論文
Sintering and Mechanical Properties of AlZrC₂

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AlZrC₂ の焼結と機械的特性

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AlZrC₂ powder prepared by solid-state reaction was sintered using a pulse electric current sintering technique in a temperature range from 1700 to 2000°C under the pressure of 40 MPa in vacuum for 5 min. The density and mechanical properties of the sintered AlZrC₂ monolith were estimated. As heating temperature increased, the density of the AlZrC₂ monolith increased and the mechanical properties were improved. The bulk density of the AlZrC₂ monolith sintered at 2000°C was 5.12 g/cm³. The maximum values of the fracture strength and Vickers’ hardness were 380 MPa and 11.1 GPa, respectively.

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Key-words : Complex carbide, AlZrC₂, PECS, Mechanical properties, Fracture strength, Vickers’ hardness

Introduction

In recent years, ternary compounds of complex carbide in Al-Ti-C system have attracted our interest because of their desirable mechanical properties, i.e. their machinability and high strength. However, research on the complex carbides of the transition elements Zr of group IV is very rare. In previous works, we sintered dense Zr₂AlC₃ using a pulse electric current sintering (PECS) technique, and characterized the physical and mechanical properties of the Zr₂AlC₃ monolith. AlZrC₂, another phase of the Al-Zr-C system was crystallographically determined by Mikhalenko in 1979. Hashimoto et al. have prepared a composite material composed of aluminum and AlZrC₂, where the AlZrC₂ powder was obtained by treatment of the composites with HCl. However, the properties of AlZrC₂ have not been studied so far.

In the present work, an AlZrC₂ powder compact was sintered by means of a PECS technique. This technique enables sintering of ceramic powders in a short time with rapid cooling. The technique can also sinter materials with poor sinterability. The mechanical properties of the sintered AlZrC₂ monolith prepared by the PECS technique are examined and discussed herein.

Experimental procedure

The starting material, AlZrC₂, was prepared from solid-state reaction using a technique described elsewhere, in which powders of Al, ZrC, and amorphous carbon from sugar were mixed at molar ratios of 21 : 14 : 15. The mixture was preformed as pellets and CIPped at 100 MPa. The pellets were then heated at 1600°C for 1 h in vacuum and ground into a fine powder. The obtained AlZrC₂ powder was heated using the PECS technique at a temperature range from 1700 to 2000°C under 40 MPa in vacuum for 5 min. After sintering, the phase of the sample was characterized by XRD. The density of the AlZrC₂ monolith was measured by Archimedes’ method using kerosene as a medium. The sintered AlZrC₂ monolith was then cut into 2 × 2 × 10 mm³ test samples for estimating fracture strength and Vickers’ hardness. The fracture strength was estimated using a three-point bending test with 8 mm span length and 0.5 mm/min cross-head speed. Vickers’ hardness was measured under the condition of 98.07 N for 15 s according to the new Japanese Industrial Standard (JIS R1610: 2003). The fracture surfaces of each sample after bending tests were observed by scanning electron microscopy (SEM).

Results and discussion

The bulk density of the AlZrC₂ monolith increased with increasing heating temperature, as shown in Table 1. The calculated theoretical density shown in JCPDS is 5.282 g/cm³ and the measured density specified in JCPDS is 5.000 g/cm³. Table 1 indicates that the bulk density of the AlZrC₂ monolith sintered at 2000°C is higher than that of Mikhalenko’s result.

The XRD patterns of the samples before and after heating are compared with the ideal XRD patterns of AlZrC₂ and

<table>
<thead>
<tr>
<th>Sintered Temperatures</th>
<th>Bulk Density (g/cm³)</th>
</tr>
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<tbody>
<tr>
<td>1700°C</td>
<td>3.60</td>
</tr>
<tr>
<td>1800°C</td>
<td>3.92</td>
</tr>
<tr>
<td>1900°C</td>
<td>4.50</td>
</tr>
<tr>
<td>2000°C</td>
<td>5.12</td>
</tr>
</tbody>
</table>

Table 1. Density of AlZrC₂ after Sintering by PECS at Various Temperatures under 40 MPa for 5 min
Fig. 1. XRD patterns of sintered AlZrC₂ by PECS at various temperatures under 40 MPa for 5 min, comparing with ideal XRD patterns.

\[ \text{Zr}_2\text{Al}_{12}\text{C}_3 \] in Fig. 1. The 2θ peaks at 33.277 and 39.418 for \( \text{Zr}_2\text{Al}_{12}\text{C}_3 \) (JCPDS No. 41-0814) found in the starting powder after synthesis \(^{11} \) disappeared after sintering. From our previous work, \(^{12} \) we can infer two reasons for this \( \text{Zr}_2\text{Al}_{12}\text{C}_3 \) loss; sublimation during sintering in vacuum or distortion of this phase under high pressure.

