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Fe-Si droplets associated with graphite on blast furnace coke

Stanislav S. Gornostayev[1)], *Timo M.J. Fabritius*[1)], *Olavi Kerkkonen*[2)], *and Jouko J. Härkki*[1)]

1) Laboratory of Process Metallurgy, University of Oulu, Oulu 90014, Finland
2) Ruukki Metals Oy, Raahe 92102, Finland
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Abstract: Fe-Si droplets on the surface of blast furnace (BF) coke from 25 to 50 cm at the tuyere level are mostly composed of Fe_3Si, which has various shapes (round, elongated, and irregular) and penetration degrees into the BF coke matrix. The shapes and penetration degrees may depend on the saturation of molten iron by silicon during interaction with the coke matrix. The droplets are covered by a tiny shell of carbon. Graphite observed inside the droplets can be divided into two categories: well-formed tabular crystals with relatively large size and flakes with structures similar as those in cast iron. The textures of the droplets reflect composition, interaction with the coke matrix, and cooling conditions.

Keywords: metallurgical coke; graphite; iron; blast furnaces

1. Introduction

Investigations on the various aspects of carbon-iron interaction are of great importance because of their extensive applications in iron-making processes [1-7]. Furthermore, carbon is an essential part of cast iron with graphite as the major compound. The form of graphite in cast iron has also been a subject of intense interest for many years. The various microstructures of cast iron have been reviewed and classified, and a number of formation mechanisms of graphite have been proposed [8-12].

Studies on Fe-Si droplets are important. The formation and evolution of the droplets in the blast furnace (BF) affect the properties of cast iron in one way or another and also determine the behaviour of the coke cone in BF [13]. Due to the difficulty in obtaining materials from such a high-temperature process, direct investigations on Fe-Si droplets in BF are complicated to be carried out. Thus, most of studies on carbon-iron interaction in BF are based on experiments conducted with the laboratory-scale equipment. The occurrence of graphite crystals on the surface of BF coke in close association with droplets of Si-bearing iron was reported earlier, and the possible formation mechanisms of graphite crystals were discussed [13]. Some features of graphite inside such Fe-Si droplets were described in this paper.

2. Samples and methods

The samples were obtained from Ruukki Metals, Raahe, Finland, and taken from the drill core at the tuyere level by a 25-50 cm interval, corresponding to the flame area. The slices of BF coke containing Fe-Si droplets were cut off from the samples and placed in a rounded plastic container with 25.4 mm in diameter which was filled with resin. The material was grinded and polished until the surfaces of Fe-Si droplets appeared. Then, the samples were studied with an Olympus SZX9 stereo microscope and a Zeiss ULTRA plus field emission scanning electron microscope (Institute of Electron Microscopy, University of Oulu, Finland). Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) analyses were also performed on the host matrix (the Fe-Si phase). In total, twenty two droplets were studied by optical microscopy (OM) and identified as Fe-Si phases with EDS spectra qualitatively, then seven of them were analyzed in details by EDS.

Corresponding author: Stanislav S. Gornostayev E-mail: ssg@cc.oulu.fi

3. Results and discussion

3.1. Occurrence, size, and shape of Fe-Si droplets

The sizes of Fe-Si droplets are within a range of 0.1-3 mm along the longest dimension as shown in Fig. 1. The morphologies of Fe-Si droplets under a stereomicroscope show that the droplets vary in shape (round, elongated, and irregular) and penetration degree into the BF coke matrix. The shape and penetration degree of Fe-Si droplets may be interrelated, as the penetration degree can be the result of reaction between a certain Fe-Si droplet and the coke matrix. Since the amount of carbon dissolved in molten iron depends on the concentration of silicon [14], droplets undersaturated with silicon may react better and penetrate deeper into the matrix, forming the irregular aggregates, as shown in Fig. 1(c). Whereas droplets saturated with silicon may not react intensively with the matrix and retain more or less the round shape, as shown in Figs. 1(b) and (d)-(f).

The extensive works were required to verify the above suggestion by electron-probe microprobe analysis (EPMA) applying wavelength-dispersive spectroscopy (WDS), which deserves the separated studies. The other work was to discuss the carbon content in the droplets and analyze the co-existed phases in detail. The samples in this paper were coated with carbon, which was the standard procedure for SEM/EDS studies; therefore, it can not be analyzed for carbon. In this regard, the other coating type should be considered for the further investigation. It also seemed obvious that the structure of coke (*e.g.*, cracks) had an impact on the droplet shape, so that the molten Fe-Si material could supply the available spaces to form the segregations with irregular outlines in the place with cracks. The longer the cracks, the deeper the penetration of material to the matrix (the "roots" of droplets in the matrix) would be.

