



# Influence of reaction of $\text{Al}_2\text{O}_3$ and carbonaceous materials in $\text{Al}_2\text{O}_3$ -C refractories on aluminum and carbon pick-up of iron

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## Abstract

Carbon-containing  $\text{Al}_2\text{O}_3$  refractory crucibles and pure  $\text{Al}_2\text{O}_3$  refractory crucible were fabricated to study the effect of carbon-containing  $\text{Al}_2\text{O}_3$ -C refractories on aluminum and carbon pick-up of iron. Refractory crucibles with pure iron powder were placed in a vacuum induction furnace and heated at 1600 °C for regular time under flowing argon atmosphere. The Al and C contents of iron samples were analyzed, and iron samples were also investigated using a field scanning electron microscope equipped with energy-dispersive spectroscopy. The results showed that carbon materials did affect the interaction of ( $\text{Al}_2\text{O}_3$ -C)/Fe system, carbothermal reduction in alumina occurred in the reaction system and the extent of reactions depended on the kinds of carbon materials.

**Keywords**  $\text{Al}_2\text{O}_3$ -C refractory · Liquid iron · Aluminum pick-up · Carbon pick-up · Carbothermal reduction

## 1 Introduction

$\text{Al}_2\text{O}_3$ -C-based refractories got a great development in iron and steelmaking in recent years and especially employed in continuous casting process for steel control in steelmaking plant due to its superior refractoriness. A lot of work has been done on the improving heats life of  $\text{Al}_2\text{O}_3$ -C refractories so as to meet the long casting sequence requirements [1–5]. With the increasing demand on high-quality steel, interactions between carbon-containing refractories and steel and their effects on the steel quality became the focus of attentions in steelmaking [6–9]. The work of Li et al. [10, 11] showed that the carbon dissolution from carbon-containing refractory lining into molten steel was the primary reason for the increase in carbon content. However, fewer attentions were paid to the aluminum pick-up of steel when such refractories were used as the lining in steelmaking.

The reaction between solid  $\text{Al}_2\text{O}_3$  and solid C will not occur below 2220 °C at atmospheric pressure in the air according to the work of Frank et al. [12]. Thus, the reaction of solid  $\text{Al}_2\text{O}_3$  and solid C was ignored in steelmaking

process which was usually proceeded at a much lower temperature. The reaction mechanism of  $\text{Al}_2\text{O}_3$ -C refractories and liquid iron is still not identified nowadays although research works on interactions of ( $\text{Al}_2\text{O}_3$ -C)/Fe system have been made during the past decade because the conflicting evidence emerged from different experiments. For instance, Khanna et al. [13–15] studied the reactions of  $\text{Al}_2\text{O}_3$ -C refractories and liquid steel, and the carbothermal reduction of  $\text{Al}_2\text{O}_3$  was confirmed in their experiment. Khanna's work was novel because the current velocity of melt which adheres to the wall of  $\text{Al}_2\text{O}_3$ -C-based submerged nozzle is almost zero in steel casting; thus, the carbothermal reduction of alumina in ( $\text{Al}_2\text{O}_3$ -C)/Fe system is possible. On the other hand, Zienert et al. [16] found that solid  $\text{Al}_2\text{O}_3$  was continuously dissolved in molten iron that enhanced the aluminum content in the melt; CO gas was produced continuously from the dissolved oxygen and carbon in the melt at the same time. Hence, it can be seen from Zienert's research that the carbothermal reduction of solid  $\text{Al}_2\text{O}_3$  and solid C could not be the explanation for the laboratory result observed in Khanna's study.

The purpose of this work was to investigate the reactions of liquid iron and  $\text{Al}_2\text{O}_3$ -based materials with or without carbon materials and their effects on the aluminum and carbon contents of iron at high temperature in order to identify whether the carbothermal reduction of alumina in  $\text{Al}_2\text{O}_3$ -C refractories is the reason for Al pick-up of iron.