The displacement (Z-axis) of the AlZrC₂ compacts during sintering by the PECS technique is shown in Fig. 2. The sintering initiation was at around 1280°C. During the soaking duration at 2000°C, the Z-axis curve plateaus out at 1 min.

The mechanical properties of the sintered AlZrC₂ monolith at various temperatures are shown in Figs. 3 and 4. Both the fracture strength and Vickers' hardness of the AlZrC₂ monolith showed the same tendency with heating temperature. At 2000°C, the AlZrC₂ monolith had maximum values of fracture strength and Vickers' hardness at 380 MPa and 11.1 GPa, respectively. The fracture strength and Vickers' hardness increased rapidly from 1800 to 2000°C, because the bulk density increased, as shown in Table 1.

SEM micrographs of the fracture surfaces are shown in Fig. 5 for the sintered AlZrC₂ bodies at various temperatures. It was found that the sinterability of AlZrC₂ is low despite using the PECS technique. The samples sintered from 1700 to 1900°C showed porous structures. The sample sintered at 2000°C showed the densest structure with only a few small pores, and each grain was not distinguished. As a result, this sintering was thought to occur through a liquid phase reaction. However, this liquid phase component during heating is not yet to be clarified.
Fig. 5. Fracture surface of AlZrC₂ after sintering by the PECS technique under 40 MPa for 5 min. (a) 1700°C, (b) 1800°C, (c) 1900°C, and (d) 2000°C.

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References
9) JCPDS card No. 32-0030.

Conclusion
We fabricated a dense AlZrC₂ monolith using a pulse electric current sintering (PECS) technique. The second phase (Zr₂Al₄C₁₈) was not found in the sintered AlZrC₂ prepared by solid-state reaction. The density, fracture strength, and Vickers' hardness increased with increasing heating temperature. The AlZrC₂ monolith obtained at 2000°C and 40 MPa in vacuum for 5 min exhibited a bulk density of 5.12 g/cm³, a fracture strength of 380 MPa, and a Vickers' hardness of 11.1 GPa.
Low-temperature synthesis of leucite crystals using kaolin

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Abstract

Synthesis of leucite crystals below 1000 °C using natural kaolin as the primary raw material was investigated. Spherical leucite crystals having a diameter of approximately 50 \textmu m were prepared by heating a powder mixture of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}, kaolin and K\textsubscript{2}SO\textsubscript{4} (in mass ratios of 3:3:15) at 900 °C for 3 h. Quartz, the main accessory phase in kaolin, and the amorphous metakaolin formed upon heating kaolin were found to be responsible for the decreased synthesis temperature.

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Keywords: A. Ceramics; A. Oxides; B. Crystal growth; C. Electron microscopy; C. X-ray diffraction

1. Introduction

Leucite (KAIS\textsubscript{2}O\textsubscript{6}) has been used as an important crystal phase in dental porcelain/glass materials [1] because of its tone, color appeal and excellent biocompatibility. Furthermore, due to its high melting point (1693 °C) [2] and high thermal expansion coefficient (3.1 \times 10^{-5} \textdegree C^{-1}, to 600 °C) [3], leucite has potential application in preparing functional coatings on metal substrates or reinforcing metal-based composites.

Leucite is generally synthesized by heating the mixture of raw materials at a temperature above its melting point and then slowly cooling the mixture to room temperature [1,3]. Recently, spherical leucite crystals with a controlled size of between several micrometers to approximately 100 \textmu m have been

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synthesized at a much lower temperature (1000 °C) by the present authors [4,5] using reagent grade Al₂(SO₄)₃, SiO₂ and K₂SO₄ as starting raw materials. Because of their spherical morphology, the synthesized leucite crystals could be well distributed in dental materials, allowing the materials (e.g. artificial teeth) to be rendered with substantially enhanced mechanical strength. In addition, the synthesized leucite crystals could be used as a raw material in the fabrication of bulk leucite ceramics or as an additive to silica glass due to having a near reflection coefficient. However, the present study is the first report of synthesis at a temperature below 1000 °C using cheaper natural materials, such as kaolin.

