Interaction of New Zealand Ironsand and Flux Materials

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New Zealand ironsand is mined for steel production. Its composition approximates that of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) containing about 60 wt% iron and 8 wt% titania. The ironsand provides an alternative source of iron to conventional iron ores. Its addition into a sinter blend is an established method of utilisation in ironmaking. Knowledge of the interaction between ironsand and flux materials during sintering is helpful to understand the sintering mechanism of titanomagnetite. In this study, two-layer interaction couples between ironsand and flux materials (CaO, MgO and dolomite) were prepared and sintered in an atmosphere of $p\text{O}_2 = 0.5$ kPa in the temperature range of 1 200–1 300°C for different times. When the ironsand was sintered with MgO, Mg^{2+} ions significantly diffused into the lattice of ironsand, which stabilised the system of $\text{FeO}_x\text{--MgO}$ and hindered the assimilation of ironsand particles. During the sintering of ironsand with CaO, a reaction zone consisting of perovskite and calcium ferrite formed between the two layers. In comparison, a reaction zone consisting of perovskite, MgO--FeO solid solution and calcium ferrite occurred during the sintering of ironsand with dolomite. Increasing sintering temperature significantly enhanced the penetration of calcium ferrite into the dolomite layer; whereas the perovskite phase and MgO--FeO solid solution remained at higher sintering temperatures due to their relatively high melting points.

KEY WORDS: sintering; ironsand; titanomagnetite; dolomite; calcia; magnesita.

1. Introduction

Ironsand deposits along the west coast of New Zealand's North Island, including those at Waikato North Head and Taharoa, are mined for iron and steel production.¹⁾ The composition and microstructure of New Zealand ironsand have been intensively examined.^{1–4)} Although the composition of ironsand is partially dependant on origin/location, it approximates that of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) containing about 60 wt% iron and 8 wt% titania (TiO_2).^{1–3)} The major impurities in the ironsand include Al_2O_3 , MgO, SiO_2 , V_2O_5 , and MnO - all but SiO_2 are typically associated with the titanomagnetite grains, occurring as solid solution components within the lattice. The other impurity elements, including part of the aluminium, are more typically associated with gangue mineral grains such as aluminosilicates (e.g. feldspars and clays), quartz and apatite.⁴⁾

New Zealand ironsand grains can be divided into two types: homogeneous grains and grains that contain exsolution lamellae. Cocker *et al.*¹⁾ examined New Zealand ironsand using electron microprobe analyses and found that homogeneous titanomagnetite particles accounted for 90 to 95 vol% and were relatively rich in Ti, containing up to 8.2 wt% TiO_2 . The exsolution lamellae appearing as bands of

variable thickness in a trellis-like pattern were of hematite-ilmenite composition with an overall high TiO_2 content of 13.1 wt%, while the titanomagnetite host was relatively low in Ti (about 1.5 wt% TiO_2). High-temperature oxidation of Fe^{2+} to Fe^{3+} in titanomagnetite can produce vacancies in octahedral sites of the {111} crystal planes, which allows increased diffusion of Ti into these regions and leads to the formation of hematite-ilmenite lamellae (1–10 μm) along the original {111} planes of the titanomagnetite host.⁵⁾

The ironsand provides an alternative source of iron to conventional iron ores. Its small particle size precludes direct charging into a blast furnace but its incorporation into sinter provides an appropriate method for its utilisation in ironmaking.⁶⁾ The behaviour of ironsand during iron ore sintering has been examined previously.⁴⁾ It was reported that the assimilation of ironsand during sintering in a reducing atmosphere started from the diffusion of calcium into the lattice of the ironsand matrix, which further decreased the melting point of titanomagnetite and accelerated the melting rate of ironsand particles. A reaction zone was formed within the ironsand particle where a perovskite ($\text{CaO}\cdot\text{TiO}_2$) phase was generated as the result of the reaction between TiO_2 and CaO.

This paper is focused on characterising the interaction between ironsand and flux materials (CaO, MgO and dolomite) in the context of iron ore sinter blends containing titanomagnetite to gain a better understanding of the sintering

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mechanism of titanomagnetite.

