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Fe–Si particles on the surface of blast furnace coke

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Abstract: This study investigates the surface of unpolished samples of blast furnace (BF) coke drilled from the tuyere zone, which hosts Fe–Si particles (mostly Fe_3Si) that vary in size, shape, depth of submersion (penetration) into the coke matrix, and contact features with the surface. Based on the shape of the particles and the extent of their contact with the coke matrix, they have been grouped into three major types: (I) sphere-like droplets with limited contact area, (II) semi-spheres with a larger contact area, and (III) irregular segregations with a spherical surface, which exhibit the largest contact area among the three types of particles. Considering the ratio between the height (h) of the particles and half of their length at the surface level (l) along the cross-section, these three types can be characterized as follows: (I) $h > l$, (II) $h \approx l$, and (III) $h < l$. All the three types of particles can be found near each other. The shape and the extent of the contact depend on the degree of penetration of the material into the matrix, which is a function of the composition of the particles. Type (I) particles were initially saturated with Si at an earlier stage and, for that reason, they can react less with carbon in the coke matrix than type (II) and (III), thereby moving faster through the coke cone. Thermodynamic calculations have shown that the temperature interval of 1250–1300°C can be considered the starting point for Si entering into molten iron under quartz-dominated coke ash. Accordingly, the initial pick-up of Si by molten iron can be assumed to be mineral-related. In terms of BF practice, better conditions for sliding Fe–Si droplets through the coke cone are available when they come into contact with free SiO_2 concentrated into small grains, and when the $SiO_2/\Sigma Me_xO_y$ mass ratio in the coke ash is high.

Keywords: blast furnace practice; metallurgical coke; molten iron; iron silicide

1. Introduction

Several phases coexist in the lower part of a blast furnace (BF): gas phase, liquid phases (iron and slag), and solid phases (coke with associated minerals, coal powder, and char) [1–2]. The smooth flow of liquids and gases in the coke bed is very important for effective operation of the BF. During their descent through a coke bed, the molten iron droplets interact with carbon and mineral matter of coke. Thus far, several studies have investigated related phenomena, including phase relationships in the Fe–Si–C system [3–4], silicon behavior in BF [5], and the dissolution of coal and coke into liquid iron [6–10]. In particular, in the case of coke, it has been observed that the "ash composition is a dominant factor that influences the rate of carbon dissolution" and it "is not just a physical barrier to carbon dissolution; it actively participates in chemical reactions at the coke/iron interface" [9]. According to the other studies, "silica has the greatest effect due to the high levels in the ash. This silicon enters the liquid iron. This is seen to dictate the carbon accumulation in iron" [10].

Despite the detailed investigations and conclusive results reported in the abovementioned reference studies, data on the physical aspects of coke-molten iron interactions are still scarce. In particular, there is no clear understanding of how the size, shape, and composition of the molten iron droplets and their contact features with the coke can affect their movement through coke cone in BF. Even general information on the phase composition of Fe–Si droplets and their distribution on the surface of BF coke are limited. This is particularly related to difficulties in obtaining samples from the BF (tuyere drilling). Our earlier investigations of Fe–Si droplets associated with the BF coke have been focused on the crystallographic features of graphite found on the surface of the coke [11], and graphite observed inside the droplets [12]. The present study describes the morphology of Fe–Si particles, their size, composition, and mechanism of interaction (contact features) with the coke matrix and ash,

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on the basis of scanning electron microscopy (SEM/FESEM) investigations, microprobe (WDS) analysis, and thermodynamic calculations. It also discusses the influence of these properties on the behavior of molten iron (the Fe–Si phase) in BF.