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**Table 1** Chemical composition of raw materials (wt.%)

Material	C	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	S	VM
Tabular alumina	–	0.02	99.420	0.02	–	–	–	0.360	–	–
Flake graphite	97.49	0.59	0.200	0.32	0.038	0.080	0.038	0.190	0.080	0.94
Petroleum coke	98.99	0.20	0.091	0.13	0.062	0.011	0.005	0.005	0.057	0.42
Microcrystalline graphite	91.76	3.87	0.730	0.55	0.160	0.090	0.210	0.050	0.090	2.54

VM Volatile matter

**Table 2** Formulation of specimens (wt.%)

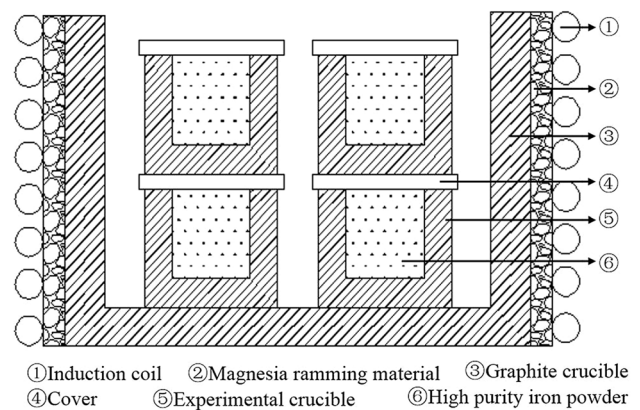
No.	Corundum			Flake graphite	Microcrystalline graphite	Petroleum coke	Phenolic resin (additional)
	3–1 mm	1–0 mm	74 μm				
1	45	25	10	20	–	–	5
2	45	25	10	–	20	–	5
3	45	25	10	–	–	20	5
4	45	25	30	–	–	–	4 (water)

Three kinds of carbon materials were introduced in Al<sub>2</sub>O<sub>3</sub>–C refractory crucible preparation, and non-carbon-containing Al<sub>2</sub>O<sub>3</sub>-based refractory crucible was also prepared.

## 2 Experimental

Tabular alumina (TA, Almatix Corp.), was mixed with flake graphite (FG, 149 μm), microcrystalline graphite (MG, 74 μm), and petroleum coke (PC, 88 μm), respectively. Carbon materials were provided by Wugang refractories company. The weight percentage of TA and carbon material was 80 and 20 wt.%, respectively, in Al<sub>2</sub>O<sub>3</sub>–C mix, and Al<sub>2</sub>O<sub>3</sub>–C mix was made as matrix for refractory crucible fabrication. Table 1 shows the composition of starting materials. The iron powders (IP) were provided by Taiyuan Iron and Steel (Group) Co. Ltd., and the composition of pure iron powder was Mn 0.00018 wt.%, Si 0.0014 wt.%, C 0.0013 wt.%, Al 0.00065 wt.%, S 0.001 wt.%, Ca 0.0017 wt.%, and Fe the balance.

The compounding of refractory crucible is shown in Table 2. Al<sub>2</sub>O<sub>3</sub>–C mix was fabricated into crucible shape and then dried at 230 °C for one day. And then, Al<sub>2</sub>O<sub>3</sub>–C refractory crucible charged with 13 g iron was put into a vacuum induction furnace (ZGIL0.01-50-4B, Jinzhou, China). The furnace was vacuumized to 200 Pa at the beginning of experiment and then purged with argon gas until  $1.013 \times 10^5$  Pa; after that, the refractory crucible with iron powder was heated at 1600 °C for 10, 20, 30, 40, 50, and 60 min, respectively, under flowing argon atmosphere (The current velocity of argon

**Fig. 1** Schematic diagram of experiment

was 10 L/min). The schematic diagram of experiment is illustrated in Fig. 1. Pure Al<sub>2</sub>O<sub>3</sub> refractory crucible (sample No. 4 in Table 2) was also made (water was used as the binder) in order to compare the results with carbon-containing Al<sub>2</sub>O<sub>3</sub>–C crucible.

Iron sample obtained in the experiment was processed and observed using a scanning electron microscope (SEM, JSM-6610, JEOL, Japan) and an energy-dispersive spectrometer (EDS, QUANTAX200-30, BRUKER, Germany), while the aluminum content of metal samples was detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an emission spectrometer (ThermoElemental Corp., USA).

