Influence of Heating Temperature, Keeping Time and Raw Materials Grain Size on Al$_4$O$_4$C Synthesis in Carbothermal Reduction Process and Oxidation of Al$_4$O$_4$C

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Several factors, influencing synthesis of Al$_4$O$_4$C in carbothermal reduction process from Al$_2$O$_3$ and C starting raw materials in argon atmosphere, and oxidation characteristics of Al$_4$O$_4$C were investigated. The formed Al$_4$O$_4$C in heated specimens was increased and Al$_2$O$_3$ and C were decreased with increase of heating temperature and extension of keeping time. Grain size of Al$_2$O$_3$ had obvious influence on synthesis of Al$_4$O$_4$C and fine Al$_2$O$_3$ was more advantageous. The activation energy of the reduction reaction from Al$_2$O$_3$ and graphite to form Al$_4$O$_4$C was calculated as 358.0 kJ/mol basing on experimental data. Al$_4$O$_4$C was observed to be oxidized from about 820°C in air. Al$_4$O$_4$C, buried in graphite powder and heated in air, was converted into Al$_2$O$_3$ and C.

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**Key-words**: Al$_4$O$_4$C, Synthesis, Al$_2$O$_3$, Graphite, Carbothermal reduction, Oxidation, Carbon-containing refractories

1. Introduction

Metal Al is frequently used in carbon-containing refractories as an additive to improve oxidation resistance and thermal properties, but it also causes some problems. For example, Al reacts with C in refractories to form Al(C$_x$)$_1$–3, which may lead the refractories to collapse for the poor hydration resistance of Al(C$_x$)$_3$.4–6

Al$_4$O$_4$C that is stable until 1890°C exists in Al$_2$O$_3$–AlC$_3$ system.5 This compound has been confirmed to have good hydration resistance and be transformed into Al$_2$O$_3$ and C at $P_{CO} = 0.1$ MPa (1 atm). So Al$_4$O$_4$C may be a better additive than metal Al for carbon-containing refractories.6–8

The authors have proceeded some research works about synthesis of Al$_4$O$_4$C from Al$_2$O$_3$ and graphite starting raw materials in argon atmosphere and it was known that the formation of Al$_4$O$_4$C started at a temperature of 1500–1550°C.7–10

However, more factors influencing synthesis of Al$_4$O$_4$C are necessary to be investigated for comprehending synthesis of Al$_4$O$_4$C in detail, and characteristics of formed Al$_4$O$_4$C are also necessary to be investigated for probable utilization in the future.

In the present work, several factors, influencing synthesis of Al$_4$O$_4$C, such as heating temperature, keeping time and grain size of Al$_2$O$_3$, and oxidation characteristics of formed Al$_4$O$_4$C were investigated.

2. Experimental procedure

2.1 Investigation on factors influencing synthesis of Al$_4$O$_4$C

Al$_2$O$_3$ (average grain size: 0.1 μm, 30 μm, 60 μm and 1 mm, purity: +99.9 mass%) and graphite (average grain size: 30 μm, purity: +99.0 mass%) were used as starting raw materials. They were weighted in proportions of C/Al$_2$O$_3$ = 1.5 (molar ratio), mixed with alcohol and dried in a vacuum-rotary evaporator. Two grams of the powder mixture put in a high purity graphite crucible was set into an electric furnace with a graphite heater (Fig. 1). Ar gas (purity: +99.9999 mass%), in which the partial pressure of O$_2$ was determined 10–20 MPa by a ZrO$_2$ sensor, was poured into the furnace after producing vacuum. The powder mixtures were heated to 1600–1700°C at a rate of 10°C/min and maintained for 3–9 h under flowing Ar of 1 L/min. Finally, the specimens were cooled to room temperature within the furnace through shutting off power supply, where the average cooling rate was 64°C/min from 1700°C to 1000°C. Phases of the heated specimens were identified by using X-ray diffraction (XRD, RINT 2200, Rigaku, Japan). Microstructure was observed using field emission scanning electron microscope (FE-SEM, JSM-6340F, JEOL, Japan). The compositions of a part of heated specimens were determined by using chemical analysis method.