2. Samples and methods

The original BF coke was taken from a drill core obtained from the tuyere zone of an operating BF at the Ruukki Steel Works (now part of Svensk Stål Aktiebolag (SSAB) Europe Ltd.) in Raahe, Finland. The selected coke was located at an interval of 25–50 cm from the tuyere level. The details of the tuyere drilling were similar to those reported by Kerkkonen [13]. After the sampling, 30 mm-long, 22 mm-wide and 5–8 mm-thick specimens were cut from the coke pieces under dry conditions [14], preserving the original surface. Subsequently, the specimens were fixed onto a glass plate of dimension 28 mm × 48 mm that fits into the specimen holder of a scanning electron microscope (SEM). In addition, more specimens were obtained from the same location, in order to prepare polished specimens. The dry-cut and the polished specimens were initially examined using a stereo microscope and optical microscope. Following that the specimens were observed using Jeol JSM-6400 SEM and Zeiss ULTRA plus field emission scanning electron microscope (FESEM), both equipped with an energy dispersive spectrometer (for EDS analysis). Furthermore, wavelength dispersive spectroscopy (WDS) analysis was performed using a Jeol JXA-8200 electron microprobe. Thermodynamic calculations under BF gas conditions were performed, in order to study the reactions between silica, carbon, and iron in the BF atmosphere.

3. Results

The investigations of unpolished sample surfaces have revealed that it hosts numerous particles, which vary in size, shape, depth of submersion (penetration) into the coke matrix (Figs. 1(a) and 1(b)), and contact features with the surface.

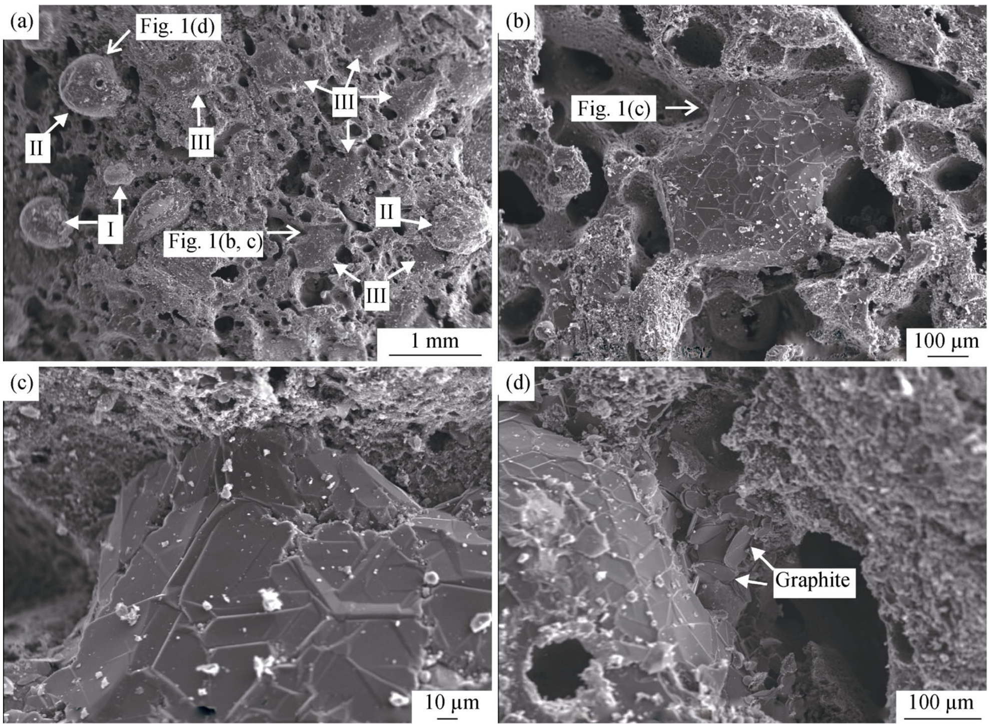

Fig. 1. Occurrence, size, and surface properties of Fe-Si particles. Jeol JSM-6400 scanning electron microscope (Institute of Electron Microscopy, University of Oulu). I, II, and III—types of particles (see text for details).