2. Experimental Procedure

2.1. Sample Preparation

The starting materials used in the interaction experiments were: New Zealand ironsand and three fluxes including synthetic calcia, CaO (Sigma Aldrich, reagent grade); synthetic magnesia, MgO (Sigma Aldrich, 99%, <325 mesh) and dolomite. The synthetic CaO powder was calcined at 1 000°C for 2 h. Ironsand and dolomite were supplied by BlueScope Ltd. and the chemical compositions examined by X-ray fluorescence (XRF) were reported previously.⁴⁾ Detailed characterisation of the ironsand has also been presented in the Ref. 4). Before use, dolomite was crushed and screened to a particle size less than 38 μm . The decomposition of dolomite particles during sintering with release of CO₂ increases the porosity of the formed MgO–CaO layer, and so may affect the contact area between ironsand and the MgO–CaO mixture. However, this affects the diffusion rates of all related elements between an interaction couple proportionally. It makes no difference to using a pure MgO–CaO mixture except for the overall diffusion extent achieved.

The interaction couple between ironsand and each flux material used in this work was prepared as follows. Ironsand particles (0.5 g) were first placed in a die with a diameter of 8 mm and pressed into a substrate in a uniaxial hydraulic press by applying 20 kN of pressure for 2 min. Then, 0.3 g of each flux material powder was placed into the same die and pressed with the ironsand substrate into an interaction couple by applying 20 kN of pressure for 2 min.

2.2. Sintering

The sintering apparatus has been described previously.⁴⁾ The setup is based on a vertical tube furnace with a working diameter of 55 mm through which a gas mixture of controlled composition can be continuously passed. Experiments were conducted at different temperatures (1 200, 1 250, 1 300 and 1 325°C) for three different times (4, 8 and 20 min) in an atmosphere of $p\text{O}_2 = 0.5$ kPa (representative of industrial iron ore sintering⁷⁾) maintained by an air–argon mixture. The furnace was preheated to a designated temperature, and then purged with the gas mixture for at least 20 min before a crucible with the interaction couples was suspended in the hot zone of the furnace. After sintering for a desired time, the samples were cooled rapidly by lifting the crucible to the cold top end of the tube furnace in order to avoid any possible transformation due to slow cooling.

2.3. Microstructure Analysis

After cooling to room temperature, the specimens were vacuum infiltrated by epoxy resin, and after hardening, sectioned perpendicular to the ironsand–flux interface. The section was ground and polished to a 1 μm finish for optical microscopic observation (Leica DM6000 Optical Microscope). The polished samples were then coated with carbon prior to analysis by scanning electron microscopy (SEM, JEOL JCM-6000) operated at 15 kV. The thickness of the reaction layers reported represents an average of 12 measurements of the layers.

3. Results and Discussion

3.1. Interaction between Ironsand and MgO

The interaction couples between ironsand and MgO were sintered in an atmosphere of $p\text{O}_2 = 0.5$ kPa in the temperature range of 1 200–1 300°C for different times. **Figure 1** presents the back-scattered electron (BSE) images of typical ironsand particles in direct contact with the MgO layer in the interaction couples sintered under different conditions. The BSE image of the interface marked in Fig. 1(b) is shown in Fig. 1(c) at a higher magnification. These sintered ironsand particles remained intact and there was no obvious morphology change due to the reaction between ironsand and MgO. There was some evidence of bonding (see the area inside the circle in Fig. 1(b)) at 1 300°C, likely due to a reaction with a silicate phase. This was not observed in

Fig. 1. Back-scattered electron (BSE) images of typical ironsand particles close to the MgO layer in the interaction couples between ironsand and MgO sintered under different conditions. (a) 1 250°C, 4 min; (b) 1 300°C, 8 min; (c) 1 300°C, 8 min, high magnification.

the sample sintered at 1 250°C (Fig. 1(a)).

