Effect of Reduction Degree on Characteristics of Slag Formed by Melting Hydrogen-Reduced DRI and Partitions of P and V between Slag and Metal

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Self-fluxing hematite pellets are reduced by hydrogen to different degrees. The reduced pellets are melted in closed MgO crucibles at 1873 K to study the effect of reduction degree on the characteristics of slag formed. The results reveal that the phosphorus content in the metallic phase can be brought down to 130 ppm merely by the self-fluxing slag, even though the slag weighs only about 8% of the metal. It shows a great potential in reducing the amount of slag formers in the steelmaking process. The slag compositions obtained by melting the reduced pellets are used to prepare small synthetic slag samples for identifying the phases after melting. The use of the small samples is to ensure efficient quenching. Microscopic examination reveals that all the self-fluxing slags contain mainly three phases, namely, magnesiowüstite, spinel, and a liquid phase. Most of vanadium is found to be in the spinel and magnesiowüstite phases. The liquid phase only contains 1–2 wt% V₂O₅. Decreased FeO content of the slag increases the vanadium oxide contents in the spinel and magnesiowüstite phases. The fact that vanadium concentrates in the solid oxide phases provides essential information for sustainable extraction of vanadium from the steelmaking slag.

1. Introduction

Between 4% and 7% of the global anthropogenic CO₂ emissions come from iron and steel production.[1] To efficiently limit CO₂ emissions from ironmaking and steelmaking, new production route(s) have become increasingly necessary. One possible solution for ore-based iron and steel producers would be to abandon the blast furnace and use hydrogen as a reductant instead of carbon. [2] Along this line, a huge project has been started in Sweden aiming at zero fossil steelmaking route, which uses hydrogen gas as the reactant.

The major differences between the hydrogen-reduced iron and the carbon-reduced iron are that the former is solid and contains no carbon and very little sulfur, as coke and carbonaceous reductants are the main sources of sulfur in blast furnace steelmaking.[3] After melting the direct reduced iron (DRI), exchange reactions will take place between the initially formed slag and the molten iron. The unreduced oxides, viz., the remaining iron oxide, the main part of all other oxides inherent to the ore, and the additives and binders added during pellet making,[4] will participate in slag formation. To utilize the advantages of DRI produced by hydrogen reduction, e.g., its low carbon and sulfur contents, optimizations of the process route are essential. One potential optimization would be the melting of the DRI in a suitable reactor followed by optimized slag–metal reactions in the vessel. This would possibly reduce the raw materials for the formation of the slag and minimize the energy consumption for heating up the slag. In this direction, a study of the structure of the initial slag formed by self-fluxing DRI would be essential. The capacity of capturing phosphorus of the self-fluxing slag would also be the base for slag optimization, as phosphorus is known to have, in many cases, detrimental effects on steel.[5] In view that some mines contain iron ore of high vanadium oxide content, e.g., the mines in Sweden, the slag optimization would require information of the vanadium partition between the initially formed slag and the metal phase.

The microstructure of the initial slag after melting of the DRI, viz., the phases present, has been studied very little. To the best of authors’ knowledge, no literature data have been published, though some recent work has reported the slag structure relevant to vanadium extraction.[6–12] In these studies, vanadium is found in high concentration in spinel phase and CaVO₃ depending on the investigated slag composition.[6–11] Al, Cr, Mg, Mn, Fe, and Ti are found together with V in the spinel phase.[6–7,9,10]

Although the partition of phosphorus between slag and liquid metal has been studied extensively with regards to the basic oxygen furnace (BOF),[13–15] very limited work has been done in the case of the initial slag after melting DRI. The initial slag after melting of DRI usually contains relatively low basicity. Some
researchers have studied phosphorus partitions between liquid steel and low basicity slags.\textsuperscript{16,20} However, synthetic slags have been used in all these works.

Also, some studies on vanadium partition between slag and liquid metal during ironmaking and steelmaking can be found in the literature.\textsuperscript{16,21–24} Selin studied the vanadium partition using synthetic slag of composition relevant to steelmaking with high fraction of charged DRI.\textsuperscript{16} However, there is no work about the V partition after melting DRI.

To utilize the advantages of DRI for material saving, energy saving, and sustainable extraction of vanadium from the iron ore, this work focuses on a characterization of the self-formed slag by melting DRI. It is very difficult to obtain very high degree of metallization in the production of DRI. Hence, the study of the effect of the degree of reduction on the slag characteristics is essential. The tasks of this study are to investigate the effects of degree of reduction on 1) the structure of the slag upon melting of hydrogen-reduced DRI pellets; 2) the partition of P between slag and metal; and 3) the partition of V between slag and metal.