3.1. Occurrence, size and surface features of Fe-Si particles

The most abundant particles which were found in the samples are 0.1–0.5 mm in size (Figs. 1(a) and 1(b)), but there are also particles up to 10 mm in size, which could be seen with the naked eye. Some droplets and segregations are surrounded by a contact zone (0.1–1.5 mm), which consists of graphite crystals (Fig. 1(d)). However, particles of 5−10 mm in size are rarely observed in the samples. This probably means that the larger droplets easily descend through the coke to the bottom of the BF. This observation can be considered when evaluating the size of the pathway necessary for smooth movement of liquid iron through the coke cone in BF. Furthermore, high-magnification observation of the specimens using SEM/FESEM (Fig. 1(c)) indicates that the surface of the particles have geometric facets bounded by ridges of triangular cross-section. These carbon (as identified using EDS analysis) facets look similar to the synthetic graphitic shells formed on top of the millimeter-sized spherical transition metal cores in high vacuum [15]. On the other hand, these geometric facets in the polished specimens look like shells of width 10–15 μm (Fig. 2(b)). Some of the particles carry occasional graphite crystals on their surface.

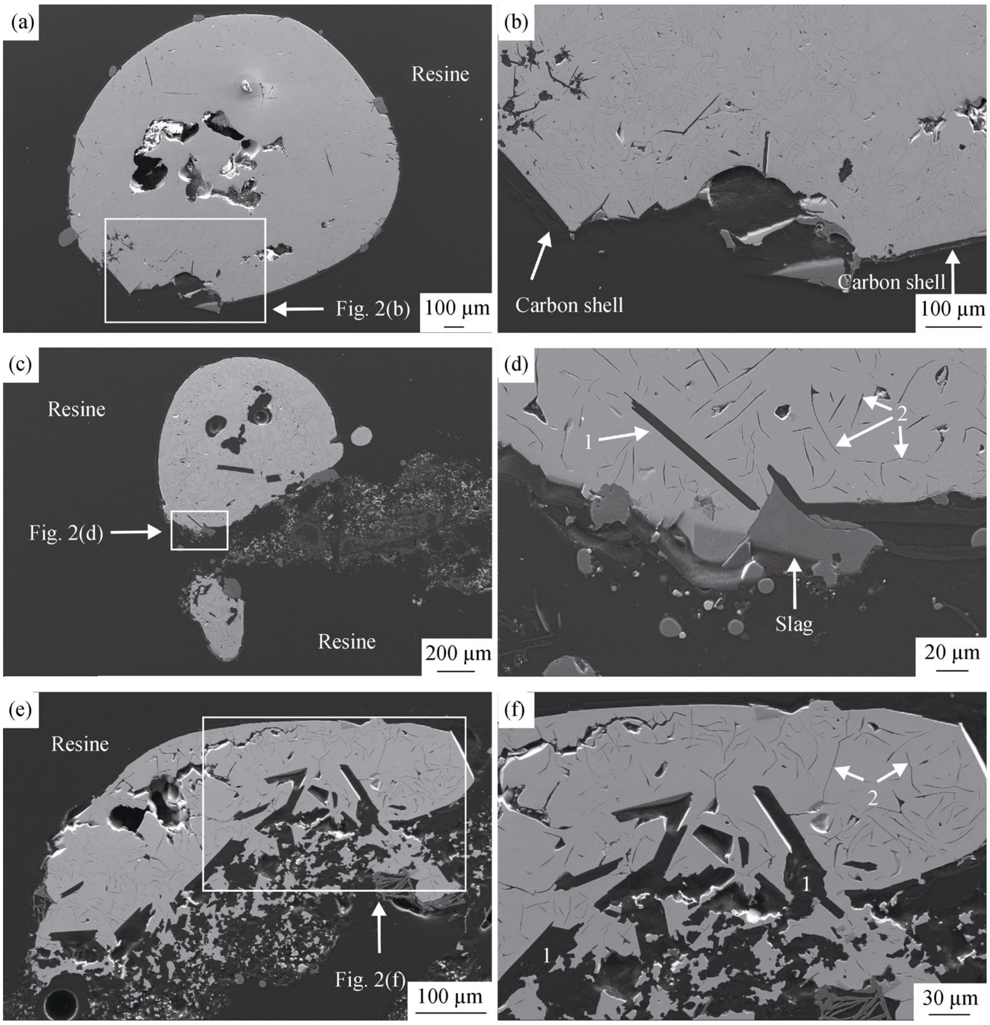

Fig. 2. Polished sections of Fe-Si particles. Zeiss ULTRA plus field emission scanning electron microscope (Institute of Electron Microscopy, University of Oulu). Note for (f): 1—graphite crystal; 2—graphite flakes with structures similar to those in cast irons [12].

