Fundamentals of Silico-Ferrite of Calcium and Aluminium (SFCA) Iron Ore Sinter Bonding Phase Formation: Effects of Basicity and Magnesium on Crystallisation during Cooling

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The effects of basicity and Mg addition on the crystallisation during cooling of complex Ca-rich ferrite iron ore sinter bonding phases SFCA and Fe-rich SFCA was investigated using *in situ* synchrotron X-ray diffraction. In synthetic iron ore sinter mixtures, cooling of a high temperature ($T = 1\,623\text{ K}$) assemblage comprising magnetite and melt showed that decreasing basicity from $B = 4.0$ to 3.0 and 2.5 resulted in the formation of a Fe-rich SFCA phase being suppressed, with SFCA being the only Ca-rich ferrite phase to form initially from the melt at $B = 2.5$. Increasing the Mg concentration in the sinter mixtures to 1 and $3\text{ wt\%}$ MgO resulted in an overall suppression of the amount of Ca-rich ferrite phase formation. However, Mg addition caused the formation of Fe-rich SFCA to be favoured over SFCA, with SFCA not observed to form at all during cooling in the $3\text{ wt\%}$ MgO mixture. The absence of SFCA in the high-Mg experiment was rationalised on the basis that the Fe-rich SFCA structure accommodates more Fe^{2+} than the SFCA structure, thereby stabilising Fe-rich SFCA relative to SFCA through replacement substitution of Fe^{2+} by Mg^{2+} . Observation of Fe-rich SFCA in sinter may be an indicator of localised high basicity, and/or, high Mg concentration, within a sinter blend.

KEY WORDS: iron ore sinter; *in situ* synchrotron X-ray diffraction; complex Ca-rich ferrite iron ore sinter bonding phases; SFCA; crystallisation during cooling; $\text{CaO}:\text{SiO}_2$ ratio; Mg addition.

1. Introduction

‘SFCA’ (Silico-Ferrite of Calcium and Aluminium) phases are key bonding materials within industrial iron ore sinter.¹⁾ Sinter is utilised extensively worldwide in the production of steel from iron ore and iron ore sinter typically constitutes more than 60% of the ferrous burden in modern blast furnaces in Japan and most of the blast furnaces in Europe.²⁾ 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 required to produce high-quality product based on the chemical composition and physical characteristics of a given iron ore sinter blend.

The SFCA in iron ore sinter has been categorised in the scientific literature on the basis of composition, morphology and crystal structure into (i) a high-Fe, low-Si form called SFCA-I which has a characteristic platy (also described as acicular) morphology.³⁾ Mumme *et al.*⁴⁾ reported that

an SFCA-I phase in industrial sinter contained $84\text{ mass\%}$ Fe_2O_3 , $13\text{ mass\%}$ CaO , $1\text{ mass\%}$ SiO_2 and $2\text{ mass\%}$ Al_2O_3 , and also synthesised Si-free SFCA-I material which had the composition $83.2\text{ mass\%}$ Fe_2O_3 , $12.6\text{ mass\%}$ CaO and $4.2\text{ mass\%}$ Al_2O_3 . Sasaki and Hida determined that acicular calcium ferrite – which we consider to be equivalent to SFCA-I – does not form *via* crystallisation from melt during cooling;⁵⁾ and (ii) a low-Fe form called SFCA which is described as having a prismatic or columnar morphology. SFCA found in industrial sinters typically contains $60\text{--}76\text{ mass\%}$ Fe_2O_3 , $13\text{--}16\text{ mass\%}$ CaO , $3\text{--}10\text{ mass\%}$ SiO_2 , $4\text{--}10\text{ mass\%}$ Al_2O_3 and $0.7\text{--}1.5\text{ mass\%}$ MgO .^{6,7)} Patrick and Pownceby⁸⁾ systematically resolved the equilibrium solid solution range and thermal stability of SFCA within the quaternary system $\text{Fe}_2\text{O}_3\text{--CaO--SiO}_2\text{--Al}_2\text{O}_3$ in air in the range $1\,513\text{ K}$ to $1\,663\text{ K}$. It should be noted that differentiation of SFCA-I and SFCA based on what may be an oversimplified morphological description of the two phases may be problematic, and the authors consider that differentiation should be made based on diffraction and/or compositional data.