2. Experimental Section

In the first part, commercial self-fluxing hematite pellets were reduced to different degrees by hydrogen and then melted at 1873 K to study the partitions of phosphorus and vanadium between steel and slag. In the second part, small slag samples along with liquid Fe were held for prolonged times at 1873 K and then rapidly cooled to investigate the high temperature phase relationship of the initially formed DRI slag.

Three different vertical resistance furnaces were used throughout the study; one for reduction, one for melting, and one for preparing samples with fast quenching. The details of the three setups are described as follows.

The hematite pellets were reduced to different degrees in the furnace, which is schematically presented in Figure 1. The pellets contained about 97% hematite, the remainder being the oxides of Al, Ca, Mg, Si, Ti, V, and P. On the supplier’s request, the detailed analysis is not given. A quartz tube was used as a reaction tube. The upper end of the quartz tube was connected to a water cooled chamber of aluminum and the lower end to a water cooled cap of aluminum. The sample was hung on a steel rod inside the furnace. The steel rod could be moved up and down using a lifting system. The gap between the steel rod and the aluminum chamber was sealed by radial seals. The thermocouple going through the bottom cap was placed 1 cm below the sample.

Iron ore pellets (160 g) were put in a basket made of a nickel–chromium (Nikrothal 80) wire and placed in the hot zone of the furnace. After sealing the furnace, it was ensured that the system was completely gas tight. The furnace was flushed with argon at a rate of 1 L min\(^{-1}\) for 30 min to remove oxygen. The furnace was then heated to 1173 K with a rate of 10 K min\(^{-1}\). After additional 30 min, the Ar gas was stopped, and the H\(_2\) gas was introduced at a rate of 0.8 L min\(^{-1}\). The hydrogen flow was stopped after different reaction times to obtain DRI with different reduction degrees. The pellets were cooled to room temperature in argon atmosphere inside the furnace. The pellets were weighted before and after reduction to calculate the degree of reduction according to Equation (1)

\[
\text{Degree of reduction} = \frac{m_2 - m_1}{m_t - m_1}
\]

where \(m_1\) and \(m_2\) are the mass of the pellets before and after reduction, respectively, and \(m_t\) is the theoretical mass of the pellets if they would be completely reduced with regards to Fe\(_2\)O\(_3\).

After reduction, the pellets were put into a closed MgO crucible (inner diameter = 3.5 cm, outer diameter = 4.2 cm, and height = 7.0 cm) and melted. It should be mentioned that no materials other than the DRI pellets were added in the crucible. The experimental setup for melting was essentially the same as that used for reduction, Figure 1, except that an alumina reaction tube was used instead. A molybdenum holder was used to attach the sample to the steel rod.

To start the experiment, the sample was introduced into the aluminium chamber, and the furnace was checked for leaks. To ensure an inert atmosphere, the furnace was evacuated and filled with argon three times. After the last evacuation and refilling, an argon flow of 0.1 L min\(^{-1}\) was maintained. The furnace was heated to 1873 K, and when the target temperature was reached, the sample was lowered to the hot zone at a speed of 15 mm min\(^{-1}\). The total time to reach the hot zone thus amounted to 30 min. The sample was held in the hot zone for 30 min. Thereafter, the sample was quickly (in \(\approx\)3 s) moved to the water cooled aluminum chamber at the simultaneous

Figure 1. Schematic drawing of the experimental setup for reduction of iron ore pellets and melting.
injection of a high flow of Ar into the chamber. The quenching gas was maintained for 30 min.

After taking out the sample from the furnace, pieces of slag and iron were collected and sent for analysis. The iron composition was analyzed with optical emission spectroscopy (OES). The slag was analyzed with X-ray fluorescence (XRF). Approximately, 2 g slag was ground and briquetted. Hence, the result of XRF could be considered representative to the composition of the whole slag sample. The phase relationship of the slag was investigated using energy-dispersive spectroscopy (EDS) in a scanning electron microscope (SEM).

To maintain the high temperature phase relationship of the slag, rapid quenching of the sample was essential. For this purpose, smaller samples of 5 g slag along with 1 g Fe were used. Figure 2 is a schematic of the experimental setup. The upper end of the alumina reaction tube was internally connected to a water cooled aluminum cap. A Mo hook and a type-B thermocouple were placed through the lid of the cap. The hook was used for holding the sample. The thermocouple was placed carefully, so that its tip was at the same height as the sample. A quenching chamber was connected to the lower end of the reaction tube with a gas tight ball valve. Mineral oil (Leybold LVO100) was used as the cooling media. The ball valve separating the reaction tube and the quenching chamber was closed during the equilibrating time, so that the oil was kept at room temperature in this period, and no vapor from the oil could come into the reaction tube. Only when dropping the sample into the oil was the ball valve opened. Splashing of oil into the reaction tube was prevented by a 50 cm long aluminum tube.

