The Phase-Formation Behavior of Composite Ceramic Powders Synthesized by Utilizing Rice Husk Ash from the Biomass Cogeneration Plant

Wenjie Yuan, Mingyu Fan, Chengji Deng, Jun Li, and Hongxi Zhu

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

Correspondence should be addressed to Wenjie Yuan; yuanwenjie@wust.edu.cn

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The development and utilization of biomass as a vital source of renewable energy were stimulated in order to reduce the global dependency on fossil fuels. A lot of rice husk ashes (RHA) were generated as the waste after the rice husk as the main fuel was burnt in the biomass cogeneration plant. The phase-formation behavior of composite ceramic powders synthesized by using rice husk ash from the biomass cogeneration plant at the different carbon ratios and temperatures was investigated. The sequence of phase formation with the calcining temperatures ranging from 1773K to 1853K was followed by $O_2 \rightarrow Sialon \rightarrow SiC + Si_3N_4 \rightarrow SiC$ in samples with $C/\text{SiO}_2 = 1:1–4:1$. Ca-$\alpha$-Sialon formed in samples with $C/\text{SiO}_2 = 5:1$ and 6:1. The results highlighted that series of reactions happening sensitively depended on $C/\text{SiO}_2$ and the temperature and demonstrated that the carbothermal nitridation provided an alternative for converting RHA waste into composite ceramic powders.

1. Introduction

The searching for renewable fuels was exigent for the industry because of the rising cost of fuel oil. As an energy source, biomass can be used directly via combustion to produce heat as a suitable candidate. The proportion of biomass was about 13% of primary energy consumption in China as early as 2000 [1]. In recent years, more and more biomass cogeneration plants were built up by support from national policies. The biomass power generation capacity of 5819 MW was constructed until the end of 2012. There are plenty of reserves of agricultural residues available in China as a large agricultural country. According to the 20% of rice husk ash by weight of the rice, the annual output of rice husk was close to 40 million tons. Therefore, the most utilized biomass for burning in cogeneration plants is rice husk, and chipped wood and straw are used as supplements in central China. Moreover, the rice husk was classified as low fouling due to the high content of ash [2]. The yield of rice husk ash (RHA) collected from the gasifier was about 25% [3]. If every kWh power generation consumed only 1.6–1.8 kg of rice husk [4], a biomass cogeneration plant with the capacity of 500 kW would generate 1600 tons of RHA in one year. However, how to deal with or utilize a tremendous amount of RHA was a big challenge. Otherwise this case could cause the resource waste and environmental repollution.

In general, rice husk ash consists of more than 90 wt.% of amorphous silica with high specific surface. Many attempts have been carried out to utilize RHA by using it as absorbents, additives, and raw materials [5]. It was reported that RHA was added into the cement to improve the durability and the early strength of concretes [6,7]. In addition, RHA was used as the filler in unsaturated polyester for sheet moulding compounds [8]. Considering RHA as raw materials, different studies were performed in order to synthesize various products such as cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) [9], lithium aluminum silicate [10], $\beta$-dicalcium silicate [11], and zeolite [12]. Indeed, RHA has been used as silica precursor for a series of silicon-based materials including silicon carbide [13], silicon nitride [14], and other silica-based material like silica gel [15] and silica aerogel [16]. On the other hand, $\text{Si}_3\text{N}_4\text{O}$ and $\text{Si}_3\text{N}_4$ formed by pyrolysing the strong acid treated rice husks under $\text{N}_2$ atmosphere [17].

