

Article

SiO₂ Promoted CaO Diffusion to C Phase at 1500 and 1700 °C

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Abstract: To better understand the mass transfer behaviors in CaC₂ production from CaO and coke, this paper studies the diffusion behaviors of CaO and graphite, with or without ash, at 1500 and 1700 °C. CaO and graphite are pressed into tablets and heated alone or in close contact. Physical and chemical changes in these tablets are analyzed by XRD and SEM+EDX. In some experiments, thin Mo wires are placed between the closely contacted CaO and graphite tablets to identify the diffusion direction. It is found that the diffusion between CaO and low-ash graphite is very limited. SiO₂ in a high-ash graphite diffuses into CaO tablet and reacts with CaO to form Ca₂SiO₄, which then diffuses into the graphite tablet easily and leads to CaC₂ formation at 1700 °C.

Keywords: calcium carbide; diffusion; Kirkendall effect; CaO; carbon; SiO₂

1. Introduction

Calcium carbide (CaC₂), produced from the reaction of coke (C) and calcium oxide (CaO) shown by Reaction (1) [1], is a major coal-derived commodity chemical used mainly in the production of polyvinyl chloride [2], polyvinyl acetate and 1,4-butanediol. China is the largest producer of CaC₂, with an annual production of more than 29 million tons in 2018.



The current CaC₂ production requires a temperature of greater than 2000 °C, which is realized by electric arc heating. This process is highly energy intensive. with an electricity consumption of about 3250 kWh/t for a CaC₂ product of 80% purity. [3] This energy requirement corresponds to 29.3 × 10⁶ kJ/t if the electricity is produced from coal-fired power generation with a thermal efficiency of 40%. To reduce the large energy loss in the power generation, auto-thermal CaC₂ production was studied, [4,5] which employs in-situ oxidation of a portion of coke to generate a high temperature environment and to provide sufficient energy for the endothermic reaction (Reaction (1)). Since the two reactants are solid while the products CaC₂ and CO are in the molten and gaseous states, respectively, under the production conditions, the overall reaction system is very complex in mass and heat transfer. [6,7] Understand these transport phenomena would help to develop more efficient CaC₂ production processes, including the auto-thermal one, which can be operated at lower temperatures to yield solid products with optimized particle size distribution and ash contents of the reactants.

The diffusion behaviors of C and CaO at high temperatures have been studied. Briefly, El–Naas et al. investigated CaC₂ production in a fluidized bed plasmas reactor and assumed solid–solid diffusion between C and CaO. [8] Kameyama reported the formation of a solid intermediate CaO·C via mutual diffusion of C and CaO at temperatures higher than 1000 °C, the formation of Ca and CO from the intermediate at 1400 °C and higher, and consequently, the formation of CaC₂. [9] Müller reported the diffusion of C ions into CaO at temperatures of 1000–1500 °C to form CaC₃O, which transformed into CaC₂ and



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CO at temperatures higher than 1500 °C. [10] Li et al. reported the formation of CaC₂ at temperatures higher than 1540 °C and attributed the reaction to diffusion of CaO into C, in the nano-crystal form at temperatures lower than 1700 °C, while in the CaC₂-CaO eutectic form at temperatures higher than 1700 °C. [11] Ji et al. studied the reaction of high purity graphite and CaO and reported CaC₂ formation through C diffusion to CaO [12]. Clearly, the diffusion behaviors reported for the CaC₂ production are not consistent in the literature, and further studies are needed, especially those using different methods.

Kirkendall effect is a well-known method for studying solid-solid diffusion at high temperatures [13]. Typical experiments include one that uses a molybdenum (Mo) wire placed in between closely contacted Cu and Ni plates to mark its position shift at high temperatures and consequently to analyze the difference in diffusion rate of the two metals. Sun [14] and Mrowec [15] studied the role of diffusion in reactions of HCl-CaO and SO₂-CaO, respectively, by placing a fine Pt film at the inter-surface of the solids. In light of the above experiments, this paper studies the diffusion behaviors of CaO and graphite at temperatures relevant to CaC₂ production using two closely contacted graphite and CaO tablets, with or without fine molybdenum (Mo) wires placed in between. The changes at the interface of the two tablets are analyzed with XRD and SEM (+EDX). The role of SiO₂ in graphite on the diffusion behavior is emphasized.