2.2 Investigation on oxidation characteristics of Al$_4$O$_4$C

1) Oxidation of Al$_4$O$_4$C in air

The specimen from mixture with C/Al$_2$O$_3$ = 1.5 heated at 1700°C for 9 h, with the highest Al$_4$O$_4$C content and a little of Al$_2$O$_3$ and graphite, was ground to into grain size of approximate 10 μm and was named Al$_4$O$_4$C product, then was used to measure oxidation characteristic in air by using TG-DTA method, where the flow rate of air was 200 ml/min and the temperature rising rate was 5°C/min. In addition, the ground-
ed powder with 10 μm grain size was reheated at 800°C for 2 h in air to remove the residual graphite and was named reheated powder, then was used to measure oxidation characteristic in air by using TG-DTA method. The graphite used in this research was also analyzed by using the same TG-DTA method.

2) Oxidation of Al₄O₄C buried in graphite powder and heated in air

Since Al₄O₄C is probable to be used as an additive into carbon-containing refractories, oxidation characteristic of Al₄O₄C coexisting with C is necessary to be determined. So oxidation characteristic of formed Al₄O₄C, buried in graphite powder and heated in air, was also investigated.

The Al₄O₄C product stated above was mixed with graphite powder in molar ratio of Al₄O₄C : graphite = 1 : 6 (Al₄O₄C product was calculated as 100% Al₄O₄C). This (Al₄O₄C product)-graphite mixture in a graphite crucible with a cover was buried into graphite powder in an alumina crucible as shown in Fig. 2. This set was heated at 400–1500°C for 1–3 h in air. The heated specimens were analyzed by using XRD to identify phases.

3. Results

3.1 Influence of various factors on synthesis of Al₄O₄C

1) Influence of heating temperature and keeping time

The powder mixtures with C/Al₂O₃ = 1.5 (Al₂O₃: 0.1 μm) were heated at 1600, 1650 and 1700°C for 3–9 h. The heated specimens were analyzed by using XRD and it was known that the phases in the heated specimens were Al₂O₃, Al₄O₄C and graphite, no other substances existing. Mass contents of the elements of Al, O and C in the heated specimens were determined and are shown in Table 1.

Figure 3(a), (b) and (c) present mass contents of the phases of Al₂O₃, Al₄O₄C and graphite in heated specimens, which were calculated from Table 1 and according to equations as

\[
\begin{align*}
[\text{Al}] & = [\text{Al}_2\text{O}_3] \times 54/102 + [\text{Al}_4\text{O}_4\text{C}] \times 108/184 \\
[\text{O}] & = [\text{Al}_2\text{O}_3] \times 48/102 + [\text{Al}_4\text{O}_4\text{C}] \times 64/184 \\
[\text{C}] & = [\text{graphite}] + [\text{Al}_4\text{O}_4\text{C}] \times 12/184
\end{align*}
\]

Where [Al], [O], [C], [Al₂O₃], [Al₄O₄C] and [graphite] are the mass contents of Al element, O element, C element, Al₂O₃ phase, Al₄O₄C phase and graphite phase in the heated specimens.

As temperature was raised, increase of Al₄O₄C and decrease of Al₂O₃ and graphite were turned into more quick. At the same time, proportion of Al₄O₄C in the heated specimens was

### Table 1. Mass Contents of the Elements of Al, O and C in Specimens from Mixtures with C/Al₂O₃ = 1.5 Heated at Various Temperatures for Different Times

