

SIGNIFICANT MINERALOGICAL DIFFERENCES BETWEEN BASIC TEST AND PRODUCTION IRON ORE SINTERS WITH EQUAL CHEMICAL COMPOSITION

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ABSTRACT

Mineralogical characterization for two ultra basic production sinter-test sinter pairs was made using optical microscopy and scanning electron microscopy. Basicities (CaO/SiO_2) of the sinter pairs were 2.1 and 2.3 respectively. Despite of the equal composition, the mineralogy and microstructure of the corresponding test and production sinters were significantly different.

The production sinters were composed mainly of fine-grained equigranular matrix rich in newly formed magnetite. Sporadically, some coarse magnetite or olivine relicts created a porphyritic-like structure. The matrix magnetite was clearly the primarily crystallized phase with interstitial vitreous slag, SFCA phase, dicalcium silicate, siliceous dicalcium titanoferrite, tertiary hematite and/or hematite-dicalcium silicate intergrowths.

The test sinters were characterized by a porphyritic-like structure with a great amount of relatively coarse magnetite and olivine relicts in a newly formed fine-grained matrix having hemicalcium ferrite as the primary phase. The interstices between the columnar hemicalcium ferrite grains were typically filled with calcium ferrite-dicalcium silicate micro-intergrowths and slightly coarse-grained droplet-like siliceous dicalcium titanoferrite grains. In places the micro-intergrowths were missing and the matrix was composed of randomly oriented acicular hemicalcium ferrite, siliceous dicalcium titanoferrite, and dicalcium silicate. Magnetite and vitreous slag did not typically exist in the test sinter matrix.

Both sinter types contained some secondary hematite existing mainly in the zone around the partially hematitized magnetite relicts.

It is proposed that the main reason for the mineralogical difference is the different melting or reaction degree originating from the difference in the sintering temperatures between the pot and production sintering processes.

INTRODUCTION

Pot sintering is not a standardized test, but it is widely used worldwide to investigate the fundamental phenomena and to test the sintering characteristics of different iron ore blends prior to full scale plant trials and plant production. As studied elsewhere in detail, the test sintering is a very sensitive method for changes in the process conditions and properties of the sinter blend materials [4, 5, 6].

At the Ruukki Production, the produced test sinter is put into different mineralogical and metallurgical tests. Estimations are made about the behaviour of the sinter mix in real sintering process and quality of the sinter and its behaviour in the blast furnace [3].

The quality of sinter is mainly governed by the structure and phase composition of the agglomerate [1, 7]. In principle, most, if not all of the properties of sinter are straightly related to the structure and mineralogy of the agglomerate. However, the sinters are typically very heterogeneous materials in macro- and micro-scale and this connection is very difficult to find out and even more difficult to prove.

Ruukki Production has developed a constant pot sintering procedure, which produces test sinters having quite well the same RDI (Reduction degradation index) values as the production sinters made from the same blend. This is basically quite astonishing, because of the known differences between the condition of the test and production sintering.

The following results were made during a co-operation project between Ruukki Production and Laboratory of Process Metallurgy, University of Oulu. The project aimed to stabilize the blast furnace operation by decreasing the quality variations of the sinter.

METHODOLOGY

Sample materials and Research Methods

The test sinters were produced according to constant pot sintering route of the Ruukki Production [3]. The sinter was screened and the fines were returned into repeated sintering until the ratio between the produced and returned sinter fines was from 0.95 and 1.05. Coke breeze was used to adjust the ratio.

The production sinter samples from Dwight-Lloyd type sinter plant of the Ruukki Production were collected using automatic sampling equipment. The same ratio between the produced and returned sinter fines was used for the sinter optimization.

The reduction degradation tests were done according to international standard (ISO 4696-1)

Polished samples from the test and production sinters were made in the mineralogical laboratory of Ruukki Production. The polished sections from the sinter samples were examined optically with Olympus BX51 polarized microscope. Compositions of the different phases were assayed with a JEOL JSM-6400 scanning electron microscope using energy dispersive spectrometry. An accelerating voltage of 15 kV and a beam current of 120 nA were used. Oxford Instruments Inca 3.03 software was used for the evaluation of the analyses.

RESULTS AND DISCUSSION

Sample Composition and Test Results

Chemical compositions and some test data for the test sinters and production sinters are seen in Table 1. The compositions are quite close to the targeted basicity values (B₂) of 2.1 and 2.3, and the Fe content and MgO-contents of 61.5% and 2.1%, respectively.