An additional phase, referred to as Fe-rich SFCA, was identified by Webster *et al.*⁹⁾ This phase was observed during *in situ* X-ray diffraction (XRD) studies where the temperature reached $1\,623\text{ K}$, resulting in a large amount of

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melt formation and a final high temperature phase assemblage consisting of magnetite + melt. During subsequent cooling and melt crystallisation the occurrence of the previously unknown Fe-rich SFCA phase was revealed (Fig. 1). **Figure 2(a)** is a backscattered electron micrograph showing Fe-rich SFCA in a synthetic sample prepared by quenching from 1 488 K while cooling under an oxygen partial pressure (p_{O_2}) of 5×10^{-3} atm.⁹⁾ Quantitative electron probe microanalysis (EPMA) gave an average composition of 84.2 mass% Fe_2O_3 , 9.6 mass% CaO, 1.8 mass% SiO_2 and 5.7 mass% Al_2O_3 , indicating it is distinct from SFCA-I and SFCA.⁹⁾ **Figure 3** shows laboratory XRD data collected for this quenched synthetic sample; the absence of the characteristic SFCA-I peaks at d-spacing = 10.7 and 9.7 Å (9.6 and 10.6° 2 θ), and the characteristic SFCA peaks at d-spacing = 8.2 and 7.6 Å (12.5 and 13.6° 2 θ), further demonstrate that Fe-rich SFCA is distinct from SFCA-I and SFCA.

It is not known whether this Fe-rich SFCA phase is pres-

ent in industrial iron ore sinter. However, a similar phase has been observed in pot-grate sinter – with bulk composition 59.00 mass% T-Fe, 8.30 mass% CaO, 5.24 mass% SiO_2 , 1.64 mass% Al_2O_3 and 1.16 mass% MgO – produced in CSIRO's facility in Pullenvale (Fig. 2(b)).¹⁰⁾ The pot-grate Fe-rich SFCA had average composition 84.8 mass% Fe_2O_3 , 9.4 mass% CaO, 2.2 mass% SiO_2 , 2.8 mass% Al_2O_3 and 1.8 mass% MgO, which was close to the composition observed in the synthetic material but with Mg present as an impurity (from the dolomite flux).

EPMA oxide totals for the Fe-rich SFCA phase were ~101 mass%, an indication that the phase contains Fe^{2+} in addition to the Fe^{3+} (i.e., the EPMA data were calculated assuming all Fe was present as Fe^{3+} . Totals of >100% indicate the presence of some Fe as Fe^{2+}). The SFCA present in Fig. 2(b) had an average composition of 72.7 mass% Fe_2O_3 , 15.3 mass% CaO, 8.2 mass% SiO_2 , 3.6 mass% Al_2O_3 and 0.7 mass% MgO (total = 100.4 mass%, with most Fe present therefore as Fe^{3+}), and the Fe_3O_4 had average composition 96.6 mass% Fe_2O_3 , 1.9 mass% CaO, 0.9 mass% Al_2O_3 and 2.6 mass% MgO (total = 102.1 mass%, indicating the Fe^{2+} content is greater than in the Fe-rich SFCA). The Fe-rich SFCA, therefore, appears to be an intermediate phase between Fe_3O_4 and SFCA in terms of composition. The Fe-rich SFCA phase in Fig. 2(b) did not appear to be significantly texturally different from the SFCA.

A number of recent investigations^{9,11–19)} have utilised *in situ* XRD in order to establish the formation mechanisms of SFCA phases under simulated sintering conditions from synthetic starting sinter mixtures in the range 298–1 623 K, under oxygen partial pressures (p_{O_2}) in the range 0.21 to 1×10^{-4} atm, and at basicity (B , = CaO: SiO_2) values in the range 2.5–5. Regarding basicity, Webster *et al.*¹⁵⁾ established the following as it relates to SFCA and SFCA-I phase formation during heating; increasing basicity significantly increased the thermal stability range of SFCA-I, from 1 363 K to 1 533 K for a mixture with $B = 2.5$, to ~1 323 K to 1 593 at $B = 5$. Increasing basicity also increased the