Figure 2 shows the chemical composition across the interface between ironsand and MgO in a sample sintered at 1 200°C for 4 min. The velocity of diffusion of an element in a solid phase can be described by the distance it diffuses in a certain time. The original ironsand particles contained about 3 wt% Mg in the titanomagnetite phase according to SEM/EDS analysis. After 4 min sintering, the Mg content was increased to about 9 wt% throughout the particle. Similarly, the Fe content in the MgO layer increased from nil to 5 wt%. In comparison, the spot analysis showed that the magnesia layer near the interface practically contained no Ti. The result shows that the diffusion of Mg within the titanomagnetite particle and iron in MgO was fast, however, Ti is hard to diffuse into the MgO phase.

Generally, one ion may take the place of another to form a solid-solution series if the difference between their ionic radii does not exceed 15% of the radius of the smaller ion.⁸⁾ Magnetite has an inverse spinel structure in which 50% of Fe^{3+} (4 coordinates, ionic radius 63 pm) occupies the tetradedral sites, while the other 50% of Fe^{3+} (6 coordinates high spin, ionic radius 78.5 pm) and all Fe^{2+} (6 coordinates high spin, ionic radius 92 pm) occupy the octohedral sites. Mg^{2+} ion (86 pm) and Fe^{2+} can substitute each other without distorting the overall structures of minerals due to their similar atomic size and identical electric charge.⁹⁾ In this study, during sintering at a high temperature, Mg^{2+} ions from MgO diffused into the lattice of titanomagnetite to form $\text{MgFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$ solid solution, and simultaneously Fe^{2+} ions diffused in the opposite direction into MgO. Ti^{4+} (74.5 pm) or Ti^{3+} (81 pm) ions are likely present as substituents of the Fe^{3+} ions at the octohedral sites considering their valency and radii. In comparison to Fe ions, Ti ions are more difficult to diffuse due to its higher electronic affinity

and stronger binding with surrounding oxygen ions. They are also hard to diffuse into MgO due to the difference in their valency; a Ti^{4+} ion needs to replace two Mg^{2+} ions to keep local electrical neutrality which has high spacial and chemical resistivities.

Figure 3 presents a BSE image of typical ironsand particles in a sample sintered at 1 300°C for 8 min, and the chemical compositions at different points marked in Fig. 3 are listed in **Table 1**. It should be noted that when an elemental content is less than 1 wt%, the number is only indicative due to the accuracy limits of EDS analysis. Points 1 and 2 represent the relict titanomagnetite particles in which the Mg content increased to over 8 wt%. Besides enhanced diffusion of ions, the higher sintering temperature also improved the sintering of ironsand particles. As shown in Fig. 3, although the contour of each ironsand particle remained intact, they were bonded together by a silicate phase (Points 3 and 4). During sintering at the high temperature, a small amount of silicate phase with low melting point was generated and melted due to the presence of impurities in the original ironsand, which was beneficial to the aggregation of ironsand particles. It is noted that the silicate phase contained approximately 7 wt% of Mg and Ca. The diffusion of Mg to the contacts between ironsand particles is likely to assist the formation of a liquid silicate phase.

However, significant diffusion of Mg^{2+} ions into the Fe_3O_4 lattice of ironsand can stabilise the system of $\text{FeO}_x\text{--MgO}$ and hinder the dissolution of ironsand particles. As shown in **Fig. 4**, the liquidus temperature of the $\text{FeO}_x\text{--MgO}$ system¹⁰⁾ increases gradually with increasing MgO content.

3.2. Interaction between Ironsand and CaO

The interaction couples between ironsand and CaO were

Fig. 2. BSE image and the chemical composition near the interface between ironsand and MgO layers in a sample sintered at 1 200°C for 4 min. (Online version in color.)

Fig. 3. BSE images of typical ironsand particles in the interaction couples between ironsand and MgO sintered at 1 300°C for 8 min.

Table 1. Elemental compositions (wt%) at the points marked in Fig. 3 and corresponding phases.

