Silico-ferrite of Calcium and Aluminum Characterization by Crystal Morphology in Iron Ore Sinter Microstructure

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Correct identification of mineral phases in iron ore sinters is key for further research, in which individual sinter properties are derived directly from mineral phases. Nowadays widespread image analysis and techniques based on the visual quantification may not exactly evaluate mineral type, what has an unfavorable effect on the overall phase analysis and all functions derived from it. Some specifics were demonstrated by microscopic examination of sinter samples and pointing out differences in calcium ferrite identification. It was found the dendritic crystallization may cause such crystal shape of low-Fe SFCA, that it ultimately looks like plates of high-Fe SFCA-I. Aggregates of SFCA-I plates crystallized adherent are misidentifiable as prismatic SFCA crystals. The pathway for SFCA-I crystals covered with SFCA was also discussed.

KEY WORDS: crystal shape; iron ore sinter; microstructure; phase identification; SFCA.

1. Introduction

A long term objective of pig iron producers is use of good quality iron ore sinters, which ensure smooth operation of blast furnace. A growing trend in research of iron ore sinters is deriving from mechanical and metallurgical properties from sinters’ microstructure and mineral phases. Because currently produced fluxed sinters have basicity CaO/SiO\textsubscript{2} ≈ 1.7, MgO level ≈ 3 wt% and SiO\textsubscript{2} level ≈ 10 wt% and MgO level ≈ 3 wt%.

There is a number of classifications of SFCA according to its crystal shape in current scientific literature. Besides the classification into only two groups, there is also a classification with transition habits between basic shapes. Besides usual columnar and acicular shapes there are also mentioned platy and sheet. Without closer examination of crystals, there was adopted a width limit of 10 μm between SFCA-I and SFCA. A ratio of 2.5 between longer and shorter side of crystal is also known. Other researches consider take into account mainly chemical composition determined by SEM-EDS.

In this research, acicular shape in cross section is denoted as platy morphology of SFCA-I and columnar as prismatic SFCA, respectively.

In this paper, there are demonstrated not only types of silico-ferrites of calcium and aluminum (SFCA) from the point of view of morphology and chemical composition in sinter samples, but also examples of such cases, in which can occur incorrect identification or confusion of SFCA types.

2. Materials and Methods

Sinters used for the study were prepared by sintering of raw materials, which are used in a real sintering plant – hematite ore, magnetite concentrate, fluxing agents lime and dolomite, to achieve the basicity of final sinter (CaO + MgO)/(SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}) ≈ 1.7, SiO\textsubscript{2} level ≈ 10 wt% and MgO level ≈ 3 wt%.

The sintering was realized in a laboratory sintering pan, parameters of which and sintering conditions have been published elsewhere. The samples were removed from sinter cakes and then prepared for observation under light microscopy: mounted into epoxy resin, grinded and polished. In order to expose the whole mineral habits in the microstructure a hydrochloric etching of amorphous phase was applied.

The chemical composition of mineral phases was obtained by SEM-EDS. The presence of concrete types of calcium ferrites in the sinter samples was confirmed by X-Ray diffraction analysis.

3. Results and Discussion

3.1. Acicular Shape

The most desirable type of sinter microstructure is bonded with SFCA-I bonding phase, i.e. the high-Fe type interpreted as acicular calcium ferrite. According to the long term research of authors, SFCA-I contains 74.7–85.1 wt% FeO\textsubscript{3}, 9–16.6 wt% CuO, 0.9–7.4 wt% SiO\textsubscript{2}, 0.5–2.8 wt% FeO and MgO level ≈ 3 wt%.

[Note]

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Al₂O₃ and up to 3.2 wt% MgO. The crystals of this ferrite are aligned closely together, have diverse directions of crystallization, and they often intersect each other. In the intercrystalline spaces are either pores or silicate phases. Fields with SFCA-I are located between coarse hematite or magnetite grains, which they bond together. An example of such microstructure is in Fig. 1(a). Chemical composition of this SFCA-I was 80.9 wt% Fe₂O₃, 11.6 wt% CaO, 5.1 wt% SiO₂, 1.5 wt% Al₂O₃ and 0.9 wt% MgO. EDS analysis confirms the high-Fe type. Because this microstructure is in etched state and the EDS spot size has not reached the edges of crystal, no other minerals have affected the measurement. The width of transected crystals is about 1–2 μm, thus under the 10 μm limit.

In Fig. 1(b) are shown narrow elongated (acicular) SFCA crystals. They are oriented in similar direction but they are not entirely parallel. It is common, that the crystals diverge towards the adjacent crystals to the right have a fish-fin-like ending. Moreover, there are also marked some intercrystallic spaces, which divide the mass of SFCA. They were filled with silicates before etching. Ordinary image analysis would classify this microstructure type as acicular calcium ferrites. But in this case, these are not plates in cross section, but an imperfectly crystalized form of prismatic SFCA. EDS proves it and detected chemical compositions as follows: 68.5 wt% Fe₂O₃, 17.8 wt% CaO, 8.8 wt% SiO₂ and 4.9 wt% Al₂O₃. Despite the microstructure is on the first sight really like SFCA-I plates, it is possible to recognize this type also visually. This is dendritic shape, which ending is quite different from SFCA-I. All long parts of crystal have almost the same direction and endings like a cauliflower head (visible in Fig. 1(b)) in the upper right corner). The outlines of SFCA prismatic shape are more clear noticeable, there and the ending of crystal together with long parts forms a compact body. Moreover, the adjacent crystals to the right have a fish-fin-like ending. A different crystallization stage of prismatic SFCA is on Fig. 1(d). Dendritic habit is more developed than that in Fig. 1(b) and is interlaced with small pores, where silicates have solidified.