Prior to mixing the synthetic slag, Al₂O₃, CaO, MgO, SiO₂, and TiO₂ powders were calcinated for 8 h at 1173 K, and V₂O₅ powder was dried at 378 K for 18 h. FeO was prepared by mixing powders of Fe and Fe₂O₃ to 49 mol% Fe and 51 mol% O, according to an earlier publication.[25] The mixture was put in a lidded Fe crucible and kept at 1123 K for 70 h in a vertical tube furnace, and TiO₂ powders were calcinated for 8 h at 1173 K, and V₂O₅ originated from the pellets themselves. Minor constituents

![Figure 2. Schematic drawing of the experimental setup used for quenching small slag samples.](image)

3. Results

The first objective of the study on melting of hydrogen-reduced iron ore pellets is to determine the effect of reduction degree on the partitions of P and V between the slag formed initially by DRI and the metallic phase. The second objective of this work is to characterize the structure of the slag formed at the melting temperature, especially the phases present. The focus of the study on the slag structure is to examine the vanadium distribution, which would provide valuable information for the study of vanadium extraction. The detailed description of the high-temperature phase relationship of the slag is based on the examination of the small quenched samples.

3.1. P and V Partition as a Function of the Degree of Reduction (FeO Content)

The iron ore pellets were reduced to reduction degrees between 91.0% and 99.3%. The experimental results along with the degrees of reduction are presented in Table 1. The table includes the concentrations of phosphorus and vanadium in the steel, the normalized slag compositions obtained by chemical analysis, as well as the calculated phosphorus partitions and vanadium partitions, L_P and L_V. Note that no other materials except the reduced pellets were added in the melting process. Both P and V originated from the pellets themselves. Minor constituents
(<1 wt%) of the slag, except P2O5, are excluded for brevity. The FeO contents of the slags, estimated from the pellets weight changes during reduction, are also listed in Table 1. It is assumed that all iron occurs as Fe2O3 before reduction, and either Fe or FeO after reduction. As shown in the table, the theoretically estimated FeO contents are in good agreement with the results of chemical analysis. The FeO contents of the self-fluxing slags vary between 72 and 22 wt% when the degree of reduction varies between 91.0% and 99.3%.

### 3.2. Existing phases

#### 3.2.1. DRI Slag

Although the fractions of different phases vary in different slag samples, in general, three different phases are found in the samples: magnesiowüstite, spinel, and a matrix “phase.” As examples, Figure 3a,b presents the typical SEM images of slags formed upon melting of DRI at 1873 K. Moreover, Table 2 shows the normalized composition ranges of these phases. The phase compositions are only indicative, as they are determined by EDS. Two to four measurements in the spinel and magnesiowüstite phases are deemed satisfactory, whereas for the matrix phase, ten analyses are needed to support the discussion later. Note that because of the big mass of the sample, the phases detected in the slag should also be considered tentative. The stable phases in the slag would need to be identified by the small efficiently quenched samples, which will be discussed later.

The magnesiowüstite phase contains mostly Mg, Fe, and oxygen with certain amount of vanadium. The composition suggests that this phase is the solid solution of wüstite. In all slags, many small spots enriched with V, Ti, and Al are found inside the magnesiowüstite phase. The spinel phase contains Al, Mg, Fe, Ti, V, and O. From observation of more than 20 SEM images of each sample, it is found that the slag from DRI reduced to 94.2% contains visibly less spinel phase than the slag of pellets

| # | Red. [%] | P (%) | V (%) | Al2O3 | CaO | FeO | MgO | P2O5 | SiO2 | TiO2 | V2O3 | Calc. FeO | Lp[1] | Lv[1] |
|---|---------|------|------|-------|-----|-----|-----|------|------|------|------|----------|-------|-------|
| 1 | 99.3    | 0.021| 0.007| 5.0   | 23.2| 22.4| 17.2| 0.7  | 21.7 | 4.5  | 5.3  | 22.7     | 15    | 501   |
| 2 | 98.7    | 0.015| 0.004| 4.7   | 20.6| 30.8| 14.1| 0.8  | 20.3 | 4.1  | 4.6  | 35.3     | 22    | 769   |
| 3 | 98.8    | 0.017| 0.003| 4.3   | 19.7| 32.6| 15.5| 0.7  | 18.8 | 3.9  | 4.5  | 33.9     | 19    | 1002  |
| 4 | 98.1    | 0.013| 0.002| 4.1   | 16.7| 39.6| 13.9| 0.7  | 17.7 | 3.3  | 4.0  | 44.2     | 23    | 1330  |
| 5 | 96.8    | 0.013| 0.001| 3.7   | 13.2| 51.7| 9.4 | 0.8  | 15.5 | 2.7  | 3.0  | 57.6     | 26    | 1994  |
| 6 | 94.2    | 0.013| <0.001| 2.7  | 8.5 | 65.6| 8.3 | 0.5  | 10.6 | 1.7  | 2.1  | 71.0     | 16    | –     |
| 7 | 91.0    | 0.020| <0.001| 2.1  | 6.2 | 72.9| 7.2 | 0.4  | 8.5  | 1.3  | 1.5  | 79.3     | 8     | –     |