### 3 Experimental results

#### 3.1 Relationship of aluminum and carbon pick-up of iron to soaking time

The relationship of aluminum and carbon contents of iron sample taken from refractory crucible with soaking time is illustrated in Fig. 2a, b, respectively. The curve 4 in Fig. 2a shows that the aluminum pick-up of iron sample obtained from pure Al<sub>2</sub>O<sub>3</sub> refractory crucible was the minimum and increased slightly with increasing the soaking time. The Al pick-up of iron sample taken from FG-containing Al<sub>2</sub>O<sub>3</sub>-C refractory crucible was the maximum, as shown by the curve 1 in Fig. 2a. The variation tendency of aluminum content of iron taken from FG and MG-containing refractory crucible was similar (the curves 1 and 2 in Fig. 2a), namely the aluminum content of iron reached the highest when the soaking time was 30 min and then decreased. The aluminum content of iron in PC-containing Al<sub>2</sub>O<sub>3</sub>-C crucible was increased with the increase in soaking time, as shown by the curve 3 in Fig. 2a. Figure 2b shows that the results of carbon pick-up of iron from different refractory crucibles were similar with those of aluminum pick-up. There was almost no carbon pick-up in iron taken from pure Al<sub>2</sub>O<sub>3</sub> refractory crucible because there was no carbon material in it.

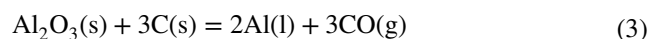
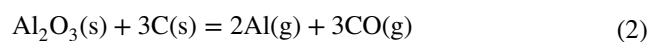
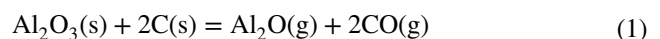
#### 3.2 SEM and EDS analysis

The electron microscopy and energy spectrum analyses on iron sample taken from different refractory crucibles and soaking time were done after experiment, and the typical results are given in Figs. 3, 4 and Table 3.

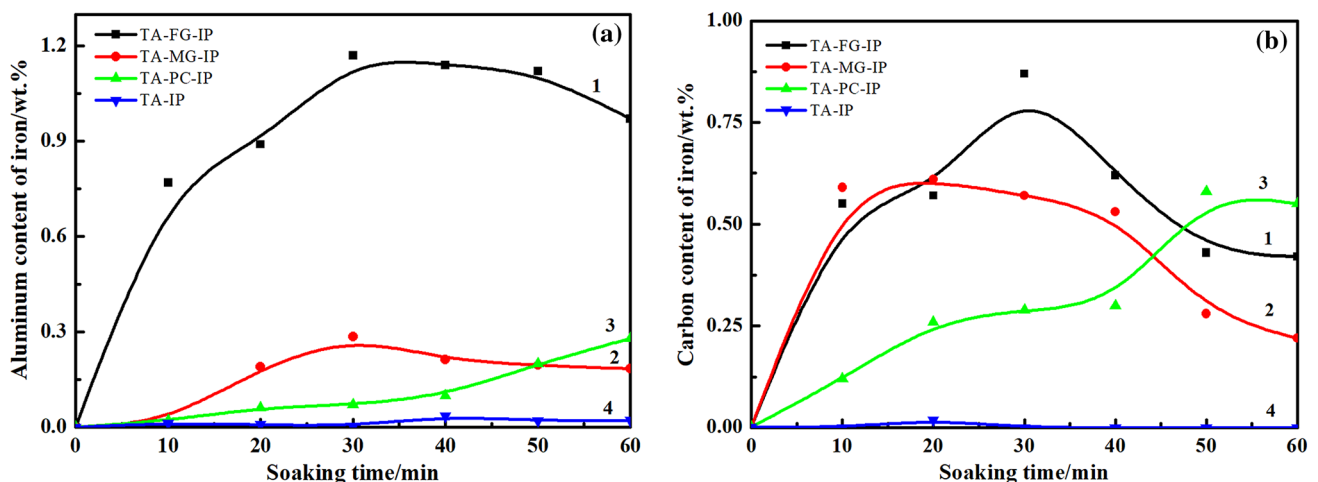
The detected elements in metal sample are shown in Table 3. Carbon cannot be detected by EDS accurately, and thus, carbon was excluded in the results. Table 3 shows that Al content in iron sample taken from FG-containing Al<sub>2</sub>O<sub>3</sub>-C refractory crucible was the maximum and aluminum content of sample taken from pure Al<sub>2</sub>O<sub>3</sub> crucible was the minimum. The Al content in the pure iron powder was 0.00065 wt.%, which meant that the detected Al in iron sample came from Al<sub>2</sub>O<sub>3</sub> materials in refractory crucible. The variation tendency of aluminum content of iron detected by EDS (Table 3) was the same as that analyzed by ICP-AES (Fig. 2a) when compared the aluminum content of iron in 30 and 60 min.

