Fundamentals of Silico-Ferrite of Calcium and Aluminium (SFCA) and SFCA-I Iron Ore Sinter Bonding Phase Formation: Effects of Titanomagnetite-based Ironsand and Titanium Addition

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The thermal decomposition of titanomagnetite-based ironsand, and the effects of ironsand addition on the formation of SFCA and SFCA-I iron ore sinter bonding phases, was investigated using *in situ* X-ray diffraction. Titanium incorporation into the SFCA and SFCA-I structures was investigated *via* phase equilibria experiments and subsequent *ex situ* characterisation. Increasing ironsand addition from 1.3 to 6.7 and to 13.8 mass% in an otherwise synthetic sinter mixture composition designed to form SFCA-I did not significantly affect the thermal stability range of SFCA-I (~1 373–1 523 K), nor did it significantly affect the maximum concentration of SFCA-I attained (42–46 mass%). The main effect of ironsand addition was a small reduction in the thermal stability range of another complex calcium-rich ferrite, γ -CFF. In comparison, increasing ironsand addition from 2.4 to 3.9 and to 11.6 mass% in an otherwise synthetic sinter mixture composition designed to form SFCA resulted in a decrease in the maximum SFCA-I concentration, from 30, to 24 and 16 mass%, respectively, with a corresponding increase in the concentration of SFCA (16, to 23 and 33 mass%). The phase equilibria studies revealed that SFCA can incorporate more titanium in its structure (up to 1.2 mass% TiO₂) than SFCA-I (0.6 mass% TiO₂). The 'total SFCA' (*i.e.* SFCA-I + SFCA) content decreased as the ironsand content increased, as well as there being a general shift to higher temperature of the total SFCA concentration curves. Such effects are likely to exert an influence on the physical properties of iron ore sinter, as well as affecting sintering fuel requirements.

KEY WORDS: iron ore sinter; ironsand; titanomagnetite; thermal decomposition; SFCA; SFCA-I; *in situ* X-ray diffraction; quantitative phase analysis; phase formation mechanisms; phase equilibria; Ti substitution.

1. Introduction

'SFCA' (Silico-Ferrite of Calcium and Aluminium) phases are key bonding materials within industrial iron ore sinter.¹⁾ Sinter is a major feedstock material of blast furnaces, utilized extensively worldwide in the production of steel from iron ore. Increased understanding of (i) the compositional and thermal stability of SFCA phases, (ii) their formation mechanisms, and (iii) the effect of different processing parameters on (i) and (ii) has the potential to improve the efficiency of the sintering process by being better able to predict optimal sintering conditions (*e.g.* temperature, oxygen partial pressure) required to produce high-quality product based on the chemical composition and physical characteristics of a given iron ore sinter mixture. Additionally, it may allow better prediction of the chemical and physical modifications of a particular iron ore sinter mixture required to produce high-quality product for given

sintering conditions.

The SFCA in iron ore sinter has been categorized in the literature on the basis of composition, morphology and crystal structure into two main types. The first is a high-Fe, low-Si form called SFCA-I which has a characteristic platy (also described as acicular) morphology. Mumme *et al.*²⁾ reported that an SFCA-I phase in industrial sinter contained 84 mass% Fe₂O₃, 13 mass% CaO, 1 mass% SiO₂ and 2 mass% Al₂O₃, and also synthesized SFCA-I material which had the composition 83.2 mass% Fe₂O₃, 12.6 mass% CaO and 4.2 mass% Al₂O₃. The second SFCA type is a low-Fe form called SFCA which is described as having a prismatic or columnar morphology. SFCA found in industrial sinters typically contains 60–76 mass% Fe₂O₃, 13–16 mass% CaO, 3–10 mass% SiO₂, 4–10 mass% Al₂O₃ and 0.7–1.5 mass% MgO.^{3,4)} Patrick and Pownceby⁵⁾ systematically resolved the equilibrium solid solution range and thermal stability of SFCA within the quaternary system Fe₂O₃–CaO–SiO₂–Al₂O₃ in air in the range 1 513 K to 1 663 K. Such a rigorous investigation of solid solution limits and thermal stability has not been performed for SFCA-I, with

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the study of Mumme *et al.*²⁾ the most detailed description of the stability of SFCA-I under equilibrium conditions. It has been suggested that a texture of intersecting microplates characteristic of SFCA-I imparts high strength and reducibility into iron ore sinter, and sinters containing significant amounts of this phase are of higher quality than those containing mostly SFCA.^{6,7)} The key to obtaining SFCA-I in sinter product is preserving it during the heating stage of the sintering process, since SFCA-I does not crystallize from melt during cooling.⁶⁾ A number of recent investigations^{8–14)} have utilised *in situ* powder X-ray diffraction (XRD) in order to establish the formation mechanisms of SFCA and SFCA-I under simulated sintering conditions from synthetic starting sinter mixtures heated in the range 298–1 623 K, under oxygen partial pressures (p_{O_2}) in the range 0.21 to 1×10^{-4} atm. XRD is an ideal technique to distinguish between SFCA and SFCA-I, since the crystal structures of the two phases are distinct.^{2,15)}