3.2. Shape, composition, mechanisms of formation, and behavior of Fe-Si particles on the surface of BF coke

Most of the particles were of round or elliptical shape (droplets). However, irregular segregations with a spherical surface could also be observed in the samples. Special attention has been paid to the shape of the particles and the extent to which they contact the coke matrix. Accordingly, the particles have been grouped into three major types: (I) sphere- (ball-) like droplets with limited contact area (Fig. 1(1a), droplets marked as "I" and Fig. 2(a)), (II) semi- (hemi-) spherical droplets (50% of spheres) with a larger contact area (Fig. 1(a), droplets "II" and Fig. 2(c)), and (III) irregular segregations with a spherical surface that offer the largest contact area among the three types of particles (Fig. 1(a), droplets "III" and Fig. 2(e)). Considering the ratio between the height (h) of the particles and half of their length on the surface level (l) along the cross-section (Figs. 2(a), 2(c), 2(e); Fig. 3), these three types of particles can be characterized as: (I) $h > l$, (II) $h \approx l$, and (III) $h < l$. As can be seen in Fig. 1(a), all the three types of particles can be found near each other. The h/l ratio and, consequently, the extent of contact and degree of penetration of the Fe–Si phase inside the coke are related to the interaction features (reaction rate) of Fe–Si with the carbon matrix. In the first case (I), the h/l ratio is greater than 1 ($h > l$). Here, the reaction of Fe–Si with carbon seems to be very limited, as it can be observed in the contact zone of the droplet (Figs. 2(a) and 2(b)). Only a few tiny graphite crystals could be observed in this area. In the second (II) case (Figs. 2(c) and 2(d)), the h/l ratio is close to 1 (semi-sphere, $h \approx l \approx$ radius). The contact area contains several graphite crystals of thickness 5 μm and length 100 μm. Besides, a few larger crystals could be observed between the contact zone and the center of the semi-sphere. Finally, the third type (III) of particles have h/l ratio below 1, which provide more noticeable fingerprints of the reaction between Fe–Si and carbon. This area hosts the largest graphite crystals (Figs. 2(e) and 2(f)). In this case, the depth of penetration of Fe–Si into the carbon matrix is close to the value of h (Fig. 2(e)). Therefore, the thickness of the Fe–Si phase inside the matrix is comparable to the height of the particles above the surface. It could be noticed that the boundary between the Fe–Si and the coke surface is quite sharp for type I and II (Figs. 2(a)–2(d)) droplets, with some slag phases present in the area. In the case of type III particles (Figs. 2(e) and 2(f)), the contact area is rather uneven, also reflecting a high rate of reaction between the Fe–Si phase and the carbon matrix. WDS analyses performed during this study (Table 1) and the EDS data of our earlier investigations [12] indicate that most of the droplets have composition closer to Fe_3Si.

