



Multiphase Reaction among Coke, Primary Slag, and Liquid Iron: Indications of a Novel Direct Reduction Mechanism

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The multiphase reaction among coke, primary slag, and liquid iron has been studied by using different experimental schemes. The influence of FeO reduction on the C content dissolved in the molten iron was determined, and the effect of FeO reduction on coke degradation in molten iron and slag was also evaluated. The reaction extent was determined by scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) and electron probe microanalysis (EPMA). The results showed that the reaction rate of C dissolution into liquid iron by coke was faster than the FeO reduction. The serious degradation of coke mainly occurs by the combined action of carbon dissolution reaction, FeO reduction reaction, and CO/CO₂ gasification reaction. Coke degradation at the slag–iron interface is significantly stronger than that in the molten slag layer and liquid iron layer because C dissolved in iron participates as a reducing agent in the FeO reduction reaction.

INTRODUCTION

Ironmaking is a complicated process used to produce liquid pig iron with the desired temperature and composition from iron ore economically and efficiently.¹ On the one hand, the separation of metal elements (mainly Fe) and oxygen elements in the ore should be realized, which is the reduction process. On the other hand, it is necessary to realize mechanical separation of the reduced metal and gangue, which is the melting and slagging process.^{2,3} Blast furnace (BF) ironmaking is the most common method of ironmaking available nowadays.^{4,5} The ore in low-temperature lump zone of BF has not been fully reduced, then quickly falls into the high-temperature zone in the lower part. Softening and melting of ore then occur, resulting in primary slag with high FeO that flows down through the coke bed. The FeO content of primary slag fluctuates in a wide range of 5% to 30%,⁶ varying depending on different BFs or different parts of the same BF. The reaction of FeO in slag

with carbonaceous materials such as coke is crucial for the smelting process, which is directly related to the pig iron yield.^{7,8} In extant literature, the reduction reaction between molten slag and carbonaceous materials (coke, char, and graphite) has been studied in depth, including the kinetics and mechanism of the reaction process. Sarma et al.⁹ studied the reduction of FeO in smelting slags by solid carbon by x-ray fluorescence spectrum, finding that gas film would be generated at the beginning of the reduction reaction. Increasing the FeO content is conducive to the chemical reaction, but the relationship is nonlinear. Teasdale et al.^{10,11} found that small iron droplets are formed on the bubble surface due to indirect reduction by CO₂/CO transformation. The FeO reduction reaction rate in slag by coke and graphite is faster than that by char. On the one hand, the slag appears to be nonwetting on char (disordered carbon structure). On the other hand, liquid Fe-C droplets were rapidly formed at the slag–C interface. Story et al.^{12,13} focused on the influence of the reaction between coke and gas phase (CO₂/CO) on the reduction reaction. When graphite is involved in the reaction, the effect of gas–carbon reaction is not obvious, but it increases significantly when the reactant is coke. Min

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et al.^{14,15} carried out a detailed analysis of the reduction reaction kinetic process and obtained the relationship between reduction rate and FeO content (activity). The Boudouard reaction is a restrictive process when the FeO content is high, while the Boudouard reaction and mass transfer of FeO in slag act together when FeO is low. The product bubbles pass through the slag and cause stirring of the melt. Se et al.¹⁶ used the constant volume pressure increase technique (CVPI) and established a model to predict the particle size of residual carbon according to the reduction reaction kinetics. Kim et al.^{17,18} experimentally studied the viscosity of a five-element slag system containing FeO.

However, existing research considers reduction of FeO in complex slag systems by solid carbon and liquid iron containing carbon. In the smelting process, molten slag, liquid iron, solid carbon, and gas phase coexist, forming a complex system. To determine the physicochemical changes between these phase directly affects the quality and production of the final molten iron. Two different experimental schemes were designed to study the multiphase coupled reaction of molten slag–liquid iron–coke–gas phase. In addition, the influence of FeO reduction on the carburizing and degradation behavior of coke was evaluated.

