Influence of SiO$_2$ and/or MnO$_2$ on the Reduction Behaviour and Structure Changes of Fe$_2$O$_3$ Compacts with CO Gas

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(Received on May 13, 2008; accepted on July 3, 2008)

Pure Fe$_2$O$_3$ and Fe$_2$O$_3$ doped with either 2.5–7.5 mass% SiO$_2$, 6.0 mass% MnO$_2$ and (6.0%MnO$_2$/H$_2$O$_2$)$1.75%$SiO$_2$) compacts annealed at 1 473 K for 6 h were prepared. The different phases were identified by X-ray diffraction (XRD) and their structures were examined by optical and scanning electron microscopes. The magnetic properties were measured with Vibrating Sample Magnetometer (VSM). Total porosity and pore size distribution were determined and their external volume was also measured. Unlike in SiO$_2$ doped samples where no new phases were detected, manganese ferrite (MnFe$_2$O$_4$) was identified in MnO$_2$-containing samples. Annealed compacts were isothermally reduced with CO at 1 073–1 373 K and the O$_2$-weight loss was continuously recorded. It was found that the reduction rate of SiO$_2$–Fe$_2$O$_3$ samples increases at the early stages with SiO$_2$ mass% due to the increase in their original porosity. At final stages, the rate was retarded due to the formation of hardly reducible fayalite (Fe$_2$SiO$_4$). In MnO$_2$-containing samples, the reduction rate was retarded at initial stages due to the presence of manganese ferrite. At later stages, the formation of fayalite–manganoan [(Fe, Mn)$_2$SiO$_4$] greatly hindered the reduction process. A catastrophic swelling ($\Delta V = 405\%$) was recorded in 6%MnO$_2$–Fe$_2$O$_3$ compacts and was greatly diminished to 55.95% in presence of 7.5% SiO$_2$ due to the decrease in size and number of metallic iron whiskers and plates. The reduction mechanism of pure and doped samples was predicted from the correlations between reduction kinetics and the microscopic examinations of partially and completely reduced samples.

KEY WORDS: iron oxides; silica; manganese oxides; reduction; fayalite; manganese–ferrite; fayalite–manganoan; swelling; reduction mechanism.

1. Introduction

Most of iron ores charged into blast furnace contain impurities such as SiO$_2$, Al$_2$O$_3$, CaO, MgO, MnO$_2$, etc. Consequently, it is practically important to clarify the effects of these impurities on the reduction behaviour of iron oxides and the accompanied structural changes which have a major influence on the process productivity. In previous work, El-Geassy et al. studied the effect of SiO$_2$ on the reducibility of ferric oxide by H$_2$, CO and CO–H$_2$ mixtures. They found that the formation of fayalite (2FeO·SiO$_2$) at later stages in presence of noncrystalline silica results in a deceleration in the reduction rate compared with crystalline form of silica. Mc-Geoge et al. found that the presence of silica increases the reducibility of ferric oxide. Baldwin found that the formation of fayalite can occur during the reduction of iron ores if the reduction temperature is higher than 1 073 K or during sintering when ferrous oxide and silica are present in absence of lime (CaO). Inami and Suzuki studied the effect of SiO$_2$ and Al$_2$O$_3$ on the lattice parameter of CaO–SiO$_2$–FeO. They observed that it decreases with the decrease of mass ratio CaO/SiO$_2$ and the amount of dissolved CaO content seems to decrease due to the formation of compounds such as CaO·FeO·SiO$_2$ and 2CaO·SiO$_2$. El-Geassy studied the influence of SiO$_2$ on the gaseous reduction of wüstite micropellets with H$_2$, CO and H$_2$–CO mixtures at 1 173–1 373 K, he observed that the highest rate at the initial stages was obtained in H$_2$ and the slowest was in CO, while with mixtures of gases the rate did not vary with the gas composition and the presence of SiO$_2$ enhanced the reduction in CO and retarded the reduction in H$_2$. Atui et al. studied joint reduction of the oxides Fe$_2$O$_3$, MnO$_2$, and NiO with carbon in an inert atmosphere. They found that the freshly reduced metallic phases accelerate oxide reduction while the solid-phase oxide interaction can retard oxide mixtures metallization. El-Geassy et al. studied the behaviour of manganese oxides during magnetizing reduction of Baharia iron ore. They found that during reduction with 20%CO–80%CO$_2$ at 873–1 073 K, magnetite was the only phase formed while at 1 173–1 273 K wüstite was partially formed with magnetite and at all reduction conditions and MnO$_2$ was reduced to MnO. It was found that impurities and associated gangue minerals play an important role on the reduction of iron oxides by its affect the swelling of pellets. Suzuki et al. studied the expansion and contraction during hydrogen reduction of...
green and pre-heated hematite compacts containing 5% of either SiO2 or Al2O3. They showed that the thermal expansion of a green compact increases when hematite particles in a matrix are uniformly reduced to magnetite while shows only slight increase in expansion when the whole compacts is reduced and become porous. Sharma et al.12) studied the effect of gangue content on the swelling of iron ore pellets during reduction with CO at 1 273 K. They reported that swelling of iron ore pellets is due to growth of iron whiskers which in turn is restricted due to the presence of gangue. In another investigation13) they found that, additives like CaO, MgO and SiO2 play important role in decreasing the maximum swelling index of the pellets.