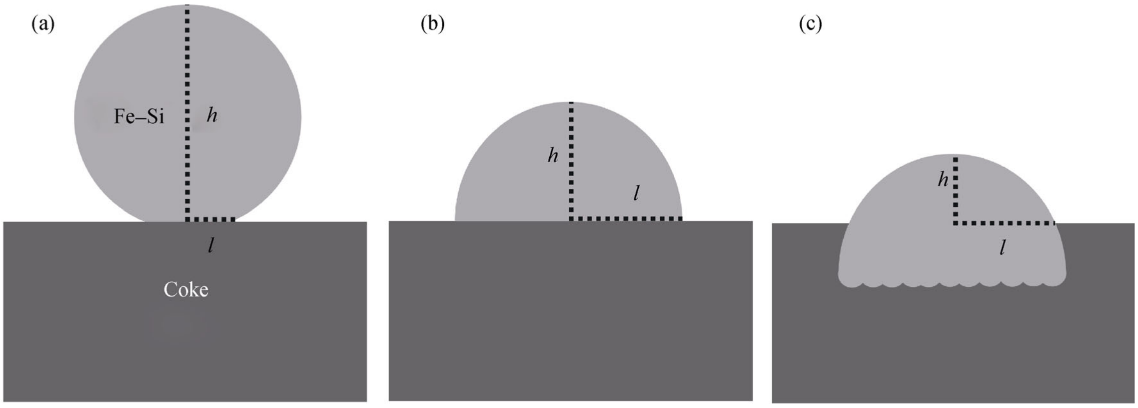

Fig. 3. *h*/*l* ratio for different types of Fe–Si particles. See text for details.

Table 1. Composition of Fe–Si droplets on BF coke

No.	Fe / wt%	Si / wt%	Formula
1	84.49	15.31	$Fe_{2.99}Si_{1.01}$
2	86.81	13.68	$Fe_{3.04}Si_{0.96}$
3	85.77	14.49	$Fe_{2.99}Si_{1.01}$

Note: WDS analysis performed using Jeol JXA-8200 electron microprobe, University of Oulu, Finland. 1—Fig. 2(a); 2—Fig. 2(c); 3—Fig. 2(e). The analyses also include trace amounts of Mn, V, Ti, and Ni.

3.3. Thermodynamic calculations

Thermodynamic calculations with FactSage software [16] (version 6.4) have been carried out for a temperature range of 1000–2000°C and BF gas conditions (44mol% CO, 4mol% H_2, 52mol% N_2 [17]). The system was set as follows: 1 mol SiO_2 + 1 mol C + 1 mol Fe + 100 mol gas. The ratio of solids and gas (1/1/1/100) was applied assuming an open system (gas flow). The results show (Fig. 4) that at lower temperatures tridymite, solid Fe–C–Si solution, and gas phases exist in the system. At approximately 1150°C, the Fe-based solid solution melts, together with a significant increase in the amount of carbon in this phase. At temperatures between 1250 and 1300°C, tridymite starts to react: SiO_2 is reduced and Si is dissolved in liquid Fe–C–Si solution. In the temperature interval of 1350–1400°C, the amount of SiO(gas) starts to increase. At about 1425°C, the silicon content in Fe–C–Si liquid solution reaches its maximum value. With further increase in temperature, more and more Si reacts into SiO(gas) and enters the gas phase. At approximately 1460°C, tridymite (what is left of it) transforms into cristobalite. Finally, at about 1725°C, all the cristobalite has reacted (mostly to gaseous SiO, but partly to Si dissolved in liquid Fe–C–Si solution).

4. Discussion

Taking into account the shape of the Fe–Si particles and the extent of their contact with the coke matrix, it can be suggested that the type I particles can easily slide on the surface of coke when compared to type II and III particles.

Consequently, type I particles move more quickly through the coke cone in BF. In terms of this study, the most favorable (for mobility through coke cone) ratio of the various types of droplets (Fig. 3) should conform to the order I > II > III. Such conditions can be achieved when the amount of silica in the system is relatively high.