Due to their unique combination of excellent mechanical properties and chemical inertness including high toughness, wear resistance, thermal shock resistance, thermal stability,
and corrosion resistance, silicon nitride and silicon carbide could be used as important structural materials [18]. Sialon is Si$_3$N$_4$-based solid solution, where aluminum and oxygen are partially substituted for silicon and nitrogen [19]. Sialon has two typical polymorphic forms: $\alpha$-Sialon with the general formula Me$_{m/3-2}$Si$_{12-2m}$O$_m$N$_{6+n}$ (where Me is metal like Y, Ca, Mg, Li, and val is valency of the metal) and $\beta$-Sialon with the general formula Si$_{6-z}$Al$_z$O$_{8-z}$N$_{2+z}$ ($0 < z < 4.2$) [20]. Furthermore, $\alpha'$-Sialon (Si$_{2-x}$Al$_{1+x}$O$_{3-x}$, 0.04 < $x$ < 0.4) as a derivative of Si$_3$N$_4$O presented a greater oxidation resistance than most of the Si$_3$N$_4$-based ceramics [21]. Due to good corrosion resistance, Si$_3$N$_4$/SiC and Sialon/SiC composites were practically and potentially applied as refractories [22–24]. One such application was in aluminum smelting cells [25].

Although the quality and performance are important, the cost of mass production should be the key factor in the commercialization of nonoxide ceramics [26]. Carbothermal nitridation process is a promising candidate for obtaining a large amount of nonoxides products. The final composition of the reaction products could be influenced by the following factors: the C/SiO$_2$ ratio, the characteristics of starting materials, the reaction gas composition, and the synthesis temperature. The percentage of rice husk in the fuel of biomass cogeneration plant was in the range from 70% to 95%. Therefore RHA from biomass cogeneration plant containing less SiO$_2$ and more impurities (such as Fe$_2$O$_3$, CaO, and Al$_2$O$_3$) was different from the common RHA. For the high efficient utilization of this kind of solid waste and the recycling economy industrial chain of energy and raw materials from biomass, composite ceramic powders were synthesized by using rice husk ash from the biomass cogeneration plant. The effects of C/SiO$_2$ ratio and the temperature on the phase composition of products were investigated. The phase-formation behavior of composite ceramic powders was discussed in order to guide the practical applications.

### 2. Experimental Procedure

The rice husk ash (average particle size < 180 mesh) provided by a biomass cogeneration plant in Hubei province, China, was used as silica source. The chemical composition of RHA is given in Table 1. Different mass percentages of RHA and carbon black (purity > 96 wt.% and particle size < 800 mesh) calculated by the ratio of C/SiO$_2$ are listed in Table 2. The starting materials were ball milled by the corundum balls with the ball to powder ratio of 2:1 for 6 h. Green bodies with the size of φ10 × 20 mm were compacted in a steel mold under 165 MPa; then samples were put into graphite crucible and calcined, respectively, at 1773 K, 1803 K, 1823 K, and 1853 K for 3 h in flowing nitrogen atmosphere (purity 99.995%).

Phase identification of each sample was performed by X-ray diffractometer (XRD, X’pert Pro MPD, PANalytical, Netherlands) with a monochromatic Cu Kα ($\lambda = 1.5406$ Å) radiation source. XRD results were quantitatively evaluated by the reference intensity ratio (RIR) method (X’pert Highscore 2.0 Plus, PANalytical, Netherlands) [27]. The microstructure and element analysis of powders were characterized by scanning electron microscopy (SEM, Nova 400 Nano, FEI, USA) and energy dispersive X-ray spectroscopy (EDX, Penta FETx3, Oxford, UK), respectively.

### 3. Results and Discussion

The carbothermal nitridation of SiO$_2$ is controlled by atmosphere, pressure, temperature, and time. For rice husk ash from the biomass cogeneration plant, it would be more complex due to the different impurities and the ratio of C/SiO$_2$. If only the reactions and products are considered, the various multiple steps could be described as few net reactions (Table 3). The expressions of the Gibbs free energy ($\Delta G$) of the above reactions are listed in Table 3 with the critical temperature $T_c$, where $\Delta G$ equals zero. The calculations were carried out by using the thermodynamic data from [28–30].

The changes in Gibbs free energy of the reactions in Table 3 are plotted with the temperature in Figure 1. It can be seen that $\Delta G$ of reaction (1) became negative when the temperature was higher than 1651 K, that is to say, Si$_3$N$_4$O firstly formed.
Table 3: Expressions for Gibbs free energy of some net reactions.