Figure 3. Phases in the slags reduced to a) 99.3% and b) 94.2%. Mapping of vanadium in the slags reduced to c) 99.3% and d) 94.2%.
of higher reduction degree. The slag of DRI reduced to 91.0% contains almost no spinel phase. The difference in the amount of spinel phase between the other slags is difficult to see by eye. The other phases are denoted as “matrix” in Figure 3a,b. The matrix, in fact, contains three phases. However, the area analysis of EDS suggests that the matrix “phase” is likely to be liquid at equilibrating temperature and becomes three phases during cooling. The area analysis in Table 2 shows that the matrix phase contains high SiO$_2$ and CaO, whereas it also contains considerable amounts of FeO, MgO, and Al$_2$O$_3$. The presence of the three phases in the matrix was, in fact, the reason to carry out the experiments with smaller samples and faster quenching (tests 8–10). This aspect is to be discussed later.

### 3.2.2. Quenched Synthetic Slag

To make sure that the phases found in the DRI slag exist at 1873 K, slag samples of smaller mass are prepared. This is done by mixing synthetic slags of similar compositions as the DRI slags and equilibrating them with Fe at 1873 K. After equilibration with liquid Fe, the sample is quenched in oil to maintain the phase relationship at 1873 K. The weighed-in compositions of the synthetic slags are given in Table 3. The examples of microscopy images are shown in Figure 4a,c,e. It is found that all three slags having different FeO contents contain the same three phases, namely, magnesiowüstite, spinel, and super cooled liquid. Confirmation of the existences of spinel phase and magnesiowüstite phase was based on 1) the compositions of the phases (EDS results); 2) previous publications for similar slags; and 3) more importantly, X-ray diffraction (XRD) analysis. Visual comparison of big amount of SEM images of the slags containing 10, 20, and 40 wt% FeO reveals that the slag with higher content of FeO contains less spinel and more magnesiowüstite. The difference between the samples containing 10 and 20 wt% FeO is quite small. While the majority of all magnesiowüstite is of the size shown in Figure 4a,c,e, all samples also contain some larger dendrites of magnesiowüstite. As an example, a microscopy image of a large magnesiowüstite is shown in Figure 5. As shown in this figure, there is a color gradient close to the surface of the large dendrites, owing to changing composition. In the surface, the FeO content is higher, whereas the MgO

### Table 2. Composition of slag phases in melted DRI.

| Red. [%] | Phase | MgO [wt%] | Al$_2$O$_3$ [wt%] | SiO$_2$ [wt%] | CaO [wt%] | TiO$_2$ [wt%] | V$_2$O$_3$ [wt%] | FeO [wt%] |
|---------|-------|-----------|-------------------|---------------|-----------|----------------|----------------|-----------|
| 99.3    | MW    | 31–33     | 0–1               | 0             | 0–1       | 0–1            | 5–9            | 58–62     |
| 98.8    | MW    | 10–15     | 0–1               | 0–3           | 0–2       | 0–1            | 1              | 77–88     |
| 98.7    | MW    | 16–18     | 0                 | 0             | 0–1       | 0              | 3              | 79–80     |
| 98.1    | MW    | 7         | 0                 | 0             | 0         | 0              | 2              | 91        |
| 94.2    | MW    | 4–5       | 0                 | 0             | 0–1       | 0–1            | 1              | 92–94     |
| 91.0    | MW    | 3         | 0                 | 0             | 0         | 0              | 1              | 95–96     |
| 99.3    | Spinel| 10–11     | 10–12             | 0             | 1–2       | 23             | 11–15          | 40–43     |
| 98.8    | Spinel| 9         | 7–9               | 0             | 1         | 21–22          | 12–13          | 47–48     |
| 98.7    | Spinel| 7         | 8                 | 0             | 1–2       | 21             | 12–14          | 49–50     |
| 98.1    | Spinel| 7–8       | 10–11             | 0             | 1         | 21–24          | 5–13           | 47–52     |
| 96.8    | Spinel| 4–7       | 7–12              | 0             | 0–2       | 17–23          | 5–9            | 57–59     |
| 94.2    | Spinel| 3–6       | 6–15              | 0–7           | 1–7       | 15–23          | 1–5            | 55–62     |
| 91.0    | Spinel| 2–3       | 5–7               | 2–5           | 1–9       | 17–20          | 0–2            | 58–70     |
| 99.3    | Matrix| 6–8       | 6–8               | 31–35         | 34–37     | 3–6            | 0–1            | 13–14     |
| 98.8    | Matrix| 6–8       | 4–8               | 34–36         | 32–42     | 0–2            | 0–1            | 11–17     |
| 98.7    | Matrix| 6–7       | 5–7               | 35–38         | 32–38     | 0–2            | 0–1            | 13–16     |
| 98.1    | Matrix| 5–7       | 5–8               | 33–35         | 32–37     | 1–3            | 0              | 15–18     |
| 96.8    | Matrix| 4–6       | 6–7               | 34–35         | 32–35     | 2–3            | 0              | 17–20     |
| 94.2    | Matrix| 4–6       | 6–7               | 33–34         | 35–37     | 0–2            | 0              | 17–21     |
| 91.0    | Matrix| 3–6       | 5–8               | 32–35         | 31–39     | 0–4            | 0              | 16–21     |