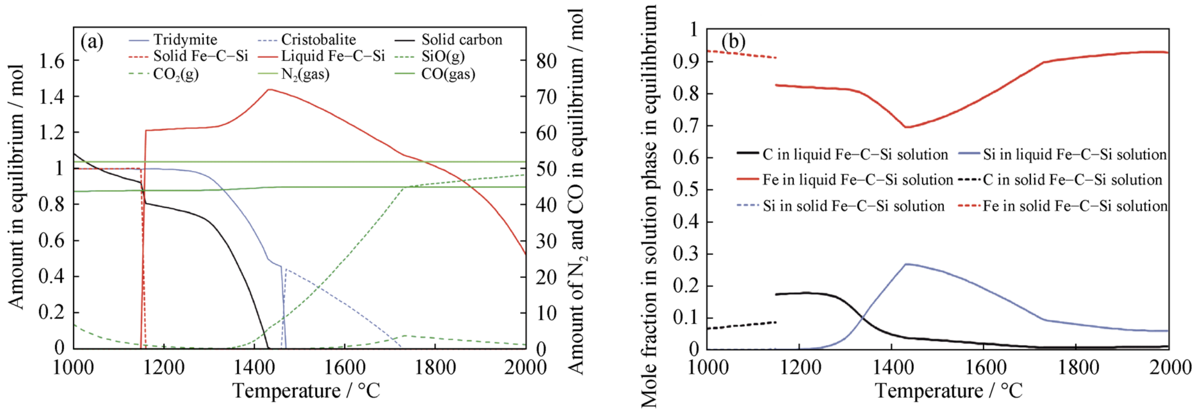

Fig. 4. Thermodynamic calculations of a system containing 1 mol SiO_2+1 mol C+ 1 mol Fe+100 mol gas (44% CO, 4% H_2, 52% N_2 at 1000–2000°C). The line "Si in liquid Fe–C–Si solution" is located close the temperature axis until 1200°C.

The most common Si-bearing mineral is quartz (SiO_2). Accordingly, it should be considered the most important Si source for formation of Fe–Si and its saturation by carbon. In coking coals, quartz occurs in its natural form (α-polymorph) [18], but it can also be formed from aluminosilicates during their thermal decomposition at coking temperatures [18]. In the latter case, it occurs as a part of complex mineral aggregate. As for the assimilation of mineral-related silicon by molten iron is concerned, there should be a contact between the melt and the Si-bearing minerals. This can happen when the Si-bearing minerals of coke are exposed to (located on) its surface and also when the silica is available in the burden material.

The WDS results presented in this study (Table 1), together with our earlier investigations [12], indicate that the droplets are mostly composed of Fe_3Si. Comparable compositions were reported for experimental Fe–Si alloys saturated with SiC or graphite at the 1523–1723 K (1250–1450°C) interval [4], which corresponds to temperatures typical of the low part of BF. The assessment of the Fe–C–Si system [3] reports the existence of Fe_3Si phase at 1200°C. This temperature is common for the area, which is located considerably above the tuyere zone. However, the Si content in our samples is much higher than that in hot metal (pig iron, 0.53wt%–2.05wt%) as reported by Yamagata *et al.* [19].

The degree of reaction of the Fe–Si phase with a carbon matrix (reflected in the shape of the particles) and, consequently, the rate of movement of molten Fe–Si particles through the coke cone in a BF depends on their composition (the whole system involving Fe, Si, and C). On one hand, "silica has the greatest effect due to the high levels in the ash. This silicon enters the liquid iron" [10]. On the other hand, the carbon content in Fe–Si alloys in general [20], and particularly in Fe_3Si [3], is limited. In the latter case, it is less than 2wt% [3]. Therefore, saturation of the Fe_3Si phase with carbon can be achieved rather quickly, provided that the thermal conditions are met in a given part of BF and that the silicon is readily available. The saturation of molten iron by Si in BF can take place by capturing it from the burden material (including minerals), coke ash (mineral form), and by the SiO [5] and Si gas phases, as discussed below. It appears that the type I particles have been saturated with Si earlier than type (II) and (III), and for that reason they can react less with the carbon of coke matrix, thus moving more quickly through the coke cone.

Thermodynamic calculations (Fig. 4) suggest that Si from tridymite (SiO_2) dissolves in liquid Fe–C–Si solution at 1250–1300°C. Thus, this temperature interval can probably be considered as the starting point for Si entering into molten iron under quartz-dominated coke ash, and perhaps, under quartz-bearing burden material. Consequently, the initial pick-up of Si by molten iron can be considered as mineral-related, probably through the capture (and/or contact) of Si-bearing minerals from the coke and burden material by the descending droplets of molten iron. The SiO(g) phase complements the saturation of molten iron with silica at higher temperatures. These estimations are in agreement with the data reported by Kamenev *et al.* [21]. However, the mechanism underlying the evolution of Si content in molten iron in the range of Fe(±Si) (upper part of BF) → Fe_3Si (tuyere) → Fe (+0.5wt%–2.0wt% Si in hot metal) deserves more detailed studies.