Recently, Bluescope's Port Kembla sinter plant has begun incorporating 2–3 mass% fine grained ($<150 \mu\text{m}$) New Zealand ironsand as a component of its iron ore sinter blend.¹⁶⁾ The ironsand is composed predominantly of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) containing 7.9 mass% TiO_2 , with minor amounts of hematite, ilmenite, quartz, pyroxene and aluminosilicates. Ironsand is a relatively cheap source of iron, and the introduction of a minor amount of titanium-bearing ore into the blast furnace burden has been demonstrated to extend blast furnace operating campaigns due to the formation of titanium carbonitrides on the hearth lining.¹⁷⁾ Early work by Bristow and Loo¹⁸⁾ found that addition of up to 2 mass% titanomagnetite did not affect sinter properties, but a bulk titanomagnetite content of greater than 3 mass% had a significant negative effect on the reduction degradation index (RDI). Paananen and Kinnunen also reported a negative effect on sinter RDI through the addition of rutile (TiO_2).¹⁹⁾ The effect of TiO_2 addition (in the form of analytical grade TiO_2) on the equilibrium sinter phases at $p_{O_2} = 5 \times 10^{-3}$ atm has recently been investigated, and reported that Ti existed mainly in perovskite, the phase concentration of which increased with increasing TiO_2 addition.²⁰⁾ This study also reported a small decrease in SFCA concentration of 45 to 42 mass% as the mass% of TiO_2 increased from 0 to 12 mass%. More recently, the effect of TiO_2 addition on the sintering behaviour of an iron ore sinter blend has been studied in laboratory tests by Dehghan-Manshadi *et al.*²¹⁾ Their results showed a considerable effect of TiO_2 on sinter strength, where the tumble index increased with increasing TiO_2 (up to 2 mass%). However, addition of more than 2 mass% TiO_2 to the blend decreased its overall strength. As with the study by Ren *et al.*,²⁰⁾ Dehghan-Manshadi *et al.* reported perovskite formation, with greater volume fractions obtained with increasing TiO_2 . Wang *et al.*¹⁶⁾ recently demonstrated that heating ironsand-doped sinter blends under reduced conditions caused individual ironsand particles to undergo assimilation beginning with diffusion of Ca from the sinter into the ironsand. This decreased the melting point of titanomagnetite which accelerated further assimilation and led to the formation of the perovskite phase.

Although the effects of titanomagnetite ironsand and TiO_2 addition on bulk sinter properties have been investigated, the effect of ironsand addition on the thermal stability

ranges of the SFCA-I and SFCA phases during heating, and the variations of the concentrations of SFCA-I, SFCA and precursor phases as a function of temperature, are not known in detail. The first aim of the current investigation was to determine the effect of ironsand addition on SFCA and SFCA-I phase formation during heating, with titanomagnetite added to two synthetic mixtures, the first having a bulk composition designed to form SFCA-I, and the other designed to form SFCA. *In situ* XRD measurements with subsequent Rietveld refinement-based quantitative phase analysis (QPA) was employed to elucidate phase evolution during heating. As part of the study, the thermal decomposition of New Zealand ironsand was also characterized in order to understand how the breakdown may influence the formation of SFCA and SFCA-I during heating. In addition, other than Ti being identified as a very minor constituent in SFCA-I by Mumme *et al.*²⁾ it is unclear as to whether Ti substitutes to any significant extent into either the SFCA or SFCA-I crystal structures. The second aim of the current investigation was to determine the extent of substitution of Ti into the SFCA and SFCA-I structures by conducting phase equilibration experiments where synthetic SFCA-I and SFCA starting compositions were doped with TiO_2 . The samples were subject to equilibration at high temperature followed by *ex situ* quantitative measurements to determine the degree of Ti incorporation.