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Element</th>
<th>Time (h)</th>
<th>0</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>Al</td>
<td>45.00</td>
<td>47.18</td>
<td>48.94</td>
<td>49.96</td>
<td>51.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>40.00</td>
<td>39.49</td>
<td>38.64</td>
<td>37.51</td>
<td>36.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.00</td>
<td>13.33</td>
<td>12.42</td>
<td>12.53</td>
<td>12.23</td>
<td></td>
</tr>
<tr>
<td>1650</td>
<td>Al</td>
<td>45.00</td>
<td>48.12</td>
<td>50.94</td>
<td>52.88</td>
<td>54.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>40.00</td>
<td>36.67</td>
<td>37.27</td>
<td>35.83</td>
<td>34.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.00</td>
<td>13.21</td>
<td>12.09</td>
<td>11.29</td>
<td>10.81</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>Al</td>
<td>45.00</td>
<td>52.53</td>
<td>55.02</td>
<td>55.93</td>
<td>56.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>40.00</td>
<td>37.11</td>
<td>36.56</td>
<td>34.9</td>
<td>34.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.00</td>
<td>10.36</td>
<td>9.42</td>
<td>9.17</td>
<td>8.42</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 3](image-url)
increased and those of Al₂O₃ and graphite were decreased for the same keeping time. It was assumed that increase of heating temperature would increase reaction speed of Al₂O₃ and graphite to form Al₂O₃C.

As keeping time was extended, proportion of Al₂O₃C in the heated specimens was gradually increased and those of Al₂O₃ and graphite were gradually decreased at each temperature. The conclusion was gained that extension of keeping time would increase reaction extend of Al₂O₃ and graphite to form Al₂O₃C.

The highest Al₂O₃C proportion was obtained at 1700°C for 9 h. In this specimen, mass content of Al₂O₃C was 91.3% and those of Al₂O₃ and graphite were 6.2% and 2.5%, respectively. According to SEM observations on this specimen, the formed Al₂O₃C grains had size in range of 10–100 μm, mainly 30–50 μm, and they hardly included pores, very dense. The residual graphite existed in the center of some Al₂O₃C grains. The residual Al₂O₃ could not be observed due to the too small size and low content.

2) Influence of grain size of Al₂O₃

The powder mixtures with C/Al₂O₃ = 1.5 (Al₂O₃: 0.1 μm, 30 μm, 60 μm and 1 mm) were heated at 1700°C for 9 h. The intensity of the highest XRD peak of each phase in the heated specimens is shown in Fig. 4.

The decrease of grain size of Al₂O₃ was advantageous for synthesis of Al₂O₃C. Increasing grain size of Al₂O₃, the reduction rate of Al₂O₃ was decreased and at the same time, Al₂C₃ was increased with Al₂O₃C decreased. It was assumed that enough fine Al₂O₃ as starting raw material is necessary for synthesis of Al₂O₃C and in this research the best grain size of Al₂O₃ was 0.1 μm.

3.2 Oxidation characteristics of Al₂O₃C

1) Oxidation of Al₂O₃C in air

The reheated powder was analyzed by using XRD and it was known that all residual graphite was oxidized; only Al₂O₃C and Al₂O₃ existed (Fig. 10(a)).

TG patterns of the Al₂O₃C product, the reheated powder and the graphite used in this research are shown in Fig. 5.

From Fig. 5, the mass of the Al₂O₃C product decreased obviously from about 610°C and again increased obviously from about 820°C. Comparing to the pattern of the graphite, it is known that the temperature of about 610°C is the starting temperature that the residual graphite was oxidized. And comparing to the pattern of the reheated powder, it is known that the temperature of about 820°C is the starting temperature that Al₂O₃C was oxidized.

2) Oxidation of Al₂O₃C buried in graphite powder and heated in air

Phases of specimens from (Al₂O₃C product)-graphite mixture heated at various temperatures and different times are shown in Fig. 6, where the intensity of graphite phase was omitted.

With increase of heating temperature and extension of keeping time, Al₂O₃C was decreased, simultaneously that of Al₂O₃ was increased. Al₂O₃C was converted into Al₂O₃ from about 600°C × 1 h and the conversion was finished at 1500°C × 3 h.

4. Discussion

1) Al₂O₃C’s formation and conversion into Al₂C₃

Figure 7 presents change of condensed phases for various partial pressures of CO (g) in the Al–O–C system, which was calculated thermodynamically (Since Al₂OC is unstable below 1715°C, Al₂OC is not included.). The formation free energy of Al₂O₃C reported by Lihrmann et al. was used in the calculation. Those of Al₂O₃, C, Al₂C₃ and CO were from NIST-JANAF Thermo-chemical Tables. The standard pressure (P°) was 0.1 MPa (1 atm).