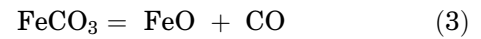
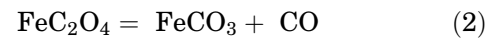
EXPERIMENTAL PROCEDURES

To study the influence of FeO on the carburizing and degradation behavior of coke, an experimental scheme was designed for pure FeO and FeO in the CaO–SiO₂–MgO–Al₂O₃–FeO slag system. High-purity electrolytic iron, ferrous oxalate dihydrate, graphite powder, and coke were selected as experimental samples. The composition of the samples is presented in Table I. The proximate analysis, ultimate analysis, and ash composition of coke are presented in Supplementary Table 1.

Experimental Scheme 1: Pure FeO

To study the effect of pure FeO, high-purity electrolytic iron, ferrous oxalate dihydrate (used for decomposition to form FeO, see Eqs. 1–3), and graphite powder were mixed to ensure sufficient

carbon for reduction of FeO and carburization of iron. The specific proportioning scheme is presented in Supplementary Table 2. Corundum crucible was used during the experiment. After reaching 1200°C at a heating rate of 20°C/min, the samples were maintained for 60 min to decompose FeC₂O₄·2H₂O.^{19,20} Heating was continued to 1550°C at a rate of 10°C/min, then this temperature was held for 60 min. After reaction, the samples were cooled to room temperature at ~ 50°C/min through the introduction of high-purity argon (5 L/min). The C content in the samples for the different schemes was determined. To eliminate experimental errors, each group was tested for four times.



Experimental Scheme 2: FeO in Slag

The effect of the FeO content in the CaO–SiO₂–MgO–Al₂O₃–FeO slag system on coke degradation and dissolution was studied in the case of coexistence of molten iron and slag. Figure 1 shows a schematic and physical diagram, while Supplementary Table 3 presents the ratios for five slag schemes with varying FeO content. Before experiment, the slag was premelted in the molybdenum crucible to reduce the volume, always being kept in Ar throughout the process. High-purity magnesia crucible (outside diameter 40 mm, inside diameter 33 mm, height 90 mm) was selected for dissolution experiment. The weight of iron and slag was calculated to ensure that the height of the liquid iron layer and molten slag layer was 8 mm and 6 mm, respectively. After the iron-slag had been heated to 1550°C at a rate of 20°C/min and had stabilized, the coke was added into the molten slag–iron, and the reaction time was controlled for 1 min without rotation in high-purity Ar (2 L/min). After the experiment, the coke sample was taken out of

Table I. Composition of experimental materials

Raw material	Composition	Manufacturer
High-purity electrolytic iron	Fe > 99.98%, C < 0.0005%, S < 0.0008%, P < 0.0005%, Co < 0.0004%, O < 0.0080%	Aladdin
Ferrous oxalate dihydrate	≥ 99%	Energy Chemical
CaO, SiO ₂ , MgO, Al ₂ O ₃	≥ 99.95%	Aladdin
Graphite powder	≥ 99.95%	Aladdin
Coke	C 84.58%, H 0.78%, N 1.12%, S 0.64%, O 0.63% FC 86.19%, M 0.20%, A 12.07%, V 1.54%	Shougang, China

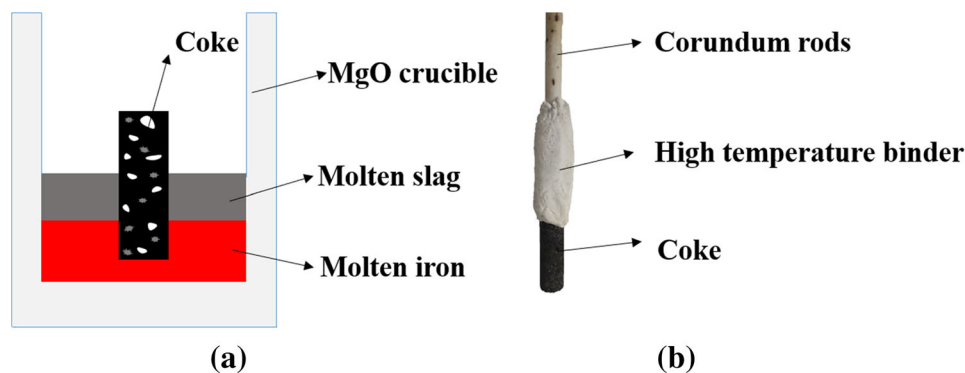


Fig. 1. Schematic diagram of reaction of coke in molten iron–slag (a) and coke connection with corundum rod for fixation (b)

the furnace and cooled in deionized water at $\sim 200^\circ\text{C}/\text{min}$ to room temperature. To facilitate the placement of coke in slag iron and control the reaction time, the coke (initial diameter 12 mm, height 60 mm) was connected with a corundum rod using a high-temperature binder. Before the experiment, the coke was preheated at $\sim 1200^\circ\text{C}$.

