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Diffusion mechanisms and reactions during reduction of oolitic iron-oxide mineral

S. NADIV* †, S. WEISSBERGER‡, I. J. LIN, Y. ZIMMELS
*Departments of Minerals Engineering and *Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel*

Diffusion mechanisms with moving reaction interfaces involved in the reduction process of oolitic iron oxide, containing small goethite particles in a kaolinite matrix, are presented. Reduction was effected by means of CO gas at 950° C, with the oolite already transformed by dehydroxylation into haematite particles and a metakaolinite matrix. The haematite particle under the $CO + O \rightarrow CO_2$ reaction taking place at its external surface develops concentric layers with unreacted haematite at the core enclosed by magnetite wustite and metallic iron, in that order. In the matrix between particles, "bridges" of a two-phase mixture of hercynite and fayalite develop by diffusion of iron ions and "reactive transport" of oxygen (by means of CO_2 molecules), thereby permitting coarsening of the metallic particles. Detailed models are presented for the diffusion mechanisms and reactions involved, and the thermodynamical picture is brought out.

1. Introduction

Direct reduction of oolite iron oxide mineral was studied. The oolite in question appears in the form of an oval particle (0.05 to 1.0 mm), containing fine particles (1 to 2 μm) of goethite ($Fe_2O_3 \cdot H_2O$) divided along concentric shells (in the large variants), or in a network pattern (in the small ones) within the matrix mineral which consists mainly of kaolinite (Al_2O_3 $2SiO_2 \cdot 2H_2O$), the relative amounts being 81% goethite, 12% kaolinite (Fig. 1).

After removal of clays, carbonates, etc. from the rest, the resulting oolite concentrate was pressed into 10 mm pellets, which were placed in an alumina crucible under a covering layer of anthracite powder, and slowly heated in an electric furnace to a preset temperature, at which it was kept for a predetermined residence time. It was then cooled (together with the furnace) to 150° C, and finally placed in a desiccator for final cooling.

Direct reduction was effected with carbon monoxide gas produced from the anthracite. In this process oxygen is removed from the iron oxide particles through the $CO + O \rightarrow CO_2$ reaction taking place at their external surface with the resulting growth of metallic iron particles. The latter become amenable to low-intensity magnetic separation after having increased in size by at least two orders of magnitude, and this fact determines the reduction temperature (25 μm average size at 1000° C).

The details of the process and the parameter interrelationship (temperature, particle size, processing time, type of reductant, etc.) are described elsewhere [1]. The same paper reports characterization data of the raw and reduced materials, and the reader interested in the pyrometallurgical aspects is referred to it.

The present paper, theoretical in nature, introduces a model based on observations and on fundamental theories whereby the overall process is controlled by mechanisms of diffusion with moving reaction interfaces. The emphasis is on insight into the thermodynamical principles underlying the process, in which the given heterogeneous solid-state open system is disturbed both thermally and chemically, and reacts nonreversibly so as to dissipate the external activation.

2. Dehydration and reduction processes

In the oolite particle, pores larger than 10 μm amounted to 5 to 33% as the size decreased from $-20 + 40$ mesh down to $-100 + 325$ mesh, respectively. The pores facilitate flow of the CO gas inside the oolite and this accelerates the reduction. Accordingly, the rate of metallization increases the smaller oolite particles. For a given heating residence time the amount of metallization as a function of temperature follows an S-shaped curve, with the steep intermediate section between 975 and 1075° C. Below 900° C only a few per cent metallization was observed, as against 90% above 1200° C. At 900° C the metal particles were one order of magnitude larger than those of the goethite, at 1100° C by two orders, and at 1200° C they coalesced into a continuous phase.

Upon heating, the goethite loses its crystal water by dehydroxylation and the formation of protohaematite at 250° C:

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O \qquad (1)$$

This takes place by the rupture of hydrogen bonds

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*Deceased November 1987.
‡*Present address*: IMI Research Institute, Haifa Bay, Israel.

