Phase Transformation of Alumina, Silica and Iron Oxide during Carbothermic Reduction of Fly Ash for Ceramics Production

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Abstract: Fly ash is a by-product from burning of coal. Utilization of fly ash by carbothermic reduction is an effective way to recover aluminum, silicon, and iron to enhance product-added value. This work was focused on the phase transformation of Al2O3, SiO2, and Fe2O3 during carbothermic reduction of fly ash in air. A comparative analysis of carbothermic reduction of fly ash in air and in nitrogen was made. Thermodynamics analysis was performed to illustrate the possible reactions for residue and condensate. X-ray diffraction (XRD), scanning electronic microscope (SEM), and energy dispersive spectrometry (EDS) were employed to characterize the phase composition, surface morphology, and microstructure of the reduced products. Results show that FeSi and FeSi appear sequentially with increasing of temperature. Al2O3N is an intermediate compound. Residue of Al2FeSi, Al, and Si, and condensate of SiC, AlN and C are obtained. β-SiAlON was not found in the residue. Nitrogen is involved in the reduction of Al2O3 but not in the reduction of SiO2 and Fe2O3. Carbothermic reduction of fly ash in air did not behave the same as fly ash in nitrogen.

Keywords: fly ash; vapor; metallic aluminum; nitridation; whisker; alloy; ceramics

1. Introduction

Fly ash emerges as a by-product mainly from the combustion of raw coal in thermal power plants. It has been reported that the present accumulating amount of fly ash in China had reached three billion tons 2020, which has resulted in serious environment pollution [1]. Only a small amount is re-utilized in low value-added products, such as concrete, brick, or cement production, and the remainder is directly impounded or landfilled. Fly ash contains mostly aluminosilicate mineral [2,3] and small amounts of iron oxide. On the profitable side, fly ash can be considered a mineral resource if the potential metal values are exploited [4–7]. Carbothermic reduction of fly ash to recover aluminum, silicon and iron can not only increase extra value of products but also reduce environmental pollution.

It was found that reduction of alumina using carbon as a reductant was favored in the presence of limited amounts of oxygen [8]. Alumina [9] decomposes into Al-containing gases and oxygen, then carbon reacts with oxygen to reduce oxygen partial pressure. The Al-containing gases reacted further to produce the final products of Al2O3 and Al2CO3. Apart from Si, SiC was obtained from the reduction of silica [10]. Carbothermic reduction of alumina improved dramatically during co-reduction of alumina and silica [11]. The presence of silicon in the system reduced the evaporation degree of aluminum [12]. Such a process could achieve advantages at the cost of course of producing an Al-Si master alloy instead of pure aluminum.
As carbothermic reduction of alumina and silica is carried out in nitrogen, the elevated nitrogen pressure [13] is beneficial for preparing coarser AlN particles; however, Forslund [14] pointed out that the conversion decreased with increasing nitrogen addition. Si₃N₄ is produced when silica is reduced by carbon in a flow of nitrogen [15]. Vlasova [16] found that α – Si₃N₄ is prepared under the condition in excess amount of carbon, and preparation of β – Si₃N₄ is promoted by Si-O-N intermediate in the absence of carbon.

When fly ash was reduced by carbon in air, Al-Si-Fe alloy was obtained at 2273 K [17]. Raw materials such as hematite [18] or iron [19] were added to reduce the initial reaction temperature of carbothermic reduction of fly ash. In addition, bauxite could be added in order to increase the aluminum content [20]. However, under a temperature of 1873K, fly ash could be used to prepare mullite with 5 wt% starch in air [21]. The NaCl-KCl molten salts medium reduced the carbothermic reduction temperature of fly ash effectively [22]. If waste with similar chemical components was used, such as red mud [23], SiC/mullite composite porous ceramics could be prepared under the optimal conditions having 15 wt% graphite and sintered at 1350 °C in air.