<table>
<thead>
<tr>
<th>Number</th>
<th>Product</th>
<th>Reaction</th>
<th>Δ𝐺 (kJ/mol product)</th>
<th>𝑇ᵣ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Si₃N₄O</td>
<td>2SiO₂(𝑠) + N₂(𝑔) + 3C(𝑠) = Si₃N₄O(𝑠) + 3CO(𝑔)</td>
<td>597.8 − 0.362𝑇</td>
<td>1651</td>
</tr>
<tr>
<td>(2)</td>
<td>O₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-</td>
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</tr>
</tbody>
</table>
Δ\(G\) of reaction (2) and (5) was negative at any temperature, which indicated that \(\text{Al}_2\text{O}_3\) could dissolve into \(\text{Si}_3\text{N}_4\text{O}\) to form \(\text{O}^\prime\)-Sialon and the excess carbon could result in the decomposition of \(\text{O}^\prime\)-Sialon all the while. \(\text{SiC}\), \(\text{Si}_3\text{N}_4\), and \(\text{Ca-}\alpha\)-Sialon formed possibly at the temperature above 1817 K.

Figure 2 presents the X-ray diffraction patterns of the products after calcination at the temperature from 1773 K to 1853 K. The phase composition of the products varied with the proportion of carbon and the temperature. Because of the impurity \(\text{Al}_2\text{O}_3\), the formation of \(\text{O}^\prime\)-Sialon \((\text{Si}_{1.83}\text{Al}_{0.17}\text{O}_{1.17}\text{N}_{1.83})\) started at 1773 K in all samples from Figure 2(a). \(\text{O}^\prime\)-Sialon occurred in the sample with less carbon ratio calcined at higher temperature (1:1–3:1 for 1803 K and 1:1 for 1853 K). The ratio of \(\text{C}/\text{SiO}_2\) for the initial formation of \(\text{Si}_3\text{N}_4\) shifted from 5:1 at 1773 K to 1:1 at 1853 K. The impurity \(\text{Fe}_2\text{O}_3\) reacted with \(\text{SiO}_2\) and \(\text{C}\) to generate \(\text{Fe}_3\text{Si}\) in all samples. The gehlenite \((\text{Ca}_2\text{Al}_2\text{SiO}_7, \text{C}_2\text{AS})\) was observed as an intermediate phase only in the samples R5 and R6 after calcination at 1773 K. Due to further reaction of the impurities \(\text{CaO}\) and \(\text{Al}_2\text{O}_3\), \(\text{Ca-}\alpha\)-Sialon formed at higher temperatures.

The relative phase content of products except for \(\text{Fe}_3\text{Si}\) calculated by semiquantitative analysis is plotted as shown in Figure 3. A small amount of \(\text{SiC}\) formed along with \(\text{O}^\prime\)-Sialon after calcination at 1773 K with low \(\text{C}/\text{SiO}_2\) \((<4:1)\), which indicated that the reactions (1) and (2) were dominant (Figure 3(a)). When the calcining temperature and \(\text{C}/\text{SiO}_2\) were elevated, the yield of \(\text{SiC}\) gradually increased. \(\text{SiC}\) finally became the unique phase in samples R3 and R4 after calcination at 1853 K (Figure 3(d)). The yield of \(\text{Si}_3\text{N}_4\) increased with the calcining temperature if \(\text{C}/\text{SiO}_2\) \(\leq 2:1\), while the amount of \(\text{Si}_3\text{N}_4\) decreased when \(\text{C}/\text{SiO}_2\) \(= 3:1–4:1\) and the calcining
Figure 4: SEM images of sample R3 after calcination at different temperatures for 3h: (a) 1773 K, (b) 1803 K, (c) 1823 K, and (d) 1853 K.