### Table 3. Weighed in composition for studying the high-temperature phase relationship of the DRI slag.

| Test | FeO [wt%] | Al$_2$O$_3$ [wt%] | CaO [wt%] | MgO [wt%] | SiO$_2$ [wt%] | TiO$_2$ [wt%] | V$_2$O$_3$ [wt%] |
|------|-----------|-------------------|-----------|-----------|---------------|---------------|----------------|
| 8    | 10.1      | 6.3               | 26.2      | 16.5      | 28.9          | 5.7           | 6.3            |
| 9    | 20.2      | 5.6               | 23.2      | 14.6      | 25.7          | 5.0           | 5.6            |
| 10   | 40.4      | 4.2               | 17.4      | 10.9      | 19.2          | 3.8           | 4.2            |
content is lower. The difference between large and small magnesiowüstites is discussed later.

3.3. Distribution of V

Element mapping is used to understand the distribution of vanadium oxide in the slag. The distribution of V in all samples is very similar. Figure 3c, d shows the relative concentration of V in slag from DRI reduced to 99.3% and 94.2%, respectively. These figures show that V is enriched in the spinel phase and in small spots inside the magnesiowüstite phase.

As mentioned previously, the smaller samples would be more representative to the equilibrium at 1873 K. Figure 4b, d, f shows the examples of how V distributes in the quenched synthetic slag samples containing 10, 20, and 40 wt% FeO. In these slags, V is found in the spinel and magnesiowüstite phases. No precipitation is seen inside the magnesiowüstite phase. It should be mentioned that as the purpose of studying the phase relationship is related to vanadium extraction, the slag containing more than 40% FeO is not studied in this respect.

EDS point (for the spinel and magnesiowüstite phases) and area (for the liquid phase) analysis are used to investigate the compositions of the phases formed in quenched synthetic slags with different FeO contents. The average compositions of the phases, based on ten measurements, are presented in Table 4. The tabulated compositions enable a semi-quantitative comparison between the samples, even though EDS is not very accurate. It is important to mention that both Fe$^{3+}$ and Fe$^{3+}$ are likely to exist in the slag; similarly, vanadium might exist as V$^{2+}$, V$^{3+}$.
V$^{4+}$, and V$^{5+}$. To make the following discussion possible, FeO and V$_2$O$_5$ are used to present the phase compositions in Table 4, even for the liquid phase. A concentration gradient is observed within the large magnesiowüstite phase shown in Figure 5. To show the size of this concentration gradient, the compositions of both the center and the surface regions of the large magnesiowüstite phase are reported in Table 4. It is important to mention that the composition of the small magnesiowüstite dendrites is very close to the composition at the surface of the big magnesiowüstite phase.

### 4. Discussion

#### 4.1. Equilibrium Phases in the Slag

While Figure 3a,b shows the examples of the phase relationships obtained in the samples of bigger mass, the present discussion regarding the equilibrium phases in the slag is mainly based on the results in tests 8–10. The smaller mass of sample along with the use of oil as cooling media would lead to better quenching and more reliable results. As shown in Figure 4a,c,e, three phases are identified, namely, magnesiowüstite, spinel, and liquid phase. A comparison of Figure 3a,b and 4a,c,e indicates that the insufficient quenching of the larger samples results in the precipitation of the matrix phases in Figure 3a,b. The matrix is, therefore, liquid at experimental temperature.