SiAlON was synthesized when fly ash was reduced by carbon in nitrogen [24]. Qiu et al. [25] found that SiAlON whiskers could be produced under conditions of lower temperature or shorter nitridation time with addition of decomposable additives. Fang et al. [26] found that alumina produced by the decomposition of mullite was partly soluted to β-SiAlON. Silica in fly ash favorably reacted with excess carbon to form SiC during the process of carbothermic reduction, and then the product was completely consumed by reaction with mullite to produce β-Sialon phases [27]. With the increase of mass ratio of SiO₂/Al₂O₃, the generated SiC changed into Si₃N₄ [28]. However, if carbothermic reduction of fly ash was in argon atmosphere, SiC was the final product [29].

Fly ash contains minor constituents such as iron oxide. Iron oxide can be completely reduced by carbon [30] at a relatively lower temperature. Accordingly, iron in the product affects the reduction of alumina and silica. Meanwhile, as fly ash is reduced by carbon in air, nitrogen will inevitably take part in the reaction. Most aluminosilicate ceramics have been prepared in nitrogen. Although there is nitrogen in air, different products are produced after carbothermic reduction of fly ash in nitrogen and in air. Atmosphere shows unavoidable impact on the carbothermic reduction of fly ash. Few studies have reported the synthesis of β-Sialon in air. As discussed above, the progress of a carbothermic reduction reaction is greatly influenced by the temperature and reduction atmosphere. In this work, the phase transformation of alumina, silica and iron oxide were investigated according to the phase analysis of the reduced product of fly ash at different temperatures. Comparison of carbothermic reduction of fly ash in air and in nitrogen was performed to better understand the effect of atmosphere.

2. Materials and Methods

2.1. Raw Materials

Fly ash from a thermal power plant in Taiyuan, Shanxi province in China was ground and screened through a standard sieve to obtain powders of 100 mesh. The chemical composition of fly ash is shown in Table 1. The X-ray diffraction pattern of fly ash is presented in Figure 1. It was observed that fly ash consists of major phases of mullite (3Al₂O₃•2SiO₂) and silica (SiO₂) and a minor phase of iron oxide (Fe₂O₃). Charcoal has the characteristics of high fix carbon, porosity, and low ash. Charcoal from Kunming Iron and Steel Holding Co., Ltd was used as a carbonaceous reducing agent. Calcium lignosulphonate (C₇H₇CaO₉(S₅)) from a paper mill was used as a binder. Industrial parameters of charcoal, such as moisture (Mad), volatiles (Vad), coal ash (Aad), fixed carbon (FCad), and ash composition, are shown in Table 2.
Table 1. Chemical composition of fly ash (wt. %).

| Composition | Al₂O₃ | SiO₂ | Fe₂O₃ | CaO | TiO₂ | MgO | MnO | C   | Others |
|-------------|-------|------|-------|-----|------|-----|-----|-----|--------|
| Content (wt.%) | 30.46 | 45.60 | 3.00  | 2.32 | 0.92 | 0.50 | 0.03 | 4.18 | 12.99  |

Table 2. Industrial analysis of charcoal.

| Property Index | Mₘ | Aₘ | Vₘ | FCₘ |
|----------------|----|----|----|-----|
| Index value wt. % (air-dry basis) | 13.0 | 5.61 | 6.55 | 87.84 |

Figure 1. XRD pattern of coal fly ash.

2.2. Experimental Setup

Experiments were carried out in a high-frequency induction furnace with a maximum operating temperature of 2473 K. The schematic of the setup is shown in Figure 2. The furnace includes a power supply unit, an infrared thermometer, and a heating device. The power supply unit provides both power and electrical control. The infrared thermometer is used for the temperature measurement. The heating device consists of a graphite crucible, a refractory filler, and an insulation layer, and a heating coil. The heating coil is cooled by circulating water.

Figure 2. Schematic of high frequency induction furnace.
2.3. Experimental Procedure

Raw materials have to be pelletized to achieve good gas permeability during the carbothermic reduction of fly ash. After examination and determination of some main relevant parameters (properties of the pellets, stoichiometric carbon addition, binder addition), the chemical composition of the raw materials combined with the optimal utilization of the setup has been investigated and improved to produce an alloy. In the experiment the refractory filler would melt if the heating time was more than half an hour at 2473 K. Therefore, the reaction temperature should be kept below 2473 K. In order to evaluate the consumption of graphite crucible caused by the reduction of fly ash, pellets consisting entirely of fly ash were heated up to 2273 K. No metallic phase was found. This meant that the effect of graphite crucible on the carbothermic reduction of fly ash could be neglected.