In spite of the several studies carried out to investigate the influence of single additives on the reduction behaviour of iron oxide, little attention was paid to the effect of more than one kind of gangue oxide.14–17) In previous work,18) they showed that hematite grains formed a relatively dense structure with more or less homogeneity distributed microstructures while EDX was used for elemental and chemical mapping of constituents in the grains. The magnetic properties were measured by the vibrating sample magnetometer (VSM, 9600). High pressure mercury pore size analyzer was used for measuring total porosity, apparent and bulk densities and the pore size distribution. The external volume of the compacts was measured by the displacement method.

Fired compacts were isothermally reduced with CO gas at 1 073–1 373 K and the O2 weight loss resulting from the reduction was continuously recorded as a function of time. The gas purification and reduction systems were described elsewhere.19) A constant CO flow rate of 1.0 l/min at STP (760 mmHg, 293 K) used in all reduction tests is sufficient to overcome the gas boundary layer effect.

3. Results and Discussion

3.1. Characterization of Pure and Doped Compacts

The physical characteristics as well as the different phases formed in the annealed compacts are given in Table 1. It can be seen that, unlike in SiO2–Fe2O3 compacts where no new phases were identified, manganese ferrite (MnFe2O4) was formed in MnO2 containing samples. The total porosity greatly increased with the increase in SiO2 content resulting in 16.57% in 7.5%SiO2–Fe2O3 samples compared with 3.05% in pure Fe2O3 which indicates that the presence of SiO2 counteracts sintering of iron oxide grains. The internal structures of pure Fe2O3, 6%MnO2–Fe2O3, 2.5–7.5%SiO2–Fe2O3 and (6%MnO2+7.5%SiO2)–Fe2O3 annealed compacts are shown in Figs. 1(a)–1(d) respectively. Figure 1(a) showed that hematite grains formed a relatively dense structure with more or less homogeneity distributed micro-pores. Figure 1(b), illustrates that hematite grains tended to be denser with the development of large pores not homogeneously distributed across the sample in which manganese ferrite phase can be distinguished as grey patches in the vicinity of the large pores. Manganese ferrite (MnFe2O4) is resulted from solid-state reaction between Fe2O3 and MnO which was resulted from the thermal dissociation of MnO2.20) Figure 1(c), showed the presence large pores and silica (gray patches) is distributed in Fe2O3 matrix. In (MnO2+SiO2)–Fe2O3 samples (Fig. 1(d)), manganese ferrite formed become less coarser than that observed in MnO2–Fe2O3 sample (Fig. 1(b)). Moreover it can be seen that SiO2 has a destructive effect on the formation of manganese ferrite which became more collapsed and accompanied by the formation of smaller pores compared to that of MnO2–Fe2O3 sample. The SEM photomicrographs of pure

<table>
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<th>compact composition</th>
<th>compact volume (mm³)</th>
<th>apparent density, (g/cc)</th>
<th>total porosity (%)</th>
<th>X-ray phase identification</th>
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<td>5.08</td>
<td>3.05</td>
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<td>2 97.5 2.5 0.0</td>
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<td>4.62</td>
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<tr>
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<td>6.65</td>
<td>4.35</td>
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<tr>
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<td>16.57</td>
<td>α-Fe2O3 + SiO2</td>
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<tr>
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<td>6.14</td>
<td>3.81</td>
<td>20.75</td>
<td>α-Fe2O3 + MnFe2O4 + SiO2</td>
</tr>
<tr>
<td>6 94.0 0.0 6.0</td>
<td>7.12</td>
<td>4.62</td>
<td>6.5</td>
<td>α-Fe2O3 + MnFe2O4</td>
</tr>
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</table>

Table 1. Characteristic and phases formed in compacts annealed at 1 473 K for 6 h.