2. Experimental

2.1. *In situ* XRD Sample Preparation

The ironsand used here was sourced from Bluescope and has previously been characterised in detail.¹⁶⁾ In summary, its bulk composition in terms of oxides is 36.0 mass% FeO, 43.4 mass% Fe_2O_3 (58.3 mass% total Fe), 7.9 mass% TiO_2 , 0.6 mass% CaO, 0.4 mass% Al_2O_3 , 2.3 mass% SiO_2 , 3.1 mass% MgO (minor amounts of Cr_2O_3 , V_2O_5 , MnO, ZrO_2 , P_2O_5 and ZnO also present), and its mineral phase composition determined by XRD is 84.1, 1.7, 3.0 and 0.5 mass% titanomagnetite, ilmenite (FeTiO_3), hematite (Fe_2O_3) and quartz (SiO_2), respectively, with the remaining 10.7 mass% being poorly crystalline or low abundance material comprised mainly of pyroxene and aluminosilicates. The titanomagnetite is assigned a formula of $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$, based on results from quantitative electron probe microanalysis (EPMA). The ironsand was micronized separately and added in progressively higher amounts to (i) the base SFCA-I mixture – bulk composition 83.2 mass% Fe_2O_3 , 12.6 mass% CaO and 4.2 mass% Al_2O_3 – previously investigated in detail by Webster *et al.*,¹²⁾ and (ii) the base SFCA mixture – bulk composition 77.36 mass% Fe_2O_3 , 14.08 mass% CaO, 3.56 mass% SiO_2 and 5 wt% Al_2O_3 – previously investigated by Scarlett *et al.*^{8,9)} and Webster *et al.*^{10,11,14)} It is important to note the base SFCA-I and SFCA mixtures were themselves composed of hematite, calcite (CaCO_3), quartz and gibbsite ($\text{Al}(\text{OH})_3$).

The ironsand/SFCA-I and ironsand/SFCA samples were mixed under acetone in a mortar and pestle with an intermediate drying and remixing stage to ensure homogenization. Three ironsand/SFCA-I samples were prepared, with ironsand contents of 1.3, 6.7 and 13.8 mass%. This equates to levels of 0.1, 0.5 and 1 mass% TiO_2 in the mixtures.

Importantly, the bulk Fe, Ca, and Al ratios were maintained at their pre-doped SFCA-I ratios by adding additional calcite and gibbsite as necessary after addition of the ironsand. It is also important to keep in mind that the compositions were designed to model the reactive ultrafine (<1 mm) coating component of a sinter mix (shown schematically in Ref. 10), rather than being representative of the bulk composition of a sinter blend containing coarse nuclei (up to 6.3 mm in size), gangue and flux particles. Three ironsand/SFCA samples were also prepared, with ironsand contents of 2.4, 3.9 and 11.6 mass% (equivalent to 0.2, 0.3 and 0.9 mass% TiO_2).

2.2. *In situ* XRD Experimentation and Quantitative Phase Analysis

For each of the ironsand/SFCA-I mixtures, as well as the unmixed, micronized ironsand, *in situ* XRD experiments were performed using an INEL diffractometer, which incorporates a CPS120 position sensitive detector allowing for simultaneous collection of up to 120° 2θ of diffraction data. The Co tube was operated at 40 kV and 35 mA. An Anton Paar HTK10 high-temperature chamber employing a Pt resistance strip heater containing a sample well measuring $\sim 20 \times 7 \times 0.2$ mm was fitted to the diffractometer. Samples were heated over the range 298–1 623 K under a flow of a 0.5 vol pct O_2 in N_2 gas mixture (to give a nominal oxygen partial pressure of $p\text{O}_2 = 5 \times 10^{-3}$ atm). The oxygen partial pressure was chosen based on the work of Hsieh and Whiteman, who determined that this $p\text{O}_2$ maximized the formation of Ca-rich ferrites whilst still producing mineral assemblages similar to those found in industrial sinters.²²⁾ XRD data were collected over the range $10^\circ \leq 2\theta \leq 120^\circ$ continuously throughout heating, with individual datasets collected for 1 min.

For the ironsand/SFCA mixtures, *in situ* synchrotron XRD (S-XRD) experiments were performed on the powder diffraction beamline at the Australian Synchrotron.²³⁾ An Anton Paar HTK 2 000 high-temperature chamber employing a Pt resistance strip heater was fitted to the beamline. XRD data were collected over the range $6^\circ \leq 2\theta \leq 86.5^\circ$ continuously throughout heating, with individual datasets collected for 1 min, using an X-ray wavelength of 1.1044 Å calibrated using LaB6 (NIST 660b line position standard). The superior angular resolution of the synchrotron data, compared to the laboratory INEL data, is beneficial to distinguish between SFCA and SFCA-I which have closely spaced reflections. The superior peak-to-background ratio of synchrotron data also assists in identifying phases with low abundance.

For each *in situ* experiment a heating rate of 20 K min^{-1} was used from 298–873 K. The rate was then reduced to 10 K min^{-1} for the 873–1 623 K interval which corresponded to the period of Ca-rich ferrite phase formation and decomposition. The temperature was measured by a Pt/PtRh10% thermocouple connected to the underside of the platinum strip directly underneath the sample. The time–temperature profile used for these experiments is significantly slower than those encountered in industrial sintering. It was chosen so as to monitor phase formation with reasonable temperature resolution and to provide XRD data with reasonable counting statistics in order to establish trends in phase behaviour with increasing ironsand concentration.