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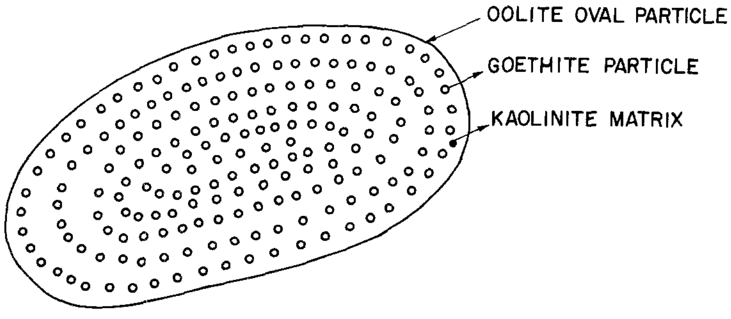

Figure 1 Oval particle of oolite : geothite particles in a matrix, with kaolinite as major constituent, plus minor minerals (schematic presentation).

between (FeO_6) octahedra layers (see Pauling [2] on the structure of the diaspore crystal) and proton delocalization preceding the dehydroxylation. The protohaematite, which initially consists of fine imperfect crystallites, recrystallizes (starting at 430° C, but mostly about 600° C) into haematite (α-Fe_2O_3) in the form of larger and perfect crystallites. Identification is possible by means of X-ray diffraction [3] or infrared absorption spectroscopy [4]. The dehydration may end with a product of about 10^{-2} $cm^3\,g^{-1}$ pore volume, comprising 0.6 to 1.0 nm micropores [5].

At 450° C the kaolinite is transformed by dehydroxylation into metakaolinite [6, 7]:

$$Al_2O_3 \cdot 2SiO_2 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \qquad (2)$$

This conversion takes place by the rupture of hydrogen bonds and proton delocalization between layers of SiO_4 tetrahedra and $AlO_2(OH)_4$ octahedra, followed by the delamination of layer packets (lamellae) and concluding with the opening of micropore channels. At 900° C this metakaolinite structure collapses into $2Al_2O_3 \cdot 3SiO_2$ spinel of γ-Al_2O_3 structure.

Within the newly formed haematite, the micropores are too narrow for easy migration of CO molecules inside the particles. Accordingly, as was in fact observed, the reduction has to follow the pattern typical for dense particulates – namely, formation of concentric layers (Fig. 2) of magnetite (Fe_3O_4), wustite (FeO) and metallic iron, around the shrinking core of haematite [8, 9]. As the reduction process advances it is assisted by diffusive migration of iron and oxygen atoms (the mechanism is described in detail in the next section). Once the external metallic layer has formed, arms rich in iron consisting of a two-phase mixture – hercynite ($FeAl_2O_4$) and fayalite (Fe_2SiO_4) – develop through dissolution of the metal in the adjoining metakaolin matrix, and eventually coalesce into continuous gangue material bridges between the particles. Formation of these bridges makes possible a ripening process, whereby the larger iron particles grow at the expense of the smaller ones as iron atoms diffuse into them from the latter, and at the same time the overall free surface energy of the particles decreases.

Above 1050° C some of the apatite $Ca_5(PO_4)_3F$ (also present in the oolite matrix material) decomposes, supplying calcium for a reaction with the hercynite and fayalite to form anorthite [1].

$$CaO + FeAl_2O_4 + 2Fe_2SiO_4 \rightarrow CaO \cdot Al_2O_3 \cdot 2SiO_2 + 5FeO \qquad (3)$$

In this reaction the bridges are destroyed, and the ripening process is arrested. At the same time pockets