3.2. Columnar Shape

The 10 μm limit is a mistake even when SFCA-I plates are fused together and the boundaries between crystals are not visible. So in cross section these crystals look like columnar SFCA. A help for identification would be the ending of crystal, which is frayed. Individual plates are perfectly parallel, but have different length. The determined chemical composition of SFCA-I in Fig. 1(c) was 79 wt% Fe₂O₃, 13.1 wt% CaO, 3.7 wt% SiO₂, 2 wt% Al₂O₃, 1.7 wt% MgO and 0.6 wt% Na₂O. These crystals were captured in a pore, which is the reason why their surface is visible, and not the polished area. An example of polished (sectioned) form is given in the paper from Cores et al.²³

Few authors state that low-Fe SFCA is the only one type of SFCA, which crystallizes directly from the melt during the cooling stage.²¹,²² In that case, the crystals need contact areas for their initial growth (so called heterogeneous nucleation). Because only magnetite is present in solid state when all other phases are melted, magnetite crystals are the contact areas. This explains a coexistence of SFCA with magnetite in the microstructure obtained at higher temperatures.¹⁴,¹⁵,²¹ But the grown of crystals cannot be euhedral and they crystallize subhedraly as is shown in SEM microphotograph in Fig. 2(a). In the SFCA/glass field, there is only one side of crystals without the influence of others, so the prisms are drawn in Fig. 2(b). As visible, the endings of crystals are not uniform. There are also marked two dash lines inside the prismatic crystal, which denote the cross sections used for demonstration of different kinds of calcium ferrites’ habits in the following Fig. 3.

3.3. Description of Ferrite Habits

The first sketch in Fig. 3(a) is the prismatic SFCA crystal. It is homogenous by contrast to other projections. In addition, there is also displayed a growth defect. There is clearly visible the nature of SFCA, which forms an angulated “C” letter in the polished microstructures (or similar).

Figure 3(b) presents plates of SFCA-I fused together. This results in the crystal shape as in Fig. 1(c). There are not any gaps between the crystals, so other phases e.g. silicates could not crystallize here. If it would be the opposite, EDS analysis would be garbled as in analysis of dendritic hematite, which is practically impossible to analyze without signals of Si and Ca from calcium silicates in intercrystalline spaces.

Aggregation of SFCA as well as SFCA-I crystals are drawn in Fig. 3(c). The core of this aggregation are the conjoined SFCA-I crystals as in the above mentioned case
(Fig. 3(b)). They are covered by SFCA crystals, which can be in plate form, too. Many authors identify these aggregations either as SFCA-I or as SFCA phase only. 6) So the further derived research of the properties cannot be correct, because it examines two different mineral phases. Based on the chemical composition of ferrites, there are differences also in shades of grey. SFCA-I contains more iron, which reveals the dendritic nature of the crystal. Crystals of type SFCA can look like as so called acicular morphology in microstructure, however it creates a characteristic ending, which act as a contact area. As a result, SFCA-I crystals with SFCA coverage occur in sinter microstructure.

The previous research of such microstructure shows the possibility of formation of the intergrown crystals. 6) If the proposal is right, that SFCA-I cannot crystallize from melt, there must be some SFCA-I preserved in a solid state during the melting period. After the melting period and the following cooling period, unmelted SFCA-I crystals act as contact areas for heterogeneous nucleation of newly crystallized SFCA. This theory would explain why SFCA crystals form the coverage of SFCA-I and not vice-versa. It was found, however, that SFCA and SFCA-I are together in the sinter microstructure even before melting period begins. 4,21)

4. Conclusions

Current researches of iron ore sinter quality need sufficiently accurate methods for classification of mineral phases. For this purpose, observation of microstructures is mainly used. The results may not be absolutely right, because the types of calcium ferrites sometimes do not crystallize in generally adopted forms. In this paper were presented examples of sinter microstructure, which can cause incorrect identification of ferrites. Dendritic crystallization of low-Fe type SFCA can look like as so called acicular morphology in microstructure, however it creates a characteristic ending, which reveals the dendritic nature of the crystal. Crystals of high-Fe SFCA-I may form aggregations of conjoined plates. The width of such aggregations is generally bigger than 10 μm. Ultimately, they resemble columnar SFCA. Low-Fe SFCA has generally a prismatic habit, but it can probably crystallize from the melt on remaining SFCA-I crystals, which act as a contact area. As a result, SFCA-I crystals with SFCA coverage occur in sinter microstructure.

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