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 \(\text{Al}_2\text{O}_3\), \(\text{Al}\), \(\text{AlN}\) and graphite, at 1700°C for 5 h in Ar atmosphere and rapid cooling down to 1400°C. In comparing with \(\text{AlN}\), it showed better hydration resistance. The obtained solid solution starts to react with \(\text{MgO}\) at 1100°C in CO atmosphere to form spinel and carbon. Therefore, the spinel-carbon clinker was prepared through heating of \(\text{MgO}-(\text{Al}_2\text{OC})_{0.5} (\text{AlN})_{0.5}\) 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 \(\text{MgO}–\text{Al}\) 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 \(\text{Al}_2\text{O}_3–\text{Al}_4\text{C}_3–\text{AlN}\) has been studied. Figure 1 presents all the compounds that have been already reported in this system.\(^2\)-\(^9\) High hydration tendency of \(\text{Al}_4\text{C}_3\) and \(\text{AlN}\) prevents their application in the monolithic refractories. Among the others, the occurrence of \(\text{Al}_2\text{O}_4\text{C}\)\(^3\),\(^4\) and \(\text{Al}_2\text{OC}\)\(^2\),\(^4\) have been confirmed by several investigations. In spinel-C formation process, reaction of \(\text{Al}_2\text{O}_4\text{C}\) with CO gas in presence of \(\text{MgO}\) results in precipitation of low amount of carbon. Although \(\text{Al}_2\text{OC}\) presents high amount of carbon during clinker formation process, it is very difficult to be obtained purely. Even after formation, \(\text{Al}_2\text{OC}\) decomposes into \(\text{Al}_2\text{O}_4\text{C}\) and \(\text{Al}_4\text{C}_3\) at 1715°C during cooling (Reaction (1)), and it would be soon entirely degraded due to the large sensitivity of aluminum carbide to moisture.\(^9\)

\[4\text{Al}_2\text{OC} = 2\text{Al}_2\text{O}_4\text{C} + \text{Al}_4\text{C}_3\] (1)

However, addition of \(\text{AlN}\) to \(\text{Al}_2\text{OC}\) has been found to stabilise \(\text{Al}_2\text{OC}\) by forming a solid solution \((\text{Al}_2\text{OC})_{1-x} (\text{AlN})_x\). Aluminum oxy-carbide, \(\text{Al}_2\text{OC}\), 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.\(^4\) \(\text{Al}_2\text{OC}\) is isostructural with \(\text{AlN}\) and its lattice differs from that of \(\text{AlN}\) 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 \(\text{AlN}\).\(^2\) Therefore, an extensive solid solution in \(\text{Al}_2\text{OC}–\text{AlN}\) system may be expected at elevated temperatures. The solubility of \(\text{AlN}\) and \(\text{Al}_2\text{OC}\) in each other to form a 2H solid solution phase was explained by Lillmann\(^5\) and Qiu et al.\(^10\). Reaction (2) shows this dissolution using the symbolic notation of Kröger and Vink.\(^9\)

\[2\text{AlN} \rightarrow 2\text{Al}^{3+} + 3\text{N}_2 + 3\text{O}^'\] (2)

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 \(\text{Al}_2\text{OC}\), 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 temperatures. \((\text{Al}_2\text{OC})_{1-x} (\text{AlN})_x\) ceramics may be of interest in future as the possible combinations of good mechanical properties (high hardness of \(\text{Al}_2\text{OC}\)) with good functional properties (high thermal-low electrical conductivity of...
AIN). But, in this work it has been considered for monolithic refractory applications. In this regard, formation of the solid solution (Al2OC)1-x(AlN)x has been investigated in the ternary diagram Al2O3-Al4C3-AlN along the quasi-binary section joining Al2OC and AlN. As a result, solid solution (Al2OC)1-x(AlN)x has been introduced as the existence 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" [4MgCO3·Mg(OH)2·5H2O], purity: more than 99% (chemical reagent grade), size: submicron
4. Al2O3: 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 (Al2OC)1-x(AlN)x

As shown in Table 1, different batches in the quasi-binary section Al2O3−AlN of the ternary diagram Al2O3−Al4C3−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. Heating and cooling rates were 10°C·min⁻¹. Ar gas was flowed at a rate of 0.21·min⁻¹ during heating and cooling. The solid solution used to form had the same conditions, 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: (Al2OC)1-x(AlN)x [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 (Al2OC)0.5(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 (Al2OC)0.5(AlN)0.5 (x=0.5)

The solid solution (Al2OC)0.5(AlN)0.5 (67mass%) and MgO (33mass%) powders were weighed, well mixed in ethanol and uniaxially pressed at 100 MPa to form compacts with diameter of 15mm and thickness of 10mm. Then, they were heated in CO gas at various temperatures for 5h in an alumina tube furnace. In all runs, CO gas was flowed at a rate of 0.21·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 parameters 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.

Table 1. Composition of the Compacts (mass%)
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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: 0.2 l·min⁻¹).

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 \((\text{Al}_2\text{OC})_{0.5}(\text{AlN})_{0.5}\), which is smaller than \(c\)-value for \(\text{Al}_2\text{OC} (0.5078\) nm) and bigger than \(c\)-value for \(\text{AlN} (0.4979\) 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
precipitates during slow cooling are AlN-rich solid solution.13)-15)

Hereafter, the phrase "solid solution (Al2OC)0.5(AlN)0.5" will be referred to the compact (c) [corresponding to (Al2OC)0.5(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 (Al2OC)0.5(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 (Al2OC)0.5(AlN)0.5(x=0.5)

Figure 8 presents hydration behavior of the obtained solid solution (Al2OC)0.5(AlN)0.5. For comparison, AlN and the formed solid solution (Al2OC)0.5(AlN)0.5 with slow cooling rate were also examined. As shown in this figure, hydration rate of the obtained solid solution (Al2OC)0.5(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 (Al2OC)0.5(AlN)0.5(x=0.5)

Assuming Reaction (3), the MgO–[(Al2OC)0.5(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%).

\[ 3\text{MgO} + 4[(\text{Al}_2\text{OC})_{0.5}\text{(AlN)}_{0.5}] + 7\text{CO} \]
\[ = 3\text{MgAl}_2\text{O}_4 + 9\text{C} + \text{N}_2 \uparrow \] (3)

But, even after heating at 1600°C for 5 h, the mass gain reached 27 mass%. As indicated in Fig. 9, (Al2OC)0.5(AlN)0.5 disappeared completely at 1500°C and spinel in accompaniment 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 Al2O3-Al4C3-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–(Al2OC)0.5(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 nm), measured by XRD–step scanning, corresponds to a normal spinel (JCPDS Card No. 21-11522)).

Fig. 9. XRD patterns of the MgO–(Al2OC)0.5(AlN)0.5 compact, after heating in CO gas for 5 h at various temperatures (CO flow rate: 0.21 min⁻¹).
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 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 continues 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 μm) and they are separately distributed throughout the matrix.

4. Conclusions
(1) Among the solid solutions (Al₂OC)₁₋ₓ(AlN)ₓ, x = 0–1, it has been found that the solid solution (Al₂OC)₀.₅(AlN)₀.₅, x = 0.₅, is easier to form by a solid state reaction.
(2) A homogenized solid solution (Al₂OC)₀.₅(AlN)₀.₅ was successfully synthesized through heating of a compact, including Al₂O₃, 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 MgO–[(Al₂O₃)₀.₅(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.

References