Pellets suffered a great mass loss. In fact, the mass loss caused by the reduction of alumina, silica, and iron oxide; decomposition of chemicals; or evaporation of volatiles reached 50% at most. Material-spraying is one of the most serious problems. Therefore, addition of raw materials was based on the complete reduction of metal oxides, except MnO (see Table 1), in 100 g fly ash to generate enough products. By calculation, the stoichiometric addition of charcoal is 30 g. Binder and water account for 6.5 and 13.7 percent of fly ash, respectively. A good intermixing of fly ash, charcoal powder, and binder was provided by uniformly mixing with water. During mixing, proportionate ingredients were combined till the required consistency was achieved. The mixture was then pressed with an external compaction in a stainless-steel die to form cylindrical pellets of \( \Phi 20 \times 25 \) mm, and dried at 150 °C for 24 h to remove moisture. A graphite crucible loaded with samples was placed into the furnace and heated to a pre-set temperature. Carbothermic reduction of fly ash proceeded continuously for 40 min to ensure a complete reduction of fly ash. After the experiments, the graphite crucible was immediately removed from the furnace and cooled at room temperature. The graphite crucible was split down the middle vertically with a saw. Residue and condensate were separated and analyzed. A flowsheet of carbothermic reduction of fly ash is shown in Figure 3.

![Figure 3. A flowsheet of carbothermic reduction of fly ash in the air.](image-url)
2.4. Analysis Methods

The internal-standard technique is currently the best method for quantitative X-ray diffraction analysis. It adopts the usual procedure of constructing a calibration curve from standards for each component sought, which is tedious, especially for multicomponent analysis. Chung [31,32] derived an intensity-concentration equation free from matrix effect. For the quantitative X-ray diffraction analysis of a mixture of \( n \) components, unknowns \( (X_i, i=1 \ldots j \ldots n) \) must satisfy the following \((n+1)\) equations:

\[
\begin{align*}
I_1 &= k_1 \cdot X_1 \\
I_2 &= k_2 \cdot X_2 \\
&\vdots
I_n &= k_n \cdot X_n \\
X_1 + X_2 + \ldots + X_n &= 1
\end{align*}
\]

Where \( I_i \) is the intensity of X-rays of component \( i \), \( X_i \) is the weight fraction of component \( i \), and \( k_i \) is a factor containing the mass absorption coefficient of the total sample. At this moment, \( k_i \) is constant for a very small variation in \( X_i \). \( k_i \) in the ratio \( k_i/k_j \) is constant for any \( X_i \). The plot of intensity ratio \( (I/I_i) \) to the weight ratio \( (X/X_i) \) of any two components is a straight line, which can provide a quantitative analysis of the processed samples.

The chemical composition of fly ash was determined by chemical analysis. Industrial parameters of charcoal measured by the national standard of the People’s Republic of China [33]. Crystalline phases were identified by X-ray diffractometer (XRD: PANALYTICAL, EMPYREAN, Cu-Kα radiation). Scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS: JEOL, JSM-6510LV) was used to examine surface morphology, microstructure and micro-area elemental composition of the reduced products.

3. Thermodynamics Analysis

Fly ash is a product of coal combustion at high temperature. The existing form of fly ash will maintain the status of coal after combustion within a certain temperature range. The transformation of coal mineral during combustion can be modeled as a mixture of individual minerals before 1500 K [34]. With increasing temperature, a number of liquid and solid solutions could possibly be formed over the reaction conditions. However, the formation of liquid and solid solutions was considered to have no significant effects on the equilibrium composition of the products [35,36]. Therefore, on the basis of the carbothermic reduction of alumina, silica, and iron oxide, a thermodynamic analysis of carbothermic reduction of fly ash was made. The carbothermic reduction temperature of fly ash is far more than 1273 K. CO predominates in the atmosphere [37,38]. Consequently, the formation of carbon dioxide was not considered.