### 4 Discussion

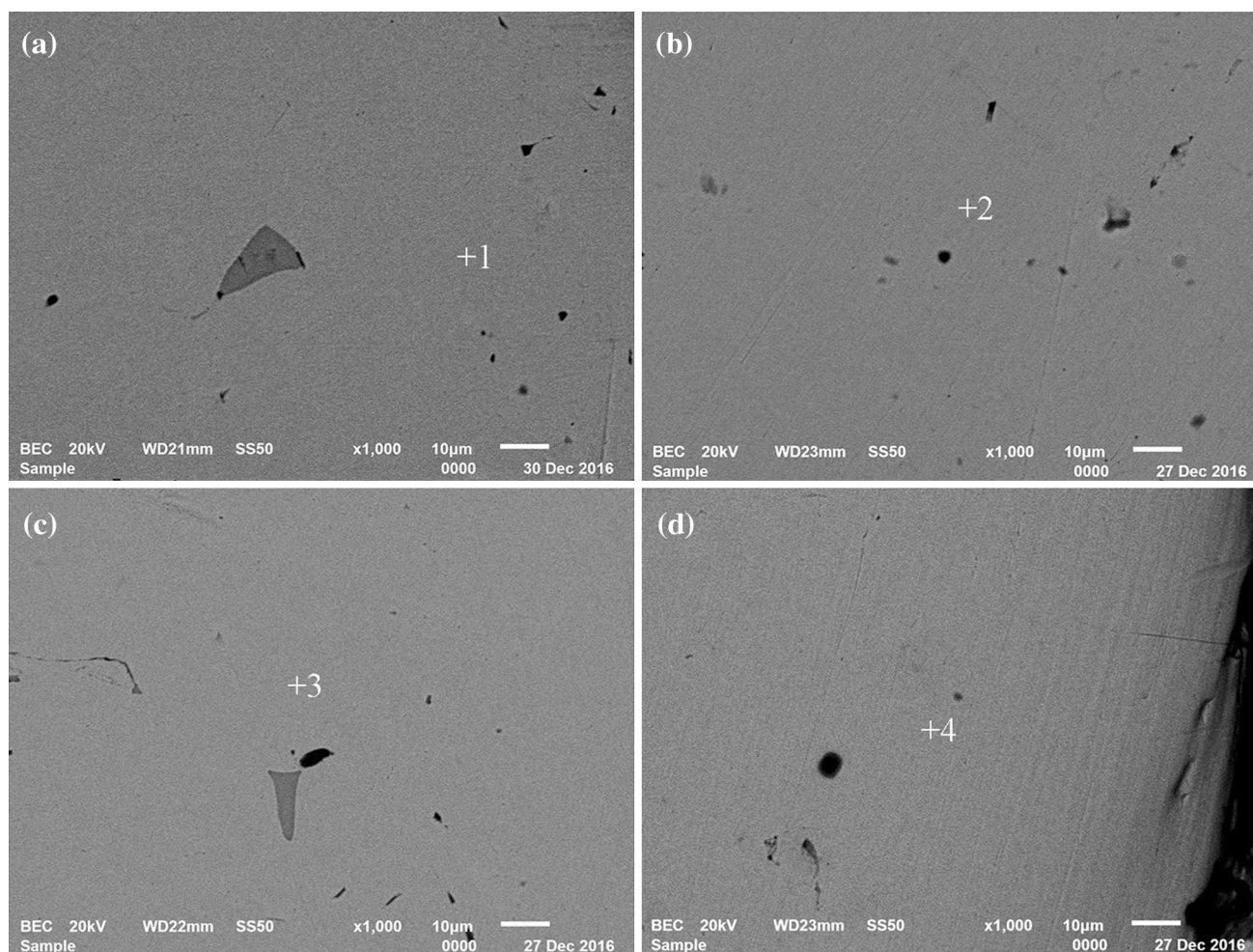
The aluminum content of iron was affected by the reactions among the (Al<sub>2</sub>O<sub>3</sub>-C)/Fe system. Reactions occurring in Al<sub>2</sub>O<sub>3</sub>-C refractories at high temperature are illustrated in reactions (1)–(3).