2. Materials and Methods

2.1. Preparation of Raw Materials

Two types of graphite were used. One contained little minerals (termed pure-C, from Qingdao Shengrui graphite Ltd., Laixi, China), while another contained 21.64 wt% minerals (termed ash-C, from Tianjin Fucheng Chemicals). The proximate and ultimate analyses of these graphite were carried out following the Chinese National Standard GB/T12-2008 and GB/T476-2008, respectively, and are shown in Table 1. The mineral composition of ash-C is shown in Table 2. Analytical-grade CaO powder was used. It was heat treated at 900 °C for 3 h in a flow of N₂ (99.999 % pure) to convert possible Ca(OH)₂ and CaCO₃ into CaO, which yielded a CaO purity of 98.26%. Mo wires with a diameter of 0.12 mm were used as the marker.

Table 1. Proximate and ultimate analyses of the graphite (wt.%).

Samples	Proximate Analysis (wt %, Air-Dry Basis)			Ultimate Analysis (wt %, Air-Dry Basis)				
	Moisture	Ash	Volatile	C	H	O	N	S
ash-C	2.64	21.64	3.78	71.28	0.99	2.67	0.39	0.39
pure-C	-	0.12	-	99.87			0.01	

Table 2. Ash contents of ash-C (mg/g).

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	SO ₃
ash-C	84.48	35.77	24.06	33.48	1.56	3.25

The graphite and CaO powders of 0.5 g were pressed separately at a pressure of 20 MPa into tablets in a die with an inner diameter of 13 mm, which yielded tablets with a thickness of 1.78 mm for CaO and 1.90 mm for the graphite. For the Kirkendall experiments, 0.5 g graphite or CaO was first pressed in the die at a pressure of 10 MPa, after laying the Mo wires on the upper surface of the sample it was pressed again at 20 MPa to yield a tablet with the Mo wires on one side of the surface.

2.2. Apparatus

The high temperature experiments were conducted in a tube furnace under an argon atmosphere. The furnace is LTF18/-/300 from Lenton Ltd. with a corundum tube of 70 mm

in diameter and 120 mm in length. A single sample tablet or a set of two tablets (one over another) was placed between two tungsten blocks that was placed in the isothermal zone of the furnace (40 mm in the center). The weight of the upper tungsten block was 170 g, which was used to ensure the close contact of the two tablets. The temperatures for the diffusion experiments were 1500 and 1700 °C. The former is lower, while the latter is higher than the initial formation temperature of calcium carbide reported (1540 °C [11]). The samples were analyzed with a scanning electron microscope (SEM, Hitachi S4700, Japan) equipped with energy dispersive (EDX) analyzers and with a powder X-ray diffraction (XRD, Bruker D8 Forcus, Germany). The XRD employs Cu K α 1 radiation and was operated at 40 KV and 40 mA, and the sample was scanned over a 2θ range of 20° to 90° at a step size of 12 °min⁻¹.

3. Results and Discussion

3.1. Physical and Chemical Changes of the Tablets

Experiments in the absence of the Mo wire marker were carried out to understand the effect of temperature on the physical and chemical changes of reactant tablets alone or in close contact. The conditions were 1500 and 1700 °C for 2 h and the data are shown in Table 3. It is seen that the heat treatment reduced the mass and size of the CaO tablet and the decreases at 1700 °C are larger than those at 1500 °C. The graphite tablets, pure-C and ash-C, decreased in mass but changed little in size. The larger mass losses of ash-C tablets than that of pure-C tablets, which were also greater than the mass of ash in the ash-C tablet, suggest that the mass losses occurred in both ash and carbon. This may be attributed to reduction of some of the ash components by C, which results in the evaporation of reduced metals and release of CO, indicating promoted ash migration or mass transfer by C.

Table 3. Mass and size of samples after the heat treatments.

Samples	1500 °C			1700 °C		
	Mass (g)	Diameter (mm)	Thickness (mm)	Mass (g)	Diameter (mm)	Thickness (mm)
CaO	0.4629	12.10	1.56	0.4465	11.62	1.46
pure-C	0.4879	13.02	1.90	0.4812	13.02	1.90
ash-C	0.3782	13.06	1.90	0.3419	12.94	1.90
Pure-C (+CaO)	0.4812	13.02	1.88	0.4793	13.02	1.88
ash-C (+CaO)	0.3763	13.04	1.92	0.3177	12.94	1.52
CaO (+pure-C)	0.4614	12.10	1.56	0.4408	11.62	1.44
CaO (+ash-C)	0.4601	12.12	1.52	0.3114	11.60	1.02
CaC ₂ (CaO+ash-C)	-	-	-	0.0852	-	0.40

Note: The original mass of CaO or graphite tablets is 0.50 ± 0.02 g and the original thicknesses are 1.78 mm for the CaO tablet and 1.90 mm for the graphite tablets. The standard deviations are 1.02% for the CaO tablets and 0.78% for the graphite tablets.