Reactions (1) – (13), concerning the residue and the condensate from literatures [1,18,39] are presented in Table 3. The relationships between change of Gibbs free energy and temperature were obtained using HSC 6.0 and Origin 7.0 software. Figure 4a shows that Gibbs free energy of the reactions (1) – (4) and (6) – (8) decreased with increasing temperature. The initial temperatures of reactions (1) – (3) were 1802 K, 1941 K, and 1837 K, respectively, suggesting carbothermic reduction of silica by the reaction (1) occurs with the most spontaneous tendency with increasing temperature. Iron oxide was readily reduced to iron by reaction (4) over 917 K. FeSi was produced by reaction (5) in the temperature range of 1711 – 2449 K. It is clear that Fe lowers the reduction temperature of silica compared with the reaction (2). The initial temperatures of reactions (6) – (7) were 2167 K and 1969 K, respectively. It can be inferred that alumina is prone to carbothermic
nitridation below 1969 K. The generated AIN reacted with SiC to produce Al and Si by reaction (8) above 1846 K.

Reaction (9) took place above 2036 K and progressed more and more with the increase of temperature. It was expected that the generated SiO would react with C to produce SiC, because the reaction (10) always happens according to the Gibbs free energy values as shown in Figure 4b. Gaseous aluminum caused by the volatilization of metallic aluminum reacted with nitrogen by reaction (11) at all the temperatures studied. Meanwhile, another possible way to produce AIN is carbothermic reduction of alumina by reaction (12) following carbothermic nitridation of Al₂O by reaction (13). The initial temperature of reaction (12) is 2353 K. In addition, from the viewpoint of kinetics, gas diffusion caused by reaction (11) is far more than the solid diffusion caused by reaction (12). Therefore, production of AIN by reaction (11) takes precedence over reaction (12).

Table 3. Chemical reactions and fitting formula of ΔrG° – T.

| Category | Number | Reaction Equations | Fitting Formula of Standard Free Energy, kJ•mol⁻¹ |
|----------|--------|-------------------|--------------------------------------------------|
| Residue  | (1)    | SiO₂ + 3C = SiC + 2CO(g) | ΔrG° = 593.3582 – 0.3293 T |
|          | (2)    | SiO₂ + 2C + Si = 2CO(g) | ΔrG° = 683.6557 – 0.3523 T |
|          | (3)    | 3SiO₂ + 6C + 2N₂(g) = Si₃N₄ + 6CO(g) | ΔrG° = 1177.8021 – 0.6410 T |
|          | (4)    | FeO₂ + 3C = 2Fe + 3CO(g) | ΔrG° = 464.3454 – 0.5063 T |
|          | (5)    | SiO₂ + 2C + 3Fe = Fe₃Si + 2CO(g) | ΔrG° = 534.4661 – 0.3123 T (873.15–2731.5K) |
|          | (6)    | 2Al₂O₃ + 3C = Al₄C₃O₆ + 2CO(g) | ΔrG° = -626.5703 + 0.2558 T (273.15–4731.5K) |
|          | (7)    | Al₂O₃ + 3C + N₂(g) = 2AIN + 3CO(g) | ΔrG° = 678.3700 – 0.3445 T |
|          | (8)    | 2AIN + SiC + 1/2O₂ = 2Al + Si + N₂(g) + CO(g) | ΔrG° = 631.6170 – 0.3421 T |
| Condensate| (9)    | SiO₂ + C = SiO(g) + CO(g) | ΔrG° = 672.8021 – 0.3305 T |
|          | (10)   | SiO(g) + 2C = SiC + CO(g) | ΔrG° = -79.2431 + 0.0011 T |
|          | (11)   | Al(g) + N₂(g) = 2AIN | ΔrG° = -1273.7815 + 0.4568 T |
|          | (12)   | Al₂O₃ + 2C = Al₂O(g) + 2CO(g) | ΔrG° = 1263.5383 – 0.5370 T |
|          | (13)   | Al₂O(g) + C + N₂ = 2AIN + CO(g) | ΔrG° = -585.1690 + 0.1924 T |

Figure 4. Diagrams of standard free energy versus temperature for reactions (1) - (13): (a) reactions of (1) – (8), (b) reactions of (9) – (13).
4. Results and Discussion