The relationship between free enthalpy change of reaction  $\Delta_r G$  and starting temperature of reactions (1)–(3) is shown in Fig. 5. It can be seen that decreasing CO partial pressure is favorable for the mentioned reactions, which means that carbothermal reduction of Al<sub>2</sub>O<sub>3</sub> can be proceeded in this experiment condition.



**Fig. 2** Relationship between aluminum (a) and carbon (b) contents of iron and soaking time. 1 Iron sample from TA-FG crucible; 2 iron sample from TA-MG crucible; 3 iron sample from TA-PC crucible; 4 iron sample from TA crucible (Al<sub>2</sub>O<sub>3</sub> crucible)



**Fig. 3** SEM photographs of iron samples after soaking for 30 min from TA-FG crucible (a), TA-MG crucible (b), TA-PC crucible (c), and TA crucible ( $\text{Al}_2\text{O}_3$  crucible) (d)

The gas products such as  $\text{Al}_2\text{O}$  and Al were moved away from the system with the flowing argon quickly. Liquid Al dissolved into molten iron and increased the aluminum concentration of iron. Reactions in  $\text{Al}_2\text{O}_3$ -C refractories were influenced significantly by carbonaceous materials; the extent of reactions among  $\text{Al}_2\text{O}_3$  and flake graphite was the maximum, while the extent of reactions among  $\text{Al}_2\text{O}_3$  and petroleum coke was the minimum, because crystalline degree and reducibility of FG were the best and those of the PC were the worst (amorphous material).

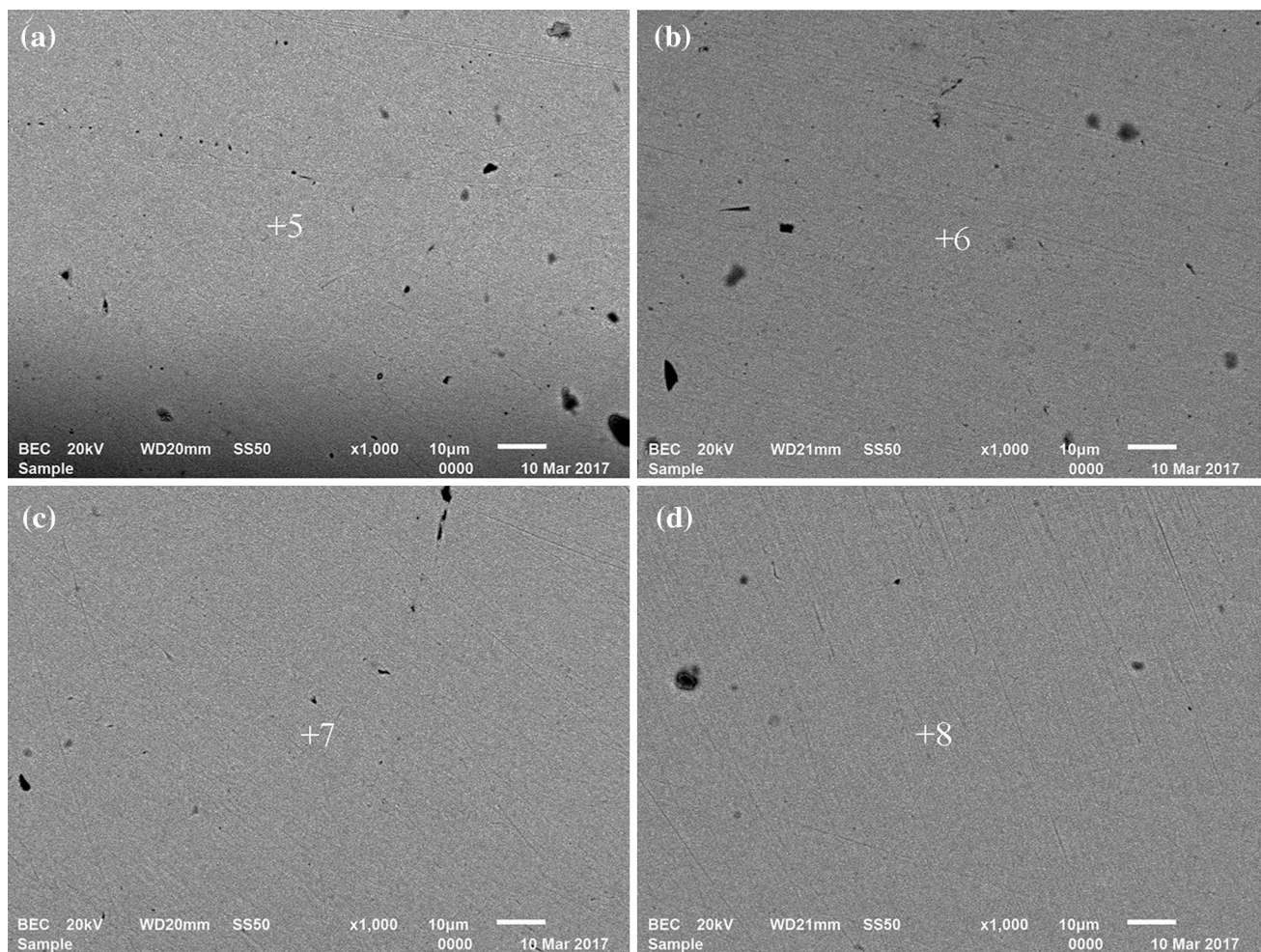
On the other hand, solid  $\text{Al}_2\text{O}_3$  dissolved into molten iron, which results in the increase in soluble Al and O contents of molten iron [17], and the soluble Al content was increased with the decreasing O content (reaction (4)).