While the distribution of the SiO(g) phase, in general, is a function of temperature and the availability of Si-bearing minerals (in the coke or/and in the burden material), there is also the practical question of what conditions would better facilitate the interaction of molten iron and mineral-related silicon in solids (minerals). It seems obvious that free grains of SiO_2 can be incorporated by (mixed with) molten iron at an earlier stage than those trapped inside the complex mineral aggregates. However, if the free SiO_2 grains are trapped inside the coke matrix, then the silica will be accessible for incorporation by molten iron only gradually, as the coke is consumed during its descent through the BF. Since investigations on the composition of the burden material was beyond the scope of this study, we restricted our discussion to coke and Fe–Si interaction. Therefore, the conditions would be better if the relative proportion of SiO_2 in the total coke ash is high. The latter can be verified by XRD measurements. Besides, indirect assessment could also be made using XRF data for $SiO_2/\Sigma Me_xO_y$ mass ratio (where Me_xO_y = $CaO + Al_2O_3 + MgO + K_2O + Na_2O$). The higher the ratio, the better the conditions will be. In addition, the grain size of the minerals could also play an important role. The smaller the quartz grains are, the more easily they can be captured by the descending droplets of molten iron and the larger the total surface area for the reaction will be. The other practical outcome of this suggestion is that a high proportion of ash in coke is not always detrimental for the BF process, provided that the $SiO_2/\Sigma Me_xO_y$ mass ratio is high. Ideally, it would be better if all coke-related ash is represented by quartz and the other elements belonging to its structure as impurities. However, “quartz has a very low tolerance for the incorporation of impurities because its void space is fairly cramped” [22] and “the most generally abundant impurity is Al, which present in the range of < 13 ppm to 15000 ppm” [22]. Thus, the maximum (desirable) limit of other elements in coke ash can be established near 1.5wt% (calculated from total ash). This means that the $SiO_2/\Sigma Me_xO_y$ mass ratio should be above 65 to indicate that most of the ash is quartz-related.

5. Conclusions

(1) The surface of BF coke hosts numerous Fe–Si particles, which vary in size, shape, depth of submersion (penetration) into the coke matrix, and contact features with the surface.

(2) WDS results obtained during this study, together with our earlier investigations [12], have found that the droplets are mostly composed of Fe_3Si.

(3) Based on the shape of the particles and the extent of their contact with the coke matrix, they have been grouped into three major types: (I) sphere-like droplets with a limited contact area, (II) semi-spheres with a larger contact area, and (III) irregular segregations with a spherical surface, which exhibit the largest contact area among the three types of particles. Considering the ratio between the height (h) of the particles and half of their length on the surface level (l) along the cross-section, these three types of particles can be characterized as: (I) $h > l$, (II) $h \approx l$, and (III) $h < l$. All the three types of particles can be found near each other.

(4) The shape and the extent of the contact depend on the degree of penetration of the material into the matrix, which is a function of the composition of the particles – they are interrelated. The higher concentration silica in the particles, the less reaction with (and penetration into) the matrix will be. This also influences the appearance of sphere- and semi-sphere shaped particles. Type I particles have been saturated with Si earlier and, for that reason, they can react less with the carbon of coke matrix, thus moving more quickly through the coke cone.

(5) Thermodynamic calculations suggest that the temperature interval of 1250–1300°C is the starting point for Si entering into molten iron under quartz-dominated coke ash. Consequently, the initial pick-up of Si by molten iron can be assumed to be mineral-related. The SiO(g) phase complements the saturation of molten iron with silica at higher temperatures.

(6) In terms of BF practice, better conditions for sliding Fe–Si droplets through the coke cone exist when they contact with free SiO_2 (preferably in small grains), and when the $SiO_2/\Sigma Me_xO_y$ mass ratio in the coke ash is relatively high.

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