The concentration gradient inside the large magnesiowüstite phase shown in Figure 5 is expected to form during cooling. The center of the large dendrites contains more MgO than the surface layer according to Table 4, suggesting that this part of the dendrites is stable at 1873 K. During cooling, the magnesiowüstite phase reacts with the liquid phase leading to higher FeO content and a decrease in the MgO content. This is in accordance with the MgO–FeO phase diagram,[27] which reveals that higher MgO content is associated with higher liquidus temperature. The MgO–FeO phase diagram indicates that the center part of the big magnesiowüstite phase is stable at 1873 K. As the contents of the other oxides (see Table 4) are considerably low, they are not expected to lower the melting temperature appreciably. The similar composition of the small dendrites and the composition at the edge of the big dendrites suggests that the smaller dendrite crystals likely are formed during cooling. Another possibility is that the small dendrites and the outer layer of the big dendrites, because of the shorter diffusion distance, have enough time to react with the liquid. This could explain why the earlier have similar composition as the latter.

Some spinel crystals appeared in the slags. To the best of authors’ knowledge, no phase diagram information is available for this multi-component system, especially for the spinel phase. Nevertheless, the shape of the spinel phase and its composition range strongly suggest that it is stable in the slag at 1873 K. The huge difference in V content between the spinel phase and the liquid phase, which contains almost no V, would further support this argument. As the slag was quenched in oil, the solidification time would be a few seconds. It is very unlikely that the liquid would become almost free of V in this short time. The presence of the spinel phase at 1573 K in a similar system has also been reported by Wu and his co-workers.[6]

A comparison of the larger and smaller samples suggests that the cooling/solidification speed would play important role for the phase relationship and microstructure of the slag. This aspect would be very interesting in future studies on vanadium extraction. As mentioned previously, iron ore pellets of lower reduction degree give a slag with considerably less spinel phase after melting. It indicates that the degree of reduction plays crucial role when vanadium extraction is concerned. It is worthwhile to mention that no more effort has been made to focus on studying the slag structure with FeO content higher than 40%. It is a common knowledge that slag with very high FeO content would not be suitable for vanadium extraction. To the best of authors’ knowledge, no study on the vanadium distribution in the slag formed by melting DRI has been reported before. It is hoped that the present results could be a starting point for the study of extraction of vanadium from the slag formed by melting of DRI.

#### 4.2. Effect of Reduction Degree on $L_P$ and $L_V$

The $L_P$ and $L_V$ determined for melted hydrogen DRI, in this work, are compared with the literature data for slag–metal systems of similar composition in Table 5. All reference compositions have been normalized to 100%. The comparison suggests that the presently determined $L_P$ and $L_V$ are in line with the literature data.
The experimentally determined partition coefficients of phosphorus and vanadium, $L_P$ and $L_V$, are plotted as the functions of the degree of reduction in Figure 6a,b, respectively. To have a better understanding, the oxygen partial pressures obtained for the experimental points using Equation (3) and (4) are included beside the points. The activity of liquid FeO is calculated by ThermoCalc, using the TCOX8 database. In view that all phases are in equilibrium at 1873 K and, therefore, have the same chemical potentials, the composition of the liquid matrix phase in the bigger samples (Table 2) is used for the calculation, neglecting $V_2O_3$ and TiO$_2$. The activity of Fe is assumed to be 1. While $L_V$ increases constantly with the decrease in reduction degree, $L_P$ shows a maximum at 96.8% degree of reduction.

The effect of FeO on the partitions is expected to be partially due to the oxygen potential in the system, whereas the FeO would also affect the slag composition, which, in turn, would affect the partitions. In addition to higher oxygen potential, lower reduction degree is associated with 1) a larger ratio of slag to metal and 2) lower basicity of the slag, which would also affect the $L_P$ and $L_V$. To consider the amount of self-formed slag and its basicity, the concentrations of P and V in the metal are plotted against reduction degree in Figure 7a,b. As shown, the P content in the metal decreases continuously with decreasing degree of reduction, until reaching a minimum of 100 ppm for reduction degrees $\leq 98.1\%$. Even at the degree of reduction of 94%, the phosphorus content in the metal can be low, about 100 ppm. However, the phosphorus content in the metal reaches 200 ppm when the reduction degree is further lowered to 91%. This can be explained by the fact that the phosphorus content in the metal depends on four factors, namely, the 1) the oxygen potential \cite{16,18}; 2) the amount of slag; 3) the basicity of the slag (more precisely, the content of CaO when both the contents of CaO and SiO$_2$ are low) \cite{16,18,19}; and 4) the temperature. In this study, the temperature is kept at 1873 K. The sample obtained with the pellets of 91% reduction has higher oxygen potential due to higher FeO content, bigger amount of slag, and lower CaO content. While the high oxygen potential and bigger amount of slag favor the removal of P from the metal to