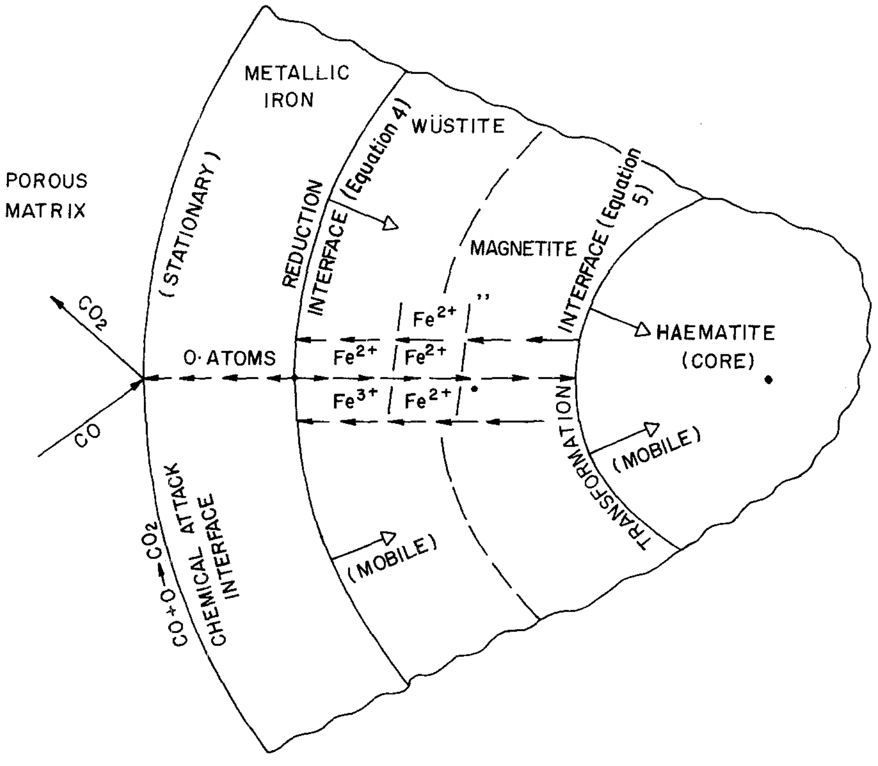

Figure 2 Reduction process mechanisms in haematite particle.

of phosphorus-rich molten iron are formed (since the solidus temperature of the iron–phosphorus system lies within the range in question), and the constitutional requirement of local equilibrium causes separation of solid iron, thus providing an alternative mechanism of metallization. This mechanism, however, falls outside the scope of the present paper, which is concerned with the situation prevailing at 950° C, with the reduction taking place by means of the CO gas only, and no molten phase being formed.

3. Reduction of iron oxide particles

As noted earlier, the reduction is effected by means of CO gas reacting with the oxygen supplied by the decomposing oxide. The bulk of the process takes place at the moving interface between the wustite and iron layers (Fig. 2), by the following reaction:

$$3\mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}| + \mathrm{O} \rightleftharpoons |\mathrm{Fe}^{2+}|'' + 2\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot} + \mathrm{FeO} \qquad (4)$$

where

$$\mathrm{FeO} \rightleftharpoons \mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}| + \mathrm{O}^{2-}|\mathrm{O}^{2-}|$$

The notation suggested by Schottky, and used by others [10], designates point defects here: $\mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}|$ is a divalent cation in the normal lattice position; $|\mathrm{Fe}^{2+}|''$ is an unoccupied divalent cation lattice position (cation vacancy); $\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot}$ is a trivalent cation in the lattice position of a divalent ion (positive hole). Divalent ion deficiency as represented by a vacancy is responsible for the excess of two negative charges at the lattice point, and must appropriately be balanced by two adjoining positive holes. Thus, migration of Fe^{2+} ions against $|\mathrm{Fe}^{2+}|''$ vacancies call for parallel interchange of charges between the divalent and trivalent iron ions, i.e. for migration of positive holes.

