Formation of Solid Solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ and Its Application in Spinel–Carbon Clinker Preparation

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$(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ 固溶体の合成とスピネル–カーボン系クリンカー作製への応用

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Among solid solutions $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$, $x=0-1$, it has been found that $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$, $x=0.5$, is easier to form by a solid state reaction. In this regard, a homogeneous solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ was obtained through heating of a compact, including Al_2O_3 , Al, AlN and graphite, at 1700°C for 5 h in Ar atmosphere and rapid cooling down to 1400°C . In comparing with AlN, it showed better hydration resistance. The obtained solid solution starts to react with MgO at 1100°C in CO atmosphere to form spinel and carbon. Therefore, the spinel–carbon clinker was prepared through heating of MgO– $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ compact in CO gas at 1500°C for 5 h. The precipitated carbon in the obtained clinker was amorphous and finely distributed among the spinel phase.

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1. Introduction

In the previous work, the spinel–carbon clinker for monolithic application was obtained through heating of an MgO–Al compact in CO gas.¹⁾ The main drawback of this method is that the clinker cannot be obtained through a single heating process, and consequently it cannot be formed in situ during practice. In order to solve this problem, use of other Al compounds, rather than Al metal, must be considered. In this regard, the ternary system of Al_2O_3 – Al_4C_3 –AlN has been studied. Figure 1 presents all the compounds that have been already reported in this system.^{2)–9)} High hydration tendency of Al_4C_3 and AlN prevents their application in the monolithic refractories. Among the others, the

occurrence of $\text{Al}_4\text{O}_4\text{C}^{3),4)}$ and $\text{Al}_2\text{OC}^{2),4)}$ have been confirmed by several investigations. In spinel–C formation process, reaction of $\text{Al}_4\text{O}_4\text{C}$ with CO gas in presence of MgO results in precipitation of low amount of carbon. Although Al_2OC presents high amount of carbon during clinker formation process, it is very difficult to be obtained purely. Even after formation, Al_2OC decomposes into $\text{Al}_4\text{O}_4\text{C}$ and Al_4C_3 at 1715°C during cooling (Reaction (1)), and it would be soon entirely degraded due to the large sensitivity of aluminum carbide to moisture.⁹⁾

However, addition of AlN to Al_2OC has been found to stabilize Al_2OC by forming a solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$. Aluminum oxy-carbide, Al_2OC , has a hexagonal crystal structure based on the wurtzite lattice in which the C and O atoms are randomly distributed over the non-metallic sites, as shown by Foster et al.⁴⁾ Al_2OC is isostructural with AlN and its lattice differs from that of AlN by 2% volume expansion of the unit cell. When aluminum oxy-carbide is written as $\text{Al}(\text{OC})_{0.5}$, it is isoelectronic with AlN.²⁾ Therefore, an extensive solid solution in Al_2OC –AlN system may be expected at elevated temperatures. The solubility of AlN and Al_2OC in each other to form a 2H solid solution phase was explained by Lihmann⁹⁾ and Qiu et al.¹⁰⁾ Reaction (2) shows this dissolution using the symbolic notation of Kröger and Vink.⁹⁾

One nitrogen atom is substituted to a carbon atom on a regular carbon site, thus creating a positive electric charge, whereas the other nitrogen atom is substituted to an oxygen atom on a regular oxygen site, thus creating a negative electric charge.

Compared with Al_2OC , the solid-solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ has two major advantages: It is easy to form by a solid-state reaction, and it is more stable at high temperature. $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ ceramics may be of interest in future as the possible combinations of good mechanical properties (high hardness of Al_2OC) with good functional properties (high thermal-low electrical conductivity of

Fig. 1. Reported compounds in Al_2O_3 – Al_4C_3 –AlN system to the accompaniment of experimental compositions (a, b, c and d in Table 1).

AlN). But, in this work it has been considered for monolithic refractory applications. In this regard, formation of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ has been investigated in the ternary diagram $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3\text{--AlN}$ along the quasi-binary section joining Al_2OC and AlN. As a result, solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ has been introduced as the easiest composition to obtain purely. Then, its participation in the formation of spinel-carbon clinker has been investigated.