4.1. Effect of Temperature on Phase Transformation of Al₂O₃, SiO₂, and Fe₂O₃

XRD analysis of the residues after carbothermic reduction of fly ash at different temperatures was made to illustrate the phase transformation of alumina, silica and iron oxide. As shown in Figure 5, it was observed that the phases are mullite (3Al₂O₃·2SiO₂), silica, iron oxide, and carbon at 1373 K and 1473 K, which was consistent with the original samples. The diffraction peaks of silica and mullite existed at 1573 K and 1673 K, but iron oxide did not, which means reduction of iron oxide occurred. Reduction of silica and alumina doesn’t take place. With the increase of temperature, the peak intensity of mullite and silica decreased prominently, and new diffraction peaks of SiC and alumina appeared at 1773 K. It was clear that mullite decomposed into Al₂O₃ and silica, and silica was reduced to SiC.

Figure 5. XRD patterns of residues at 1373 K–1773 K.

Figure 6 shows diffraction patterns of the residues in the temperature range of 1873 – 2273 K. It was found that the residue contained Al₂O₃, SiC, and Fe₃Si at 1873 K. The increasing peak intensity of alumina matched the disappearance of mullite due to its decomposition. The generated silica and original silica were both reduced into SiC and Fe₃Si by reactions (1) and (5), respectively. Thermodynamic comparative analysis of the reactions between (2) and (5) showed that the presence of Fe reduced the reduction temperature of silica. However, an Si phase was not observed at 1873 K.
At 1973 K the decrease of peak intensity of alumina revealed that the reduction of alumina occurred. FeSi phase was detected. If FeSi was produced by an individual reaction, the newly generated FeSi and already generated FeSi at 1873 K remained in the reduced sample. Given the disappearance of FeSi diffraction peak, it is possible to conclude that the generated Si dissolves into FeSi phase to produce FeSi. Accordingly, it could be found that the diffraction peak of FeSi widened and shifted towards a high angle in comparison with that at 1873 K, which is consistent with the decrease of the lattice constant of iron [40]. The appearance of a Al2O3N diffraction peak means nitrogen in air is involved in chemical reactions as a result of carbothermic reduction. This can be explained by the fact that nitrogen reacts with Al2O3 to produce AlN by the reaction (7), then the generated AlN reacts with Al2O3 to produce Al2O3N [41–43].

A stronger diffraction peak of FeSi appeared at 2073 K, suggesting more and more Si was produced and dissolved into the FeSi phase. The increase of Al2O3N peak intensity coincided with the decrease of alumina peak intensity because of the reaction between AlN and Al2O3. Si and AlN were detected in the residue at 2173 K. With the increase of Al2O3 peak intensity, the decrease of Al2O3N peak intensity showed that Al2O3N were decomposed into AlN and Al2O3 [44,45]. The peak intensity of SiC decreased progressively, which is in accordance with the appearance of a weak diffraction peak of Si according to reaction (8).

At 2273 K diffraction peaks of Al2O3, Al2O3N, AlN and FeSi were not found in the residue; however, Al and Al3FeSi3 peaks were. The disappearance of the Al2O3N diffraction peak indicated that Al2O3N was decomposed. The generated Al2O3 was transformed into AlN by reaction (7), which sequentially reacted with SiC to produce Al and Si by reaction (8). The speculation coincided with the decrease of peak intensity of SiC and the increase of peak intensity of Al and Si. It can be inferred that AlN promotes
production of Al and Si. The generated Al and Si will react with the already disappeared Fe:Si to produce Al:FeSi3.

Based on the discussion above, it was found that the phase transformation of Al2O3, SiO2, and Fe2O3 during the carbothermic reduction of fly ash in air could be divided into four stages in terms of temperature: (1) iron oxide was reduced in the temperature range of 1373 K~1573 K; (2) decomposition of mullite (3Al2O3∙2SiO2) and reduction of silica occurred at temperatures between 1673 K and 1873 K; (3) the formation and decomposition of Al5O6N took place within 1973 K~2173 K; (4) Al9FeSi3, Al, and Si were obtained at 2273 K.