Characterization of Samples

The observed objects were cut from the selected sample under dry condition and fixed by resin using an Opal 480 mounting machine. The fixed samples were ground using silicon carbide paper to 2000 grit, then polished by diamond paste until $1\ \mu\text{m}$ particle size using lubrication fluid. The samples were coated with gold for scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS, Zeiss Gemini 500 and ULTIM MAX). Electron probe microanalyzer (EPMA, Shimadzu 1720) was applied for nondestructive elemental analysis of micron-scale volume on the surface of the material.

RESULTS AND DISCUSSION

Effect of FeO Content on Carbon Dissolution into Liquid Iron

The results for the carbon content in the samples after the end of experiment scheme 1 are shown in Fig. 2. With increasing FeO, the carburizing amount in liquid iron decreased gradually. The final iron sample was observed by SEM; the results are shown in Fig. 3. Backscattered SEM images showed an uneven distribution of C in the microscopic appearance of iron after cooling, which cannot directly prove its uneven dissolution at high temperatures. However, the uneven precipitation of dissolved carbon during the cooling process can prove the unevenness of the sample composition and indirectly prove the unevenness of carbon dissolution. Reduction reaction of FeO included direct reduction using C and indirect reduction using CO. Reaction of C with CO_2 in a gasification reaction is one route for carbon consumption (Eqs. 4–6). It also proved that the reaction rate of

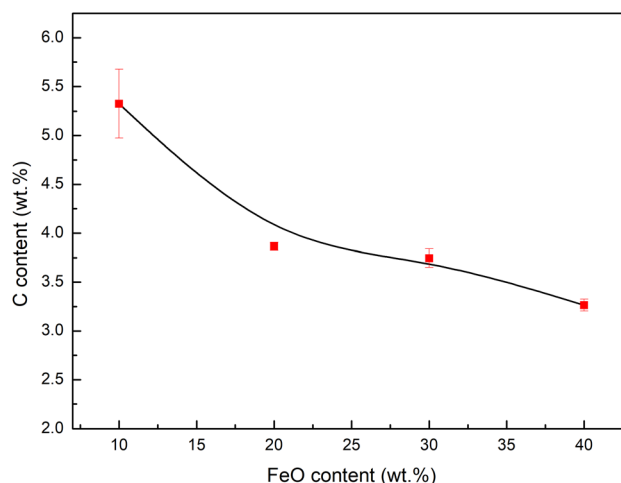
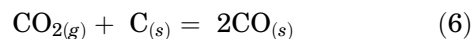
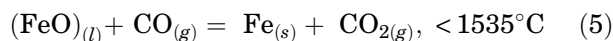
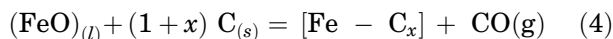


Fig. 2. Carbon content in liquid iron with different FeO contents

C dissolution into liquid iron was better than that of FeO reduction.



Effect of FeO Content in Slag System on Coke Degradation

The macroscopic size of coke after dissolution in molten iron and different slags was determined (through an average of five measurements); the calculation results are shown in Fig. 4a. It can be seen that the size of coke in the slag–iron junction part was significantly smaller than that in the molten slag layer and liquid iron layer. With increasing FeO content in the slag system, the size of these three parts showed a decreasing trend, indicating greater carbon consumption. This effect was more obvious for coke located in the slag–iron