The internal part of some droplets contains voids, which represent a large fraction of volume in some cases, as shown

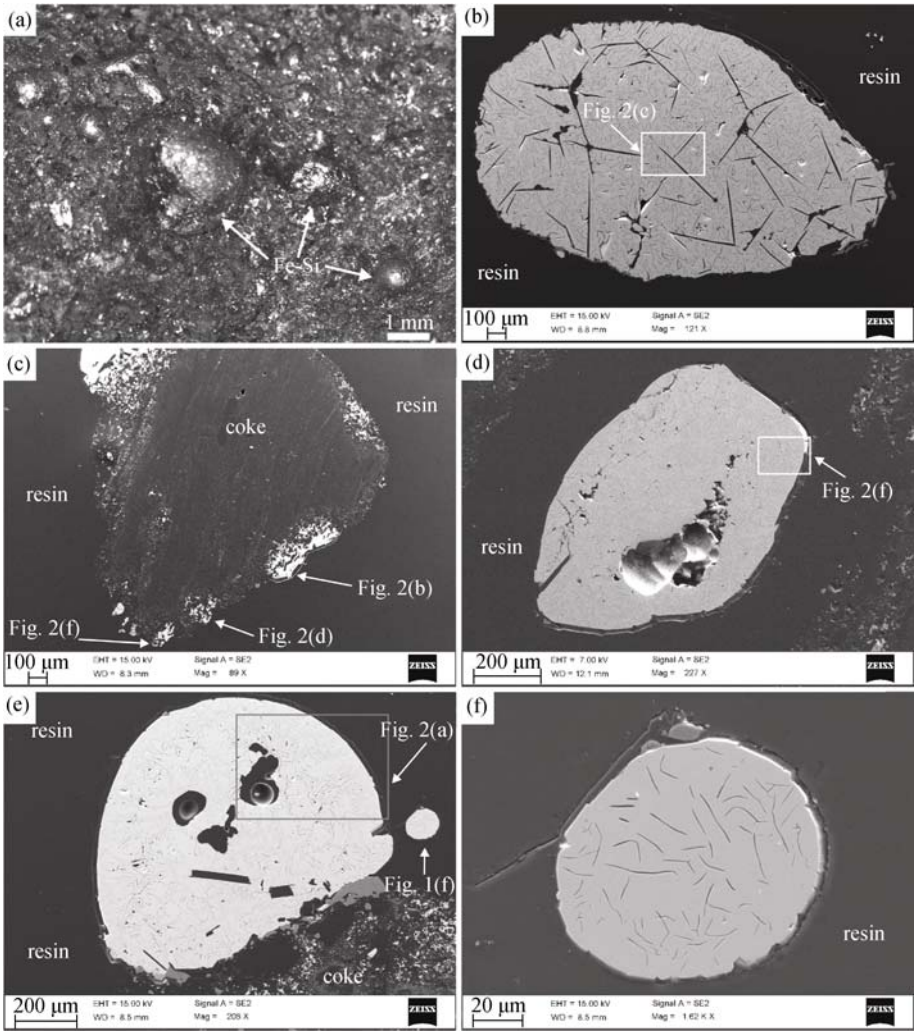

Fig. 1. Morphologies of Fe-Si droplets: (a) OM image on the original surface of BF coke; (b)-(f) SEM images in polished sections with different scales.

in Fig. 1(d). The droplets are covered by a thin shell of carbon in the thickness of 10-15 μm, as shown in Fig. 2(a), which has the geometrical facet bounded by the ridges of triangular cross-section, as reported earlier [13].

3.2. Composition of Fe-Si droplets

EDS analyses in Table 1 show that, most of droplets are quite close to $Fe_{0.75}Si_{0.25}$ in composition, which corresponds to Fe_3Si (the $D0_3$ modification of body-centered cubic phase). The only exception is an elliptic droplet, which has the formula of $Fe_{0.87}Si_{0.13}$. It should be mentioned that the EDS method employed here is regarded as a semi-quantitative one; for that reason, the separate study involving the WDS technique and more representative analytical dataset should be needed to describe the compositions of Fe-Si droplets in BF coke.