Carbon dissolution reaction from carbonaceous materials occurred soon after iron sample was melted in  $\text{Al}_2\text{O}_3$ -C refractory crucible as follows:



The carbon pick-up of iron obtained from FG-containing  $\text{Al}_2\text{O}_3$ -C refractory crucible was the maximum at the beginning of the melting (the curve 1 in Fig. 2b) because the crystalline degree of flake graphite was the best; and then, the carbon pick-up of iron was decreased due to the formation of decarburization layer at the boundary between iron and refractory crucible [18]. The variation tendency of carbon content in iron sample taken from FG and MG-containing refractory crucible was similar (the curves 1 and 2 in Fig. 2b). The carbon pick-up of iron sample taken from MG-containing  $\text{Al}_2\text{O}_3$ -C refractory crucible was less than that taken from FG-containing  $\text{Al}_2\text{O}_3$ -C refractory crucible because the crystalline degree of MG



**Fig. 4** SEM photographs of iron samples after soaking for 60 min from TA-FG crucible (a), TA-MG crucible (b), TA-PC crucible (c), and TA crucible (Al<sub>2</sub>O<sub>3</sub> crucible) (d)

**Table 3** EDS result of points in Figs. 3 and 4

Point	Weight percentage/%		Atomic percentage/%	
	Fe	Al	Fe	Al
1	98.83	1.17	97.60	2.40
2	99.72	0.28	99.42	0.58
3	99.94	0.06	99.88	0.12
4	99.98	0.02	99.96	0.04
5	99.02	0.98	97.99	2.01
6	99.83	0.17	99.65	0.35
7	99.70	0.30	99.38	0.62
8	99.96	0.04	99.92	0.08