The temperatures of phase formation/transformation given throughout the manuscript are those at the start – which is when the temperatures were automatically recorded – of the relevant data set. The uncertainty in these temperature values, therefore, was the difference between the temperatures at the start of successive data sets. The decomposition of precursor phases and the formation of new phases as the experiments progressed was visualized by stacking the datasets to produce plots of accumulated data with temperature plotted vs 2θ , viewed down the intensity axis.

Rietveld refinement-based QPA was performed on the individual datasets using TOPAS (Version 5).²⁴⁾ The crystal structure data of Blake *et al.*, Maslen *et al.*, Saalfeld and Wedde, Lager *et al.*, Schulz and Tscherry, Oftedal, Berastegui *et al.*, Decker and Kasper, Arakcheeva *et al.*, Arakcheeva and Karpinskii, Mumme *et al.*, Hamilton *et al.*, Hamilton, Wechsler *et al.*, Pecharroman *et al.*, Becerro *et al.* and Pauling were used for Fe_2O_3 , CaCO_3 , $\text{Al}(\text{OH})_3$, $\alpha\text{-SiO}_2$, $\beta\text{-SiO}_2$, CaO , $\text{C}_2(\text{F}_{1-x}\text{A}_x)$, CF, CFA, $\gamma\text{-CFF}$, SFCA-I, SFCA, Fe_3O_4 , $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$, $\gamma\text{-Fe}_2\text{O}_3$, perovskite and Fe_2TiO_5 , respectively.^{2,15,25–39)} The use of the QPA algorithm embodied in TOPAS returns relative, rather than absolute, concentrations for crystalline phases in a system if amorphous material, including melt phases, are present. Previous work has demonstrated that amorphous Al_2O_3 is present in these systems after the decomposition of $\text{Al}(\text{OH})_3$.^{8–14)} Therefore, absolute phase concentrations as a function of temperature were determined, *via* an ‘external standard’ methodology.¹²⁾

2.3. Phase Equilibria Experiments and *Ex situ* Characterisation

Table 1 shows the bulk composition of the samples in terms of mass% oxides and elements. TiO_2 was added to the base SFCA and SFCA-I mixtures described in Section 2.1 in the form of a 94 mass% rutile/6 wt% anatase powder (Aldrich, 99.99%). Approximately 0.5 g of each sample was pelletised and heated at temperature (1 513 K for the SFCA-I-1 TiO_2 , -2 TiO_2 , -3 TiO_2 samples, and 1 533 K for the SFCA-1 TiO_2 , -2 TiO_2 and -3 TiO_2 samples, with both temperatures below the melting points) for 48 hr (with intermediate grinding and re-pelleting after 24 hr) in a platinum crucible in a vertical tube furnace in air. The samples were confirmed to be at equilibrium by establishing that XRD

Table 1. Nominal compositions, in mass% oxides, of the mixtures used in the phase equilibria experiments (all Ti added as TiO_2) designed to determine the extent of substitution of Ti into SFCA and SFCA-I.

Sample	Concentration (oxide mass%)				
	Fe_2O_3	CaO	SiO_2	Al_2O_3	TiO_2
SFCA-I-1 TiO_2	82.32	12.48	–	4.20	1.00
SFCA-I-2 TiO_2	81.49	12.36	–	4.16	2.00
SFCA-I-3 TiO_2	80.66	12.23	–	4.11	3.00
SFCA-1 TiO_2	76.59	13.94	3.52	4.95	1.00
SFCA-2 TiO_2	75.81	13.80	3.49	4.90	2.00
SFCA-3 TiO_2	75.04	13.66	3.45	4.85	3.00

patterns collected for the samples after 24 hrs heating, and after 48 hrs, were the same. The temperature adjacent to the crucible was measured using a Pt/PtRh13% thermocouple connected to an ice-point cell, and temperatures are considered accurate to ± 10 K. Samples were rapidly quenched by dropping the crucible to the cold end of the furnace. Samples were crushed and prepared for *ex situ* EPMA, which was performed using a JEOL JXA-8900R Superprobe. Hematite, wollastonite (CaSiO_3 , CS), “Magalox” (a synthetic spinel, composition MgAl_2O_4) and rutile were used as standards for the microprobe analyses which were conducted in wavelength dispersive mode using an accelerating voltage of 15 kV, a beam current of 20 nA, a beam diameter of 5 μm and counting times of 15 sec on the peak and 7.5 sec on the background.