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Fe₂O₃, MnO₂–Fe₂O₃, SiO₂–Fe₂O₃ and (SiO₂/MnO₂)–Fe₂O₃ samples are shown in Figs. 2(a)–2(d) respectively which showed different grain structures. In Fig. 2(a), hematite grains have a shape of roundish to flat smooth pebble with an average size range of 3–10 μm coalesced to each other to form dense structure. Figure 2(b) shows that the matrix structure of hematite grain size increased due to the presence of MnO₂. The structure given in Fig. 2(c) showed that hematite grains take a deformity globular and the coalition between grains decreased. In (MnO₂/SiO₂)–Fe₂O₃ compacts, hematite grains are relatively smaller than that in 7.5%SiO₂–Fe₂O₃.

The magnetic properties of pure and doped compacts were measured and given in Fig. 3. It showed that magnetization increased in the order Fe₂O₃<(SiO₂/MnO₂)–Fe₂O₃<MnO₂–Fe₂O₃ and the presence of SiO₂ decreases the saturation magnetism of MnO₂–Fe₂O₃ samples. This is resulted from the decrease in the amount of manganese ferrite which is considered as a weak magnetic material. In SiO₂ containing samples, the magnetization decreased due to the effect of SiO₂ which considered as magnetically dead particle distributed in the MnO₂-doped Fe₂O₃ matrix.

3.2. Reduction Behavior of Pure and Doped Compacts

The isothermal reduction curves of pure Fe₂O₃ and 2.5–7.5mass%SiO₂–Fe₂O₃ compacts obtained at 1 073, 1 173, 1 273 and 1 373 K are shown in Figs. 4(a)–4(d) respectively. At initial and intermediate stages, the reduction rate increased with SiO₂ mass% due to the increase in their original porosity (Table 1) which facilitates gas diffusion to and from the iron oxide grains. After certain extent of reduction, the presence of SiO₂ retarded the reduction of Fe₂O₃ due to the presence of hardly reducible fayalite phase (Fe₂SiO₄). This retardation is influenced by SiO₂ mass% and the reduction temperature. The higher the SiO₂ content, the larger amount of fayalite developed and consequently the higher the slowing down in the rate was detected. At ≤1 273 K, the reduction of SiO₂-containing compacts was not completed and stopped at different extents depending on the SiO₂ mass%. In order to clarify the influence of SiO₂ on the reduction behaviour of iron oxide more clearly, the rate of reduction (dr/dt) at initial and final stages was plotted against the corresponding temperature as shown in Fig. 5. For a given compact composition, the rate of reduction increased with temperature. At a given temperature, the value of (dr/dt) increased with the increase in SiO₂ mass% at the initial stages, while it decreased at later stages.

On the other hand, the isothermal reduction curves of Fe₂O₃, MnO₂–Fe₂O₃, SiO₂–Fe₂O₃ and (SiO₂/MnO₂)–Fe₂O₃ compacts with CO at 1 073–1 373 K were given and discussed elsewhere. It can be observed that the reduction of pure and doped compacts was greatly influenced by both of temperature, doping species and reduction extents as follows; 1) at ≤1 173 K, the reduction rate at early stages decreased in the order SiO₂–Fe₂O₃<Fe₂O₃<(SiO₂/MnO₂)–Fe₂O₃<MnO₂–Fe₂O₃ due to both of porosity and the MnFe₂O₄ effects. At final stages, the rate is changed to the order Fe₂O₃>MnO₂–Fe₂O₃>SiO₂–
Fe₂O₃/(SiO₂/H₂O)/(MnO₂)–Fe₂O₃ due to the formation of both of hardly reducible fayalite (2Fe₂O₃·SiO₂) and/or fayalite–manganoan [(Fe, Mn)₂SiO₄] phases as were identified by XRD.