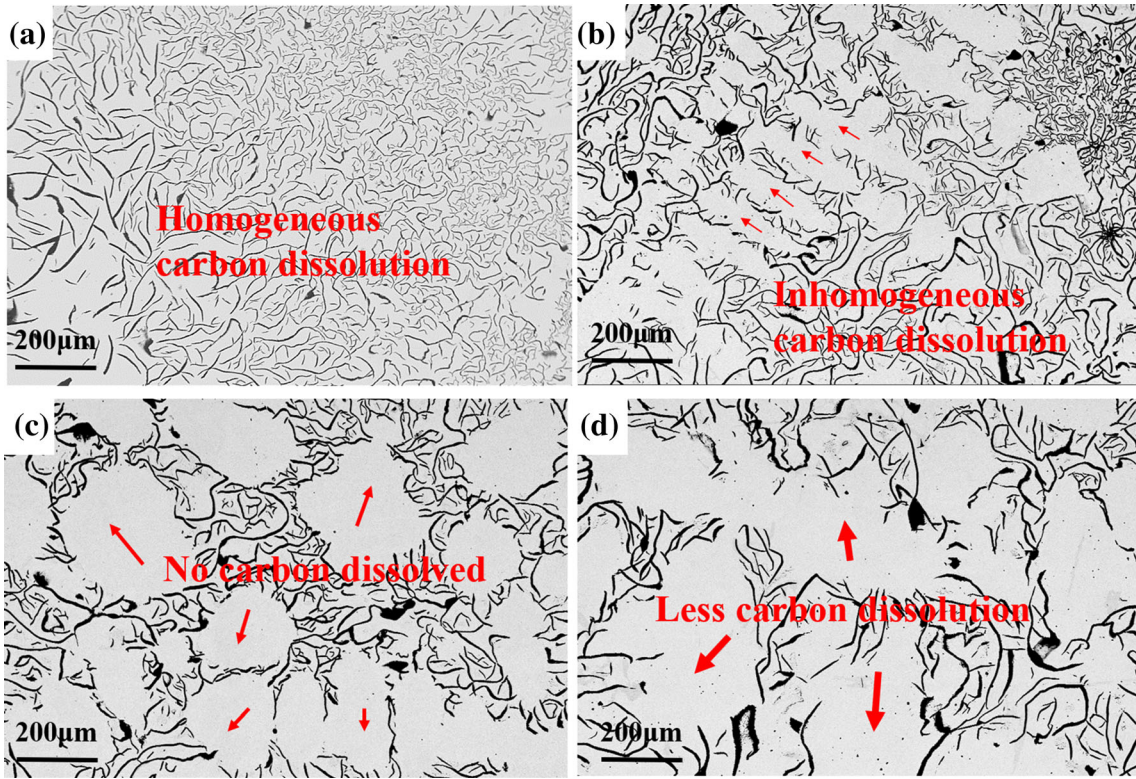


Fig. 3. SEM of iron after carbon dissolution with different FeO content: (a) 3 wt.%, (b) 6 wt.%, (c) 9 wt.%, and (d) 12 wt.%