3. Results and Discussion

3.1. *In situ* Thermal Decomposition of Ironsand

Figure 1 shows a plot of accumulated *in situ* XRD data, viewed down the intensity axis and with temperature plotted vs 2θ , for the experiment performed to examine the thermal decomposition of the ironsand sample. Reflections for $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ (ICDD card no. 01-075-1374 is the closest match), Fe_2O_3 (ICDD no. 33-0664) and quartz (SiO_2 , ICDD 33-1161) were observed at room temperature. Reflections for FeTiO_3 (ICDD 29-0733) are closely adjacent to the Fe_2O_3 reflections, and are therefore not separately labeled in Fig. 1. Above ~ 573 K, maghemite ($\gamma\text{-Fe}_2\text{O}_3$, ICDD 01-076-3169) reflections were observed, above ~ 973 K reflections for pseudobrookite (Fe_2TiO_5 , ICDD 41-1432), and above ~ 1523 K reflections from a spinel phase (designated Fe_3O_4 because the concentrations of Ti and other possible impurity elements in this phase are unknown).

Figure 2 shows the Rietveld fit for the ironsand sample at 298 K, and Fig. 3 shows the results of the Rietveld refinement-based QPA for the unmixed ironsand sample over the range 298–1623 K. Notably, oxidation of $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ to $\gamma\text{-Fe}_2\text{O}_3$ was extensive by 653 K (*i.e.* the concentration of $\gamma\text{-Fe}_2\text{O}_3$ at this temperature was 59 mass%), and the decrease in $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ concentration in the range 505–653 K was

Fig. 1. *In situ* XRD data collected for the New Zealand ironsand sample, viewed down the intensity axis, over the range 298–1623 K at $p_{\text{O}_2} = 5 \times 10^{-3}$ atm. (Online version in color.)

61 mass%). This suggests that the Ti was incorporated into the $\gamma\text{-Fe}_2\text{O}_3$ structure to form a titanomaghemite phase. In the range 653–831 K the $\gamma\text{-Fe}_2\text{O}_3$ concentration initially reaches a plateau before further oxidation of $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ results in the formation of additional Fe_2O_3 and minor FeTiO_3 . In the range 860–1070 K, $\gamma\text{-Fe}_2\text{O}_3$ converts to Fe_2O_3 (*i.e.* hematite) and, similar to the oxidation of $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ to $\gamma\text{-Fe}_2\text{O}_3$, the conversion is effectively complete with the result being titanium-bearing Fe_2O_3 and minor ferrous pseudobrookite (Fe_2TiO_5). Finally, at $T > \sim 1523$ K the Fe_2O_3 reduces to titanium-bearing magnetite (designated as Fe_3O_4 in Figs. 1 and 3 since the Ti concentration in the phase is unknown).

3.2. Effect of Ironsand on SFCA-I Formation in Mixtures Designed to form SFCA-I

Figure 4 shows the plot of accumulated *in situ* XRD data for the 6.7 mass% ironsand/SFCA-I mixture (0.5 mass% TiO_2). Reflections for Fe_2O_3 , $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$, CaCO_3 (ICDD 5-0586) and $\text{Al}(\text{OH})_3$ (ICDD 33-0018) were observed at room temperature. Due to their low abundance (< 0.1 mass%) in this mixture, reflections for FeTiO_3 and SiO_2 were not observed. The first event was the decomposition

Fig. 2. Rietveld fit to the dataset collected for the ironsand sample at 298 K. Experimental data are shown as open circles, the calculated pattern a continuous solid line and the difference pattern the solid line below. The vertical lines are the Bragg reflection markers for (upper to lower) Fe_2O_3 , SiO_2 , $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$, FeTiO_3 and the Pt sample stage. (Online version in color.)

Fig. 3. Results of Rietveld-based QPA showing absolute phase concentrations as a function of temperature, for the ironsand sample. (Online version in color.)

Fig. 4. *In situ* XRD data collected for the 6.7 mass% ironsand/SFCA-I mixture. (Online version in color.)

of $\text{Al}(\text{OH})_3$ to amorphous Al-oxide which was complete by 591 K. Then, CaCO_3 decomposed to CaO (ICDD 37-1497), which was complete by 936 K. Similar to what was observed for the ironsand sample discussed in Section 3.1, oxidation of $\text{Fe}_{2.73}\text{Ti}_{0.27}\text{O}_4$ to $\gamma\text{-Fe}_2\text{O}_3$ was complete by 672 K, with the conversion of $\gamma\text{-Fe}_2\text{O}_3$ at higher temperature resulting in the formation of additional (4.4 mass%) and Ti-bearing Fe_2O_3 .