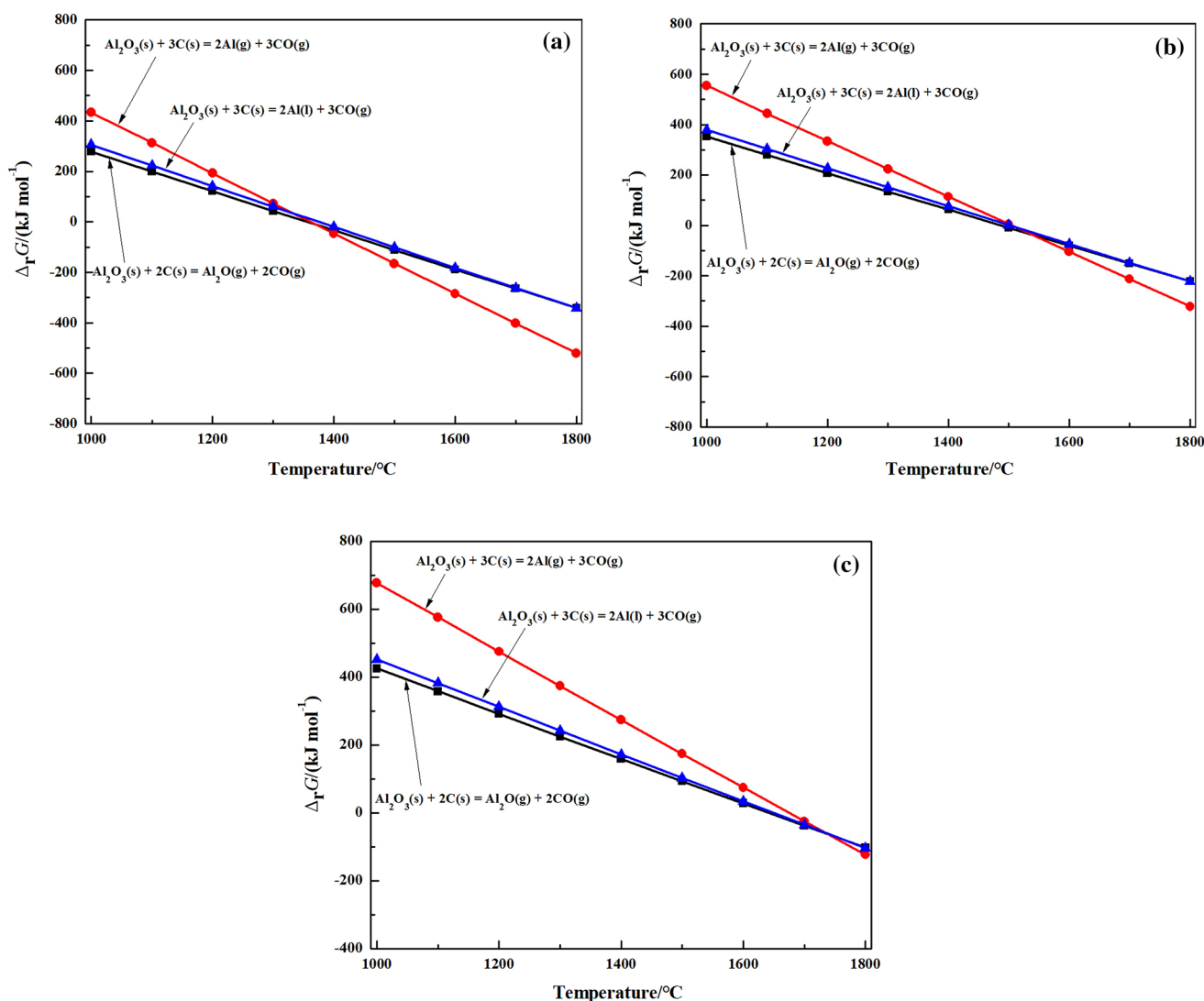
was less than that of FG. Loose structure emerged in PC-containing Al<sub>2</sub>O<sub>3</sub>-C refractory crucible, resulting from microstructure evolution of petroleum coke during heating [19]; thus, liquid iron penetrated into the PC-containing

Al<sub>2</sub>O<sub>3</sub>-C refractories in the experiment and the enlarged contact area between liquid iron and refractories was beneficial to the carbon pick-up of iron. Although the crystalline degree of PC was the worst, the carbon pick-up of iron obtained from PC-containing Al<sub>2</sub>O<sub>3</sub>-C refractories was steadily increased, as shown by the curve 3 in Fig. 2b.

CO was produced by the reaction of [C] and [O] at subsequent stage of the experiment which was shown in reaction (6).