4.2. Surface Morphology and Phase Analysis
4.2.1. Residue

Figure 7a presents the cross-section morphology of residue at the bottom of crucible after experiment at 2273 K. Three sections with different colors are labeled as A, B, and C, respectively. EDS of the sections A, B, and C are shown in Figure 7b–d, respectively, and the elemental compositions are shown in Table 4.

![Figure 7](image_url)

**Figure 7.** SEM-EDS patterns of the residue; (a) SEM image of the residue with three sections, (b) EDS of section A, (c) EDS of section B, (d) EDS of section C.

**Table 4.** Elemental compositions of the sections A, B and C.

|   | A       |   | B       |   | C       |   |
|---|---------|---|---------|---|---------|---|
| Element | Mass% | Atom% | Element | Mass% | Atom% | Element | Mass% | Atom% |
| Al     | 1.58   | 1.24  | Al      | 36.96 | 41.09  | Al      | 41.67 | 51.95 |
| Si     | 74.09  | 55.8  | Si      | 36.71 | 39.21  | Si      | 21.68 | 25.97 |
| C      | 24.33  | 42.90 | Ca      | 26.33 | 19.70  | Fe      | 36.65 | 22.09 |

The grey section marked A contains Al, Si and C. The calculated Si/C atomic ratio is 1.3, which is more than the theoretical value of SiC with Si/C atomic ratio of 1. It can be deduced that an individual Si phase exists in addition to SiC. The light grey section
marked B contains Al, Si, and Ca. Calcium comes from fly ash, binder, and ash of charcoal. Al, Si and Fe are found in the silver section marked C. The content of Fe is much more than the theoretical value of Al:FeSi₂, which puts in evidence that Fe is excessive in the residue. It was found that Fe was not distributed among these three sections in a balanced way. It is possible FeO₃ in fly ash is reduced first because of the lower reduction temperature. The generated Fe aggregated into droplets and led to excess of iron in a specific region. Subsequently, the iron-containing phase was formed, seen in FeSi, Fe₃Si and AlFeSi₂. If there were no iron droplets in a specific region, SiO₂ and Al₂O₃ would be reduced into Si and Al, respectively, such as in the light grey region marked B.

4.2.2. Condensate

During carbothermic reduction of fly ash at 2273 K, a small amount of grey cotton-shaped condensate was produced on the top and wall of crucible. The condensate was composed of SiC, AlN and C, as shown in Figure 8a. At high temperatures SiO₂ was reduced by carbon to produce gaseous SiO [46], and the generated SiO continued to react with carbon to produce SiC by reaction (10). Al₂O₃ was unavailable to react with C by the reaction (12) due to the excessive initial reaction temperature of 2353K. Production of AlN was more likely to happen by reaction (11) instead of reaction (13). Aluminum vapor required by the reaction (11) came from the volatilization of metallic aluminum [47]. Composite ceramics of AlN-SiC offer the advantages of high thermal conductivity and good mechanical properties [48]. The condensate provides the right material for preparing AlN-SiC composite ceramics by burning the residual carbon. It is noted that the formation of condensate did not always happen. This was closely related to the heating rate.

The scanning electron microscope image of the condensate shown in Figure 8b indicates that most whiskers have distinct droplets at the top, which is considered to be the main evidence of VLS mechanism (V: vapor feed gases; L: liquid catalyst; S: solid crystalline whisker) [49,50]. Al and SiO vapor phase [51,52] may form an oxygen-rich liquid phase at the top of the whiskers after nucleation, and C can enter the liquid phase and produce SiC and AlN whiskers by reactions (1) and (7).

![Figure 8](image)

**Figure 8.** XRD pattern and SEM image of condensate; (a) XRD patterns of condensate, (b) SEM image of condensate.

4.3. Phase Transformation Analysis

The appearance of an FeSi diffraction peak at 1873 K as shown in Figure 6, is exactly in the temperature range of 1711 – 2449 K in reaction (5). Over the initial reaction temperature of 1941 K, more and more silicon was produced by reaction (2) and dissolved into FeSi phase to produce FeSi. The diffraction peak of the generated FeSi at 1973 K is found in Figure 5. The results show that the presence of iron reduces the reduction temperature of SiO₂, which is consistent with findings [18]. The FeSi phase and the Fe₃Si phase coincide well with the binary phase diagram of silicon and iron [53,54].
However, the FeSi phase is not found in Figure 6. It can be speculated that sufficient iron is required for the formation of Fe-Si intermetallics. Although the content of SiO₂ in fly ash is more than that of Fe₂O₃, lots of SiO₂ is reduced into SiC or SiO. The generated Fe₅Si participates in the production of Al₃FeSix.