It was found that the closely contacted CaO and pure-C tablets did not adhere to each other at these temperatures. The mass losses of these two tablets are about 1% more than those heated alone, but no new product was visible at the interface, indicating the occurrence of some trace reactions at the interphase that cannot be identified by the method used here. Similar behaviors were also found for the CaO and ash-C tablets in close contact at 1500 °C. The closely contacted CaO and ash-C tablets at 1700 °C, however, lost much more mass than the tablets heated alone, about 30% for CaO tablet and 7% for ash-C tablet, and a new product layer was found at the interface, about 0.0852 g. The product was CaC₂ because it released acetylene upon mixing with deionized water. The incremental mass losses correspond to a CaO:C molar ratio of about 1:2, which is significantly different from the stoichiometric CaO:C ratio of Reaction (1), 1:3. This indicates that some amounts of CaO diffused out of the CaO tablet, possibly through dissolution into CaC₂ to form an eutectic, a reaction between CaO and CaC₂ to form gaseous Ca and CO as reported in the

literature [16], and the reaction of CaO with the ash in the ash-C tablet. [17] These indicate that the mass transfer of CaO is promoted by the ash in the ash-C tablet.

To better understand the mass transfer behavior, all the samples in Table 3 were subjected to XRD and SEM+EDX analyses. Figure 1 shows that the XRD spectra of the CaO tablets under the 3 conditions, alone at 1500 °C (spectrum (a), left) and in close contact with the pure-C tablet at 1500 (spectrum (b), left) and 1700 °C (spectrum (c), left), are very similar; so are the XRD spectra of pure-C tablets (spectra (a), (b) and (c), right). Figure 2 shows that the SEM+EDX (×1000) spectra of the CaO tablets under the 3 conditions are also similar and so are the SEM+EDX spectra of pure-C tablets. These behaviors support the findings discussed earlier that little mass transfer can be found between the CaO and pure-C tablets under these temperatures, even though they were in close contact.

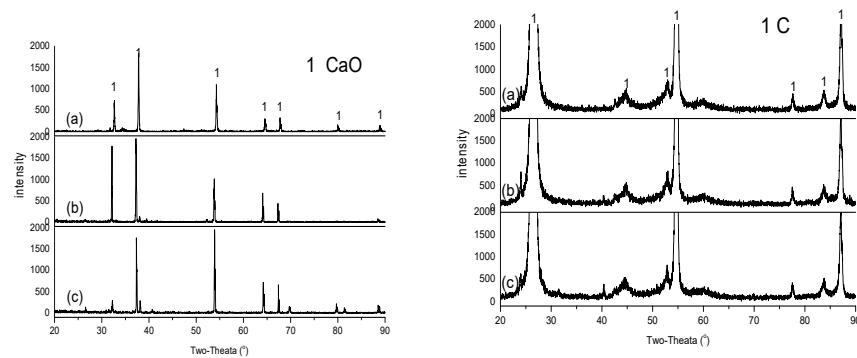


Figure 1. XRD analysis: (a) CaO and pure-C (1500 °C); (b) CaO+pure-C (1500 °C); (c) CaO+pure-C (1700 °C).

Figure 3 shows the XRD spectra of CaO and ash-C tablets after being heated individually or in close contact. Different from the CaO tablet heated alone at 1500 °C (spectrum (a), left), the CaO tablets heated in close contact with the ash-C tablet show Ca_2SiO_4 (spectrum (b), left), which can be ascribed to a reaction of CaO with SiO_2 , as reported by Wang et al. [18], indicating migration of SiO_2 from the ash-C tablet. The absence of Ca_2SiO_4 at 1700 °C may be ascribed to its decomposition, as reported by Huffman et al. [17]. The absence of CaC_2 and SiC peaks at 1700 °C (spectrum (c), left) indicates little C diffusion from the ash-C tablet to the CaO tablet. The appearance of the single C peak at 2θ of 26° at both temperatures (spectra (b) and (c), left) is somewhat surprising, since other major C peaks are absent. Its origin, therefore, is not clear at present.