2. Experimental procedure

2.1 Raw materials

The raw materials used in this study are as follows:

- (1) Carbon: natural graphite, purity: more than 99%, size: less than 10 μm
- (2) Al: purity: more than 99%, size: less than 10 μm
- (3) MgO: calcined "Basic Magnesium Carbonate" $[4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$, purity: more than 99% (chemical reagent grade), size: submicron
- (4) Al_2O_3 : purity: more than 99.99%, mean size: 0.23 μm
- (5) AlN: purity: more than 99%, mean size: 2 μm

2.2 Synthesis of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$

As shown in Table 1, different batches in the quasi-binary section $\text{Al}_2\text{OC--AlN}$ of the ternary diagram $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3\text{--AlN}$ (Fig. 1) were weighed, well mixed in ethanol, dried, isostatically pressed (at 100 MPa) and finally heated in an alumina tube furnace at 1700°C for 5 h in Ar gas. The heating and cooling rates were 10°C·min⁻¹. Ar gas was flowed at a rate of 0.2 l·min⁻¹ during heating and cooling. The all above mixtures were also heated in the same condition, but they were rapidly cooled down to 1400°C (ca. 100°C·min⁻¹) by circulating cold water around heating chamber. Then, phase compositions of the heated compacts were examined by X-ray diffraction (XRD) test. Microstructure of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ [the compact (c) after heating at 1700°C and rapid cooling] was observed by scanning electron microscope (SEM). Finally, lattice parameters of the obtained solid solution were measured through step scanning-XRD with rotation step of 0.005° and detecting time constant of 4 s in each step.

2.3 Hydration behavior of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x=0.5$)

Since monolithic refractories deal with moisture, hydration must be considered as an important phenomenon that can degrade the refractories. Therefore, the obtained solid solution was subjected to hydration test inside a humid chamber at 70°C with humidity of 90%.

2.4 Spinel-carbon clinker preparation by using the obtained solid-solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x=0.5$)

The solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ (67 mass%) and MgO (33 mass%) powders were weighed, well mixed in ethanol and uniaxially pressed at 100 MPa to form compacts with diameter of 15 mm and thickness of 10 mm. Then, they were heated in CO gas at various temperatures for 5 h in an alumina tube furnace. In all runs, CO gas was flowed at a rate of 0.2 l·min⁻¹. After heating at each temperature, mass changes were recorded and phase compositions were determined (by XRD). Microstructure of the obtained clinker was observed by SEM. Element analysis was also conducted on the prepared clinker by a SEM equipped with an energy-dispersive X-ray analyser (EDX-SEM). Finally, lattice parameter of the formed spinel phase in the obtained clinker was measured through XRD-Step Scanning with rotation step of 0.005° and detecting time constant of 4 s in each step. Oxidation behavior of the prepared clinker (powder) was analysed by differential thermogravimetry (DTG) in air. Heating rate was always 10°C·min⁻¹. For comparison, an unheated mixture, including spinel (80 mass%) and graphite (20 mass%), was also examined. Pore size distri-

Table 1. Composition of the Compacts (mass%)

Compacts ($\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$	(a) Al_2OC ($x=0$)	(b) $(\text{Al}_2\text{OC})_{0.83}(\text{AlN})_{0.17}$ ($x=0.17$)	(c) $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x=0.5$)	(d) $(\text{Al}_2\text{OC})_{0.33}(\text{AlN})_{0.67}$ ($x=0.67$)
Raw materials				
Al_2O_3	41.46	37.32	27.64	20.73
Al	43.90	39.51	29.27	21.95
Graphite	14.64	13.17	9.76	7.32
AlN	---	10.00	33.33	50.00

bution of the prepared clinker was measured by a mercury porosimeter.

