Synthesis of aluminum oxycarbide (Al$_2$OC) by selective microwave heating

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Aluminum oxycarbide (Al$_2$OC) is known as a promising material for refractory and abrasive uses. However, Al$_2$OC is synthesized at high temperatures with a long reaction time by an electric furnace. Microwaves are known as a low energy heating method due to its heating mechanism; rapid heating and cooling, selective and internal heating, etc. Therefore, Al$_2$OC was synthesized from amorphous carbon and alumina using a microwave furnace. The reaction ratio and particle shape were measured by XRD, SEM and TGA. The results showed that the reaction ratio increased by the microwave heating versus conventional heating, because the carbon and alumina interface was efficiently heated by the microwaves.

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Aluminum oxycarbide (Al$_2$OC) is known as a promising material for refractory and abrasive uses.1,2) The composite of Al$_2$OC with SiC and AlN (SiCaION), shows excellent mechanical properties like hardness, bending strength, etc. In this composite, Al$_2$OC acts as a sintering aide and has the advantage of a low sintering temperature comparable to the SiC monolith.3-5) SiCaION ceramics can be fabricated by hot pressing mixture of SiC, AlN, Al$_2$O$_3$ and Al$_4$C$_3$. In these processes, Al$_2$O$_3$ and Al$_4$C$_3$ form a liquid phase of Al$_2$OC as described by Eq. (1).

$$\text{Al}_4\text{C}_3 + \text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{OC} \quad (1)$$

$$\text{Al}_2\text{OC} + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_4\text{O}_4\text{C} \quad (2)$$

However, in addition to Al$_2$OC, a byproduct of Al$_4$O$_4$C also forms as shown by Eq. (2). Moreover, Al$_4$C$_3$ as the starting powder generates inflammable H$_2$ gas by reacting with moisture present in the air. Therefore, it is preferable to synthesize Al$_2$OC without going through the explosive reactions. Despite its importance, there are very few reports in the literature about synthesizing Al$_2$OC. Rwyablokov et al. synthesized Al$_2$OC from carbon and Al$_2$O$_3$ at 1700°C for four hours.6) In this study, in order to decrease the reaction temperature and shorten the reaction time, the microwave heating method was applied.

Microwave heating has found wide applications in material synthesis because of its many advantages such as rapid heating and cooling, selective and internal heating and dramatically reduced reaction time.7,8) In conventional heating methods, heat is transferred from the outside of the sample to the inside. In contrast, during microwave heating, the electromagnetic energy converts to thermal energy, which is absorbed by the materials, thus the materials are directly heated. This internal heat leads to advantages such as reduction of the processing time/cost and high yield as well as making new material synthesis possible by selectively heating the sample. It is known that materials with a high dielectric constant can be selectively heated. For example, carbon black, graphite and carbon fibers are well known materials heated by microwaves due to their high dielectric constant and low loss factor against the microwave frequency of 2.45 GHz.9-15)

There are many reports about the synthesis of carbide compounds by microwave heating.16-22) Hashimoto et al.23) synthesized SiC powder using silica and carbon by microwave heating. They suggested that some hot spots were generated inside the sample during processing, which accelerated the formation of SiO(g) and the subsequent reaction with carbon to form SiC. As a result, SiC was synthesized at a low temperature and a short time.

In this study, Al$_2$OC was synthesized from alumina and amorphous carbon by microwave radiation at low temperatures and short reaction times as compared to conventional heating methods. The carbon was revealed to be selectively heated by the microwaves due to its dielectric constant higher than that of alumina. Compared with the sample heated by a conventional heating method, the carbon and alumina interface in the sample heated by the microwaves was effectively heated.

Figure 1 shows the experimental setup in which a powder mixture of aluminacarbon with the 1:4 molar ratio was mixed by a mortar for 10 min. A 3 g sample of the powder was added to a crucible that had a hole (φ6 mm) in the side for gas inlet. The crucible was put in a larger crucible with the inner side pasted with SiC to prevent heat radiation. This crucible was then placed in the chamber. The crucible was surrounded by alumina insulation to prevent heat radiation. Argon gas (99.999%) flowed at the rate of 1.0 L/min into the crucible to prevent the carbon from burning. The gas was purged for 30 min before the heating. Microwaves irradiated the sample using a microwave furnace (MWKB-3.0; Takasago Institute Corporation; frequency: 2.45 GHz; maximum output power: 3 kW). The furnace was heated to the required temperature at the rate of 15°C/min. After heating, the irradiation was stopped and the furnace was naturally cooled to room temperature. The temperature was measured by a radiation thermometer during the heating.

An electric furnace (IDX-5, Kuno science) was used as the conventional heating method for comparison. In a typical procedure, 3 g samples were placed in a cubic graphite crucible (Inside diameter: 20 mm, Outer diameter: 30 mm, Height: 20 mm) and covered by a graphite plate. After evacuation to 35 Pa by a rotary pump, high-purity argon gas was introduced into the furnace at the flow rate of 2.0 L/min and maintained at a positive pressure.
of 50 kPa throughout the entire experiment. The furnace was first heated to 1000°C at the rate of 15°C/min, then to the target temperature at the rate of 10°C/min. After heating, the furnace was naturally cooled to room temperature. Table 1 summarizes the heating condition.

The X-ray diffraction patterns of the as-received products were recorded by an X-ray diffractometer (XRD, Rigaku, Ultima IV) with Cu Kα (λ = 1.5406 Å) radiation. A thermogravimetric analysis (TGA, Rigaku, Thermo Plus TG-8120) was used to evaluate the non-reacted carbon contents in the heated samples. The heated samples were characterized by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7600F) and energy-dispersive X-ray spectroscopy (EDS, JEOL, JED-2300) in order to investigate their shape and composition.