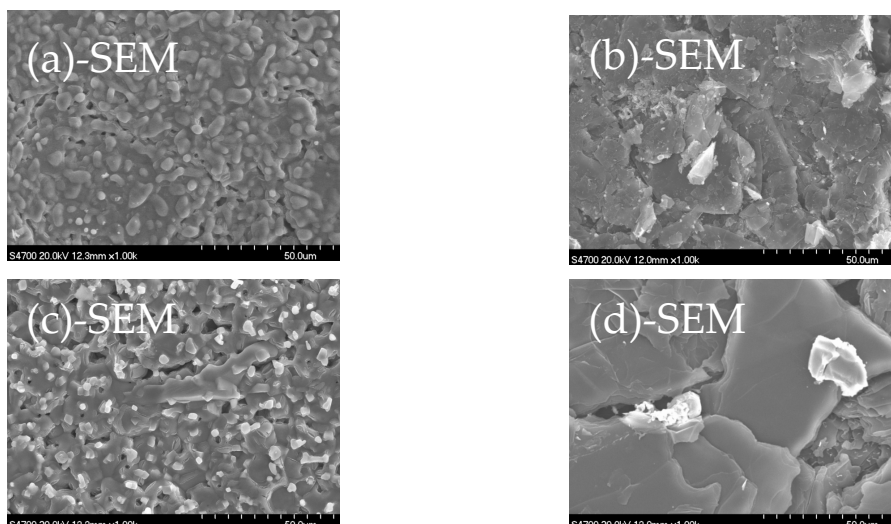


Figure 2. Cont.

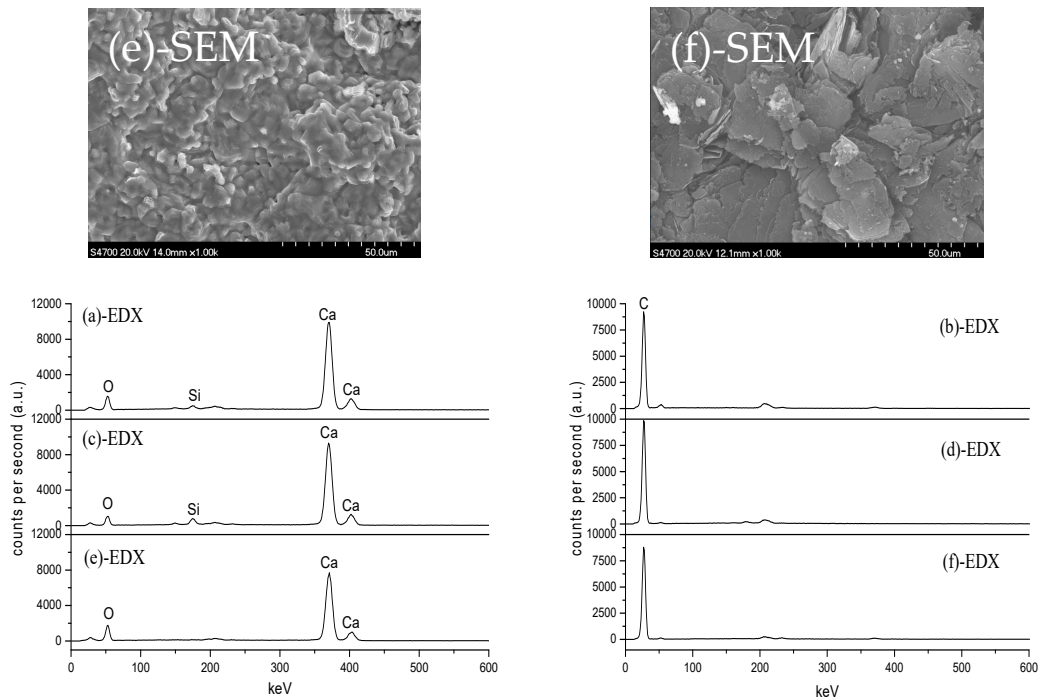


Figure 2. SEM+EDX analyses: (a) CaO (1500 °C); (b) pure-C (1500 °C); (c) CaO (+pure-C, 1500 °C); (d) pure-C (+CaO, 1500 °C); (e) CaO (+pure-C, 1700 °C); (f) pure-C (+CaO, 1700 °C).