3. Results and discussion

3.1 Synthesis of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$

Figure 2 presents XRD patterns of the different compacts (mentioned in Table 1) after heating at 1700°C for 5 h in Ar gas. XRD pattern of the heated compact (a), corresponding to Al_2OC , confirms formation of a little Al_2OC (so called α' - $\text{Al}_2\text{OC}^{11}$) with JCPDS Card No. 36-0149¹²⁾ but a large amount of unexpected $\text{Al}_4\text{O}_4\text{C}$ and Al_4C_3 . As a result, it is very difficult to obtain pure Al_2OC through a simple heating process. On the other hand, addition of a little AlN to Al_2OC [Fig. 2(b)] not only prevents $\text{Al}_4\text{O}_4\text{C}$ formation and retards Al_4C_3 formation but also enhances formation of the 2H solid solution phase $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ (so called α' - $\text{Al}_2\text{OC}^{11}$) with JCPDS Card No. 36-0148¹²⁾. More addition of AlN ($x=0.5$), as Fig. 2(c) shows, results in formation of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$ without any $\text{Al}_4\text{O}_4\text{C}$ or Al_4C_3 residual. Although further addition of AlN ($x=0.67$) enhances formation of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$, some part of AlN remains undissolved after heating process [Fig. 2(d)]. As shown in Fig. 3 [calculated from the experimental results of the Refs. (9) and (10)], the Al_2OC -rich solid solutions thermodynamically form only at high temperature, and addition of AlN decreases the forming temperature of the solid solution. Therefore, formation of a complete solid solution cannot be easily expected by addition of a little AlN, as shown in Fig. 2(b) ($x=0.17$). On the other hand, although the AlN-rich solid solutions thermodynamically form at lower temperatures, demixing of AlN during cooling may easily take place at higher AlN content.⁹⁾ This is in a good agreement with the XRD results in Fig. 2(d). The volume changes of unit cell of the solid solution $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$, as a function of x , is plotted in Fig. 4.⁹⁾ As this figure shows, there are two linear volume variation regions, which are separated by an abnormal variation region from $x=0.5$ to $x=0.6$. This important abnormal volume variation can be seen as characteristic of a new ordering phenomenon, which leads to the formation of a new ordered phase at about $x=0.57$, as $\text{Al}_{10}\text{O}_3\text{C}_3\text{N}_4$.⁹⁾ This phase is itself able to dissolve noticeable amounts of AlN in its lattice, as suggested by the second linear variation region. Extrapolation of the first linear variation to $x=0$ leads to the pure Al_2OC , while extrapolation of the second linear variation to $x=1$ leads to the pure AlN. Because of low hydration resistance of AlN and high hydration resistance of Al_2OC , a solid solution similar to the Al_2OC structure is simply expected to show better hydration resistance than a solid solution similar to the AlN structure. Therefore, the solid solution is preferred to be in the linear range between $x=0$ and $x=0.5$. Besides, as mentioned before, higher amount of AlN addition facilitates formation of the solid solution. As a result, the best composition is supposed to be $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x=0.5$). XRD pattern in Fig. 2(c) verifies forma-

Fig. 2. XRD patterns of the compacts in Table 1, after heating at 1700°C for 5 h in Ar gas (heating and cooling rate: 10°C·min⁻¹; Ar flow rate: 0.21·min⁻¹).

Fig. 3. Thermodynamical stability of the solid solution $(\text{Al}_2\text{O}_3)_{1-x}(\text{AlN})_x$ in the Al_2O_3 – AlN system, calculated based on data of Lihmann et al.⁹ and Qiu et al.¹⁰

Fig. 4. Volume variation of the unit cell of $(\text{Al}_2\text{O}_3)_{1-x}(\text{AlN})_x$ solid solution; from Lihmann et al.⁹

Fig. 5. XRD pattern of the compact (c) $[(\text{Al}_2\text{O}_3)_{0.5}(\text{AlN})_{0.5}]$ after heating at 1700°C for 5 h in Ar gas and rapid cooling (Ar flow rate: 0.21·min⁻¹, heating rate: 10°C·min⁻¹, cooling rate: 100°C·min⁻¹).

Fig. 6. Step scanning-XRD patterns of the compact (c) $[(\text{Al}_2\text{O}_3)_{0.5}(\text{AlN})_{0.5}]$ after heating at 1700°C for 5 h in Ar gas and (a) slow cooling: 10°C·min⁻¹, (b) rapid cooling: 100°C·min⁻¹. (Ar flow rate: 0.21·min⁻¹; heating rate 10°C·min⁻¹).

tion of the 2H solid solution phase without any residual.

Although XRD test results of the heated compacts (a), (b) and (d) after rapid cooling were almost same as those after slow cooling, an obvious difference was observed in the case of compact (c). As shown in Fig. 5, XRD pattern of the compact (c) after rapid cooling confirms presence of a homogeneous single-phase 2H solid solution as the only detected phase, while the same compact with a slow cooling rate (10°C·min⁻¹) exhibited peak splitting in Fig. 2(c), suggesting the presence of two 2H solid solutions in coexistence. Step scanning-XRD results of the heated compact (c) with slow and rapid cooling in Fig. 6 make the mentioned peak splitting clearer. These results also indicate lattice parameter of $c = 0.5061$ nm for the rapid-cooled solid solution $(\text{Al}_2\text{O}_3)_{0.5}(\text{AlN})_{0.5}$, which is smaller than c -value for Al_2O_3 (0.5078 nm) and bigger than c -value for AlN (0.4979 nm) (JCPDS Card Nos. 36-0148 and 25-1133, respectively).¹² Comparison of the two XRD patterns in Fig. 6 shows that the splitting of (002) peak in the Fig. 6(a) occurs on the high-angle side, which implies that the formed

Fig. 7. SEM pictures of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ (fractured surface).

precipitates during slow cooling are AlN-rich solid solution.^{13)–15)}

Hereafter, the phrase “solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ” will be referred to the compact (c) [corresponding to $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$], which was heated in Ar gas at 1700°C for 5 h and rapid-cooled to 1400°C, with an XRD pattern presented in Fig. 5. SEM images of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ (fractured surface) are presented in Fig. 7. Although structure of the bulk sample is quite porous, a fine size powder with dense grains can be obtained after enough grinding (less than 5 µm).