The critical P°C/PO of Al₂O₃C and Al₂C₃ formation increases with rise of temperature from Fig. 7. Since the con-
version critical temperature of Al$_2$O$_3$→Al$_2$O$_3$C is less than that of Al$_2$O$_3$C→AlC, at same partial pressure of CO ($g$), Al$_2$O$_3$C would be formed firstly according to Re. (1) and then be converted into AlC according to Re. (2) as temperature was raised.

$$
2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow \text{Al}_2\text{O}_3\text{C}(s) + 2\text{CO}(g) \quad (1)
$$

$$
\text{Al}_2\text{O}_3\text{C}(s) + 6\text{C}(s) \rightarrow \text{Al}_4\text{C}_3(s) + 4\text{CO}(g) \quad (2)
$$

The changes sequence of condensed phases in the Al–O–C system with increase of temperature is as the following.

$$
\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al}_2\text{O}_3\text{C} + \text{C} \rightarrow \text{Al}_4\text{C}_3 + \text{C}
$$

In addition, since the stable area of Al$_2$O$_3$C is very narrow, the formed Al$_2$O$_3$C would quickly be reduced by C to form AlC as temperature was raised.

Re. (1) should only occur in the reaction-starting period of Al$_2$O$_3$ and C, after Al$_2$O$_3$ was separated from C by formed Al$_2$O$_3$C, Al$_2$O$_3$C would be formed mainly according to Re. (3) and (4). Similarly, Re. (2) should also only happen in the reaction-starting period of Al$_2$O$_3$C and C, as long as Al$_2$O$_3$C was separated from C by formed Al$_4$C$_3$, Al$_4$C$_3$ would be formed mainly according to Re. (5) and (6). Overall reaction of Re. (3) and Re. (4) is same with Re. (1) ((3) + 3 × (4) = (1)). Overall reaction of Re. (5) and Re. (6) is same with Re. (2) ((5) + 6 × (4) = (2)).

$$
2\text{Al}_2\text{O}_3(s) + 4\text{CO}(g) \rightarrow \text{Al}_2\text{O}_3\text{C}(s) + 3\text{CO}_2(g) \quad (3)
$$

$$
\text{CO}_2(g) + \text{C}(s) \rightarrow 2\text{CO}(g) \quad (4)
$$

$$
\text{Al}_2\text{O}_3\text{C}(s) + 8\text{CO}(g) \rightarrow \text{Al}_4\text{C}_3(s) + 6\text{CO}_2(g) \quad (5)
$$

Since this research was conducted in argon atmosphere with partial pressure of O$_2$ as $10^{-20}$ MPa as statement, O$_2$ should have reacted with the graphite heater, the graphite crucible, and the graphite in mixtures into CO (1/2O$_2(g)$ + C(s)→CO (g)) with a partial pressure as approximately $2 \times 10^{-20}$ MPa. But, even if $P_{CO}$ is $10^{-18}$ MPa, very higher than $2 \times 10^{-20}$ MPa, the starting temperature of Al$_2$O$_3$C formation is 1180°C (1453 K) in thermodynamics from Fig. 7. The actual starting temperature is 1500–1550°C as statement, about 350°C higher than the former. The difference should be attributed to the activation energy of Re. (1). Using the data in Fig. 3 and according to the formula reported by Arrhenius ($k=A \exp(-E/RT)$), the activation energy of Re. (1) was calculated as 358.0 kJ/mol.

2) Influence mechanism of change of Al$_2$O$_3$ grain size on Al$_2$O$_3$C synthesis

The change of Al$_2$O$_3$ grain size had obvious influence on composition of synthesized product as statement. The influence mechanism is discussed as the following.

The contents of phases in the heated specimens from Al$_2$O$_3$ with 0.1 μm in grain size and that from Al$_2$O$_3$ with 1 mm in grain size were extremely different (Fig. 4). The formation mechanisms of these products were emphatically discussed.