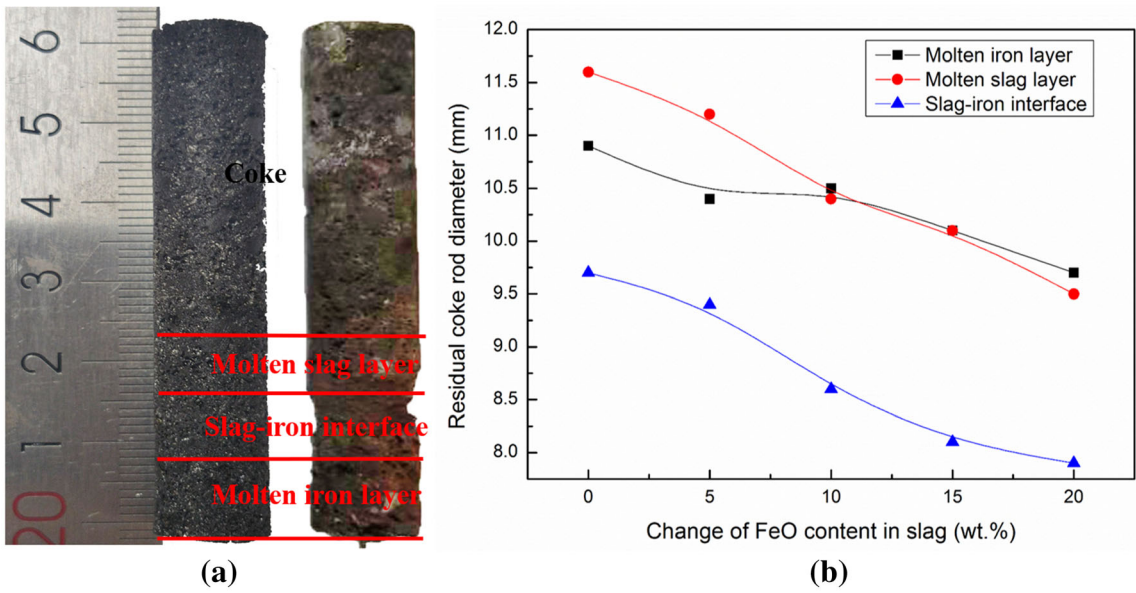


Fig. 4. Macromorphology of coke before and after dissolved in molten iron (a) and slag and change in size with different FeO contents (b)

interface, followed by the coke located in the slag layer, and finally the iron layer. In addition, the carburization of iron layer was less affected by the composition of the slag system in a short period of time. Also, the fluctuation range was monitored to be less than 5%, even though the C consumption at the slag–iron interface reduces the C contact with liquid iron. The overall conclusion is that the reduction rate of FeO in slag by coke is lower than that of coke dissolution into molten iron.

The morphology of coke in the slag layer after experiment 2 was observed by SEM. Taking the slag containing 15% FeO as an example, the results are shown in Fig. 5. A small amount of slag adheres to the coke surface, and the composition of slag was still mainly CaO–SiO₂–MgO–Al₂O₃–FeO. The deterioration of coke in slag was not serious, despite the combination of indirect and direct reductions. The formation of bubbles by Boudouard reaction also intensifies the contact of various reactants and enhances the degradation of coke. EDS analysis revealed that its composition was mainly the same as that of ash in unreacted coke.^{21,22} The weight loss of coke after dissolution into molten iron–slag was only about 1 g. This means that only ~ 0.12 g ash in coke dissolved into the slag. Therefore, it is assumed that the composition of the slag will not change during the experiment.

The morphology of coke in the molten iron layer was observed and is shown in Fig. 6a. The change of the average diameter of coke in molten iron layer was more obvious, indicating that the dissolution of coke in liquid iron was stronger than slag. The wettability between liquid iron and coke is poor, and the surface of coke does not show attached iron drops.^{23,24} The composition of ash in coke did not change significantly, remaining in the silicate

aluminate system. The coke morphology at the slag–iron interface is shown in Fig. 6b. FeO in slag is reduced by C in liquid iron to form a CO/CO₂ gas phase, which makes the reduction reaction proceed continuously. Meanwhile, small iron drops from FeO reduction appear at the interface between coke and molten slag, flowing to the side of liquid iron after aggregation. Figure 6c shows a backscattered image of the slag phase attached to the coke surface. EPMA revealed that the slag phase was mainly silicate, magnesia–aluminum spinel, and SiO₂. A small amount of metal Fe and solid solution are included. The FeO in the slag was almost completely reduced, and the molten iron and slag entered the pores of coke.

Dissolution and Degradation Mechanism of Coke Caused by Slag–Iron

The reason for the serious coke dissolution and degradation at the interface can be explained based on Fig. 7. When the FeO content is lower than 20%, the softening and melting temperatures of slag are significantly reduced. The most basic reactions at the interface include dissolution of C into liquid iron and reduction of FeO in slag. However, there are two reasons for the faster dissolution of coke at slag–iron interface. On the one hand, the C dissolved in liquid iron can participate in direct reduction of FeO on the molten layer side.^{25,26} On the other hand, the C concentration in molten iron decreases because of reduction of FeO, which accelerates the dissolution of coke. The CO generated in this process can continue to participate in the indirect reduction reaction to generate CO₂ gas, resulting in a liquid boiling phenomenon.²⁷ With