Point no.	Fe	Ca	Ti	Mg	Si	Al	Phase identified
1	62.0	0.1	5.2	8.1	0.1	1.9	Titanomagnetite
2	61.5	0.1	5.5	8.7	0.2	2.1	Titanomagnetite
3	12.3	7.6	3.2	7.6	22.5	6.9	Silicate
4	12.2	7.8	3.8	7.3	23.6	6.6	Silicate

sintered in an atmosphere of $pO_2 = 0.5$ kPa in the temperature range of 1 200–1 325°C for different times. The microstructure of formed mineral phases was examined by optical microscope and SEM/EDS.

A reaction zone between the ironsand and CaO layers was generated in the specimens during sintering in this study. **Figure 5** presents the BSE images of the interface between the ironsand and CaO layer sintered under different conditions. As shown in Fig. 5(a), a reaction zone with a width of approximately 3 μm was formed at the boundary of iron-sand particles and CaO sintered at 1 200°C for 4 min. The reaction zone thickness increased with increasing sintering time (see Fig. 5(b)), showing a reaction zone of thickness of ~ 12 μm after 20 min. A morphological change of the

reaction zone with sintering temperature was also observed. Figure 5(c) shows the interface between the ironsand and CaO layers in samples sintered at 1 250°C for 4 min and the thickness of the reaction zone increased to approximately 8 μm . When sintered at 1 300°C for 4 min, the average thickness of the reaction zone increased significantly to about 30 μm , as shown in Fig. 5(d).

Figure 6 shows the BSE image and elemental distribution of a reaction zone between ironsand and CaO in a specimen heated at 1 200°C for 20 min. The chemical compositions at different points presented in Fig. 6 were examined by EDS analysis and are listed in **Table 2**. The reaction zone contained a high concentration of Ca which was relatively uniformly distributed. However it can be noted from the distributions of Fe and Ti that there was a narrow band within the reaction zone next to the titanomagnetite matrix, corresponding to a band in the BSE image with a slightly darker colour. EDS analysis shows that the band (point 3) had a distinct composition from the major part of the reaction zone (points 4 and 5), but was the same as those distributed dark areas (point 2) within the titanomagnetite matrix. As shown in Table 2, the major part of the reaction zone was dominated by a calcium ferrite phase containing about 27 wt% Ca and 36 wt% iron, while the Ti-rich subzone and the distributed dark areas in the titanomagnetite matrix was a perovskite phase of Fe and Ca, containing 16–24 wt% of Ti. Similar perovskite phase was also found around the peripheries of some relict ironsand particles in an industrial sinter with addition of 3 wt% of ironsand.⁴⁾

Point 6 in Fig. 6 proved to be in the lime layer, which also contained low levels of iron (3.71 wt%). Problems in sample preparation resulted in some loss of CaO. As a result the CaO side of the ironsand-CaO couple shown in Fig. 6 was not in the same plane as the other part of the sample, mak-

Fig. 4. Liquidus temperature of FeOx-MgO system.¹⁰⁾

Fig. 5. BSE images of the interaction couples of ironsand and CaO sintered under different conditions. (a) 1 200°C, 4 min; (b) 1 200°C, 20 min; (c) 1 250°C, 4 min; (d) 1 300°C, 4 min.

Fig. 6. BSE image and EDS mapping of a reacted zone between ironsand and CaO in a specimen sintered at 1 200°C for 20 min. (Online version in color.)

Fig. 7. BSE image and EDS mapping of an interaction couple between ironsand and CaO sintered at 1 300°C for 20 min. The details of the small areas marked as a, b and c are presented in Fig. 8. (Online version in color.)

Table 2. Elemental composition (wt%) of grains marked in Fig. 6 and corresponding phases.

Point no.	Fe	Ca	Ti	Mg	Si	Al	Phase identified
1	63.8	1.0	2.48	3.5	0.3	2.7	Titanomagnetite
2	14.5	24.0	23.6	0.3	0.4	0.6	Perovskite
3	22.3	27.7	16.0	0.2	2.8	1.4	Perovskite
4	35.7	27.4	1.3	0.2	0.8	2.0	Calcium ferrite
5	36.2	27.0	1.2	0.4	0.3	1.4	Calcium ferrite
6	3.7	57.9	0.1	2.0	0.6	0.1	CaO

ing the absolute signal strength of Ca in this area weaker.