In Equation 4 an Fe^{2+} ion diffuses from the Fe/FeO interface into the wustite layer, against an $|\mathrm{Fe}^{2+}|''$ and two $\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot}$ positive holes. Annihilation of the vacancy at the Fe/FeO interface supplies in fact the two electrons needed to annihilate the two positive holes. The local stress situation is one of compression exerted by the denser rim of the iron layer on the wustite, in conjunction with the capillary forces at the curved interface, which assist the FeO decomposition. The O^{2-} anion is transformed into an oxygen atom capable of interstitial diffusion through the metallic iron rim lattice towards the outer surface, where the reaction with the CO molecule takes place. The released electrons neutralize an iron cation attached to the inner side of the iron layer, whereby the Fe/FeO interface moves towards the core direction.

The other important interface is the $\mathrm{Fe_2O_3/Fe_3O_4}$, which surrounds the residual haematite core of the reducing particle. Here, reduction of the α-$\mathrm{Fe_2O_3}$ takes place by means of the inward-diffusing Fe^{2+} ions, presumably through the reaction

$$\mathrm{Fe_2O_3} + \mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}| \rightleftharpoons |\mathrm{Fe}^{2+}|'' + 2\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot} + 3\mathrm{FeO}$$

$$\text{(component of magnetite)} \qquad (5)$$

where

$$\mathrm{Fe_2O_3} \rightleftharpoons 2\mathrm{Fe}^{3+}|\mathrm{Fe}^{3+}| + 3\mathrm{O}^{2-}|\mathrm{O}^{2-}|$$

At this interface the most important event is "opening" of the close-packed hexagonal (CPH) anionic sub lattice of α-$\mathrm{Fe_2O_3}$ into the cubic close-packed (CCP) one of spinel form, carrying an excess of cation vacancies. The reaction which takes place is

$$\mathrm{Fe_2O_3}\left.\begin{array}{l}\nearrow \text{transformed } \mathrm{Fe_2O_3}\\ \searrow \text{deficient FeO}\end{array}\right\}\begin{array}{l}\mathrm{Fe_2O_3\cdot FeO}\text{ spinel}\\ \text{(complex } \mathrm{Fe_3O_4}\\ \text{oxide)}\end{array} \qquad (6)$$

The complex oxide $\mathrm{Fe_3O_4}$ resulting from the solid-state reduction is imperfect compared with magnetite produced by chemical precipitation. Rearrangement of atoms is only possible through crystalline imperfections. The state of stress at the interface must be such that the new product on the outer side of the $\mathrm{Fe_2O_3/Fe_3O_4}$ interface would be under tension. It should be emphasized again that the reduction process proceeds exclusively by cation diffusion, with no anions taking part.

No sharp interface could be discerned between the $\mathrm{Fe_3O_4}$ and FeO layers as the latter oxide is non-stoichiometric; it derives from the transformed $\mathrm{Fe_2O_3}$ component of the complex $\mathrm{Fe_3O_4}$, and is deficient in iron to some extent. This transition likewise follows Equation 5. The unit-cell formula of the inverse spinel structure of magnetite is $(\mathrm{Fe}^{3+})_8[\mathrm{Fe}_8^{2+}\,\mathrm{Fe}_8^{3+}]\mathrm{O}_{32}$ where [ ] stands for octahedral, and ( ) for tetrahedral cationic sites. Its iron content is 42.86 at %, and the unit cell parameter 0.83 nm. Out of the 32 available octahedral sites only 16, and out of the 64 available tetrahedral sites only 8, are occupied. The unit cell can be divided into eight cubic octants [11] close-packed with oxygen anions and resembling an fcc system (Fig. 3). In all octants, six octahedral sites at edge midpoints (out of 12 available) are equally occupied by Fe^{2+}, Fe^{3+} ions. Apart from this common feature two types of octant can be distinguished: Type A has two tetrahedral sites occupied by Fe^{3+} ions, facing each other along the diagonal (three-fold rotation axis) on either side of the central octahedral site; it represents the transformed $\mathrm{Fe_2O_3}$ component of the magnetite (resembling a modification of γ-$\mathrm{Fe_2O_3}$ structure). In Type B only this octahedral site is occupied by a Fe^{2+} ion, while the two adjoining tetrahedral sites (as in Type A) are empty; it represents the deficient FeO component. The octants of these different types are packed together in the manner of a three-dimensional chequer-board.