The image analysis revealed that the phase composition of the production and test sinters were very different. The production sinters were higher in magnetite (MA) and lower in hematite (HE) than the test sinters (See Table 1). The difference in FeO content (titrated analysis) is also an indication of this. The actual content of calcium ferrites (CF) is somewhat uncertain, due to the difficulties to distinguish different calcium ferrites from magnetite. Both the glass phase and the crystals of silicate phases (olivine relicts) are classified as part of the vitreous slag (VS).

Table 1: Composition and test data for test sinters (TS1 and TS2) and production sinters (PS1 and PS2)

Sample	Fe	CaO	SiO ₂	MgO	Al ₂ O ₃	Ti	FeO	B ₂	RDI	CF	HE	MA	VS
TS1	60,28	7,55	3,57	2,08	0,58	0,23	5,20	2,11	21,7	18,8	31,1	38,8	11,3
TS2	60,43	7,62	3,24	2,15	0,54	0,23	6,00	2,35	18,6	21,2	30,0	37,2	11,7
PS1	60,44	7,45	3,40	1,99	0,59	0,25	10,87	2,09	20,7	15,9	18,7	53,6	11,9
PS2	61,04	7,16	2,97	1,72	0,57	0,27	10,95	2,30	21,6	19,2	16,9	49,9	14,0

The measured RDI values of the test and production sinters were quite low and indicated good behaviour in the blast furnace.

Mineralogy and Structure

*Production Sint*ers

The production sinters were highly magnetite dominated. The total magnetite content was at least 50-60%. Most of the sinter fragments (Figure 1) consisted of newly formed, fine grain granular magnetite (Ma, light grey) matrix with interstitial minor phases (darker areas). Some coarse grain magnetite relicts (Figure 2), partially oxidized to hematite (He, white), occurred sporadically making the structure look porphyritic-like. Proportion of the relicts in the production sinter was about 20%. At the reaction zone between the magnetite relicts and magnetite rich matrix, hybridomorphic secondary hematite grains were identified.

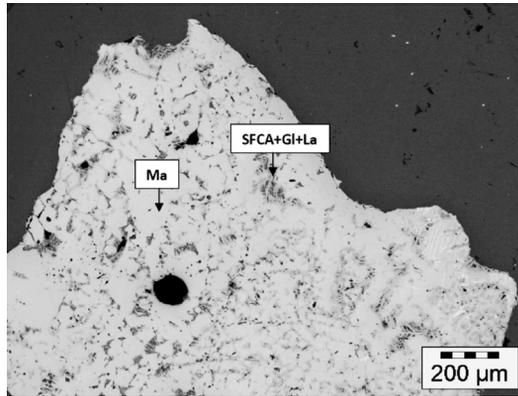


Figure 1: Typical equigranular-like structure of production sinter

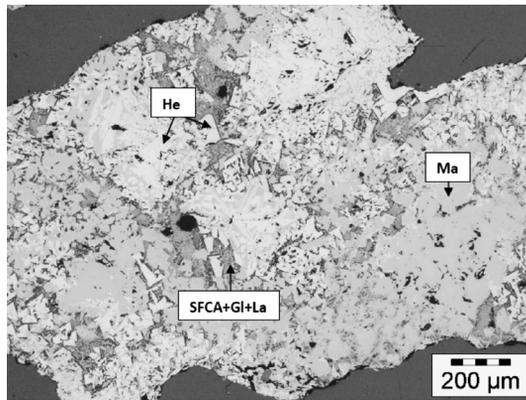


Figure 2: Typical porphyritic-like structure of production sinter

Closer look into the matrix interstices revealed the existence of two kinds of main phase associations. In the first one (Figure 3), matrix magnetite (Ma, light grey) was surrounded by SFCA phase (SFCA, medium grey, columnar) with intervening glass phase (Gl, dark grey, smooth) and dicalcium silicate (La, dark grey, granular). In some cases a few grains of siliceous dicalcium titanoferrite (not seen in Figure 3) was also detected.

The second association (Figure 4) consisted of magnetite with interstitial ternary hematite (He, white), existing mainly as dendritic crystals and as micro-intergrowths with dicalcium silicate. Some glass phase and a few grains of the siliceous dicalcium titanoferrite (DCTif, medium gray, a few grains around the glass phase in the central part of the photo) were typically present.

Variations in phase proportions and mixing and gradation of the types into each other were not rare.