2. Experimental

Reagent grade Al₂(SO₄)₃·14-18H₂O and K₂SO₄, and 2–10 μm Chinese kaolin (Fujian, China), the chemical composition of which is shown in Table 1, were used as starting materials. The XRD patterns shown in Fig. 1 reveal that, apart from the primary crystal phase, i.e. kaolinite (Al₂O₃·2SiO₂·2H₂O), SiO₂ (quartz) and muscovite are present in kaolin as accessory phases. The quartz content is estimated to be approximately 6.7 wt% based on the chemical compositions shown in Table 1.

Al₂(SO₄)₃ was prepared by heating Al₂(SO₄)₃·14-18H₂O for more than 12 h at 300 °C in air. The heated Al₂(SO₄)₃ was then mixed with kaolin and K₂SO₄ in mass ratios of 3:3:15 using a mortar in order to obtain a melted phase for the crystal growth of leucite during heating. A mass of this powder mixture (approximately 20 g) was heated in an alumina crucible (high: 75 mm, diameter: 55 mm) to 850–1100 °C at the rate of 10 °C/min and was maintained at temperature for 0–3 h. After heating, the furnace was allowed to cool naturally to room temperature. The reactant mass remaining at the bottom of the crucible was soaked in 3% hydrochloric acid at 70–80 °C for 1–2 h to dissolve the remaining K₂SO₄–Al₂(SO₄)₃ system components. Subsequently, the remaining sample was rinsed with distilled water, dried well at approximately 80 °C for 1 h and sifted with an 88-μm sieve to obtain pure reaction products. The resulting crystalline phases in the reaction products were examined by X-ray diffraction (XRD: Model XD-D1, Shimazu Co., Ltd., Kyoto, Japan) and their microstructures were examined using a scanning electron microscope (SEM: Model JEL 5200, Nihondensi Co., Ltd., Tokyo, Japan). In order to clarify the formation mechanism of leucite crystals, crystalline phases in the reactant masses before the hydrochloric acid treatment were also examined by XRD.

<table>
<thead>
<tr>
<th>Chemical composition of kaolin (mass%)</th>
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<tbody>
<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>MgO</td>
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<tr>
<td>K₂O</td>
</tr>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>Ig. loss</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Effect of temperature and time on the formation of leucite crystals

Figs. 2 and 3 show XRD patterns and SEM micrographs of the samples after heating the powder mixture at 850—1100 °C for 3 h and further treating with hydrochloric acid, respectively. At 850 °C, only quartz (but no leucite) was identified by XRD, and the microstructure reveals an extensive formation of grains of less than 10 μm in diameter. As the temperature increased to over 850 °C (900–1100 °C), the quartz disappeared and only leucite remained. Nevertheless, depending on the temperature, the formed leucite crystals showed different morphologies. At 900 °C, spherical leucite crystals having a diameter of approximately 50 μm were observed. However, at 1000 °C, the leucite crystals began to lose their spherical morphology. A further increase in temperature to 1100 °C led to the formation of leucite crystals of two different diameters, approximately 50 μm and 10–20 μm. At 900 °C, the number of leucite nuclei formed in the sample decreased. Therefore, a comparatively small number of leucite crystals appeared to be responsible for the increase in the size of leucite crystals, which is thought to cause the formation of large monocrystals. In contrast, upon increasing the temperature to 1100 °C, a large number of leucite nuclei formed, so that each of the leucite crystals became smaller and showed a tendency to form crystal agglomerations. Thus, these results indicated that when kaolin was used as the primary raw material, spherical leucite crystals of homogeneous size could be synthesized by heating the

![XRD pattern of the Chinese kaolin used.](image)

![XRD patterns of the samples after heating the mixture kaolin and K₂SO₄ (in mass ratios of 3:3:15) at 850–1100 °C for 3 h and further treating with hot hydrochloric acid.](image)
powder mixture at 900 °C, which is lower than that (1000°C) reported in previous studies using reagent grade SiO₂ as a starting raw material [4,5].

Fig. 4 presents XRD patterns and SEM micrographs of the samples after heating the powder mixture at 900 °C for various time periods and further treating with hot hydrochloric acid. SiO₂ quartz and muscovite (but no leucite) were detected by XRD in the sample that was heated at 900 °C for 0 h. That is, the sample was heated to 900 °C but was not maintained at this temperature. No spherical grains were seen in the corresponding microstructure. After 1 h at 900 °C, leucite was observed to form, but SiO₂ quartz and muscovite were still present, and spherical grains were still not formed in the microstructure. However, after heating at 900 °C for 2 h, quartz and muscovite had almost disappeared and only leucite was identified by XRD, and the microstructure reveals the formation of spherical grains having a diameter of approximately 30 μm.