Fig. 2. Backscattered electron micrographs collected for (a) a synthetic sample, quenched from 1 488 K during cooling at $p_{O_2} = 5 \times 10^{-3}$ atm, showing the Fe-rich SFCA phase,⁹⁾ and (b) a pot-grate sinter sample showing association of SFCA, Fe-rich SFCA and Fe_3O_4 (magnetite) phases. $C_2S = 2CaO \cdot SiO_2$.¹⁰⁾

Fig. 3. Laboratory XRD data collected for the synthetic material for which a backscattered electron micrograph is shown in Fig. 2(a). The characteristic Fe-rich SFCA peak at d-spacing = 3.2 Å (32.5° 2 θ) is labelled. Also labelled are magnetic peaks, and peaks matched with a Ca-Al-silicate phase (Internal Centre of Diffraction Data entry no. 01-088-1797).

amount of SFCA-I formed, from 18 mass% for the mixture with $B = 2.5$ to 25 mass% for the $B = 5$ mixture. There was a corresponding decrease in the amount of SFCA which formed from $B = 2.5$ to $B = 5$. In another of these investigations the effect of Al_2O_3 concentration (with $B = 4$) on the crystallisation of Fe-rich SFCA and SFCA was established.⁹⁾ Increasing the Al_2O_3 content (i) increased the temperature at which both the Fe-rich SFCA and SFCA phases crystallised from the melt, and (ii) decreased the range of temperature over which Fe-rich SFCA exists before the SFCA phase formed. Whilst the effects of alumina on the formation of Fe-rich SFCA and SFCA during cooling have been established, the effect of basicity on the crystallisation of Fe-rich SFCA and SFCA has not been investigated. Establishing the effects of basicity is the first aim of this paper.

The Fe-rich SFCA phase present in Fig. 2(b) contained Mg, and dolomite, $(\text{Ca,Mg})\text{CO}_3$, and other MgO-bearing materials such as olivine, $(\text{Fe,Mg})_2\text{SiO}_4$, and serpentine, $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$, are commonly used in addition to limestone, CaCO_3 , as flux components for the production of iron ore sinters.²⁰⁾ The MgO content of the resulting sinter gives blast furnace slag good flowability and desulphurisation properties,⁶⁾ and the addition of up to 3 mass% MgO to sinter feed is typical. The second aim of this paper is to determine the effects of Mg on the crystallisation of Fe-rich SFCA and SFCA during cooling of Mg-doped sinter. We have chosen to focus on the cooling since the effects of Mg addition on phase behavior during heating – overall suppression of complex calcium ferrite formation and the expense of magnesio-ferrite, but with Mg favouring the formation of SFCA-I relative to SFCA – are well established.^{20–22)}

2. Experimental

2.1. *In situ* XRD Sample Preparation

Table 1 shows the concentration of each mixture, in terms of mass% of oxides. The base mixture, SM4/5, with $B = 4.0$ and containing 5 wt% Al_2O_3 has been utilised in a number of our previous investigations.^{9,13–19)} The SM3/5 and SM2.5/5 mixtures, with $B = 3.0$ and 2.5, respectively, were designed to examine the effect of basicity. The SM4/5-1MgO and 3MgO mixtures, with 1 and 3 wt% addition of MgO to SM4/5, respectively, were designed to examine the effect of Mg concentration. The mixtures were prepared from fine grained synthetic hematite, Fe_2O_3 (Acros Organics, 99.999%); calcite, CaCO_3 (Thermo Fisher, 99.95%); quartz, SiO_2 (Sigma Aldrich, 99.995%); gibbsite, $\text{Al}(\text{OH})_3$ (Alcan OP25 Super White, 99.9%); and magne-

site, MgCO_3 (99.9%). Weighed powders were micronised in ethanol for 4 min g^{-1} , centrifuged and dried at 333 K overnight. They were then remixed by hand in a mortar and pestle to ensure homogeneity.

2.2. *In situ* XRD Experimentation and Data Analysis

In situ synchrotron XRD (S-XRD) experiments were performed on the powder diffraction beamline at the Australian Synchrotron.²³⁾ An Anton Paar HTK 2000 high-temperature chamber employing a Pt resistance strip heater was fitted to the beamline. XRD data were collected over the range $5^\circ \leq 2\theta \leq 85.5^\circ$ continuously throughout heating, with individual datasets collected for 24 sec, using an X-ray wavelength of 1.1061 Å calibrated using LaB6 (NIST 660b line position standard).