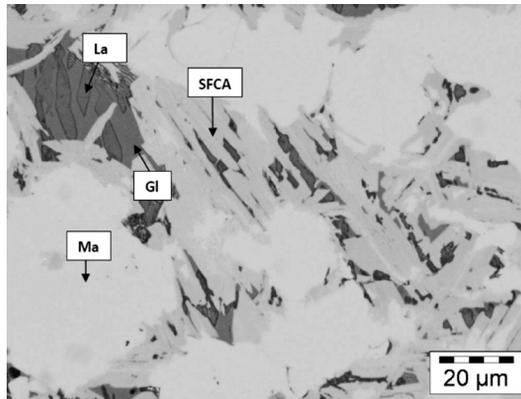


Figure 3: Typical phase association of the production sinter

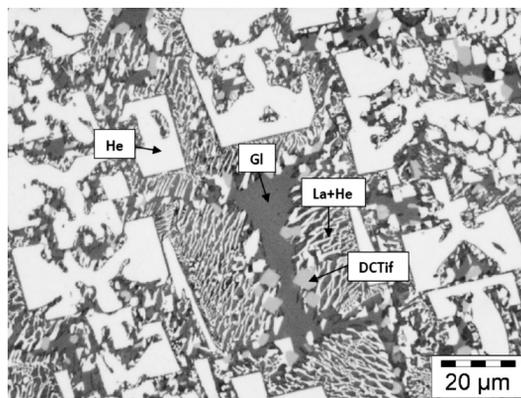


Figure 4: Typical interstitial phase association of the production sinter

Test Sinters

The test sinters were totally different from the production sinters. Most of the test sinter fragments were very distinctively characterized by a porphyritic-like structure (Figures 5 and 6). The relatively coarse grain magnetite and occasional olivine relicts, making up about 50% of the sinter, were surrounded by newly formed fine grain hemicalcium ferrite rich matrix. Oxidation of the magnetite relicts to hematite was generally more pronounced than in the production sinters.

At the contact zone between the magnetite relicts and matrix, idiomorphic secondary hematite was observed.

With very few exceptions, magnetite and vitreous slag were absent from the test sinter matrix.

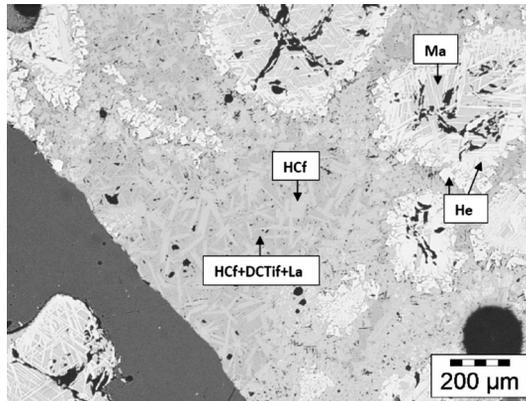


Figure 5: Typical structure of the test sinters

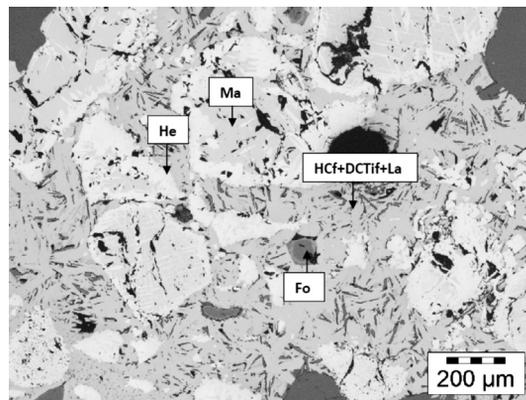


Figure 6: Typical structure of the test sinters

The test sinter matrix had two main phase associations characterized by specific microstructures. In most sinter fragments, the matrix was characterized by randomly oriented columnar hemi-calcium ferrite (Figure 7). Between the hemicalcium ferrite columns (HCf, light grey) existed allotriomorphic droplet-like grains of siliceous dicalcium titanoferrite (DCTif, medium grey) and very fine grain intergrowth of dicalcium silicate and some form of calcium ferrites (almost white with darker spots), probably the hemicalcium ferrite.

The second type of the matrix (Figure 8) was characterized and dominated by randomly oriented acicular to columnar hemicalcium ferrite (HCf, light grey), long-shaped dicalcium silicate grains (La, dark grey) and allotriomorphic siliceous dicalcium titanoferrite (medium grey). Grain size of the phases was quite alike. Amount of the dicalcium silicate and dicalcium ferrite phase was low in places.

Variations in phase proportions of the main types and mixing and gradation of the types into each other were not rare.