The first Ca-rich ferrite to form was alumina-substituted dicalcium ferrite (designated hereafter as $\text{C}_2(\text{F}_{1-x}\text{A}_x)$ (ICDD 01-089-8667) at ~ 1053 K, followed by CF (*i.e.* monocalcium ferrite, where C = CaO and F = Fe_2O_3 , ICDD 3-065-1333) and CFA (a phase with average composition 71.7 mass% Fe_2O_3 , 12.9 mass% CaO , 0.3 mass% SiO_2 and 15.1 mass% Al_2O_3 ,⁹ ICDD 1-077-0676) at ~ 1233 K. As the temperature increased further, SFCA-I (ICDD 52-1258) and $\gamma\text{-CFF}$ (nominal composition $\text{Ca}_{3.0}\text{Fe}_{14.82}\text{O}_{25}$, ICDD 1-078-1675) formed, at ~ 1373 K. Incongruent melting (*i.e.* solid 1 $\rightarrow$ liquid + solid 2) of SFCA-I, which was complete by 1535 K (*i.e.* liquidus temperature), produced a phase assemblage of Fe_3O_4 (designated so because of the low overall Ti concentration in this mixture (0.5 mass%), and the significant level of Ca and Al substitution into the Fe_3O_4 which has been observed in previous work¹⁰) in a Fe_2O_3 -(Fe_3O_4)- CaO - SiO_2 - Al_2O_3 -rich melt. In addition, similar to the results of Webster *et al.*,¹² i) decomposition of $\gamma\text{-CFF}$ resulted in the formation of an unknown phase (observed in the range 1465–1511 K) for which no suitable matches in the ICDD database could be found, and ii) SFCA was not observed. Similar events were observed in the *in situ* XRD data collected for the 1.3 and 13.8 mass% ironsand/SFCA-I mixtures. There was no evidence in the *in situ* XRD data for the formation of perovskite, which was the major Ti-bearing phase reported in the studies of Zhang *et al.*,¹⁶ Ren *et al.*²⁰ and Dehghan-Manshadi *et al.*²¹ Minor amounts of perovskite may be below the detection limit of this laboratory-based experimentation.

Figure 5 shows the results of the Rietveld refinement-based QPA for the 1.3 (Fig. 5(a)), 6.7 (Fig. 5(b)) and 13.8 mass% (Fig. 5(c)) ironsand/SFCA-I mixtures. The increasing concentration of ironsand did not significantly affect

Fig. 5. Results of the Rietveld-based QPA for the (a) 1.3 mass%, (b) 6.7 mass% and (c) 13.8 mass% ironsand/SFCA-I mixtures over the range 298–1623 K. (Online version in color.)

the thermal stability range of SFCA-I, extending from 1370–1531 K for the 1.3 mass% mixture to 1366–1535 K for the 13.8 mass% mixture. In addition, the maximum SFCA-I concentration attained was not markedly different between experiments; this was 42, 46 and 45 mass% for the 1.3, 6.7 and 13.8 mass% mixtures, respectively. The main effect of ironsand addition was a small reduction in the thermal stability range of $\gamma\text{-CFF}$, from 1405 to 1496 K in the 1.3 mass% ironsand mixture, to 1405 to 1472 K in the 13.8 mass% ironsand mixture. The scatter in Fe_3O_4 concentration observed for the 1.3 mass% ironsand mixture, in particular, is due to poor particle statistics in the region where significant melt generation has occurred (*i.e.* a relatively small number of Fe_3O_4 crystallites in a significant amount of melt phase).^{12,13} The amount of Fe_3O_4 which formed, therefore, was similar in each experiment (~ 25 mass%).

In each of the SFCA-I/ironsand mixtures investigated here, the maximum concentrations of the precursor phases

(i.e. Fe_2O_3 , $\text{C}_2(\text{F}_{1-x}\text{A}_x)$, CF and CFA) were similar in each experiment, further suggesting a lack of effect of the iron-sand on SFCA-I formation and stability. The di- and mono-calcium ferrites are known to incorporate ~ 5 mass% TiO_2 substituting for Fe_2O_3 ,⁴⁰⁾ and it is likely that the Ti has been primarily incorporated into these early-formed phases. The main implication of the results presented here in Section 3.2 is that any degradation in sinter quality with increasing iron-sand concentration, up to levels of 13.8 mass% addition of iron-sand to the ultrafine component of a sinter blend, is not likely to be due to a reduction in the abundance of SFCA-I in the final sinter microstructure. Further work is required to establish at what level of iron-sand addition a significant effect on SFCA-I formation becomes important.