To obtain FeO out of the $\mathrm{Fe_3O_4}$ [12] without upsetting the electrostatic charge balance, the Fe^{3+} ions should be replaced by 1.5 times as many Fe^{2+} ions occupying some of the vacant edge midpoint sites as well. Thus, the 16 Fe^{3+} ions of the $\mathrm{Fe_3O_4}$ unit cell must be replaced by 24 Fe^{2+} ions, thus bringing the latter to a total of 32, occupying exclusively octahedral sites in the NaCl-type crystallographic system. The resultant FeO will have an equivalent supercell parameter of 0.856 to 0.860 nm with a non-stoichiometric iron content of 47.7 to 48.8 at %, respectively.

4. Transformation of matrix phase

Once the reduced metallic layer has formed in the

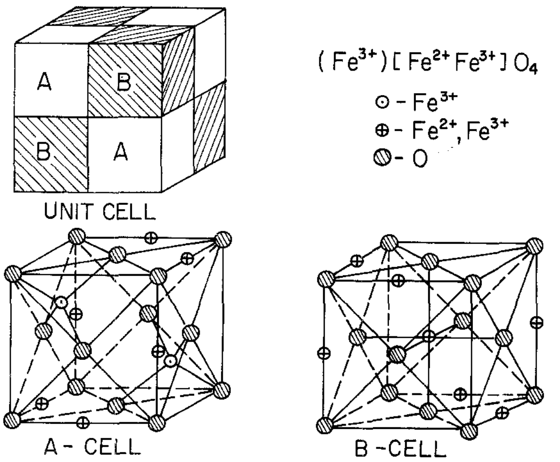

Figure 3 Unit cell of magnetite, resembling a three-dimensional chequer-board of different type octants [11], forming an inverse spinel structure.

particle, a reaction interface moves away from the outer surface and advances radially into the matrix. The matrix, which originally consisted mainly of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), had already been dehydrated, through detachment of bound water molecules at 450° C, into metakaolinite ($Al_2O_3 \cdot 2SiO_2$), which is in turn transformed at the moving reaction interface, with a constant supply of iron and oxygen, into a mixture of two compounds: hercynite ($FeAl_2O_4$) and fayalite (Fe_2SiO_4), following the reaction

$$\underset{\text{metakaolinite}}{Al_2O_3 \cdot 2SiO_2} + 5FeO \rightarrow \underset{\text{hercynite}}{FeAl_2O_4} + \underset{\text{fayalite}}{2Fe_2SiO_4} \tag{7}$$

with

$$\Delta G^0_{1100\,\mathrm{K}} = -290\,\mathrm{kcal\,mol^{-1}} \quad (-1214\,\mathrm{kJ\,mol^{-1}})$$

Being an interface reaction, it takes place by the redistribution of aluminium and silicon ions through interfacial diffusion at the moving interface. The process as a whole is one of reoxidation, with both species supplied in parallel with the major reduction process: the oxygen atoms diffusing throughout the external metallic layer (induced by the $CO + O \rightarrow CO_2$ reaction), and Fe^{2+} ions dissolved from the same layer into the adjoining already-transformed matrix (Fig. 4). As atoms of both types arrive at the reaction interface (as is described below), a chain of reactions takes place sequentially [6, 7] instead of the one represented by Equation 7, probably as follows