AlN is found in the condensate, as shown in Figure 8. The favorable reaction path is the nitridation of aluminum by reaction (11). Al₂O₃N can be decomposed into AlN again. The generated AlN reacts with SiC to produce Al by reaction (7), which is in accordance with the decrease of diffraction peak intensity of SiC at 2273 K as shown in Figure 6. Eventually, Al₃FeSix, Al, and Si are obtained. According to the analysis above, a schematic diagram of phase transformation of Al₂O₃, SiO₂, and Fe₂O₃ during carbothermic reduction of fly ash in air is presented in Figure 9.

![Figure 9. Schematic diagram of phase transformation.](image)

4.4. Comparative Analysis of Carbothermic Reduction of Fly Ash in Air and Nitrogen

SiAlON is a compound containing Si, Al, O, and N. Si₅N₄ is the matrix of β-SiAlON in which a solid solution is formed by the substitution of Si and N atoms by Al and O atoms, respectively. AlN was produced in the current study, which is consistent with the carbothermic reduction of alumina in nitrogen [55].

SiC, instead of Si₅N₄, is produced when silica in fly ash is reduced in air. For the synthesis of SiAlON by carbothermal reduction and nitridation, it was reported that the carbon environment of the raw materials would significantly influence the phase composition and chemical composition of the products [56]. Qiu [35] pointed out that when the carbon concentration [C] > 28 wt%, the amount of SiAlON decreases and the SiC content increases. There is a weight loss during nitridation caused by escape of SiO and generation of CO. In this study, carbon content was about 23 wt%. There must be something else that plays a critical role for the synthesis of β-SiAlON. Several mechanisms have been proposed for the synthesis of SiC, but in all of them, there is an initial stage with the formation of silicon monoxide. Generally, the accepted mechanism is the reaction of silicon monoxide with carbon (reaction 10) [57]. The mechanism is also supported by the generated SiC in the condensate. When fly ash is reduced by carbon in nitrogen, the gas that SiO can react with is restricted to nitrogen. This was supported by carbothermic reduction of silica to produce Si₅N₄ in nitrogen [15]. When fly ash is reduced by charcoal in air, Si₅N₄ is not produced. It is reasonable to conclude that SiO reacts with oxygen preferentially.
As for carbothermic reduction of fly ash in nitrogen, iron in fly ash may act as a promoting agent for the growth of a β-Sialon whisker due to its role in reducing the melting point of products [58]. However, during carbothermic reduction of fly ash in air, iron in fly ash decreases the reduction temperature of silica and participates in the formation of FeSi and Fe2Si phases.

Therefore, carbothermic reduction of Al2O3 in air is in tune with that in nitrogen, but that is not true for FeO3 and SiO2. The consequence of this effect is that carbothermic reduction of fly ash in air may not behave the same as for fly ash in nitrogen.

5. Conclusions

(1) The phase transformation of Al2O3, SiO2 and FeO3 can be divided into four stages, i.e., 1373 K–1573 K, reduction of FeO3; 1673 K–1873 K, decomposition of mullite and reduction of silica; 1973 K–2173 K, formation and decomposition of Al2O3N; 2273 K, production of AlOFeSi, Al, and Si.

(2) During carbothermic reduction of fly ash in air, the reduction of Al2O3 is consistent with that in nitrogen, but that is not true for FeO3 and SiO2.

(3) With increasing temperature, FeSi first appears, then FeSi follows. The presence of Fe promotes the reduction of SiO2. No FeSi was found. The generated FeSi participates in the production of AlOFeSi. Growth of condensate of SiC, AlN, and C follows the VLS mechanism.

(4) During carbothermic reduction of fly ash in air, much of the SiO2 is reduced into SiC or SiO. SiO reacts with oxygen preferentially, and SiN4 was not produced. That is why β-Sialon cannot be prepared in air.

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