3.2. Formation mechanism of leucite crystals

The processes that occur upon firing natural kaolin have been well documented. Upon heating at approximately 550 °C, kaolin loses structural water to form dehydrated amorphous metakaolin. In a ²⁷Al and ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS-NMR) study of the kaolinite–mullite transformation [6], Sanz et al. reported that the tetrahedral sheet of kaolinite begins to break down at
Fig. 4. XRD patterns and SEM micrographs of the samples after heating the mixture of \( \text{Al}_2(\text{SO}_4)_3 \), kaolin and \( \text{K}_2\text{SO}_4 \) (in mass ratios of 3:3:15) at 900 \( ^\circ \text{C} \) for 0–2 h and further treating with hot hydrochloric acid.

approximately 600 \( ^\circ \text{C} \) and continues to break down until reaching 900 \( ^\circ \text{C} \). The formed metakaolin then becomes very active. Madani et al. have also studied zeolite formation from alkali-leached kaolinite using the MAS-NMR technique [7]. They found that the formed metakaolin further decomposes to form \( \gamma-\text{Al}_2\text{O}_3 \) and amorphous \( \text{SiO}_2 \) by increasing the heating temperature to approximately 980 \( ^\circ \text{C} \) [6,8].
Based on these findings, the XRD peaks of SiO$_2$ (quartz) detected in the samples heated for 3 h at 850 °C (Fig. 2) and for 0 h at 900 °C (Fig. 4) should be attributed to the original SiO$_2$ (quartz) present in the as-received kaolin (Fig. 1). As revealed in a previous study [5], SiO$_2$ (either in crystalline or amorphous form) in starting materials accelerates the nucleation of leucite crystals. Therefore, the SiO$_2$ quartz from kaolin should play a similar role in the present experiment. Fig. 5 shows XRD patterns of samples of the powder mixture that were heated to 900 °C and maintained for 0 or 3 h without acid treatment. K$_2$SO$_4$ and K$_3$Al(SO$_4$)$_3$ were detected in both samples. Although the phase diagram of the K$_2$SO$_4$–Al$_2$(SO$_4$)$_3$ system is not available, the low melting point of K$_3$Al(SO$_4$)$_3$ (690 °C) [9] means that a K$_2$SO$_4$–Al$_2$(SO$_4$)$_3$ liquid should form in the sample heated at 900 °C. As a result, the leucite crystals, upon forming via nucleation and subsequent growth, would become spherical so as to decrease the high surface energy (Figs. 3 and 4). The accelerated nucleation (due to the SiO$_2$ quartz) and crystallization (due to the reactive amorphous metakaolin) in this process are believed to be responsible for the decrease in the synthesis temperature from 1000 °C [4,5] to 900 °C (see Section 3.1).

4. Summary

Low-temperature synthesis of leucite crystals using natural kaolin was investigated. After a powder mixture of Al$_2$(SO$_4$)$_3$, kaolin and K$_2$SO$_4$ (in mass ratios of 3:3:15) was heated at 900 °C for 3 h, spherical leucite crystals having a diameter of approximately 50 μm were obtained. SiO$_2$ (quartz), the accessory phase in kaolin, and the amorphous metakaolin formed upon heating kaolin contributed to the decreased synthesis temperature of leucite crystals.

References

Comminution of Asbestos by a Mechanical Grinding and its Sinterability
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When asbestos (chrysotile: Mg₃Si₂O₅(OH)₃) was heated at 600°C for 3 h, dehydration reaction of it had been almost finished, changing to an amorphous phase in crystallography. Then the remaining fiber became brittle, because the structure of fiber could be easily ground till <1 μm diameter in grain size using a mortar. When the compact body made by pressing the ground asbestos fiber at 80 MPa was heated at 1300°C for 1 h, the relative density of the compact reached 90%. Then the crystal phase of the compact was mainly forsterite (Mg₃Si₂O₅), but a small amount of chroenoestatite (Mg₃Si₂O₅) was also detected.