2) At 1273 K, the rate at their early stages is in the order SiO₂–Fe₂O₃ > MnO₂–Fe₂O₃ > Fe₂O₃ > (SiO₂ + MnO₂)–Fe₂O₃. At final stages, the rates were changed to MnO₂–Fe₂O₃ > Fe₂O₃ > SiO₂–Fe₂O₃ > (SiO₂ + MnO₂)–Fe₂O₃ due to the presence of fayalite and fayalite–manganoan phases at such reduction conditions.

3.3. Reduction Kinetics and Mechanism

The rate controlling mechanism in the reduction of pure and doped compacts at both the initial and final stages was predicted from the correlation between both of:

a) apparent activation energy values computed from Arrhenius equation,\(^\text{15}\) b) application of the different formulations derived from

Fig. 4. Typical reduction curves of pure Fe₂O₃ and Fe₂O₃ doped with 2.5–7.5 mass% SiO₂ compacts at (a) 1073 K, (b) 1173 K, (c) 1273 K, (d) 1373 K.

Fig. 5. Effect of temperature on the reduction rate of pure Fe₂O₃ and Fe₂O₃ doped with 2.5–7.5 mass% SiO₂ at (a) initial stages, (b) final stages.
gas–solid reaction model\textsuperscript{21, 22}) and c) microscopic examinations of partially and completely reduced samples.

The values of the apparent activation energy (Ea) obtained from Arrhenius plots where the rate of reduction (\(\log dr/dt\)) was plotted against the reduction temperature (1/TK) for pure and doped compacts at initial (5\%) and final (80\%) reduction stages. The computed (Ea) values obtained are given in Table 2. At initial reduction stages these values reveal that, the reduction of compacts is controlled by the combined effect of gaseous diffusion and interfacial chemical reaction processes. At final stages, a combined effect of interfacial chemical reaction and solid-state diffusion mechanism seems to be the rate determining step. The contribution of solid-state diffusion in the mechanism increases with the increase in SiO\textsubscript{2} mass\% due to formation of hardly reducible fayalite with CO and solid state diffusion play a major part in the reduction of this phase which is also temperature dependant.

The gas diffusion, interfacial chemical reaction and mixed reaction formulations derived from gas–solid reaction model\textsuperscript{21–23}) were also tested against the experimental results obtained at 1 073–1 373 K. As a result of these applications, it was found that a set of straight lines was only obtained on applying the mixed control reaction formulation as shown in Figs. 7(a)–7(d) in which the reduction time (\(t\)) was plotted against \([1−(1−x)^{0.5}+x+(1−x)\ln(1−x)]]; (x is the fractional reduction at given time). This indicates that a combined effect of gaseous diffusion and interfacial chemical reaction is the rate determining step at early stages up to certain reduction extents which is temperature dependant. At later stages, the interfacial chemical reaction formulation resulted straight lines as shown in Figs. 8(a)–8(d), in which \((t)\) was plotted against \([1−(1−x)^{0.5}]\). The deviation from straight lines at the later stages indicated that solid-state diffusion is contributed in the reduction process and its effect decreased with rise in temperature.