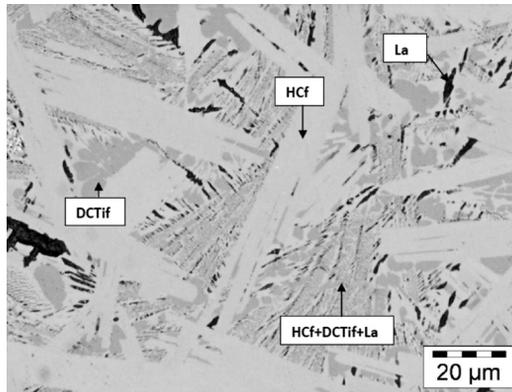


Figure 7: A typical phase association of the test sinter matrix

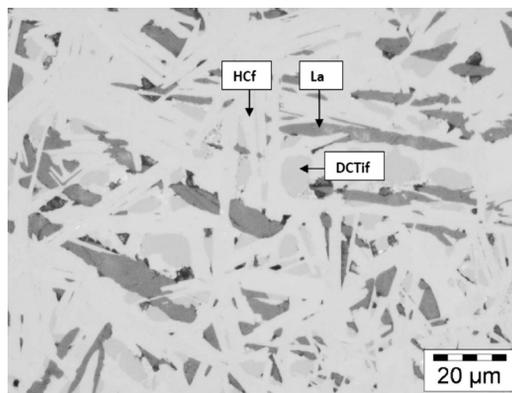


Figure 8: Another typical phase association of the test sinter matrix

Optical microscopy revealed the differences between the production and test sinters. It seems most obvious, that the main reason for the difference in the mineralogy and structure was the sintering temperature. The lower sintering temperature in the pot sintering process created a lower reacting and melting degree for the material. Because about half of the magnetite grains were not involved in the reactions, the reacting material was lower in Fe and higher in CaO and SiO₂. This caused that primary crystallization started from the hemicalcium ferrite phase field instead of the magnetite field of the Fe-richer system taking part in the sintering reactions in the production sinter.

Mineral Chemistry

Typical chemical compositions of the production and test sinter phases are presented in Tables 2 and 3 respectively. Numbers of the first column in Table 2 refers to phases: magnetite/matrix (1 and 2), magnetite/relict (3), olivine/relict (4), hematite/secondary (5), hematite/ternary (6), dicalcium silicate (7), siliceous dicalcium titanoferrite (8 and 9), vitreous slag (10), and SFCA phase (11). In Table 3 the numbers refer to phases: hemicalcium ferrite (1 and 2), magnetite/relict (3), olivine/relict (4), hematite/secondary (5), dicalcium silicate (6), siliceous dicalcium titanoferrite (7 and 8). All Fe is calculated as total FeO (FeO_T).

In general, magnetite and olivine relicts of different sinter types were quite comparable in chemical composition. The same was true for the hematite oxidation lamellas, secondary hematite grains and dicalcium silicate. The matrix magnetite of the production sinters had always clearly increased CaO and MgO contents.

Table 2: Typical chemical compositions of the phases existing in the test sinters

No.	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	V ₂ O ₅	MnO	FeO _t
1	5,52	0,00	0,00	3,57	0,00	0,00	1,08	77,21
2	1,92	0,00	0,00	2,12	0,00	0,00	0,00	85,01
3	0,00	0,00	0,00	0,00	0,00	0,00	0,00	85,08
4	47,60	0,00	39,01	0,00	0,00	0,00	0,00	8,72
5	0,00	0,78	0,00	0,97	1,68	0,00	0,00	83,57
6	0,00	0,70	0,00	1,51	2,07	0,00	0,00	79,21
7	0,00	0,00	31,63	62,17	0,00	2,08	0,00	1,93
8	0,00	0,44	10,03	40,88	23,18	0,00	0,00	18,13
9	0,00	0,00	10,57	41,46	6,29	1,06	0,00	30,73
10	0,00	0,53	30,94	39,68	5,01	5,45	0,00	10,32
11	0,00	2,21	7,62	16,35	1,68	0,00	0,00	62,59

Table 3: Typical chemical compositions of the phases existing in the test sinters

No.	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	V ₂ O ₅	MnO	FeO _t
1	0,00	0,93	1,94	14,55	0,00	0,00	0,00	70,16
2	1,50	0,53	0,00	9,75	0,00	0,00	0,00	75,52
3	0,00	0,39	0,00	0,00	0,00	0,00	0,00	87,28
4	50,64	0,00	40,11	0,00	0,00	0,00	0,00	7,62
5	0,00	0,53	0,00	0,43	0,50	0,00	0,00	84,37
6	0,00	0,00	30,63	59,84	0,00	1,81	0,00	1,97
7	0,00	0,56	8,75	40,13	11,01	0,00	0,00	31,01
8	0,00	0,00	10,11	39,60	1,73	0,81	0,00	38,04

Composition of the calcium ferrites of the production sinters and test sinters are compared in Figure 9. Although there was some overlapping in the compositions, production sinters usually contained the higher SiO₂ containing SFCA phase. In the test sinters the calcium ferrite was typically a hemicalcium ferrite with lower SiO₂ content.