### Table 5. $L_P$ and $L_V$ determined in this work in comparison with relevant references.

| Test or Ref. | $T$ [K] | Steel | Slag | $L_P$ [1] | $L_V$ [1] |
|-------------|---------|-------|------|----------|----------|
| [16]        | 1866    | 0.02  | –    | 29.5     | 18.4     |
| [17]        | 1873    | 0.07  | –    | 28.6     | 15.7     |
| [18]        | 1873    | 0.04  | –    | 30.6     | 24.1     |
| [22]        | 1873    | 0.0007| –    | 28.9     | 16.5     |
| 1           | 1873    | 0.02  | 0.007| 5.0      | 23.2     |
| [16]        | 1866    | 0.01  | –    | 27.3     | 15.6     |
| [16]        | 1866    | 0.01  | –    | 29.9     | 14.2     |
| [18]        | 1873    | 0.02  | –    | 25.1     | 20.4     |
| 2           | 1873    | 0.02  | 0.004| 4.7      | 20.6     |
| [17]        | 1873    | 0.09  | –    | 18.9     | 13.8     |
| [22]        | 1873    | 0.0005| –    | 21.0     | 16.6     |
| 4           | 1873    | 0.01  | 0.002| 4.1      | 16.7     |
| [17]        | 1873    | 0.2   | –    | 7.9      | 13.7     |
| 6           | 1873    | 0.01  | <0.001| 2.7     | 8.5      |

Figure 6. a) $L_P$ and b) $L_V$ versus reduction degree. The calculated oxygen potential in [Pa] is indicated beside each experimental point.

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slag, the CaO content of the slag is too low (too high FeO content) to maintain P in the slag. This is why the sample reduced to 91% has very poor phosphorus removal. It is worthwhile to point out that a phosphorus content of 130 ppm would meet the specifications of many steel grades. On the other hand, for some other high steel grades, the phosphorus content must be further lowered. Decreasing the phosphorus concentration could be done by increasing the oxygen potential\cite{18} by increasing the amount of slag, by adding certain amount of basic oxides such as CaO\cite{18,19} and by decreasing the temperature.\cite{19} This aspect is to be studied in very near future, whereas the present results could be a reliable starting point for the study.

A mass balance calculation reveals that a degree of reduction of 98.1% corresponds to a slag amount of 8 wt% of the metal, whereas a degree of reduction of 94.2% corresponds to a slag amount, which is 17 wt% of the metal. In industrial practice, it is difficult to reach a degree of reduction higher than 95% without considerable increase of cost. The present results imply that even 95% reduction would be acceptable when only dephosphorization is concerned. The V concentration in the metal also decreases with decreasing degree of reduction. For degrees of reduction $\leq 94.2\%$, the V concentration in the metal is below the detection limit of the analysis equipment of 10 ppm, indicating thereby that almost all vanadium ends up in the slag.

4.3. Distribution of V in the Slag

As listed in Table 3, the highest concentration of V$_2$O$_3$ is found in the spinel phase. The magnesiowüstite phase has the next highest concentration of V$_2$O$_3$. The matrix phase, viz., the liquid phase, has the lowest concentration of V$_2$O$_3$, only about 1–2 wt%.

Wu and his co-workers studied the factors affecting spinel phase formation at 1573 K in the system CaO–SiO$_2$–MgO–FeO–Al$_2$O$_3$–V$_2$O$_3$–P$_2$O$_5$. They found that, when the wüstite phase appeared in the slag, most of V$_2$O$_3$ was concentrated in the spinel phase\cite{30}. Their results are in accordance with the present findings.

Wu et al. also found that the V$_2$O$_3$ content of the spinel phase was constant when changing FeO content when magnesiowüstite was present\cite{66}. Such correlation could not be found in the present work, as shown in Table 4. The difference in the finding could be due to the difference in the composition ranges studied in the two investigations.

It is interesting to notice that the spinel phase contains most of the vanadium after melting of the DRI obtained from Swedish ore. This observation would throw some lights on the V extraction from the slag formed by melting DRI.

In addition, the V$_2$O$_3$ dissolved in the magnesiowüstite phase also needs some attention. To the best of the present authors’ knowledge, there is no reported study on the solubility of V$_2$O$_3$ in the magnesiowüstite containing MgO and FeO for direct comparison. On the other hand, it is interesting to mention that Coetsee and Pistorius report that 15 wt% V$_2$O$_3$ dissolves in liquid FeO at 1873 K and $p_{O_2} = 2.3 \times 10^{-3}$ Pa in the FeO–V$_2$O$_3$ system\cite{20}. A somewhat higher dissolution of V$_2$O$_3$ is reported by Huang et al. and Zeng et al., whose experiments are conducted in Ar atmosphere\cite{29,30}. Furthermore, according to the findings by the present authors, 26 wt% V$_2$O$_3$ dissolves in MgO phase in the V$_2$O$_3$–MgO system at 1873 K and $p_{O_2} = (3.55 \pm 0.3) \times 10^{-3}$ Pa\cite{21}. Further study of the magnesiowüstite phase is definitely needed for the development of the process of V extraction from slag.