The RLM photomicrographs of SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3} and (SiO\textsubscript{2}/MnO\textsubscript{2})–Fe\textsubscript{2}O\textsubscript{3} compacts reduced up and to 20\% and 80\%
extents at 1173 K are shown in Figs. 9 and 10(a)–10(d) respectively. Figure 9(a) illustrates the presence of three distinctive layers (outer, middle, and inner layers). These layers indicate that, the reduction proceed in topochemical reaction mode. At the surface of compact, the resistance to CO diffusion was very slow and therefore the chemical reaction had major effect as a controlling step. Figure 9(b) shows the structure of the interface zone between the outer and middle layers in which some metallic iron grains together with lower oxides (magnetite and wüstite) were observed. As the reduction proceeds and the gas penetrated inside the compact, the resistance to gas diffusion is also increases. Therefore, the reduction is controlled by combined effects of chemical and gaseous diffusion processes. The microstructure 80% reduced samples given in Fig. 9(c) shows that the outer layer consists of dense metallic iron grains distributed in porous matrix of relatively large macropores. The inner layer given in Fig. 9(d) showed the fayalite was entrapped inside dense metallic iron grains. The presence of these relics pointed out to that solid-state diffusion has considerable effect in the reduction process at the final stages. The RLM photomicrograph of 20% reduced (SiO₂-Fe₂O₃)–Fe₂O₃ compact given in Fig. 10(a) illustrates the presence of three layers (outer, middle and inner). The outer layer consists of metallic iron while lower oxides are concentrated in the middle layer and unreduced hematite is in the core. This indicating that the reduction is proceeds in a topochemical mode of reaction. Figure 10(b) illustrates the diffused interface between the outer and middle layer in which some metallic iron grains diffused into the middle layer and this implies that the gaseous diffusion played a considerable effect in the reduction process. The microstructure of 80% reduced compacts (Fig. 10(c)) shows that fayalite and wustite are was entrapped inside the metallic iron grains. Figure 10(d) shows that metallic iron was nucleated at outer surface of fayalite (Fe₂SiO₄) and/or fayalite–manganon (Fe, Mn)₂SiO₄ grains resulting entrapped relics. The thickness of iron layer increases with reduction time. The presence of these relics hindered the gas diffusion and the reduction could be preceding by solid-state diffusion of anion and cations at their final reduction stages.¹⁵

3.4. Volume Changes of Compacts during Reduction Process

The volume change (ΔV) of pure and doped compacts
was calculated from the relationship\textsuperscript{18}:

\[ \Delta V\% = [(V_f - V_i)/V_i] \times 100 \] .................(2)

where, \( V_f \) and \( V_i \) are the volume of reduced and unreduced compacts respectively.

The effect of reduction temperature on the \((\Delta V)\) values of

Fig. 8. Testing of experimental data against the mixed control mathematical formulation at the final stages for (a) pure Fe\textsubscript{2}O\textsubscript{3}, (b) 2.5\%SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}, (c) 5\%SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}, (d) 7.5\%SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}.

Fig. 9. Microstructure of 7.5\% SiO\textsubscript{2}-doped Fe\textsubscript{2}O\textsubscript{3} compacts partially reduced at 1173 K at (a) 20\% reduction extent, (b) 20\% reduction extent, (c) 80\% reduction extent, (d) 80\% reduction extent.

Fig. 10. Microstructure of (7.5\%SiO\textsubscript{2}+6\%MnO\textsubscript{2})–Fe\textsubscript{2}O\textsubscript{3} compacts reduced at 1173 K at (a) 20\% reduction extent, (b) 20\% reduction extent, (c) 80\% reduction extent, (d) 80\% reduction extent.
pure Fe$_2$O$_3$, SiO$_2$–Fe$_2$O$_3$, (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$ and MnO$_2$–Fe$_2$O$_3$ compacts reduced at 1 073–1 373 K are given in Fig. 11. It shows that while the presence of SiO$_2$ greatly hindered the swelling of Fe$_2$O$_3$ compacts, the presence of MnO$_2$ enhances the swelling effect. The catastrophic swelling that was detected in pure Fe$_2$O$_3$ compacts at 1 198 K ($\Delta V' = 255\%$) was greatly inhibited in presence of 7.5 mass% SiO$_2$ to $< 60\%$. On the other hand, the presence of 6 mass% MnO$_2$ in Fe$_2$O$_3$ compacts enhancing the swelling of compacts and reached to $\Delta V' = 405\%$ at 1 248 K. The effect of reduction temperature on the volume change of SiO$_2$–Fe$_2$O$_3$ and MnO$_2$–Fe$_2$O$_3$ compacts showed that it sharply decreased with further rise in temperature. In (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$ compacts, the compacts behave more or less like SiO$_2$–Fe$_2$O$_3$ indicating that SiO$_2$ has a great influence rather than MnO$_2$. The external shape, profile and the calculated $\Delta V'$% values of reduced pure Fe$_2$O$_3$, 7.5%SiO$_2$–Fe$_2$O$_3$, (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$, and MnO$_2$–Fe$_2$O$_3$ compacts at 1 073–1 373 K are shown in Figs. 12(a)–12(d) respectively. In pure Fe$_2$O$_3$ compacts Fig. 12(a), the profile of reduced compact starts to change at 1 173 K showing maximum deformation at 1 198 K. The SiO$_2$-containing compacts showed that the compacts still have the original profile up to 1 373 K and no considerable deformation in shape is observed. This indicating that the presence of SiO$_2$ preserves the shape and profile of reduced compacts and greatly decreased the swelling of compacts even in presence of MnO$_2$ as shown in Figs. 12(b), 12(c).