For each *in situ* experiment a heating rate of 50 K min^{-1} was used from 298–1 623 K. The rate was then reduced to 5 K min^{-1} during cooling between 1 623–1 273 K, and then increased to 50 K min^{-1} from 1 273 to 298 K. 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, especially during cooling, is significantly slower than those encountered in industrial sintering. It was chosen so as to monitor phase crystallisation with reasonable temperature resolution in order to establish trends with compositional variation.

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. An error of $\pm 10 \text{ K}$ is assigned to these values consistent with previous work.⁹⁾

The decomposition of precursor phases and the formation of new phases as the experiments progressed was visualised by stacking the datasets to produce plots of accumulated data with temperature plotted vs 2θ , viewed down the intensity axis.

Throughout heating and cooling the Anton Paar chamber was fed by a continuous flow of a 0.5% O_2 in N_2 gas mixture ($p\text{O}_2 = 5 \times 10^{-3} \text{ atm}$). Hsieh and Whiteman concluded that this $p\text{O}_2$ maximised the formation of Ca-rich ferrites while still producing mineral assemblages similar to those found in industrial sinters.²⁴⁾

3. Results and Discussion

Figure 4 shows a plot of accumulated *in situ* XRD data, viewed down the intensity axis and with temperature plotted vs 2θ , for the experiment performed for SM4/5-1MgO mixture. During heating the sequence of phase decomposition/formation events were as follows: decomposition of $\text{Al}(\text{OH})_3$; decomposition of MgCO_3 ; decomposition of CaCO_3 ; formation of lime (CaO); formation of dicalcium ferrite (C_2F , *i.e.* $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$); formation of calcium ferrite (CF , *i.e.* $\text{CaO} \cdot \text{Fe}_2\text{O}_3$); formation of SFCA-I; and formation of SFCA. At the peak temperature the phase assemblage was Fe_3O_4 in a $\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ melt. During cooling the Fe-rich SFCA began to crystallise from the melt at 1 506 K, followed by SFCA at 1 481 K. Secondary Fe_2O_3 was observed to form below 1 393 K. **Table 2** shows the temperatures of Fe-rich SFCA and SFCA formation during

Table 1. Nominal compositions, in mass% oxides, of the mixtures used in the *in situ* S-XRD experiments.

Sample	Concentration (oxide mass%)					Basicity
	Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	
SM4/5	77.36	14.08	3.56	5.00		4.0
SM3/5	73.78	15.87	5.35	5.00		3.0
SM2.5/5	70.20	17.67	7.13	5.00		2.5
SM4/5-1MgO	76.59	13.94	3.52	4.95	1.00	4.0
SM4/5-3MgO	75.04	13.66	3.45	4.85	3.00	4.0

cooling for each mixture. The results for SM4/5 are in good agreement with those determined previously.⁹⁾

In terms of the crystallisation temperature of the Fe-rich

Table 2. Temperatures of the Fe-rich SFCA and SFCA crystallisation events during cooling.

Sample	Temperature (K)	
	Fe-rich SFCA	SFCA
SM4/5	1 489	1 475
SM3/5	1 501	1 496
SM2.5/5	1 484	1 484
SM4/5-1MgO	1 506	1 481
SM4/5-3MgO	1 443	–

Fig. 1. *In situ* S-XRD data showing the formation of Fe-rich SFCA and SFCA during cooling from a magnetite + melt phase assemblage at 1 623 K and $p_{O_2} = 5 \times 10^{-3}$ atm in a synthetic iron ore sinter mixture. Adapted from Ref. (9).

SFCA and SFCA phases in Table 2, there does not appear to be a significant variation with basicity given the ± 10 K uncertainty assigned to temperature values. There was, however, a suppression in the formation of the Fe-rich SFCA phase with decreasing basicity (**Fig. 5**), with only a very small amount of the Fe-rich SFCA phase observed for the B = 2.5 mixture (Fig. 5(c)). There was also a reduction, with decreasing basicity, of the temperature range where Fe-rich SFCA was present before SFCA began to form, with both phases forming simultaneously during cooling at B = 2.5. We note that the basicity of the Fe-rich SFCA phases discussed in Section 1 was high – in the range B = 4.3 to 5.3 – and so it is not surprising that a higher basicity in the reacting mixture would promote the formation of the Fe-rich SFCA phase.