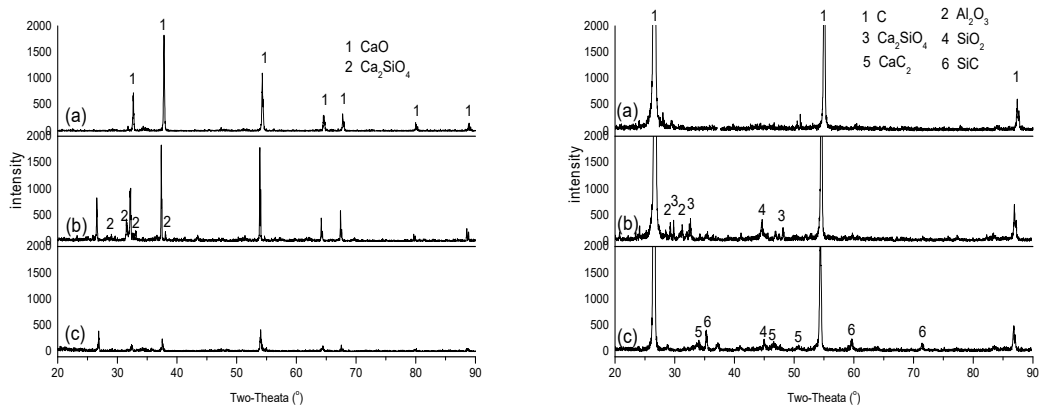


Figure 3. XRD analyses: (a) CaO (left) and ash-C (right) alone at 1500 °C; (b) CaO (left) and ash-C (right) when they were in close contact at 1500 °C; (c) CaO (left) and ash-C (right) when they were in close contact at 1700 °C.

Figure 3 also shows that the ash-C tablets in close contact with the CaO tablet are very different from that heated alone, including the appearances of SiO₂, Al₂O₃ and Ca₂SiO₄ at 1500 °C (spectrum (b), right) and SiC and CaC₂ at 1700 °C (spectrum (c), right; note: a CaC₂ layer is formed between the CaO and the ash-C tablets at 1700 °C). These phenomena indicate the diffusion of CaO to the ash-C tablets, which leads to a reaction of CaO with SiO₂ at 1500 °C to form Ca₂SiO₄ [17] and a reaction of CaO with C at 1700 °C to form CaC₂. The disappearance of Ca₂SiO₄ at 1700 °C may be attributed to its reaction with C that forms CaC₂ and SiC [19].

It is worth noting that few Al- and Fe-containing compounds can be observed in Figure 3, even though their contents in ash-C are not minute; about 42 wt.% and 28 wt.% of SiO₂ in ash-C, respectively. These seem to suggest that the diffusion rates of Al₂O₃ and Fe₂O₃ are not as fast as SiO₂ in graphite and/or their reaction with CaO are slower

than SiO_2 . This is in agreement with that reported by Li et al., i.e., effect of SiO_2 on CaC_2 formation is larger than that of Al_2O_3 and Fe_2O_3 . [19]

Figure 4 shows SEM+EDX results of the samples analyzed in Figure 3. Clearly, the morphology of the closely contacted CaO and ash-C tablets is different from that when heated alone. The contact of ash-C tablet makes the surface of CaO tablet melt at $1500\text{ }^\circ\text{C}$ and form spherical granules of about $5\text{ }\mu\text{m}$ in diameter at $1700\text{ }^\circ\text{C}$. This is accompanied by an increase in Si content at $1500\text{ }^\circ\text{C}$ (12.02%) and the disappearance of Si at $1700\text{ }^\circ\text{C}$, which agrees with the behavior shown in Figure 3, i.e., the formation of Ca_2SiO_4 at $1500\text{ }^\circ\text{C}$ and the disappearance of Ca_2SiO_4 at $1700\text{ }^\circ\text{C}$. The contact of CaO tablet makes the surface of ash-C tablets change too; surface erosion by increased Ca and Si contents at $1500\text{ }^\circ\text{C}$ and surface recovery at $1700\text{ }^\circ\text{C}$ due to the disappearance of Ca.