$$\begin{aligned}
&\text{(a)}\quad \underset{\text{metakaolinite}}{2(Al_2O_3 \cdot 2SiO_2)} \\
&\qquad \rightarrow \underset{\text{spinel-type phase}}{2Al_2O_3 \cdot 3SiO_2} + \underset{\text{amorphous}}{SiO_2} \\
&\text{(b)}\quad \underset{\text{spinel-type phase}}{2Al_2O_3 \cdot 3SiO_2} + 2FeO \\
&\qquad \rightarrow \underset{\text{cyanite}}{2(Al_2O_3 \cdot SiO_2)} + \underset{\text{fayalite}}{2FeO \cdot SiO_2} \\
&\text{(c)}\quad \underset{\text{cyanite}}{Al_2O_3 \cdot SiO_2} + 3FeO \\
&\qquad \rightarrow \underset{\text{fayalite}}{2FeO \cdot SiO_2} + \underset{\text{hercynite}}{FeO \cdot Al_2O_3}
\end{aligned} \tag{8}$$

The spinel-type phase is believed to be some form of γ-alumina [6]. Structurally, its unit-cell formula is $(Si_8)[Al_{10\frac{2}{3}}]O_{32}$. It is metastable to the extent that with FeO as mineralization agent it decomposes and transforms. All forms in the chain reactions are close-packed anion sublattices. The cyanite is an aluminium orthosilicate (Al_2SiO_5), a CCP structure with all aluminium atoms in the octahedral sites; above 800° C it decomposes into a mixture of hercynite ($FeAl_2O_4$) and fayalite (Fe_2SiO_4), the first having a normal (CCP) spinel structure with iron atoms in tetrahedral and aluminium in octahedral sites, and the second resembling olivine (CPH) in structure with silicon atoms in tetrahedral and iron in octahedral sites. It is reasonable to assume that the chain of reactions takes place by reshuffling of the anionic sublattice to permit proper accommodation of the newly arrived oxygen and incorporation of the newly arrived Fe^{2+}, in parallel with local redistribution of silicon and aluminium. The diffusion of the latter is not necessarily coupled,

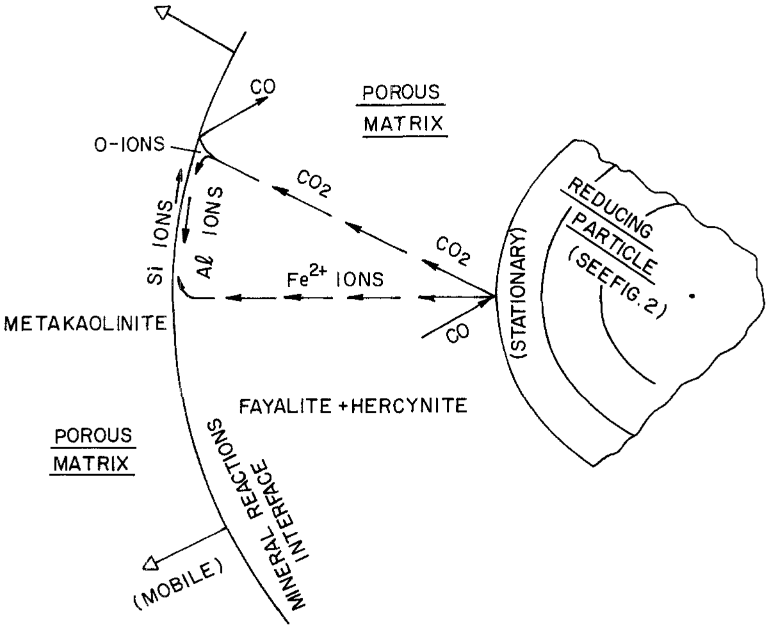

Figure 4 Mineral reactions in the inter-particle matrix material.

and since the formation reaction of the hercynite and fayalite are of topotactic nature [1] (since the cation lattice positions in the reacting and product phases are conserved, namely: aluminium in octahedral sites of hercynite as in alumina, and silicon in tetrahedral sites of fayalite as in silica), the compounds can be formed simultaneously without mutual interference.