3.3. Effect of Ironsand on SFCA-I and SFCA Formation in Mixtures Designed to form SFCA

Figure 6 shows the plot of accumulated *in situ* XRD data for the 11.6 mass% ironsand/SFCA mixture (0.9 mass% TiO_2). Similar phases and phase formation/decomposition events were observed here when compared to what was observed in Fig. 4, with the exception of (i) the presence of quartz (ICDD 33-1161), (ii) the detection of minor perovskite (designated as $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, ICDD 01-072-4765) in the experiment performed for the 11.6 mass% mixture, (iii) the formation/decomposition of SFCA (ICDD 46-0037), and (iv) the lack of formation of significant γ -CFF. With respect to quartz, the transformation of α - SiO_2 to β - SiO_2 was completed by 860 K which is within experimental uncertainty of the 846 K value reported by Kihara⁴¹⁾ and gives confidence in the accuracy of the temperature measurements.

Figure 7 shows the results of the Rietveld refinement-based QPA for the 2.4 (Fig. 7(a)), 3.9 (Fig. 7(b)) and 11.6 mass% (Fig. 7(c)) ironsand/SFCA mixtures. Most significantly, increasing ironsand concentration affected both the thermal stability range and the maximum concentration of the SFCA-I and SFCA phases. For SFCA-I, the thermal

stability range was reduced from between ~ 1307 – 1521 K for the 2.4 mass% mixture to between ~ 1346 – 1513 K for the 11.6 mass% mixture, and the maximum concentration reduced from 30, to 24 and 16 mass% for the 2.4, 3.9 and 11.6 mass% ironsand mixtures, respectively. For SFCA, the thermal stability range was reduced from ~ 1354 – 1521 K for the 2.4 mass% mixture to ~ 1442 – 1560 K for the 11.6 mass% mixture, whereas the maximum concentration increased from 16, to 23 and 33 mass% for the 2.4, 3.9 and 11.6 mass% ironsand mixtures, respectively.

The trends in maximum SFCA-I and SFCA concentrations suggest that SFCA is likely to incorporate more Ti in its crystal structure than SFCA-I, and the EPMA compositional results summarised in Tables 2 and 3 confirm this hypothesis. SFCA-I contains up to 0.6 mass% TiO_2 , and SFCA 1.2 mass% in air and at equilibrium. The results also confirm the presence of Ti in Fe_2O_3 , as well as indicating that the perovskite contains a significant amount of Fe.

Fig. 6. *In situ* S-XRD data collected for the 11.6 mass% ironsand/SFCA mixture. (Online version in color.)

Fig. 7. Results of the Rietveld-based QPA for the (a) 2.4 mass%, (b) 3.9 mass% and (c) 11.6 mass% ironsand/SFCA mixtures over the range 298–1623 K. (Online version in color.)

Table 2. Summary of the EPMA compositional results for the products of the phase equilibria experiments (all Ti added as TiO₂) performed for SFCA-I-TiO₂, SFCA-I-2TiO₂ and SFCA-I-3TiO₂ at 1 513 K.

Phase	Composition (oxide mass%)					Total
	Fe ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	
<i>SFCA-I</i>						
SFCA-I-1TiO ₂	82.14 (0.37)	13.33 (0.08)	0.04 (0.01)	4.74 (0.06)	0.33 (0.02)	100.59 (0.37)
SFCA-I-2TiO ₂	82.15 (0.43)	13.17 (0.07)	0.04 (0.01)	5.08 (0.04)	0.43 (0.05)	100.88 (0.40)
SFCA-I-3TiO ₂	80.41 (0.69)	13.03 (0.31)	0.04 (0.01)	6.29 (0.57)	0.63 (0.23)	100.41 (0.40)
<i>Fe₂O₃</i>						
SFCA-I-1TiO ₂	97.88 (0.64)	0.36 (0.06)	0.00 (0.01)	1.00 (0.06)	0.97 (0.12)	100.21 (0.63)
SFCA-I-2TiO ₂	98.08 (0.44)	0.38 (0.08)	0.00 (0.01)	1.13 (0.02)	1.15 (0.03)	100.74 (0.43)
SFCA-I-3TiO ₂	97.48 (0.37)	0.31 (0.07)	0.00 (0.01)	1.34 (0.13)	1.25 (0.13)	100.38 (0.41)
<i>Perovskite</i>						
SFCA-I-1TiO ₂	17.80 (2.56)	39.05 (1.62)	0.06 (0.02)	0.74 (0.19)	41.08 (2.20)	98.73 (1.12)
SFCA-I-2TiO ₂	14.01 (1.92)	40.12 (0.67)	0.13 (0.04)	0.51 (0.13)	44.87 (1.75)	99.63 (0.53)
SFCA-I-3TiO ₂	11.71 (1.59)	40.05 (1.04)	0.09 (0.02)	0.53 (0.15)	46.15 (1.62)	98.52 (0.82)

Table 3. Summary of the EPMA compositional results for the products of the phase equilibria experiments (all Ti added as TiO₂) performed for SFCA-1TiO₂, SFCA-2TiO₂ and SFCA-3TiO₂ at 1 533 K. The numbers in parentheses are the standard deviation of the ~10 point analyses for each phase. Where numbers in parentheses are not present, the composition is from an individual point.