When vanadium is produced as a co-product to steel and iron, vanadium is oxidized to a slag phase through oxygen blowing of hot metal from the reduced ore\cite{32,33}. Alkaline salt roasting followed by water leaching is the most common method in industry to recover vanadium from this slag\cite{34}. For environmental reasons, it is preferred to use soda, Na$_2$CO$_3$, during alkaline salt roasting\cite{32}. The purpose of soda roasting is to produce water soluble sodium vanadate, which first requires oxidation of vanadium to V$_2$O$_5$. The reactions taking place during soda roasting are complex. First, iron is oxidized, and silicates, spinels, and titanates are decomposed. Second, sodium vanadates, titanates, silicates, and ferrates are formed, depending on the amount of soda used. Different roasting reagents would have different selectivity to vanadium\cite{33}. It is expected that different phases in the slag will behave differently in the roasting procedure. The present characterization of the self-formed slag by melting DRI provide a starting point for the study on sustainably extraction of vanadium. It is evident that the phase relationship of the slag is needed for fundamental understanding of the extraction process\cite{7,35–37}. Several investigators have reported that vanadium slags intended for alkaline salt roasting and water leaching

Figure 7. Concentration of a) P and b) V in the metal versus reduction degree.
contain silicate phases and a vanadium enriched spinel phase.\textsuperscript{[7,10,35,37]} The types of phases present in the slag have great impact on the roast-leach route, because their thermodynamic properties determine, for example, at which temperatures the roasting reactions take place depending on the added roasting reagent(s).\textsuperscript{[38,39]} In the DRI slag studied in this work, vanadium occurs in both spinel and magnesiowüstite phases. Hence, the development of a process for hydrometallurgical extraction of vanadium from this slag would include finding a way to recover vanadium from both the spinel and magnesiowüstite phases, without negative interference from the matrix phase. Much more work is needed to find a way to extract vanadium in the new hydrogen steelmaking route.

5. Conclusion

This study focused on the characterization of the self-formed slag when melting DRI produced by hydrogen reduction. The partitions of phosphorus and vanadium between slag and metal were related to the degree of reduction in the range of 91.0–99.3%. The phases formed in the slag after melting were characterized. Melting of the DRI at 1873 K with different degrees of reduction resulted in different FeO contents in the slag, varying between 72% and 22%. The partition of phosphorus was found to increase with decreasing reduction degree (increasing oxygen potential) until reaching a maximum at 96.8% reduction. The partition of vanadium was found to increase continuously with oxygen potential. It was found that the phosphorus content in the metal phase could be brought down to quite low level by merely the self-fluxing slag in the DRI. Only at very low degree of reduction, e.g., 91% reduction, the slag became very poor for dephosphorization. This finding would form a fundamental base for material saving and energy saving in the following steelmaking process. Microscopical examination of the slag structure revealed magnesiowüstite phase, spinel phase, and a matrix consisting of three phases. The three phases in the matrix were believed to be formed during cooling. Vanadium mainly existed in the spinel and magnesiowüstite phases. To clarify the phase relationship of the self-fluxing DRI slag at 1873 K, additional experiments with faster quenching were made in the second part of this work. Small amounts of synthetic slag were equilibrated with Fe in closed crucibles at 1873 K. The slags contained 10, 20, and 40 wt% FeO, whereas the mass ratio between the other oxides was kept constant. The samples were quenched in oil. Three phases existed in all samples, namely, spinel, magnesiowüstite, and quenched liquid. The presence of the liquid phase confirmed that the matrix “phase” found in the slag in the first part of the study was liquid at 1873 K. The vanadium oxide content was highest in the spinel phase, although vanadium oxide was also present in the magnesiowüstite phase. The liquid only contained 1–2 wt% V$_2$O$_5$. The vanadium oxide contents of the spinel and magnesiowüstite phases increased with decreased FeO content of the slag. On comparison of the slags containing 10 and 40 wt% FeO, it was visible that the slag with more FeO contained more magnesiowüstite and less spinel phase. The present characterization of the self-formed slag by melting DRI would hopefully provide a starting point for the study on sustainable extraction of vanadium.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hydrogen-reduced iron, phosphorus partition, self-fluxing slag, sustainable steelmaking, vanadium partition

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