The temperature was higher than 1803 K. The products in samples with C/SiO₂ = 5:1–6:1 consisted of Ca-α-Sialon, Si₃N₄, and SiC after calcination at 1803 K and 1823 K (Figures 3(b) and 3(c)), whereas Si₃N₄ was absent in those after calcination at 1853 K (Figure 3(d)). Therefore, with the increase of the temperature and C/SiO₂, the main reactions were transferred from (4) and (5) to (3) and (6) in the mixtures with C/SiO₂ ≤ 4:1. For the samples with higher C/SiO₂ ratio (5:1 and 6:1), reactions (3), (4), and (7) simultaneously happened at 1803–1823 K; moreover, reactions (3) and (4) were replaced by (6) at 1853 K. The ratio of α- and β-Si₃N₄ was proportional with the carbon content in starting mixtures and decreased with the increase in the calcining temperature (Table 4), which was consistent with [31]. The other work indicated that β-Si₃N₄ just appeared at 1773 K while α-Si₃N₄ was the major phase in the reaction product. It could be deduced that a liquid phase played a key role according to the reduction of α/β ratio [32]. The α-β transformation was inhibited by high SiO vapour pressure [33]. On the other hand, Si vapour generated when C/SiO₂ ratio is above a certain level. Gaseous Si and N diffused and reacted with impurity Fe. The nucleation and growth of α-Si₃N₄ would start from Fe-Si-N liquid if the concentration of Si-N exceeds the saturation level [34]. The growth of α/β ratio with C/SiO₂ could be explained from the above arguments.

The scanning electron micrographs of sample R3 after calcination at different temperatures for 3 h are shown in Figures 4(a)–4(d). Combined EDS results, the phases were further identified. Columnar SiC and O’-Sialon were observed growing from Fe-Si droplets at 1773 K (Figure 4(a)), which suggested typically vapor-liquid-solid (VLS) growth mechanism [35]. At 1803 K, the product consisted of the SiC with irregular and whisker shape and short rod-like

<table>
<thead>
<tr>
<th>Temperature</th>
<th>C/SiO₂ (molar ratio)</th>
<th>Ratio of α- and β-Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1773 K</td>
<td>5:1</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>6:1</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>6:1</td>
<td>0.58</td>
</tr>
<tr>
<td>1803 K</td>
<td>5:1</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>6:1</td>
<td>0.50</td>
</tr>
<tr>
<td>1823 K</td>
<td>5:1</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>6:1</td>
<td>0.50</td>
</tr>
</tbody>
</table>
\( \beta\)-Si\(_3\)N\(_4\) as shown in Figure 4(b). With the temperature increasing, hexagonal \( \beta\)-Si\(_3\)N\(_4\) particles conglomerated together at 1823 K (Figure 4(c)). SiC grains in the sample calcined at 1853 K were composed of the agglomerate of long string just like the angleworm (Figure 4(d)), which is completely different from others.

4. Conclusions

This study demonstrated that it is feasible to prepare composite ceramic powders using rice husk ash from the biomass cogeneration plant. The series of reactions in the carbothermal nitridation sensitively depended on the proportion of carbon and the temperature. The formation of \( \alpha\)-Sialon, SiC, Si\(_3\)N\(_4\), and Ca-\( \alpha\)-Sialon can be explained through the above-mentioned mechanisms. The sequence of phase-formation with the calcining temperatures ranging from 1773 K to 1853 K was followed by \( \alpha\)-Sialon \( \rightarrow \) SiC + Si\(_3\)N\(_4\) \( \rightarrow \) SiC in the samples at the ratio of carbon to SiO\(_2\) with 1:1–4:1. Ca-\( \alpha\)-Sialon formed in the samples at the ratio of carbon to SiO\(_2\) with 5:1 and 6:1. Fe\(_5\)Si which formed from iron impurity in rice husk ash can participate in reaction as the catalyst. The ratio of \( \alpha\) - and \( \beta\)-Si\(_3\)N\(_4\) was proportional to the carbon content in starting mixture and decreased with the increase in the calcining temperature.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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