Phase	Composition (oxide mass%)					Total
	Fe ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	
SFCA						
SFCA-1TiO ₂	75.92 (0.69)	14.45 (0.17)	3.36 (0.17)	5.44 (0.11)	1.17 (0.03)	100.34 (0.51)
SFCA-2TiO ₂	74.71 (0.50)	14.72 (0.20)	3.66 (0.24)	5.93 (0.23)	1.23 (0.08)	100.25 (0.47)
SFCA-3TiO ₂	73.95 (1.67)	14.99 (0.43)	3.94 (0.51)	6.82 (0.83)	1.17 (0.10)	100.86 (0.52)
Fe ₂ O ₃						
SFCA-1TiO ₂	97.47 (0.67)	0.39 (0.04)	0.02 (0.02)	1.02 (0.02)	1.62 (0.02)	100.52 (0.41)
SFCA-2TiO ₂	96.34 (0.74)	0.53 (0.14)	0.02 (0.02)	1.10 (0.04)	1.79 (0.03)	99.77 (0.82)
SFCA-3TiO ₂	98.31 (0.43)	0.45 (0.04)	0.02 (0.02)	1.08 (0.02)	1.92 (0.07)	101.78 (0.69)
Perovskite						
SFCA-1TiO ₂	16.31	40.76	2.59	0.55	38.94	99.15
SFCA-2TiO ₂	17.63 (4.48)	39.26 (2.17)	2.67 (0.36)	0.79 (0.47)	38.76 (3.95)	99.12 (1.08)
SFCA-3TiO ₂	15.04 (1.60)	39.82 (1.22)	2.33 (0.21)	0.59 (0.09)	40.49 (1.72)	98.28 (1.18)

Perovskite in the CaO – iron oxide – TiO₂ system in air can accommodate as much as 83% of Fe in substitution for Ti.⁴⁰⁾ The Ti substitution mechanism(s) within SFCA and SFCA-I are unclear from the data in Tables 2 and 3, and further work is required to determine this.

The trends in maximum concentrations may also help to explain the observations of Bristow and Loo¹⁸⁾ – *i.e.* that titanomagnetite content of greater than 3 mass% had a significant negative effect on sinter properties – since SFCA-I is generally considered to be the more desirable bonding phase for promoting sinter quality than SFCA. Furthermore, **Fig. 8** shows a plot of the ‘total SFCA’ concentration (*i.e.* SFCA-I + SFCA) produced for each of the ironsand/SFCA mixtures. The area under the curve decreases as the ironsand

content in the starting sinter mixture increases, and so the likelihood of retaining the key bonding matrix materials in the sinter microstructure during heating are also reduced. Figure 8 also shows that in order to maximise the amounts of bonding matrix material during heating, higher sintering temperatures would be required as the ironsand content is increased. This would likely have implications for fuel (*i.e.* coke breeze) consumption and overall productivity. As well, it is noted that Bristow and Loo¹⁸⁾ postulated that the addition of titanium decreased the fracture toughness of the retained glass, typically the weakest phase in iron ore sinter, thereby increasing the vulnerability of the sinter to crack propagation and lowering the RDI. It is important, therefore, to investigate the effect of ironsand addition on phase for-

Fig. 8. Total SFCA (i.e. SFCA-I + SFCA) concentration as a function of temperature for the 2.4, 3.9 mass% and 11.6 mass% ironsand/SFCA mixtures.

mation during cooling using *in situ* diffraction, to determine the nature and abundance of phases (including SFCA) which crystallise from the melt during cooling, thereby affecting the retained glass.

4. Conclusion

The effects of ironsand addition on the thermal stability and concentration of SFCA-I and SFCA iron ore sinter bonding phases during heating were determined using *in situ* diffraction techniques with subsequent Rietveld refinement-based quantitative phase analysis. Results showed that, for starting sinter mixtures with bulk compositions designed to form SFCA-I, increasing the ironsand concentration up to 13.8 mass% did not significantly affect the thermal stability range of SFCA-I or the maximum concentration of SFCA-I. However, for starting sinter mixtures with bulk compositions designed to form SFCA, increasing the ironsand concentration from 2.4 to 3.9 and 11.6 mass% resulted in a reduction in the thermal stability range of both SFCA and SFCA-I, and caused a reduction in the amount of SFCA-I with an associated increase in the amount of SFCA. Phase equilibria experiments showed that SFCA accommodates more Ti in its crystal structure than SFCA-I. Future work will investigate the effect of ironsand addition/Ti on phase formation during cooling, since retained glass and SFCA phases which have crystallized from the melt are a significant component of the microstructure of typical industrial sinters.

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