CO was exuded out of the furnace with the flowing argon, which was favorable for the reaction shown in reaction (6) and caused the decrease in [O] concentration. At the meantime, the dissolution of solid Al<sub>2</sub>O<sub>3</sub> in melt was speeded up with the decrease in [O] concentration (reaction (4)); therefore, the concentration of [Al] was increased (Fig. 2a).



**Fig. 5** Relationship between  $\Delta_r G$  and temperature for reactions (1)–(3). **a** CO partial pressure of 10 Pa; **b** CO partial pressure of 100 Pa; **c** CO partial pressure of 1 kPa

Magnetic field accelerated the diffusion of carbon in the molten iron [20]. The crystalline degree of FG is the best among these carbon materials, the second is MG, and the PC is the worst. Therefore, the matching degree between flake graphite and magnetic field was the best and the matching degree between petroleum coke and magnetic field was the worst. Thus, the reaction of [O] and [C] was accelerated by the increment of [C] in FG-containing  $\text{Al}_2\text{O}_3$ –C refractories; [O] was decreased by the formation of CO, which accelerated the dissolution of solid  $\text{Al}_2\text{O}_3$  into the melt.

Al content in iron sample taken from TA-FG crucible reached the maximum when soaking time was 30 min and then decreased (the curve 1 in Fig. 2a), because an isolated zone was generated on the interface of molten iron and refractory crucible after 30 min due to the oxidation of carbon [10]. The formation of isolated zone was the result of

the reaction of  $\text{Al}_2\text{O}_3$  and flake graphite, and then, pores were remained in this area. The reaction of  $\text{Al}_2\text{O}_3$  and flake graphite was inhibited later due to the increasing partial pressure of CO, which results in no liquid Al formation and the increase in [Al] was stopped. At the meantime, [Al] was consumed by the reaction with [O] in the molten iron; thus, the aluminum content of iron was decreased with the soaking time after 30 min. There is the similar reason for the variation in the aluminum content of iron sample taken from TA-MG crucible.

The ash content in microcrystalline graphite was the maximum, which prohibited the carbon from dissolving in the liquid iron because ash oxides transformed into glass phase at high temperature; thus, carbon content of iron sample was decreased and the carbothermal reduction of  $\text{Al}_2\text{O}_3$  was prohibited, as revealed by the curve 2 in Fig. 2a.

The extent of reactions among  $\text{Al}_2\text{O}_3$  and petroleum coke was the slowest because petroleum is a kind of amorphous material. Hence, Al content of iron taken from TA-PC crucible was increased slightly with increasing the soaking time compared with that of FG/MG-containing crucible (the curve 3 in Fig. 2a). Meanwhile, the porous microstructure was formed in TA-PC crucible, which results from the transformation of pore configuration of PC at high temperature [19], and the temperature on the interface was increased slowly, which was unfavorable for the dissolution process of carbon into liquid iron, and thus, the carbon content of iron increased gradually with the soaking time, too.

Iron sample taken from  $\text{Al}_2\text{O}_3$  crucible had a minimal Al content (curve 4 in Fig. 2a), which indicated that [Al] generated by decomposition of solid  $\text{Al}_2\text{O}_3$  was very low (reaction (4)). Therefore, the aluminum pick-up of iron was mainly due to the carbothermal reduction among ( $\text{Al}_2\text{O}_3\text{-C}$ )/Fe system in this study.

## 5 Conclusion

The influence of reaction of  $\text{Al}_2\text{O}_3$  and carbonaceous materials in ( $\text{Al}_2\text{O}_3\text{-C}$ )/Fe system on aluminum and carbon pick-up of iron was investigated. Different carbonaceous materials containing  $\text{Al}_2\text{O}_3\text{-C}$  refractories have various effects on the aluminum and carbon pick-up of iron. Flake graphite-containing  $\text{Al}_2\text{O}_3\text{-C}$  refractories have significant effect on the aluminum and carbon pick-up of iron, and the aluminum and carbon pick-up of iron taken from petroleum coke-containing  $\text{Al}_2\text{O}_3\text{-C}$  refractories kept growing with the soaking time. The aluminum pick-up of iron sample taken from non-carbon-containing  $\text{Al}_2\text{O}_3$  refractory crucible was the minimal, which indicated that the decomposition process of solid  $\text{Al}_2\text{O}_3$  in liquid iron was rather slow.

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