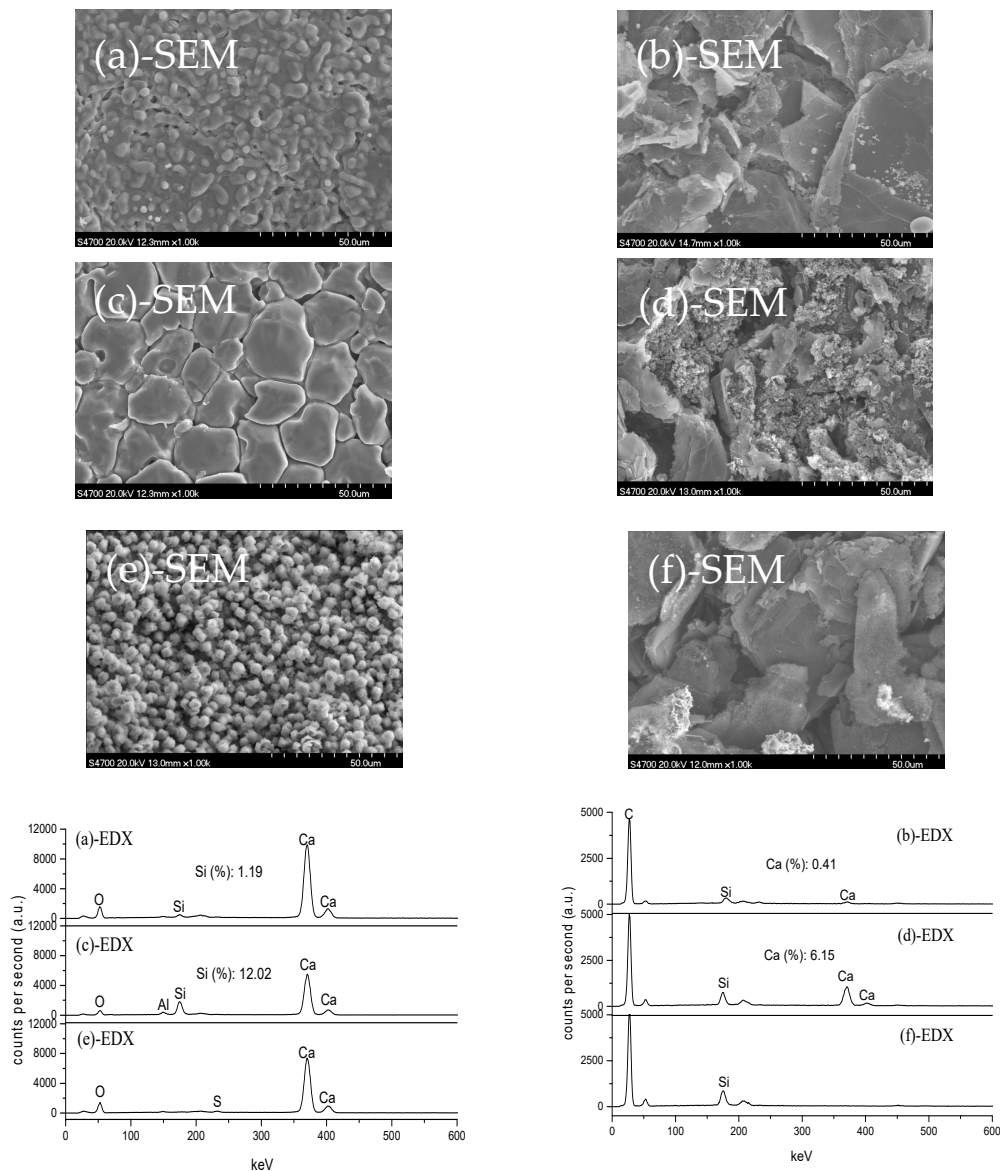


Figure 4. SEM+EDX analyses: (a) CaO ($1500\text{ }^\circ\text{C}$); (b) ash-C ($1500\text{ }^\circ\text{C}$); (c) CaO (+ash-C, $1500\text{ }^\circ\text{C}$); (d) ash-C (+CaO, $1500\text{ }^\circ\text{C}$); (e) CaO (+ash-C, $1700\text{ }^\circ\text{C}$); (f) ash-C (+CaO, $1700\text{ }^\circ\text{C}$).

Figure 5 shows XRD and SEM+EDX results of the CaC_2 layer (about 0.4 mm in thickness) formed between the closely contacted CaO and ash-C tablets at $1700\text{ }^\circ\text{C}$. It is clear that the sample contains CaC_2 and CaO as well as trace amounts of Si and Al.

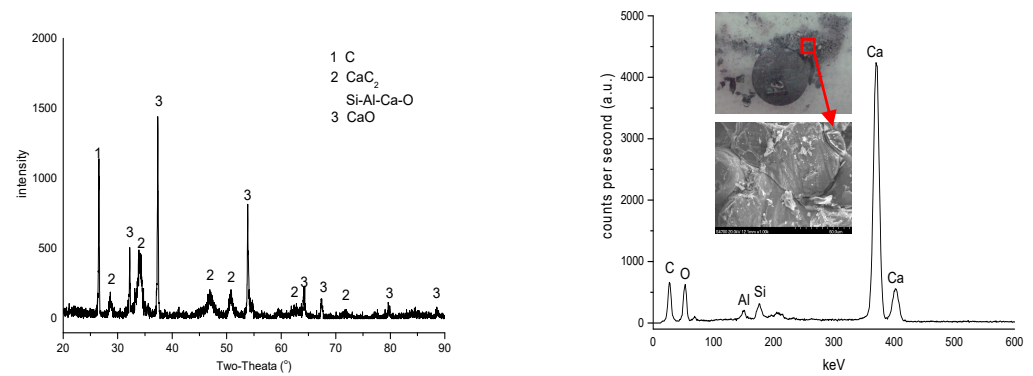


Figure 5. The analyses of CaC_2 layer: XRD (left) and SEM+EDX (right).