3.2 Hydration behavior of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x = 0.5$)

Figure 8 presents hydration behavior of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$. For comparison, AlN and the formed solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ with slow cooling rate were also examined. As shown in this figure, hydration rate of the obtained solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ (rapid cooled) is lower than that of the slow-cooled solid solution. Precipitation of AlN-rich solid solution during slow cooling, which has higher hydration tendency than low-AlN solid solutions, can explain impaired hydration resistance of the slow-cooled solid solution.

3.3 Spinel–carbon clinker preparation by using the obtained solid-solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ ($x = 0.5$)

Assuming Reaction (3), the MgO – $[(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}]$ compact must gain 45.8% mass after heating in CO gas, and final phase composition is supposed to be spinel (79.8 mass%) and carbon (20.2 mass%).

But, even after heating at 1600°C for 5 h, the mass gain reached to 27 mass%. As indicated in Fig. 9, $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ disappeared completely at 1500°C and spinel in ac-

Fig. 8. Mass gain of AlN and the obtained $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ powders during hydration (70°C, 90% humidity).

Fig. 9. XRD patterns of the MgO – $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ compact, after heating in CO gas for 5 h at various temperatures (CO flow rate: 0.2 l·min^{−1}).

companion to unreacted MgO were the main detected phases. Two unknown peaks with 2θ of 33.83° and 60.47° were also detected. As mentioned in the introduction, since the Al_2O_3 – Al_4C_3 –AlN system has not been completely cleared yet, these peaks might be related to one of the phases in this system or combination of them with MgO. Hereafter, the work “clinker” will be referred to the MgO – $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ compact that was heated at 1500°C for 5 h in CO gas. Figure 10 presents SEM images of the obtained clinker. The clinker is made of very fine grains. EDX–SEM element analysis confirmed formation of a homogenous structure in which the formed spinel and carbon to the accompaniment of unreacted MgO were distributed uniformly. Lattice parameter of the formed spinel ($a = 0.883 \text{ nm}$), measured by XRD–step scanning, corresponds to a normal spinel (JCPDS Card No. 21–1152¹²⁾).

XRD patterns of the obtained clinker and the unheated spinel–graphite mixture are presented in Fig. 11. Since car-

Fig. 10. SEM micrographs of the obtained clinker (fractured surface).

Fig. 11. XRD patterns of the obtained clinker and spinel-graphite mixture.

bon peaks in the clinker are quite broad, the precipitated carbon must be amorphous. This amorphous carbon is simply expected to show higher oxidation tendency than graphite. DTG results of the both samples in Fig. 12 confirm above statements. The exothermic peak of carbon burnout occurs at 647°C for the clinker and at 835°C for the spinel-graphite mixture. As TG curves show, oxidation of

Fig. 12. DTG results of the obtained clinker and spinel-C mixture in air (heating rate: $10^\circ\text{C}\cdot\text{min}^{-1}$).

Fig. 13. Pore size distribution of the obtained clinker.

carbon in the obtained clinker starts around 550°C, but graphite burnout starts at higher temperature around 650°C. Porosimetry analysis in Fig. 13 presents a very fine and narrow distribution of open pores in the obtained clinker. Therefore, since the spinel grains do not make an impermeable continuous framework, they cannot protect carbon from oxidation and their surrounding effect around precipitated carbon must be negligible. This could be expected from SEM pictures in Fig. 10 and EDX-SEM element analyses. As this figure shows the spinel grains are too small (less than $1\mu\text{m}$) and they are separately distributed throughout the matrix.

4. Conclusions

- (1) Among the solid solutions $(\text{Al}_2\text{OC})_{1-x}(\text{AlN})_x$, $x=0-1$, it has been found that the solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$, $x=0.5$, is easier to form by a solid state reaction.
- (2) A homogenized solid solution $(\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}$ was successfully synthesized through heating of a compact, including Al_2O_3 , Al, AlN and graphite, at 1700°C for 5 h in Ar atmosphere and rapid cooling down to 1400°C .
- (3) The obtained solid solution showed quite better hydration resistance in comparing with AlN.

(4) A spinel-carbon clinker was prepared through heating of the $\text{MgO}-(\text{Al}_2\text{O}_3)_{0.5}(\text{AlN})_{0.5}$ compact at 1500°C for 5 h in CO gas.

(5) The precipitated carbon phase in the obtained clinker was amorphous and finely distributed among the formed spinel and remaining MgO grains.

(6) Low oxidation resistance of the obtained spinel-C clinker implies that surrounding of the precipitated carbon by the formed spinel cannot protect carbon from oxidation.

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