The Fe^{2+} ions arrive by diffusion through both phases of the transformed matrix, moving mostly via vacant tetrahedral cationic sites. The oxygen ions arrive by "reactive transport" via CO_2 gas molecules formed by the reduction process at the particle interfaces and flowing through the porous matrix (Fig. 4). The molecular decomposition of CO_2 into CO and oxygen supplies the oxygen needed at the reaction interface. Thus the carbon serves as a carrier for the oxygen.

Carbon monoxide and dioxide molecules have resonating bond structures [13]: in the CO molecule the most probable (50%) mode out of the four possibilities is $^{(-)}{:}\mathrm{C}{\equiv}\mathrm{O}{:}^{(+)}$ (in contrast to the purely covalent mode such as $:\mathrm{C}{=}\ddot{\mathrm{O}}{:}$). The direction of the molecular dipole moment corresponds to a positive charge on the oxygen atom, accounting for 16% of the partial ionic bonding. In carbon dioxide, all four modes are of equal probability such as $^{(-)}{:}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{-}\mathrm{C}{\equiv}\mathrm{O}{:}^{(+)}$ (in contrast to the purely covalent mode such as $:\ddot{\mathrm{O}}{=}\mathrm{C}{=}\underset{\cdot\cdot}{\mathrm{O}}{:}$), which makes for easy retransformation into a CO molecule by donation of an O^- ion. The CO molecule is somewhat more stable than CO_2, with resonance energy (relative to ketonic double-bonded type) 83 kcal mol^{-1} (348 kJ mol^{-1}) as against 33 kcal mol^{-1} (138 kJ mol^{-1}) for the latter.

At the chemical-attack interface (Fig. 2) take place the transformations $Fe \rightarrow Fe^{2+} + 2e$ (with the two free electrons serving for formation of CO_2 molecules of partially ionic character) and $Fe^{2+} \rightarrow |Fe|'' + 2Fe^{3+}|Fe^{2+}|^{\cdot}$ (as a basis for the diffusion mechanism in the transformed matrix phases). The Fe^{2+} ions arriving at the interface of mineral reactions (Fig. 4) meet there $2O^-$ ions provided by reactive transport, and there ensues the chain of reactions described above. Although the exact kinetics of the overall process in the matrix are not yet well established, it is likely that mass drift towards the particles, as well as the closing of pores, compensate for the volumetric changes accompanying the reactions.

5. Coarsening process

As the reaction interfaces, moving away from the reducing particles, impinge on one another within the matrix, and the bridges of gangue material referred to earlier form between the particles, diffusion of Fe^{2+} ions from the smaller into the larger particles sets in as a necessary step in the coarsening process (Fig. 5). At this stage reduction of the particles proper is still far from complete and from now on both processes take place simultaneously.

The coarsening process (known also as "Ostwald ripening") can be described as follows [14]: when dispersed particles are soluble in the containing matrix, smaller particles tend to dissolve and subsequently precipitate on larger ones. The driving force derives from the attendant decrease in the overall interfacial energy. This effect is often observed in metal alloys, but rarely in minerals. The concentration of solute in the matrix adjoining a particle is inversely related to the radius of the latter (as in the well-known Gibbs – Thomson equation): the smaller the particle the higher this concentration. In these circumstances a downward gradient of Fe^{2+} ion concentration develops between the smaller and larger particles, along which the iron ions diffuse.

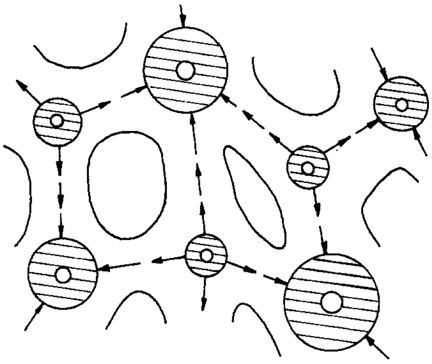

Figure 5 Probable diffusion directions of Fe^{2+} ions along gangue material bridges during the coarsening process of the particles (schematic presentation).