3.2. Diffusion Behavior Identified by Mo Wire Marker

The above data and discussion indicate that the major mass transfer at 1500 and 1700 °C is CaO , from the CaO tablet to the ash-C tablet, but it is visible mainly in the presence of SiO_2 . The SiO_2 , in this case, migrates from the ash-C tablet to the CaO tablet. This mutual diffusion is somewhat complex. The formation of CaC_2 layer between the CaO and ash-C tablets may also be complex because the diffusion of C may be influenced by CaC_2 when it is formed at the interface. To better understand the extent of diffusion of CaO and C, Mo wire markers were placed between the CaO and the ash-C tablets before heating (Sample a in Figure 6). The models in Figure 6 are used as guidelines to identify the mass transfer behaviors. It is seen that after heating if the Mo wires locate at the top of CaC_2 layer (keeping contact with CaO , Model b), the main diffusion should be CaO to ash-C, i.e., the decrease of the CaO tablet in thickness and the appearance of a new layer of CaC_2 ; if the thickness of the ash-C tablet decreases but the Mo wires keep at the top surface of the ash-C tablet (Model c), the main diffusion should be C in ash-C to CaO ; if the Mo wires stay in the middle of CaC_2 layer (Models d), the main diffusion should be mutual for the two reactants. The result of an experiment at 1700 °C in Figure 7 shows that the location of Mo wires are similar to Model b, i.e., away from the ash-C side (close to the CaO tablet that has been removed from the top of the CaC_2 layer), indicating the diffusion of CaO to ash-C. This behavior is confirmed by Figure 8, in which the Mo wires were placed on the CaO tablet surface before heating and were found remaining at the CaO side after heating to 1700 °C.

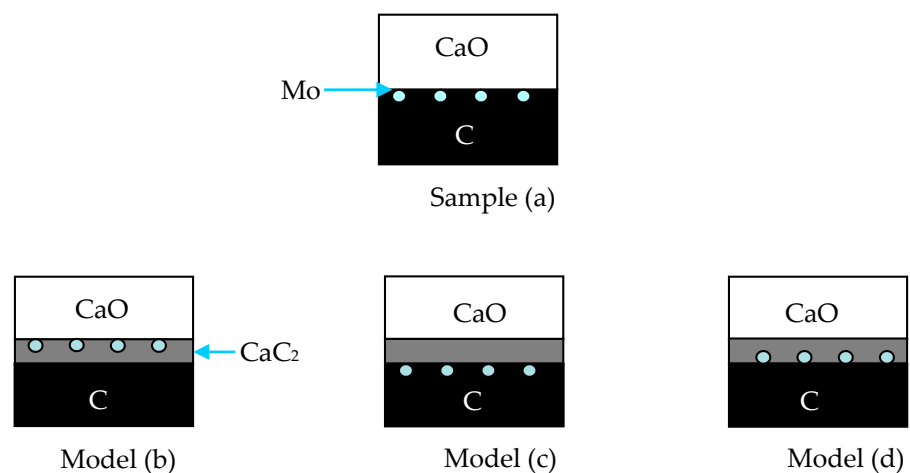


Figure 6. Diffusion models between CaO and ash-C distinguished by the Mo wires: (a) Sample a; (b) CaO diffuses into C; (c) C diffuses into CaO ; (d) mutual diffusion of CaO and C.

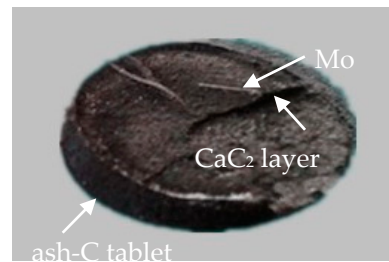


Figure 7. Location of Mo wires after the sample (CaO+ash-C with Mo wires) after the heat treatment at 1700 °C.

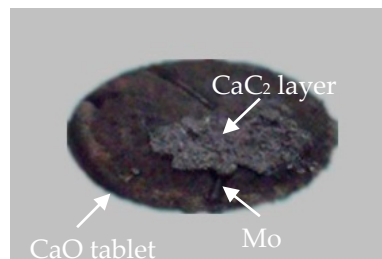


Figure 8. Location of Mo wires after the sample (ash-C+CaO with Mo wires) after the heat treatment at 1700 °C.