It is known that the reactions between CaO and Fe₂O₃ or TiO₂ are favoured thermodynamically which can be presented as follows:

The standard Gibbs free energy changes of the reactions were calculated using data from Binnewies and Milke¹¹⁾ in the range of 1 200 to 1 325°C. Thermodynamically, the reaction between TiO_2 and CaO is favoured over that between Fe_2O_3 and CaO .

When the interaction couples of ironsand and CaO were sintered, Ca^{2+} ions (with radius 114 pm) from CaO diffused into the lattice of Fe_3O_4 , while Fe^{2+} , Fe^{3+} and Ti^{4+} ions from ironsand diffused in the opposite direction into CaO . As a result, a reaction zone which was rich in Ca, Fe and Ti was generated between the two layers. Due to the low diffusivity of Ti^{4+} , it was accumulated near the titanomagnetite matrix boundary and combined with relatively mobile Ca^{2+} and formed the perovskite phase. Ca^{2+} also diffused inside the titanomagnetite matrix and formed distributed perovskite phase where the Ti content was much higher than the average after Fe diffused away. Meanwhile, a calcium ferrite phase was formed close to the CaO layer due to the reaction between CaO and iron oxides and the relatively higher diffusion rates of Fe^{2+} and Fe^{3+} . It is interesting that the difference between the radii of Ca^{2+} and the octahedral Fe^{2+} ions is up to 24%, yet Ca^{2+} can quickly diffuse in the titanomagnetite lattice. The reason behind may be that substitution of octahedral Fe^{3+} ions by smaller Ti^{4+} ions with higher electron affinity creates more space for Ca^{2+} next to the coordinating O^{2-} ions. On the other hand, iron diffused into the CaO layer perhaps via a surface diffusion mechanism. Fine CaO powder provided high surface area for the diffusion to take place.

Figure 7 shows the BSE image and EDS mapping of an interaction couple between ironsand and CaO heated at 1 300°C for 20 min. A coarsened reaction zone was observed around the interface of the two layers whose development may have been affected by separation from the ironsand layer. The Ti rich and Fe rich bands in the reaction zone can be clearly identified from the Fe and Ti distributions. A part of Fe-rich subzone penetrated into CaO layer (region 'c'), which was repeated in specimens sintered at this severe sintering condition, but was never observed in other conditions. This excludes the possibility of mixing ironsand particles into the CaO layer, and penetration of Fe into CaO was through diffusion of Fe. It can also be seen that Ca penetrated deeply into the ironsand layer and distributed between the titanomagnetite particles.

The BSE images of three different typical areas in Fig. 7 are shown in **Fig. 8** with higher magnification. The chemical compositions at different points presented in Fig. 8 obtained by EDS analysis are summarised in **Table 3**. Figure 8(a) represents the microstructure of the ironsand layer after sintering. Although ironsand boundaries were still clearly seen, they were intimately bonded by a perovskite phase (Points 3 and 4) and a lesser amount of silicate phase (Point 5). The reaction zone presented in Fig. 8(b) consisted of perovskite (Points 6 and 7) and calcium ferrite (Points 8 and 9) phases. Small amounts of iron oxides were also finely distributed in the reaction zone (Points 10 and 11). Figure 8(c) shows the microstructure of calcium ferrite penetrated into the CaO layer. Many calcium ferrite particles were aggregated together (as represented by Point 12) as well as finely distributed in the CaO layer (Point 13).