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Key-words: Asbestos, Chrysotile, Heat treatment, Amorphous phase, Mechanical grinding, Sinterability

1. 総 言

アスベストは熱の源に産する繊維状の酸塩鉱物の総称で、主に石棉系およびカクセシ系に分かれる。現在ではカフラン系が熱水変化を受けたときに生成する石棉系鉱物のクリソサイト（Mg₃Si₂O₅(OH)₃）のみが輸入利用されている1)。これに続くクリソサイトを指しアスベストと称していることが多いが、本論ではクリソサイトをアスベストとして扱う。このアスベストは、一般に0.02 μmから0.1 μmの径をもつ繊維状鉱物が束状になった構造をしており、融点が高く（1521°C）、高い抗張力を持ち、軟性があり、加工しやすく、耐熱性、耐熱性に優れ、耐熱性を有するなどの特性を持ち2)。そのため、主にセメントと複合化され、腐朽材や建材などの建築材として1950年ごろから戦後の経済復興に合わせて利用が始まり、特に1960年代の経済成長期に急速にその需要が伸びた。1970年代の最盛期には、年間3500トンもの量が使用された3), 4)。欧米では、早から発がん性などアスベストに起因する健康障害5)が指摘され、使用規制・禁止の措置がとられていた。わが国では1975年に、労働者健康の立場からアスベストの吹き付け工事は原則禁止された。しかしその後もアスベストの使用は続けられ、近年でも年間5〜10万トンの使用量がある。最近になって、大手建材メーカーがアスベストを自主的に使用禁止にと発表し、今後の使用量は大幅に減少するものとみられる。しかししながらアスベストを含んだ建築材の量は累計で数千トンに達し、2010年から2020年までに向けその廃棄のピークを迎えるといわれている。アスベスト含有建築物は現在特定管理物質に指定され、撤去や埋め立て廃棄も厳重な管理下で行われている。

アスベスト含有建築物の無害化、さらにはその有効利用に関する研究は急務であり、現在多くの民間企業や公的研究機関で取り組まれている。溶融する高温まで加熱することによるアスベストの微細変質6)、酸処理によるアスベストの組成変質7)、アルミナ8)、都市のごみ焼却灰9)、アルミニウム製材時の副生精錬灰10)、ケイ酸ソーダやケイ酸カリウム11)など種々の添加物を加えて加熱することで、新たな低融点物質を形成させる無害化など、その多くは特許として公開されているが、いまだ低コストで安全に大量処理できる画期的な処理技術といわれているものはない。

本研究では、基礎的におまっアスベスト単体について着目し、その毒性の主原因と言われる繊維状鉱物12)を機械的に破壊することによって、それを無害化できないか考えてみた。アスベストを単純に加熱しても、その繊維状鉱物は融点近くまで保持される3)。またアスベストは室温では発熱性に優れた材料であるが、加熱による脱水により引張り強さは低下する3)。しかししながらそれ以外においては、アスベストの耐火性と機械的特性変化に関連付ける報告は少ない。そこで、アスベストの加熱に伴う組織変化と機械的強度変化の関連性について検討した。加えて、アスベスト粉塵物の有効利用法を発開する基礎研究として、粉塵末から成形体を作製し、その焼結性について調べた。アスベスト単体は、高温で加熱すると主な結晶相としてはフォースステイト（Mg₃Si₂O₅）となるため13)，高温或は電気鍍銅の原料としての利用も期待される。また、本基礎研究は、アスベストを含む複合建築物廃棄物の無害化において、熱処理と機械的破壊の同時処理が有効である可能性を示唆し、加えてその有効利用法の開発にも新しい方向性を示すものになると考えられる。

2. 実験方法

用いたアスベストはカナダ・ケベック州産クリソサイトで、その化学組成を表1に、走査型電子顕微鏡（SEM）によりその微細組織を観察した結果を図1に示す。主に径0.2 μmの繊維質が束状に集まっているのが観察される。アルミナの他（高さ75 mm、幅60 mm、容積150 cm³）にクリソサイト約3 gを入れ、それを電気炉に入れて加熱した。電気炉の昇温速度は10°C/minとし、550°Cから1000°Cの温度で所定時間加熱した。加熱後、炉の電源を切り、炉は炉内で自然放出させた。加熱処理によるアスベストの組成変化を粉末X線回折（XRD）分析により調べた。

11
アスベストの粉末実験は、未処理及び加熱処理後のアスベストをののの約0.5g秤量し、直径1cmのSiN₄製の乳鉱と乳棒を使って人工によく粉末（すりつぶす磨碎）した。同時作業者により毎秒1回転、そして乳棒と乳鉱の接触には常に2〜3kgの重荷が加わる条件で行った。粉末処理されたアスベストの微細組織をSEMにより観察した。