The sample weight was measured based on Eqs. (3) and (4) and the reaction rate was calculated.

Figure 2 shows XRD patterns of the samples with varying treatment temperatures. The diffraction peaks at 2θ = 32.78, 36.04, 37.44° are the (100), (002), and (101) reflections of the Al2OC structure (JCPDS Card No. 00-036-0149), respectively. The stronger (100) diffraction peak intensity of Al2OC gradually increased with the treatment temperature. The peak intensity of the M1700-30 was the strongest. In contrast, the C1700-120 had a very low intensity in spite of heating for 120 min.

Table 2 shows the TG results for calculation of the quantity of non-reacted carbon and reacted carbon in samples which were heated at different temperatures and reaction times.

The X-ray diffraction patterns of samples heated at the target temperatures (800, 1400°C). The carbons were burned at 800°C in air and Al2OC was oxidized at 1400°C. The peaks after heating at 800°C were the same as M1700-30 in
Therefore, Al₂OC was synthesized at a low temperature and short time, because carbon was selectively heated by microwaves. It was synthesized at a low temperature (1600°C) and short reaction time (no keeping) by the microwaves, because the carbon was directly heated. Therefore, the carbon and alumina interface was more efficiently heated by the microwaves than by conventional heating.

It is important for the reaction that the carbon and alumina are vaporized at high temperatures. Microwaves directly heated the carbon. In this study, Al₂OC was synthesized from amorphous carbon and alumina by microwave heating and compared to conventional heating. It was synthesized at a low temperature (1600°C) and short reaction time (no keeping) by the microwaves, because the carbon was directly heated. Therefore, the carbon and alumina interface was more efficiently heated by the microwaves than by conventional heating.

Table 3. The ratio of carbon, alumina and Al₂OC in samples which were heated at different temperatures and reaction times

| Sample     | Carbon/wt% | Al₂O₃/wt% | Al₂OC/wt% |
|------------|------------|-----------|-----------|
| C1700-20   | 31.3       | 67.9      | 0.8       |
| M1700-30   | 22.0       | 53.0      | 25.0      |
| M1700-0    | 25.8       | 61.6      | 12.6      |
| M1650-0    | 28.8       | 65.3      | 5.9       |
| M1600-0    | 33.0       | 64.0      | 3.0       |

Fig. 4. SEM images of (A) M1700-30 heated 800°C, (B) enlarged picture of the Al₂OC particle of (A).

Figs. 3(b) and 3(c), because this carbon has no crystalline structure. Figure 3(d) shows that the peaks of Al₂OC completely disappeared. This result illustrates that Al₂OC was oxidized to alumina.

Table 3 shows the weight ratio of carbon, alumina and Al₂OC in the samples. The Al₂OC weight ratio was calculated using the weight loss based on Eq. (4). The molar weight of Al₂OC was lower than that of Al₂O₃. Therefore, when Al₂OC was oxidized to alumina, the weight increased. The quantity of Al₂OC was calculated using the following equation.

\[
\text{Quantity of } \text{Al}_2\text{OC} = \frac{m_{\text{M}_{\text{Al}_2\text{O}_3}}}{(M_{\text{Al}_2\text{O}_3} - M_{\text{Al}_2\text{OC}})} \tag{5}
\]

Where \( m \) is the mean weight gain in mg, \( M_{\text{M}_{\text{Al}_2\text{O}_3}} \) is the mean molecular weight of \( \text{Al}_2\text{O}_3 \) (101.96 g/mol), and \( M_{\text{Al}_2\text{OC}} \) is the mean molecular weight of \( \text{Al}_2\text{OC} \) (101.96 g/mol). The quantity of Al₂OC gradually increased with the higher synthesizing temperature, and the sample heated at 1700°C for 30 min by the microwaves contained the highest quantity of Al₂OC (25.0 wt%). On the other hand, C1700-120 included only 0.8wt% Al₂OC. These results were also the same as the XRD and TG analysis results in Fig. 2 and Table 1. M1600-0 included 3 wt% Al₂OC. Therefore, Al₂OC was synthesized at a low temperature and short time by using microwaves. This result shows that microwaves promoted this reaction, because carbon was selectively heated by the microwaves and the interfaces of carbon and alumina were efficiently heated. On the other hand, the outer portion of the samples was heated and not its interfaces by conventional heating, because it is heated by heat conduction of the air.

Figure 4 shows SEM images of M1700-30 heated at 800°C for removing the carbon. In Fig. 4(A), the small particles were Al₂OC and the big ones were sintered alumina, which were confirmed by EDS. Therefore, alumina particles grew to 1–5 μm by heating at 1700°C due to the microwave radiation. Figure 4(B) is an enlarged picture of the Al₂OC particles that were confirmed by EDS. The Al₂OC particle size was about 10 nm that was smaller than the carbon and alumina of the raw materials. If this reaction proceeded as a solid–solid reaction or solid–vapor reaction by the vaporization of carbon, Al₂OC was obtained as alumina particles coated with it. However, Al₂OC was obtained as small particles. This shows that the alumina and carbon reacted by the vapor–vapor reaction. These reactions are given below.

\[
\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al}(g) + 3\text{CO}(g) \tag{6}
\]

\[
2\text{Al}(g) + \text{CO}(g) \rightarrow \text{Al}_2\text{OC}(s) \tag{7}
\]

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