Enhanced sintering conditions (higher temperature and

Fig. 8. Higher magnification BSE images of the areas marked in Fig. 7.

longer sintering time) significantly improved the assimilation between ironsand and CaO and correspondingly resulted in a coarsened reaction zone. The formation of low melting point calcium ferrite phase in the Fe-rich subzone greatly promoted mass transfer and further penetration of calcium ferrite into the CaO layer. In contrast, the TiO_2 -rich subzone became wider and did not melt since TiO_2 stabilised the system of $\text{CaO-TiO}_2\text{-FeO}_x$ ¹⁰⁾ and hindered its dissolution any further (**Fig. 9**). The liquidus temperature increases gradually with the introduction of TiO_2 along the tie-line from $\text{CaO-Fe}_2\text{O}_3$ (mono calcium ferrite) to CaO-TiO_2 (perovskite).

3.3. Interaction between Ironsand and Dolomite

Investigation of the decomposition of dolomite showed that under CO_2 the reaction takes place in two distinct stages. Dolomite decomposes into calcite and magnesium oxide in the range of 550–800°C (Reaction 3), and then calcite dissociates (Reaction 4) in the range of 900–960°C.

Table 3. Elemental composition (wt%) of grains marked in Fig. 8 and corresponding phases.

Point no.	Fe	Ca	Ti	Mg	Si	Al	Phase identified
1	71.4	0.7	3.5	1.6	0.3	1.5	Titanomagnetite
2	69.4	1.1	4.4	1.4	0.5	1.6	Titanomagnetite
3	12.0	27.8	23.7	0.3	1.0	0.7	Perovskite
4	10.8	27.2	26.0	0.2	0.8	0.6	Perovskite
5	11.8	30.1	3.8	0.5	13.2	3.6	Silicate
6	29.0	29.4	9.4	0.4	1.6	1.1	Perovskite
7	26.9	28.2	10.7	0.5	1.4	1.0	Perovskite
8	36.6	28.6	2.4	0.4	0.8	1.4	Calcium ferrite
9	37.6	28.9	2.3	0.3	0.9	1.6	Calcium ferrite
10	65.5	3.6	0.5	4.4	0.2	1.7	Iron oxides
11	66.1	3.7	0.7	4.3	0.3	1.6	Iron oxides
12	37.3	28.6	1.8	0.7	0.6	1.4	Calcium ferrite
13	31.4	24.9	1.6	1.1	0.5	1.4	Calcium ferrite

Fig. 9. Liquidus temperature of CaO–TiO₂–FeO_x system.¹⁰⁾

Fig. 10. BSE images of the interaction couples of ironsand and dolomite sintered under different conditions. (a) 1 200°C, 4 min; (b) 1 200°C, 20 min; (c) 1 250°C, 4 min; (d) 1 300°C, 4 min.

As a result, the interaction between ironsand and dolomite layers practically involved ironsand with CaO and MgO. This was investigated in an atmosphere of $p\text{O}_2 = 0.5$ kPa in the temperature range of 1 200–1 325°C for different times. The morphological changes of the interaction couples with sintering temperature and time were observed, as shown in **Fig. 10**. A reaction zone was formed between

the two layers with an average thickness of $3.8 \mu\text{m}$ after sintering at 1 200°C for 4 min, as shown in **Fig. 10(a)**. Its interface towards the dolomite face was sometimes jagged, but with no sharp edges or straight sides. The thickness of the reaction zone increased to about $13 \mu\text{m}$ as sintering time increased to 20 min (**Fig. 10(b)**). **Figure 10(c)** shows the reaction zone in a specimen sintered for 4 min at 1 250°C with an average thickness of $7.8 \mu\text{m}$. It is common in **Figs. 10(a)–10(c)** that some of the reaction product penetrated into the dolomite layer, which became extreme in **Fig. 10(d)** where the specimen was sintered at 1 300°C for 4 min. The

formation of the reaction zone was significantly enhanced with a distinct increase in the average thickness to over 100 μm . The reaction zone consisted of several different sub-zones as shown by their difference in brightness.