The RLM and SEM photomicrographs of pure Fe$_2$O$_3$, MnO$_2$–Fe$_2$O$_3$, SiO$_2$–Fe$_2$O$_3$ and (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$ compacts reduced at their maximum swelling temperatures are given in Figs. 13 and 14(a)–14(d) respectively. The structure of pure Fe$_2$O$_3$ compacts reduced at 1 198 K given in Fig. 13(a) illustrates that, the majority of metallic iron appear in the form of flakes with elongated shape and distributed in a porous matrix result in catastrophic swelling of compacts ($\Delta V' = 255\%$). In MnO$_2$–Fe$_2$O$_3$ reduced compacts at 1 248 K, a matrix structure consists of separated metallic iron flakes in a highly porous structure as shown in Fig. 13(b). The growing of metallic iron flakes impinges on adjacent grains and push them apart causing wider and wider macropores and catastrophic swelling ($\Delta V' = 405\%$). Figures 13(c), 13(d) illustrate the effect of silica on the shape of metallic iron grains which become relatively dense and thus hindered the formation of flakes and result in small increase in volume change ($\Delta V' = 60\$) compared to that of pure Fe$_2$O$_3$ or MnO$_2$–Fe$_2$O$_3$ compacts. The SEM photomicrographs given in Fig. 14(a) illustrates the formation of metallic iron plates and whiskers which are most probably responsible for the catastrophic swelling occurred in pure
The structure observed in SiO$_2$-containing whiskers which accompanied by highly porous matrix catastrophic swelling by more growing of metallic iron effect on the size and number of metallic iron plates and whiskers result in small increase in the volume increase the compact strength and restricted the growth of whiskers. The formation of fayalite and fayalite–manganoan [(Fe, Mn)$_2$SiO$_4$].

Fe$_2$O$_3$. Figure 14(b) shows the promotion of MnO$_2$ to the catastrophic swelling by more growing of metallic iron whiskers which accompanied by highly porous matrix structure. The structure observed in for SiO$_2$-containing samples (Figs. 14(c), 14(d)) reveals the SiO$_2$ has a negative effect on the size and number of metallic iron plates and whiskers. The formation of fayalite and fayalite–manganoan increase the compact strength and restricted the growth of whiskers and plates result in small increase in the volume change of compacts during reduction process.

4. Conclusion

Fe$_2$O$_3$, SiO$_2$–Fe$_2$O$_3$, MnO$_2$–Fe$_2$O$_3$ and (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$ compacts annealed at 1 473 K were isothermally reduced by CO at 1 073–1 373 K, the results obtained can be summarized as follow:

1) Unlike in SiO$_2$–Fe$_2$O$_3$ annealed compacts where no new phases were detected, manganese ferrite was formed in MnO$_2$-containing samples. The total porosity of compacts increased with the SiO$_2$ mass%.

2) The rate of reduction of SiO$_2$–Fe$_2$O$_3$ compacts increased as the SiO$_2$ content increased at the initial stages. At the final stages the presence of SiO$_2$ retarded the reduction of Fe$_2$O$_3$ due to the development of hardly reducible fayalite (Fe$_2$SiO$_4$) phase. For (SiO$_2$+MnO$_2$)–Fe$_2$O$_3$ compacts, the rate of reduction decreased due to the formation of hardly reducible fayalite–manganoan [(Fe, Mn)$_2$SiO$_4$].

3) The reduction of pure and doped samples was controlled by a combined effect of chemical reaction and gaseous diffusion at the initial stages. At final stages, a combined effect of chemical reaction and solid-state diffusion controlling the reaction and the contribution of latter increased with doping oxide contents and decreased with rise in temperature.

4) The presence of silica had a negative effect on the size and number of metallic iron plates and whiskers result in small increase in the volume of compacts (ΔF=58%) compared to 255% in pure Fe$_2$O$_3$ and thus inhibited the catastrophic swelling. Catastrophic swelling in reduced samples was detected in MnO$_2$–Fe$_2$O$_3$ samples reduced at 1 248 K resulting 405%.

REFERENCES