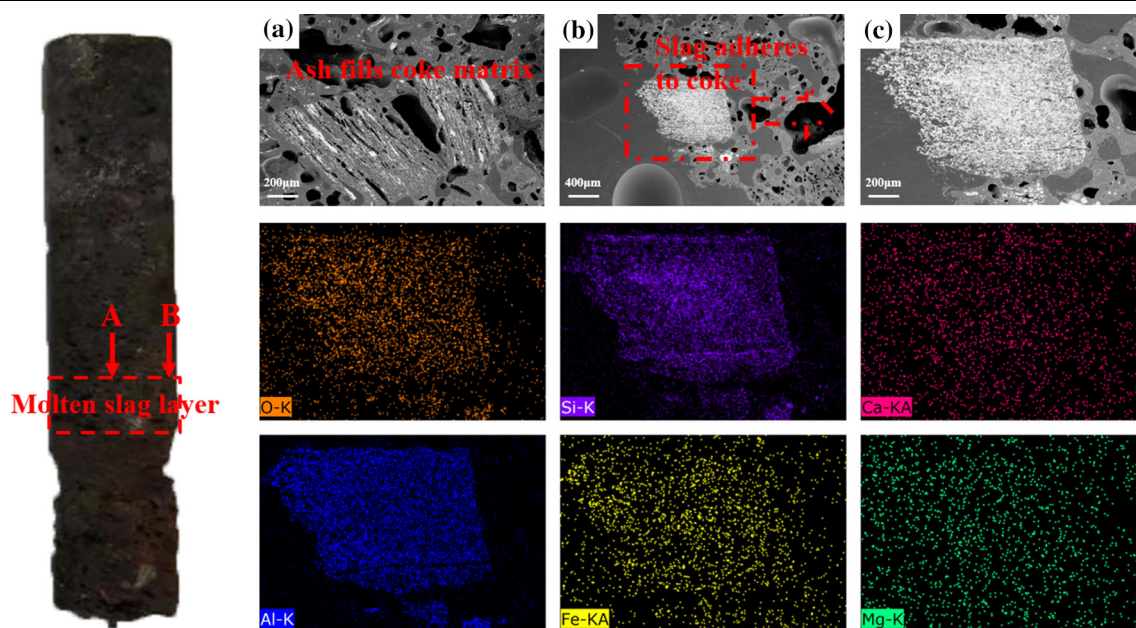


Fig. 5. Morphology and maps of coke in slag layer: (a) internal morphology of coke; (b, c) surface morphology of coke. EDS mapping for (c)