3.3. Behaviors of SiO_2 and Ca_2SiO_4

The above discussion shows that the diffusion of SiO_2 from the ash-C tablet to the CaO tablet plays an important role in promoting CaO diffusion, possibly via the formation of Ca_2SiO_4 . To better understand these behaviors, the CaO and the ash-C tablets in close contact were subjected to heating at 1500 °C for 1, 2 and 4 h and analyzed by XRD. Figure 9 shows that CaO peaks (left, CaO tablets) decrease while Ca_2SiO_4 peaks appear in 1 and 2 h heating, indicating diffusion of SiO_2 from the ash-C tablet to the CaO tablet and consequently the reaction between SiO_2 and CaO to form Ca_2SiO_4 . The Ca_2SiO_4 peaks, however, disappear in 4 h and a peak ascribed to the CaO- Ca_2SiO_4 eutectic appears. The low melting point of CaO- Ca_2SiO_4 eutectic, 1454 °C, [20] suggests increased mass transfer of Ca species, which would promote CaC_2 formation, provided that the temperature is sufficiently high, greater than 1540 °C, [11] for example.

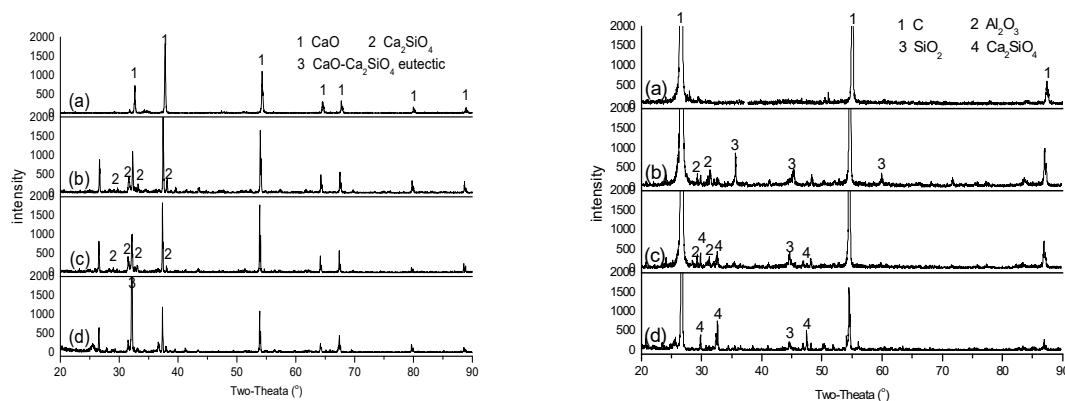


Figure 9. XRD analysis of CaO (left) and ash-C (right) after being heat treated at 1500 °C for different time: (a) CaO or ash-C alone; (b) CaO+ash-C (1 h); (c) CaO+ash-C (2 h); (d) CaO+ash-C (4 h).

Figure 9 also shows that the surface of ash-C tablet (right, ash-C tablets) was enriched with SiO_2 and Al_2O_3 in 1 h heating and then SiO_2 converted to Ca_2SiO_4 in 2 and 4 h,

indicating again the diffusion of CaO from the CaO tablet to the ash-C tablet with the aid of SiO₂. The above information agrees with that reported by Ji et al. [21]. The absence of Ca₂Al₂O₅ and calcium aluminosilicates in these XRD spectra also indicates that Al₂O₃ is not as active as SiO₂ in reacting with CaO at the temperature.

4. Conclusions

At temperatures of 1500 and 1700 °C, which are lower and higher than the initial formation temperature of CaC₂ from CaO and C (1540 °C), respectively, little diffusion can be found between CaO and a low-ash graphite (pure-C) in 2 h. The SiO₂ in a high-ash graphite (ash-C) diffuses into the CaO phase and reacts with CaO to form Ca₂SiO₄ at these temperatures. A CaO-Ca₂SiO₄ eutectic may be formed at temperatures lower than 1500 °C, which promotes diffusion of Ca species into graphite and results in CaC₂ formation at 1700 °C. Little graphite diffusion into the CaO phase is evidenced under the conditions. SiO₂ is faster in mass transfer and more reactive with CaO than Al₂O₃ and Fe₂O₃ at the temperatures studied.

Author Contributions: Z.L. and Q.L. designed the study and revised the paper; L.N. performed the experiments and drafted the paper; R.W. and J.W. made intellectual contributions to this study and did some supporting work; Y.P. edited the paper form and did some supporting work. All authors have read and agreed to the published version of the manuscript.

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