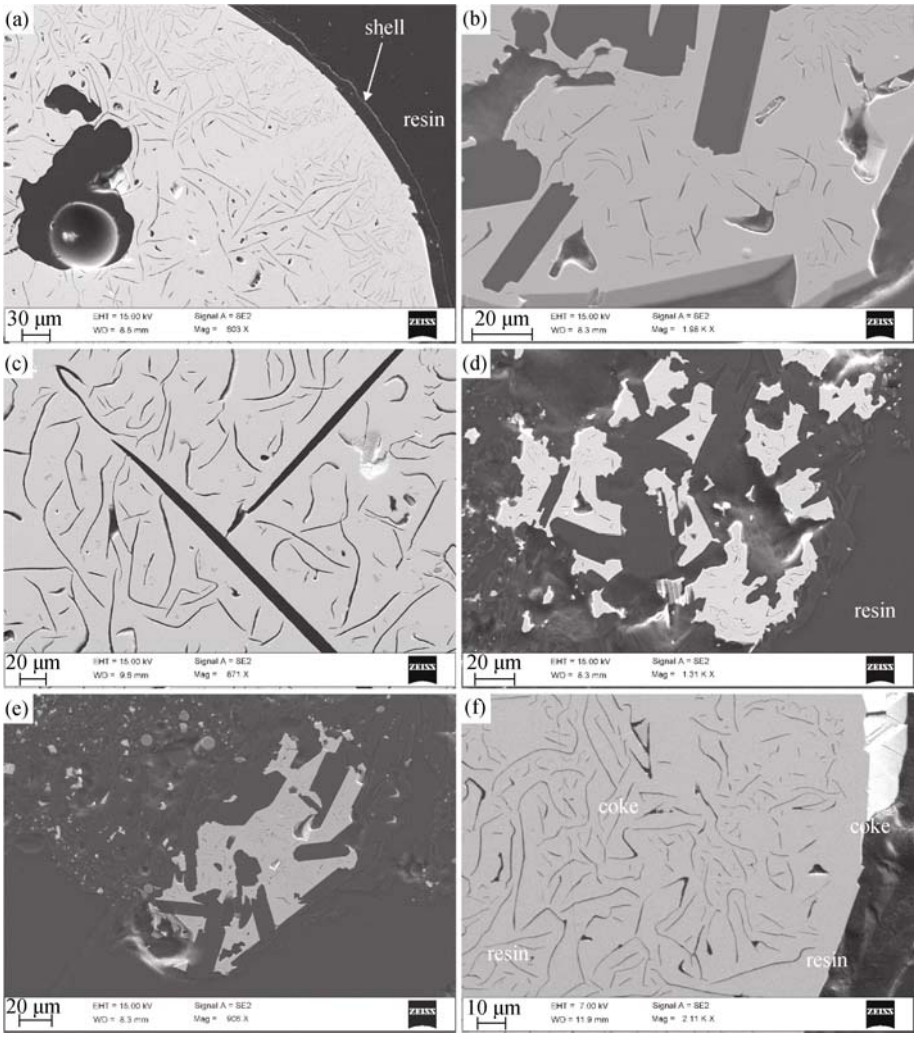

Fig. 2. SEM images of graphite in polished sections of Fe-Si droplets with different scales.

Table 1. EDS analyses of Fe-Si droplets

No.	Location	Composition of Fe-Si droplets		
		Fe content / wt%	Si content / wt%	Formula
1	Fig. 1(f)	84.99	12.78	$Fe_{0.77}Si_{0.23}$
2	Fig. 2(a)	86.07	12.63	$Fe_{0.77}Si_{0.23}$
3	Fig. 2(b)	85.17	13.68	$Fe_{0.76}Si_{0.24}$
4	Fig. 2(c)	92.22	7.21	$Fe_{0.87}Si_{0.13}$
5	Fig. 2(d)	85.41	13.23	$Fe_{0.76}Si_{0.24}$
6	Fig. 2(e)	82.47	14.33	$Fe_{0.74}Si_{0.26}$
7	Fig. 2(f)	85.38	13.08	$Fe_{0.77}Si_{0.23}$

3.3. Graphite in Fe-Si droplets

The shapes of graphite observed in the droplets can be divided into two categories: (1) well-formed tabular crystals and their aggregates with the relatively large size; (2) flakes with the structures similar as those in cast iron. Some of the droplets own both types of graphite.