From SEM observation on the unheated mixtures, when Al$_2$O$_3$ was 0.1 μm and graphite was 30 μm, Al$_2$O$_3$C grains were adhering on the surface of graphite grains modeled in Fig. 8 (a), and when Al$_2$O$_3$ was 1 mm and graphite was 30 μm, graphite grains were adhering on the surface of Al$_2$O$_3$ grains, modeled in Fig. 9 (a).

As temperature was increased, Al$_2$O$_3$ reacted with graphite to form Al$_2$O$_3$C. When Al$_2$O$_3$ was 0.1 μm, Al$_2$O$_3$C would be formed in the contacting area of Al$_2$O$_3$ and graphite according to Re. (1) and in the Al$_2$O$_3$ grains area according to Re. (3) and (4) due to the diffusion of CO (g) and CO$_2$ (g). Even if a part of formed Al$_2$O$_3$C reacted with C or CO (g) to form AlC, the formed AlC would react with Al$_2$O$_3$ again to form Al$_2$O$_3$C according to Re. (6).
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The formed \( Al_2O_3 \) was modeled in Fig. 8(b). The formed \( Al_2O_3 \) was dense grains as former statement. Since dense \( Al_2O_3 \) grains packed the residual graphite and so no gas was allowed to diffuse, the residual graphite could not further react with \( Al_2O_3 \) to form \( Al_4C_3 \). And because the formed \( Al_2O_3 \) estranged the residual graphite and the residual \( Al_2O_3 \), the residual graphite and \( Al_2O_3 \) also could not react with each other and so were remained in the last product, as modeled in Fig. 8(c).

When \( Al_2O_3 \) was 1 mm, the reduction of \( Al_2O_3 \) was slow and difficult and even a part of \( Al_2O_3 \) could not be reduced at last. \( Al_2O_3 \) would be formed on the surface of \( Al_2O_3 \) grains as modeled in Fig. 9(b). Since the formed \( Al_2O_3 \) and \( C \) or \( CO(\text{g}) \) coexisted for a long time, \( C \) was excessive for the formed \( Al_2O_3 \); the formed \( Al_2O_3 \) would further be reduced to form \( Al_4C_3 \) according to Re. (2), (5) and (6). The formed \( Al_4C_3 \) was packing the grains of \( Al_2O_3 \) from observation of the heated product. From Fig. 4, besides \( Al_2O_3 \) and \( Al_4C_3 \), there are a little of residual \( Al_2O_3 \) and \( C \) in the heated specimen. The residual \( Al_2O_3 \) is considered a part of the formed \( Al_2O_3 \) that was near the unreduced \( Al_2O_3 \) and was not reduced into \( Al_4C_3 \). Another probability is the residual \( Al_2O_3 \) is the result of the reaction between the formed \( Al_4C_3 \) and the unreduced \( Al_2O_3 \) according to Re. (6). The residual \( Al_2O_3 \) should locate between unreduced \( Al_2O_3 \) grain and formed \( Al_4C_3 \). The reason that residual \( C \) existed is considered that, because the formed \( Al_4C_3 \) had estranged \( C \) from \( Al_2O_3 \) and \( Al_2O_3 \), \( C \) could not react with \( Al_2O_3 \) or \( Al_2O_3 \) and was remained on the surface of grains as modeled in Fig. 9(c). When \( Al_2O_3 \) was 30 \( \mu m \) and 60 \( \mu m \), the reaction tendencies were between the two states as discussed above.

