H}_2\text{O}$ ($\times 2440$).

4. Discussion

4.1. Non-stoichiometry of fayalite

According to our results, this is not so wide as given in the literature. However, such a property is very sensitive to the possible presence of non-combined wüstite, as we found was the case in the work of Divanach [14] and Ory [15]. More work is needed on this problem, with *in situ* measurements such as Sockel's [16], but over a wider range of oxygen pressures.

4.2. Kinetics of oxidation

The shapes of the isotherms and the observations with SEM lead to the conclusion that the first oxidation stage is the formation of a compact polycrystalline layer. This includes nucleation and growth, both lateral and vertical, which are accelerated by increasing temperature, as seen in Fig. 1.

Once the surface is covered by the new formed phases, the oxidation should proceed via some solid state diffusion process. It is difficult to know

which is the diffusive species. The value of activation energy of 230 kJ mol^{-1} corresponds to the value given for oxygen diffusion through silica during silicium oxidation [17]. This could explain the promoter role of water vapour, as it is known that OH groups diffuse quite easily through silica [18]. Iron oxide can be ignored in this process for it is probably in the form of separate grains surrounded by silica. This explains why it is difficult to achieve complete oxidation even at 1000°C with pure oxygen.

Finally, it should be noticed that a discontinuity, such as the one observed at 840°C , is quite usual, and comes from the volume increase from quartz to cristobalite (+ 13%).

4.3. Whisker growth

In order to understand this phenomenon, two complementary sets of experiments were carried out:

(1) Wüstite and kirschsteinite (FeCaSiO_4) were oxidized under the same conditions as fayalite.

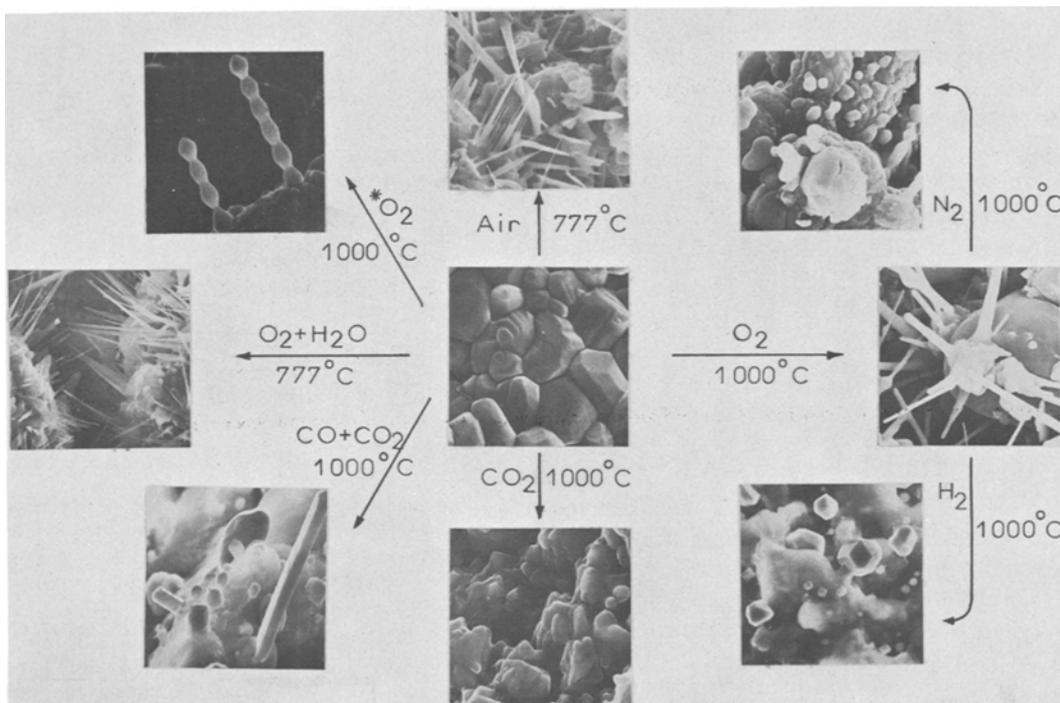


Figure 5 Results of physical and chemical treatments applied to the whiskers ($\times 2460$).
 *Low flow rate $\sim 81\text{h}^{-1}$.

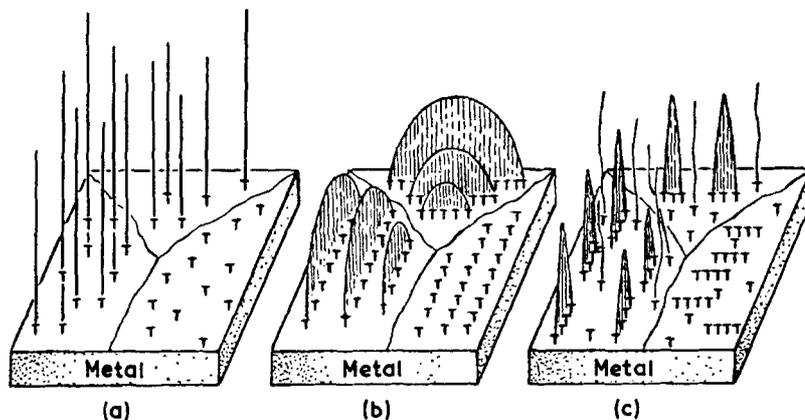
Neither produced whiskers, which points to the favourable action of free silica, for kirschsteinite oxidation supplies $\text{Fe}_2\text{O}_3 + \text{CaSiO}_3$.

(2) A series of physical and chemical treatments were applied to the whiskers, as shown in Fig. 5, which summarizes the morphological observations in fayalite oxidation. An interesting feature that can be emphasized is the presence of periodic grown whiskers, due either to starvation of oxygen during oxidation, or to evolution from classical whiskers under heat treatment in nitrogen. Such periodic whiskers of Si have been obtained by Givargizov

[19, 20] who interprets this as an oscillation between some parameters of the growth from the vapour phase ($\text{SiCl}_4 + \text{H}_2$) taking into account the superficial tension.

The question as to which is the mechanism of whisker growth cannot be answered with certainty. However, whatever mechanism operates, the following point can be stressed: the whiskers have a strong tendency to align themselves and then to condense, in some cases into plates, and often hexagonally shaped plates in the presence of H_2O . They condense along linear defects in the substrate

Figure 6 Gulbransen's observations on iron oxidation [21]. (a) Annealed pure iron, dry oxygen, 400°C ; (b) cold worked pure iron, dry oxygen, 400°C ; (c) annealed or cold worked pure iron, H_2O vapour, 400°C .



(lines of dislocations, grain boundaries. . .) which can act as favourable sites for whisker nucleation. This recalls Gulbransen and Copan's observations on iron oxidation [21] (see Fig. 6).

Finally, it is worth mentioning that oxidation of fayalite by CO₂ is extremely slow. At 1000° C only 3% is transformed after 10 days. This can be associated with a similar sluggishness of fayalite towards reduction with CO [7].

Acknowledgements

One of the authors (S. M. El Raghy) was financially supported by a French Government grant during his sabbatical leave from the Faculty of Engineering, Cairo University, Egypt. The authors thank M. A. Kohler for his efficient work in obtaining SEM micrographs, and Dr F. Jeannot for the preparation of different samples of fayalite.

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Received 5 July 1977 and accepted 17 January 1978.