Graphite crystals of the first category are found in some relatively large-sized droplets, which occur in the peripheral parts at the boundary between the droplet and coke in most cases, as shown in Figs. 1(c), 1(e), 2(b), 2(d), and 2(e). The crystals often have a tabular morphology and appear in the form of various intergrowths and aggregates, although the crystals of single well-formed shape have been observed in some cases, as shown in Figs. 2(b) and (e). The sizes of crystals varied from 5 μm in width to 200 μm in length with a width/length ratio between 1:3 and 1:5. It was proposed that the crystals of large size were formed during coke-iron interaction [1]. This suggests the penetration of the carbon matrix by molten iron through carbon dissolution and the precipitation reactions, which may produce the well-ordered graphitic carbon. When the penetration moved further into the carbon matrix, the precipitated small graphite crystals would be transformed into large flakes in later recrystallization steps [1].

The flakes with the structures similar as those in cast iron are observed in all the droplets studied here, as shown in Figs. 1(b), (d)-(f), and Fig. 2. Since Fe-Si droplets represent a parent material for cast iron, it seems reasonable to compare the graphite morphologies both in the droplets and cast iron by classification already developed. Such comparisons can also yield some advantages in the interpretation of results. The ASTM A247 classification divides all graphite flakes into five types: A) the randomly oriented flakes in uniform distribution; B) the rosette pattern of graphite flakes; C) the randomly oriented flakes in widely varied sizes; D) the fine pattern of flakes without graphite around; E) the graphite flakes with the preferred orientation and a quasi-regular pattern [10-11].

The appearances of graphite flakes vary from one droplet to another. The smallest rounded droplet with 0.1 mm in size includes the uniformly distributed and randomly oriented flakes (Figs. 1(e)-(f)). These flakes are 5-25 μm in length and 1 μm (or less) in thickness, which can be compared with the type A of ASTM. This A-type graphite can also be found in larger droplets, as shown in Figs. 1(e), 2(a), and 2(f), which possesses more complex shapes (linear, arc-like, folded) and more variations in length for hypoeutectic grey iron [15]. The droplets with arc-like and folded morphologies (Figs. 1(d) and 2(f)) have several interconnected voids as "a chain of bubbles" with the irregular shape, representing a relatively large total volume as shown in Fig. 1(d). The formation of these voids probably indicates the convection of molten material during the droplet movement on the surface of coke. In some cases, the areas containing graphite of type A are adjacent to the elongated zones, which are free of graphite in Fig. 2(a). Type A is also recorded in samples of the first category in Figs. 1(e), 2(b), 2(d), and 2(e), which coexists with large graphite flakes. According to Alp *et al.* [11], the presence of type A graphite reflects a higher cooling rate than that of type B graphite, which is not observed in the samples.

The straight and needle-like crystals are found in one droplet which has an unusual composition of the hosting Fe-Si phase (shown in Table 1 and Figs. 1(b) and 2(c)). Individual crystal can reach 500 μm in length and 10 μm in thickness. This graphite can be attributed to type C of ASTM A247 and similar in appearance to graphite C as "kish graphite" from hypoeutectic grey iron [15]. Such straight crystals are named as proeutectic flakes and primary flakes [12], when they grow in the liquid, unencumbered by the presence of austenite [12]. This graphite coexists in the droplets with smaller straight or arc-like flakes of type A.

4. Conclusions

Fe-Si droplets on the surface of BF coke samples are mostly composed of Fe_3Si and have various shapes (rounded, elongated, and irregular) and penetration degrees into the BF coke matrix. It is suggested that the shape and penetration level may depend on the saturation of molten iron by silicon during its interaction with the coke matrix and on the structural features of coke (cracks). The droplets are covered by a carbon shell of 10-15 μm in thickness. The graphite observed inside the droplets can be divided into two categories: (1) well-formed tabular crystals and their aggregates with the relatively large size; (2) flakes with the structures similar as those in cast iron, as the graphite of ASTM types A and C. Some of the droplets host both types of graphite.

The textures of the droplets probably reflect their composition, interaction with the coke matrix, and cooling conditions. This means that the droplets can be quite different even within one sample of coke. The differences in composition can be caused by the primary features of burden material (*i.e.*, the parent mineral association of piece of ore) and

also the amount and composition of minerals associated with the coke, which react with the droplets, moving down through the coke cone.

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