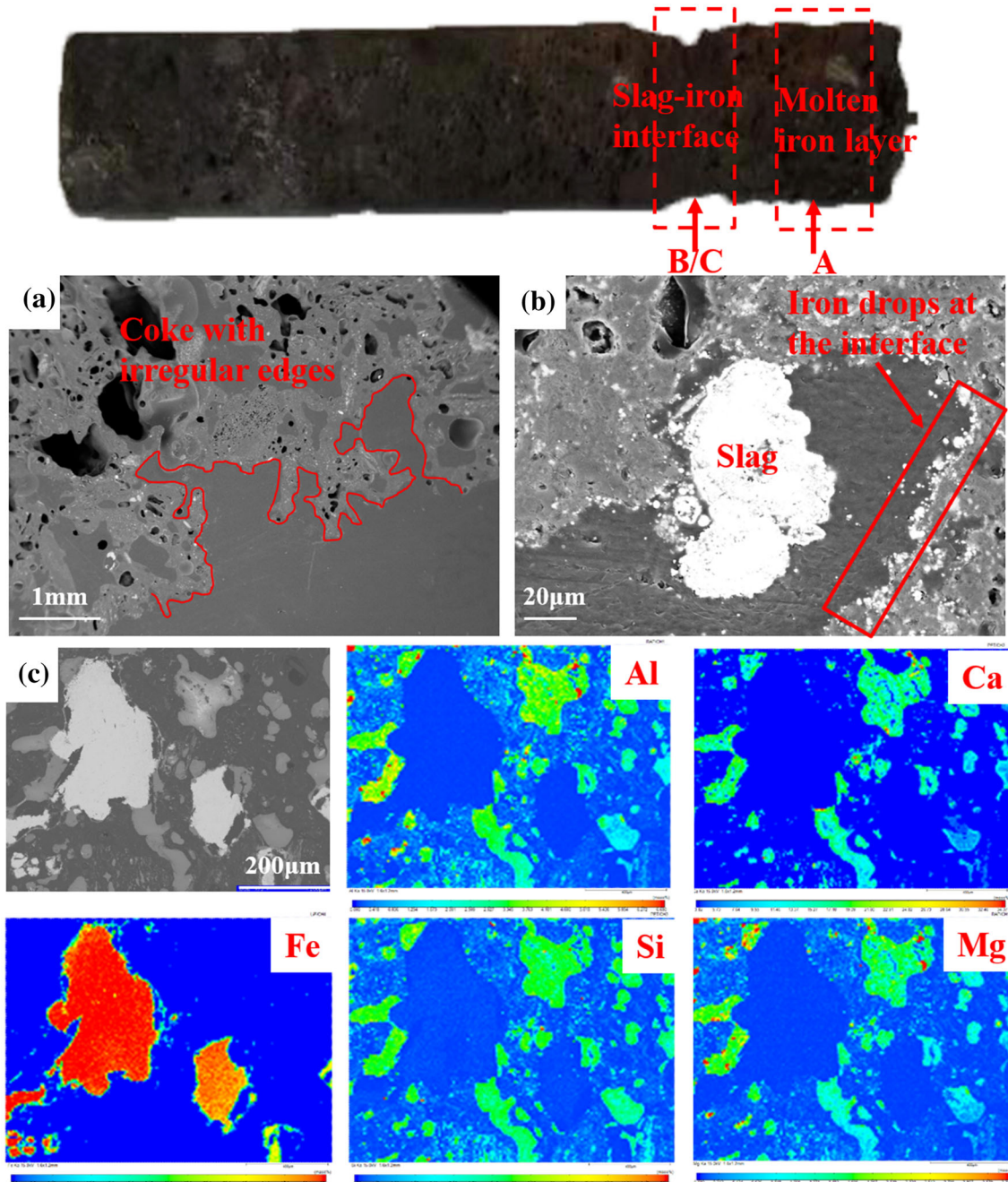


Fig. 6. Morphology of coke sample in molten iron layer (a), morphology of coke at slag-iron interface (b), and slag adhering to coke in slag-iron interface with corresponding element distribution (c)

increasing FeO content, the reduction reaction intensifies and promotes further carburizing.

CONCLUSION

The interaction between molten slag-liquid iron-coke-gas phase was investigated by using two different experimental schemes. The influence of the presence of FeO on the C dissolved in molten iron and the degradation of coke by molten iron and slag was obtained. The results are as follows:

1. The reaction rate of C dissolution into liquid iron was faster than that of FeO reduction. The degradation of coke at the slag-iron interface was obviously stronger compared with that in the molten slag layer or molten iron layer. Increasing the FeO content caused further degradation of coke.
2. The composition of the slag system had little influence on the dissolution of C into liquid iron. The serious degradation of coke at the interface is mainly the result of the combined action of

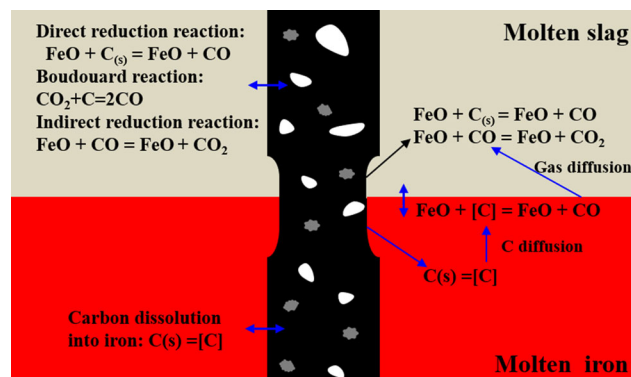


Fig. 7. Multiphase reaction mechanism among coke, primary slag, and liquid iron

carbon dissolution reaction, reduction reaction, and gasification reaction.

- The reduction of iron oxides below the soft melting zone in BF is seriously affected by the carbon dissolution reaction into molten iron. The influence of C dissolution on FeO reduction also plays an important role besides coke gasification reaction.

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DECLARATIONS

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there are no conflicts of interest.

SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at <https://doi.org/10.1007/s11837-021-04915-4>.

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