Figure 11 shows the BSE images and EDS mapping of the interaction couple between ironsand and dolomite heated at 1 300°C for 20 min. Discrete titanomagnetite particles with very limited Ca and Mg concentrations were present within the ironsand layer (area 'a'). A coarsened (diffused edge on the dolomite side) reaction zone with broad penetration of Fe and Ti into the dolomite layers was observed. From the elemental distribution of the reaction zone, Fe, Ca, Ti and Mg were non-uniformly distributed. At least three subzones can be identified, one being the broadest part which penetrated into the dolomite layer and contained high levels of Fe and Ca, while another was close to the unreacted ironsand layer with relatively high Ti and Ca contents, which formed a discontinuous boundary on the ironsand layer. Between these two subzones was a band appearing similar to the perovskite band observed in the sintered iron-sand and CaO reaction couple, but containing a significant amount of Mg. The first broadest subzone was represented

by the areas 'c' and 'd' in the BSE image in Fig. 11, and the last two narrow subzones were included in area 'b'.

The BSE images of the four different typical areas in Fig. 11 are shown in **Fig. 12** at higher magnification. The chemical compositions at different points marked in Fig. 12 were examined by EDS analysis and summarised in **Table 4**. As shown in Fig. 12(a), the morphology of the ironsand layer after sintering at 1 300°C for 20 min was very similar to that occurring in sintered reaction couples of ironsand and MgO (Fig. 3). The ironsand particles remained intact and were weakly bonded by narrow necks. A small amount of silicate bonding phase (Points 3 and 4) contained relatively low concentrations of Ca and Mg, indicating that the assimilation between the ironsand particles which were located several particles away from the interface was not affected by the presence of dolomite. The concentrations of Mg and Ca in the relict titanomagnetite particles (Points 1 and 2) were also hardly changed.

Figure 12(b) shows the microstructure of the Ti-rich subzone and Mg-rich subzone in samples sintered at 1 300°C for 20 min. The Ti-rich subzone marked by Point 7 and next to the titanomagnetite (Points 5 and 6) proved to be com-

Fig. 11. BSE image and EDS mapping of an interaction couple between ironsand and dolomite sintered at 1 300°C for 20 min. The detailed information in areas *a* through *d* is presented in Fig. 12. (Online version in color.)

Fig. 12. BSE images of phases marked in Fig. 11.

Table 4. Elemental composition (wt%) of grains marked in Fig. 12 and corresponding phases.

Point no.	Fe	Ca	Ti	Mg	Si	Al	Phase identified
1	65.9	0.4	5.6	3.0	0.3	1.9	Titanomagnetite
2	68.1	0.2	4.8	2.6	0.3	1.4	Titanomagnetite
3	21.0	3.5	4.3	1.9	20.9	5.8	Silicate
4	16.7	5.7	5.2	1.6	22.8	7.3	Silicate
5	65.3	1.3	1.1	7.0	0.4	1.7	Titanomagnetite
6	67.5	0.5	1.5	4.1	0.3	1.6	Titanomagnetite
7	12.4	26.5	22.4	1.1	0.6	0.9	Perovskite
8	20.4	27.4	15.4	1.7	1.5	1.2	Perovskite
9	25.5	27.3	10.4	1.7	0.9	0.9	Perovskite
10	25.9	0.3	0.5	42.0	0.4	0.8	MgO–FeO
11	24.5	0.8	0.7	44.7	0.3	0.9	MgO–FeO
12	24.4	0.6	0.4	43.4	0.4	1.1	MgO–FeO
13	33.7	28.2	3.8	2.1	1.0	1.4	Calcium ferrite
14	36.9	28.7	1.8	1.8	0.5	1.3	Calcium ferrite
15	6.2	0.7	0.4	59.7	0.4	0.4	MgO–FeO
16	36.7	28.4	2.3	2.3	0.6	1.2	Calcium ferrite

plex perovskite phase containing some Fe. The phase with brightness between perovskite and titanomagnetite (Point 8), which was also found to be distributed in the dark grey area (Point 9), was another form of perovskite containing less Ti but more Fe. The Mg-rich band shown in Fig. 11 was seen to consist of round dark grey grains (Points 10 and 11), and contained mainly MgO–FeO solid solution. The microstructure of the subzone rich in Fe and Ca is presented in Fig. 12(c), which was found, as expected, to mainly consist of

Fig. 13. A diffusion model describing phase formation during sintering of an interaction couple between ironsand and dolomite. (Online version in color.)

calcium ferrite (Points 13 and 14) but also contained discrete fine particles of MgO–FeO solid solution (Point 12). Figure 12(d) shows the penetration of calcium ferrite particles into the dolomite layer. A large amount of fine calcium ferrite particles and MgO–FeO particles (Point 15) were distributed in the dolomite layer.