Increasing Mg concentration up to 3 wt% MgO for the SM4/5-3MgO mixture lowered the crystallisation temperature of Fe-rich SFCA significantly, while SFCA was not

Fig. 4. *In situ* S-XRD data collected for the SM4/5-1MgO sample, viewed down the intensity axis, during heating and cooling in the range 298–1 623 K and at $p_{O_2} = 5 \times 10^{-3}$ atm. CF = $CaO \cdot Fe_2O_3$, $C_2F = 2CaO \cdot Fe_2O_3$.

Fig. 5. *In situ* S-XRD data collected between 1 623 and 1 323 K during cooling and over the range $19^\circ < 2\theta < 20^\circ$ for the (a) SM4/5, (b) SM3/5, (c) SM2.5/5 and (d) SM4/5-3MgO mixtures. The colours in the plots are proportional to X-ray intensity, with red more intense than green, and green more intense than blue.

Fig. 6. *In situ* S-XRD data collected over the range $19^\circ < 2\theta < 20^\circ$ at 298 K for the SM4/5, SM3/5, SM2.5/5, SM4/5-1MgO and SM4/5-3MgO mixtures.

observed to crystallise during cooling in this experiment (Fig. 5(d)). The general suppression of complex Ca-rich ferrite phase formation (*i.e.* SFCA phases) with increasing Mg content is consistent with previous work.^{20,21)} The presence of Mg here also favoured the formation of Fe-rich SFCA compared to SFCA, in a similar manner to the presence of Mg favouring the formation of SFCA-I compared to SFCA during heating.²²⁾ Considering the sizes of the Mg^{2+} and Fe^{2+} cations (0.86 and 0.92 Å for Mg^{2+} and Fe^{2+} in octahedral coordination, respectively²⁵⁾), and the significantly larger size of the Ca^{2+} cation (1.16 Å), we postulate that Mg substitutes for Fe^{2+} in the Fe-rich SFCA and SFCA crystal structures. A greater solubility of Mg in Fe-rich SFCA, as evidenced by the formation of this phase being favoured over SFCA as Mg content increases, is consistent with this phase incorporating a higher proportion of Fe^{2+} (see Section 1). **Figure 6** shows that for each mixture that the Fe-rich SFCA phase formed, the characteristic peak of Fe-rich SFCA at 19.7° 2θ (d-spacing = 3.2 Å) was observed down to 298 K.

4. Conclusion

The effects of basicity and Mg concentration on the crystallisation of Fe-rich SFCA and SFCA phases during cooling of iron ore sinter mixtures heated and cooled in the range 298–1 623 K and at $p_{\text{O}_2} = 5 \times 10^{-3}$ atm have been investigated using *in situ* S-XRD. Decreasing basicity from $B = 4.0$ to 2.5 resulted in the formation of a Fe-rich SFCA phase being suppressed, with SFCA becoming the only Ca-rich ferrite phase to crystallise from the melt during cooling at $B = 2.5$. An opposing effect was observed with increasing Mg addition, with Mg stabilising Fe-rich SFCA relative to SFCA.

It is unknown whether Fe-rich SFCA is observed in industrial sinter. However, given that industrial sinter blends are typically fluxed to basicity < 2.0 , any observation *via* electron microscopy of the Fe-rich SFCA phase in industrial or pilot scale pot-grate sinter may be an indicator of localised high basicity, and/or, localised high Mg concentration in a sinter blend.

Future work will investigate the effect of Ti content on the crystallisation of Fe-rich SFCA and SFCA during cooling, since the introduction of a minor amount of titanium-bearing sinter into the blast furnace burden is a strategy used by steelmakers to extend blast furnace operating campaigns.²⁶⁾ Given that it has been previously shown that the SFCA crystal structure can accommodate more Ti than the SFCA-I crystal structure,¹⁷⁾ it is hypothesised here that increasing Ti content will suppress Fe-rich SFCA formation relative to SFCA formation during cooling. Future work could also investigate the effect of cooling rate on the formation of the Fe-rich SFCA and SFCA phases.

Regardless of whether or not Fe-rich SFCA is actually present in industrial sinter, this study progresses the fundamental knowledge of iron ore sintering reactions, since Fe-rich SFCA may form as an intermediate phase during cooling even if it is not preserved in cooled sinter product.

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