3) Oxidation mechanism of \( Al_2O_3 \)

When \( Al_2O_3 \) product was oxidized in air by using TG-DTA method, since the sample size was little and the flowing rate of air was high, \( Al_2O_3 \) should be sufficiently oxidized from about 820°C by \( O_2 \) in air to form \( Al_2O_3 \) and \( CO \) according to Re. (7).

\[
Al_2O_3(s) + 2O_2(g) \rightarrow 2Al_2O_3(s) + CO_2(g) \quad (7)
\]

From Fig. 5, it is also observed that the mass increase was turned into slow from about 1060°C to 1090°C for not only \( Al_2O_3 \) product but also the reheated powder. XRD patterns of the reheated powder and the specimens from reheated powder analyzed by using TG-DTA at 1060°C and 1250°C in air are shown in Figs. 10(a), (b) and (c), respectively. Comparing Fig. 10(b) with Fig. 10(a) and (c), a higher degree of amorphous phase was found in the specimen analyzed at 1060°C. Probably this amorphous phase affected the mass variation from 1060°C to 1090°C.

When \( Al_2O_3 \) product buried in graphite powder was heated in air, \( Al_2O_3 \) should be oxidized according to Re. (8) to form \( Al_2O_3 \) and \( C \), because the main gas is \( CO(g) \) in carbon-containing refractories at high temperature.\[^{11}\]

\[
Al_2O_3(s) + 2CO(g) \rightarrow 2Al_2O_3(s) + 3C(s) \quad (8)
\]

\[
2C(s) + O_2(g) \rightarrow 2CO(g) \quad (9)
\]

Since \( CO \) was generated according to Re. (9), the overall reaction in this case is Re. (10) \((= (8) + (9))\).

\[
Al_2O_3(s) + O_2(g) \rightarrow 2Al_2O_3(s) + C(s) \quad (10)
\]

4) Advantage of \( Al_2O_3 \) as an additive for carbon-containing refractories

From Fig. 7, when partial pressure of \( CO(g) \) is lower than the critical \( CO(g) \), partial pressure of \( Al_2O_3 \) to \( Al_2O_3 \) \( (s) \) exists stably. It means that Re. (1) happens. When partial

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![Fig. 9. Reaction models of \( Al_2O_3 \) with 1 mm grain size and graphite during heating \((a) \rightarrow (b) \rightarrow (c)\).](image)

\[
4Al_2O_3(s) + Al_4C_3(s) \rightarrow 3Al_2O_3C(s) \quad (6)
\]

As long as \( C \) was not excessive \((C/Al_2O_3 \leq 1.5)\), \( Al_4C_3 \) would not exist in the last product. This is the reason that the products shown in Fig. 3 included only \( Al_2O_3 \), \( Al_2O_3 \) and \( C \), no \( Al_4C_3 \). In these cases, overall reaction of Re. (2) and Re. (6) is same with Re. (1) \((0.5 \times (2) + 0.5 \times (6) = (1))\), and overall reaction of Re. (4), (5) and (6) is also same with Re. (1) \((3 \times (4) + 0.5 \times (5) + 0.5 \times (6) = (1))\). The reaction procedure was modeled in Fig. 8(b).
pressure of CO \((g)\) is higher than the critical value, \(\text{Al}_2\text{O}_3(s)\) exists stably. It means that Re. (8) happens. Because the main gas is CO \((g)\) in carbon-containing refractories at high temperature as statement, when \(\text{Al}_2\text{O}_4\text{C}\), C and \(\text{Al}_2\text{O}_3\) coexist in carbon-containing refractories and the refractories were used at working temperature in air, the main happening reaction will be Re. (8), but not Re. (1). Similarly, in carbon-containing refractories, \(\text{Al}_2\text{O}_4\text{C}\) as additive will not be reduced into \(\text{Al}_4\text{C}_3\) according to Re. (2).

Since \(\text{Al}_2\text{O}_4\text{C}\), added into carbon-containing refractories, will be oxidized into \(\text{Al}_2\text{O}_3\) and C by CO. The formation of C will cause the fact that carbon raw material in the refractories is not reduced, even if the carbon raw material reacts with O\(_2\) into CO. \(\text{Al}_2\text{O}_4\text{C}\)’s role of oxidation resistance is concluded. The formed \(\text{Al}_2\text{O}_3\) is a phase of enduring high temperature, it will not decrease the characteristic of erosion resistance of carbon-containing refractories. On the other hand, when Re. (8) is proceeded, the accompanying volume change is \(-2.1\%\). However, when Re. (11) is proceeded, the volume change is \(+170.5\%\). The later great expansion can play a role of increasing density and decreasing porosity; however, this role is little because the porosity is already very low in carbon-containing refractories. At this time, the spalling caused by great expansion can not be neglected.