Composition of the siliceous dicalcium titanoferrite is clarified on the basis of 92 SEM assays in Figure 10. This phase had quite stable CaO and SiO₂ contents and variable TiO₂ and FeO contents. TiO₂ content in the production and test sinters varied from 6.3% to 23.2 % and from 1.6% to 11.0% respectively. It was obvious, that Ti is replacing Fe in the siliceous dicalcium titanoferrite structure. Despite of numerous mineralogical characterizations made for different test and production sinters [1, 2, 3, 7], this kind of siliceous dicalcium titanoferrite has not been reported earlier for iron ore sinters.

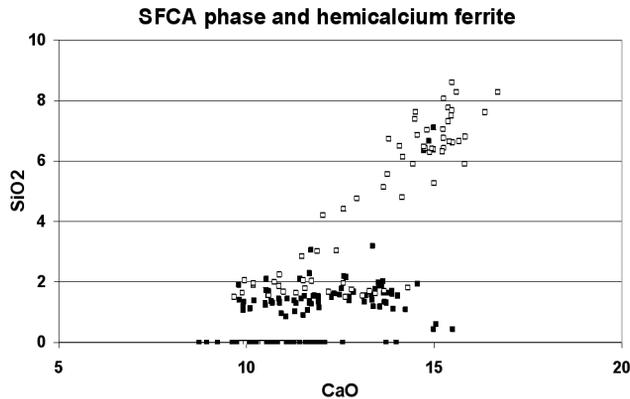


Figure 9: Composition variation of the SFCA phase and hemicalcium ferrite from production sinters (black open squares) and test sinters (black full squares). Scales are in oxide w-%

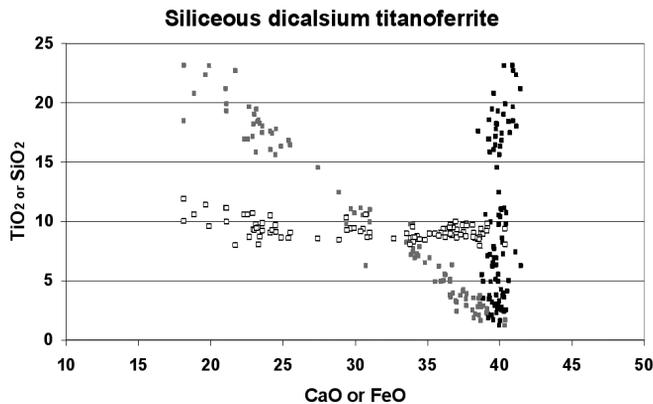


Figure 10: Composition variation of the siliceous dicalcium titanoferrite expressed as CaO vs. TiO_2 (black full squares), FeO vs. SiO_2 (black open squares), and FeO vs. TiO_2 (full gray squares). Scales are in oxide w-%

Part of the variation in the composition is analytical error due to the very fine grain size of the phase, especially in the case of the production sinters. This generates increased variation in the CaO and SiO_2 content especially for the high TiO_2 (low FeO) compositions.

CONCLUSIONS

RDI values of test sinters made using a pot sintering equipment has been observed to predict quite well the RDI values of the production sinter made from the same mix. Mineralogy and structure of the test sinter-production sinter pairs with basicity of 2.1 and 2.3 was made using optical and scanning electron microscopy.

Results revealed that mineralogy and texture of the test and production sinter made from mix was totally different. The structure and phase composition of the production sinters were dominated by newly formed magnetite matrix with some magnetite relicts, while in the test sinters were dominated by hemicalcium ferrite rich matrix with a great amount of magnetite relicts. In both sinters a new type of dicalcium ferrites was

identified. It was a siliceous dicalcium titanoferrite with constant SiO_2 and CaO contents and varied TiO_2 contents up to 23%.

It is proposed that the reason for the mineralogical difference is the different melting or reaction degree of the production and test sinters, in turn caused by differences in the sintering temperature between the pot and production sintering processes.

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