6. Conclusions

1. When a thermodynamical heterogeneous solid-state open system is disturbed through thermal (isothermal heating) and chemical (a reducing gas in the present case) activation, it drives for a situation of minimum build-up of free energy. In our system, the increase in free energy of the haematite particles by their reduction into metallic iron is counteracted by transformation of the matrix phase and the subsequent ripening process, which lower the overall free energy of the system as far as possible.

2. The mechanism by which the different processes take place in both the particles and the matrix is diffusion of divalent iron ions. Simultaneously, some oxygen is transferred by interstitial atomic diffusion in the newly formed metallic phase, and by reactive transport (with the oxidized CO_2 gas as carrier) through the porous matrix.

3. In kinetical terms, the problem becomes one of diffusion with moving reaction interfaces. The main reduction interface lies below the outer interface of the particles, at which wustite decomposes and liberates both divalent iron ions and oxygen atoms. The chemical attack interface, at which the intruder CO gas is oxidized to CO_2, coincides with the outer surface, and remains stationary throughout. Apart from these, there are two important moving interfaces. The first is located within the core of the particle, where the haematite, on arrival of diffusing Fe^{2+} ions, opens its CPH anionic sublattice by transforming into a CCP one of magnetite, producing both cation vacancies and positive holes. The second, located within the matrix, is an interface of mineral reactions, whereby local interfacial diffusion of aluminium and silicon ions, enriched by bulk diffusion of Fe^{2+} ions, and oxygen brought by reactive transport with CO_2 gas as

a carrier, leads to the metakaolinite matrix transforming into iron-bearing mineral phases.

4. When the interfaces of mineral reaction, in their motion away from the initial particles, impinge on one another, bridges of gangue-material phases form across which the Fe^{2+} ions move and permit coarsening of the particles, thereby lowering the overall interfacial energy of the system.

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References

1. S. WEISSBERGER, Y. ZIMMELS and I. J. LIN, *Met. Trans. B* **17B** (1986) 433.
2. L. PAULING, "The Nature of the Chemical Bond", 3rd Edn (Cornell University Press, Ithaca, 1960) p. 483.
3. H. P. ROOKSBY, "The X-ray Identification and Crystal Structure of Clay Minerals" (Mineralogical Society, London, 1961) p. 354.
4. S. YARIV and E. MENDELOVICI, *Appl. Spectrosc.* **33** (1979) 410.
5. M. L. GARCIA-GONZALEZ, P. GRANGE and B. DELMON, "Reactivity of Solids" (Plenum, New York, 1977) 755.
6. G. W. BRINDLEY, "Kinetics of High-Temperature Processes", edited by W. D. Kingery (Wiley, MIT, Oxford, 1959) p. 220.
7. S. SOLACOLU, "Physical Chemistry of Technical Silicates", (Publishing House, Bucarest, 1968), pp. 53, 385–386.
8. L. Von BOGDANDY and H. J. ENGEL, "The Reduction of Iron Ores" (Stahleisen, Dusseldorf, 1971) p. 164.
9. H. SCHMALZRIED, "Solid-State Reactions" (Academic, New York, 1974) pp. 195–203.
10. L. Von BOGDANDY and H. J. ENGEL, "The Reduction of Iron Ores' (Strahleisen, Dusseldorf, 1971) p. 90.
11. A. J. M. KUIPERS, PhD thesis, Eindhoven (1978) p. 95 (as quoted by G. Galeczki, DSc thesis, Technion Haifa (1979) p. 3).
12. A. F. WELLS, "Structural Inorganic Chemistry" (Clarendon, Oxford, 1962) pp. 490–492.
13. L. PAULING, "The Nature of the Chemical Bond", 3rd Edn (Cornell University Press, Ithaca, 1960) pp. 265–269.
14. G. W. GREENWOOD, "The Mechanism of Phase-Transformations in Crystalline Solids" (Institute of Metals, London, 1969) pp. 103–110.

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