\[
2\text{Al}(s) + 3\text{CO}(g) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{C}(s) \tag{11}
\]

The spalling is one of the main factors of carbon-containing refractories damage. Particularly for MgO–C refractories, the formed \(\text{Al}_2\text{O}_3\) will react with MgO into spinel with additional volume expansion, the combination of this expansion and the expansion of Re. (11) should greatly affect the spalling resistance of the MgO–C refractories. \(\text{Al}_2\text{O}_4\text{C}\) additive can slightly decrease the affection of expansion of spinel formation. So \(\text{Al}_2\text{O}_4\text{C}\) additive is considered better than Al additive on spalling resistance of refractories.

Furthermore, since \(\text{Al}_2\text{O}_4\text{C}\) will not be transformed into \(\text{Al}_4\text{C}_3\), \(\text{Al}_2\text{O}_4\text{C}\) as an additive in carbon-containing refractories will not lead the refractories to collapse. \(\text{Al}_2\text{O}_4\text{C}\) also can be used in unshaped refractories containing water. When the used carbon-containing refractories with Al additive were recycled for using again, the formed \(\text{Al}_4\text{C}_3\) in the refractories from reaction of Al and C was a serious problem. In general, these used refractories were especially dealt for removing the \(\text{Al}_4\text{C}_3\). This process is complex and time-consuming. Using \(\text{Al}_2\text{O}_4\text{C}\) additive, this problem does not exist.

Moreover, although \(\text{Al}_2\text{O}_4\text{C}\) started to be oxidized from about 820°C by O\(_2\) later than graphite (from about 610°C by O\(_2\)), \(\text{Al}_2\text{O}_4\text{C}\) started to be oxidized at almost the same temperature with graphite when buried in graphite powder and heated in air. This indicates that \(\text{Al}_2\text{O}_4\text{C}\) can play a role of decreasing the oxidation of graphite in the carbon-containing refractories. \(\text{Al}_2\text{O}_4\text{C}\), even if milled to very fine, has not combustible danger and so does not involve risks in utilization.

From the discussion above, \(\text{Al}_2\text{O}_4\text{C}\) is considered a promising additive for carbon-containing refractories.

5. Conclusions
Several dynamics factors influencing synthesis of \(\text{Al}_2\text{O}_4\text{C}\) and oxidation characteristics of \(\text{Al}_2\text{O}_4\text{C}\) were investigated and results are concluded as the following.

(1) The formed \(\text{Al}_2\text{O}_4\text{C}\) was increased with increase of heating temperature and extension of keeping time. Grain size of \(\text{Al}_2\text{O}_3\) had obvious influence on synthesis of \(\text{Al}_2\text{O}_4\text{C}\) and enough fine \(\text{Al}_2\text{O}_3\) should be used for synthesizing \(\text{Al}_2\text{O}_4\text{C}\) and avoiding \(\text{Al}_4\text{C}_3\) formation.

(2) The activation energy of reaction of \(\text{Al}_2\text{O}_3\) and graphite to form \(\text{Al}_2\text{O}_4\text{C}\) was calculated as 358.0 kJ/mol.

(3) \(\text{Al}_2\text{O}_4\text{C}\) started to be oxidized from about 820°C when heated in air.

(4) \(\text{Al}_2\text{O}_4\text{C}\), buried in graphite powder and heated in air, started to be oxidized at almost the same temperature with graphite and was converted into \(\text{Al}_2\text{O}_3\) and C. \(\text{Al}_2\text{O}_4\text{C}\) was considered a promising additive for carbon-containing refractories.

References
Influence of Heating Temperature, Keeping Time and Raw Materials Grain Size on 
\( \text{Al}_4\text{O}_4\text{C} \) Synthesis in Carbothermal Reduction Process and Oxidation of \( \text{Al}_4\text{O}_4\text{C} \)