The mechanisms of phase formation in the interaction couple of ironsand and dolomite can be summarised in Fig. 13. During sintering, Mg^{2+} and Ca^{2+} ions from the dolomite (MgO and CaO) layer diffused towards the ironsand layer, while Fe^{2+} , Fe^{3+} and Ti^{4+} ions from ironsand diffused in the opposite direction into MgO and CaO. Consequently, the reaction zone which was rich in Ca, Fe, Mg and Ti was generated between the two layers. Since Ti^{4+} diffused at a slower rate than Fe^{2+} and Fe^{3+} , a perovskite phase was formed as a result of reaction between CaO and accumulated TiO_2 close to the relict ironsand layer. This perovskite acted as a barrier to the diffusion of Mg^{2+} ions, which accumu-

lated next to the perovskite layer and combined with Fe to form a FeO–MgO solid solution. In Fig. 12(a), the contents of Mg in silicate bonding phase and ironsand were low, since the presence of perovskite phase hindered the diffusion of Mg into ironsand layer. In contrast, in sintered ironsand–MgO couple shown in Fig. 3, Mg significantly diffused into ironsand layer and benefited the generation of silicate bonding phase. This FeO–MgO solid solution hindered further diffusion of CaO towards the ironsand layer. Finally, further phase formation was due to the relatively higher diffusion rates of Fe^{2+} and Fe^{3+} through the perovskite and MgO–FeO solution barriers, and Fe and Ca combined to form calcium ferrite phase close to the CaO–MgO layer. This mechanism explains why Mg and Ca can individually diffuse into the titanomagnetite matrix and even penetrate deeply into the ironsand layers, but very little diffuses into the ironsand layer from the MgO–CaO mixture. It also shows that the assimilation process developed mainly in the direction of the MgO–CaO layer through the diffusion of Fe.

With increasing sintering temperature, the calcium ferrite phase (low melting point) in the Fe-rich subzone started to melt first and promoted further spread of calcium ferrite into the dolomite layer, as shown in Fig. 11. The perovskite phase and MgO–FeO solid solution remained stable at the higher sintering temperature due to their higher melting points.

4. Conclusions

In this study, the reaction couples between ironsand and flux materials (CaO, MgO and dolomite) were sintered in an atmosphere of $p\text{O}_2 = 0.5$ kPa in the temperature range of 1 200–1 300°C for different times. The main conclusions are as follows.

(1) Mg^{2+} ions significantly diffused into the lattice of ironsand when the ironsand was sintered with MgO, which stabilised the system of FeO_x –MgO and hindered the assimilation of ironsand particles.

(2) During sintering of ironsand with CaO, a reaction zone consisting of perovskite and calcium ferrite occurred

between the two layers. When sintered at higher temperature (1 300°C), the ironsand particles were intimately bonded by mainly perovskite and a lesser amount of silicate phases. Partial melting of calcium ferrite phase greatly promoted mass transfer and further penetration of calcium ferrite into the CaO layer.

(3) In terms of sintering of ironsand with dolomite, perovskite and calcium ferrite were also generated in the reaction zone. A MgO–FeO solid solution was formed close to the perovskite phase, since the formation of perovskite phase hindered further diffusion of Mg^{2+} ions into the ironsand layer. Increasing sintering temperature significantly enhanced the penetration of calcium ferrite phase into the dolomite layer; whereas the perovskite phase and MgO–FeO solid solution remained at high sintering temperature due to their higher melting points, which hindered penetration of Ca and Mg into the ironsand layer and suppressed the bonding between ironsand particles.

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