次に、加熱処理後粉砕したアスベスト粉末の焼結性について検討した。粉末されたアスベスト粉末を20×20mmの正方形型に入れ、80 MPaの一軸加圧成形を行い、得られた粉末成形体を電気炉にて1000℃〜1400℃の所定温度で1h焼成した。昇温速度は10℃/minとし、加熱保持後に炉の電源を切り、試料は炉内で自然冷却させた。得られた試料の大きさ密度及び真密度を含水法及びアルカリメソ法によりそれぞれ測定し、両者から相対密度を算出した。XRD分析により加熱試料の構成結晶相を同定した。比較のために、未加熱処理アスベストを出発原料に用いて同様の成形体を作製し、これも1000℃〜1400℃の温度で焼成した。加熱後の試料の微細組織を観察し、処理後粉砕したアスベスト粉末の焼結性について検討した。

3. 結果と考察
3.1 アスベストの被粉砕性
図2は、アスベストを550℃から1000℃までの各温度で3h

加熱した試料のXRD分析結果を示す。550℃で加熱した試料からは、クリソタイルが同定された。600℃の場合、クリソタイルの回折線はほぼ消滅し、わずかにフォルステライトの回折線が検出されるものの、その回折線強度は低く非晶質に近い状態であるとみられた。700℃から1000℃まで加熱温度が上昇するのに伴い、フォルステライトの回折線強度は大きくなくなる傾向を示したが、それ以外の新たな結晶相は同定されなかった。この加熱に伴う構成結晶相の変化は、以前の報告結果と一致するもの。図3に、550℃、600℃、800℃及び1000℃で3h加熱した各試料を乳鉱で5min粉砕した試料、SEMでそれぞれの微細組織を観察した結果を示す。550℃の場合、纖維が短くなっているものの、纖維状形態は失われていなかった。一方600℃の試料では、纖維状組織は破壊され、ほとんどが1μm以下の微細な粒にまで粉砕されていた。800℃及び1000℃の加熱の場合も600℃での加熱の場合と同様で、いずれも纖維状形態は破壊され、1μm以下の粒にまで粉砕されていた。次に、600℃で3h加熱し、その後乳鉱による粉砕時間を10sから120sまで変えてしたもののが、試料のSEM観察結果を図4に示す。600℃で加熱した試料は短く、10s間の粉末では纖維状組織は残存しているが、20s間の粉砕後には纖維長が20〜30μm以下に破壊さ
Fig. 4. SEM microphotographs of asbestos ground for various seconds using a mortar after heating at 600°C for 3 h.

Fig. 5. XRD patterns of asbestos ground for 5 min using a mortar after heating at 600°C for various hours.

Fig. 6. SEM micrographs of asbestos ground for 5 min using a mortar after heating at 600°C for various hours.

Fig. 7. Relative densities of the compacts made by asbestos with grinding for 5 min after heating 600°C for 3 h and raw asbestos without heat treatment, which were heated at 1000-1400°C for 1 h.

かった。60秒間の粉砕後に生じた繊維状組織はみられなかったが、さらに120秒間の粉砕後の試料では、図3に示した600°Cで5分粉砕した試料とほぼ同程度の1μm以下の微細な粒のみに変化した。本実験条件では、120秒間の粉砕処理で、加熱処理したアスベストの繊維状組織がほとんどの破壊されることが分かった。しかしながら、その後の実験では、十分な破壊を行う目的から、粉砕時間は5分とした。図5及び図6には、600°Cでアスベストを加熱し、その温度での保持時間を別の試料のXRD分析結果、及びそれらの試料をのおのおの5分粉砕処理した後、SEMによりその繊維組織を観察した結果を示す。600°Cまで加熱した保持を行った試料にクリソタイルが検出され、同試料の繊維組織観察からは試料中に繊維状組織が多く残存しており、繊維状組織が破壊されにくいことが分かった。0.5h保持した試料は、クリソタイルの回折強度は小さくなり、またその場合の試料の繊維長は短く切断され、そのほとんどが長さ10μm以下になった。1h保持した試料は、さらにクリソタイルの回折強度は小さくなり、また粉砕により繊維長も数μmとなり、一見して繊維とは判別できないまでの状態になった。2h保持した試料のXRD回折強度は弱く、粒はさらに細かく粉砕されて1μm以下となり、図2、図3に示された600°Cで3h加熱保持した試料のXRD図形及びそれを5分粉砕した試料のSEM観察結果の粒形態とほぼ同じとなった。以上の結果より、アスベストは600°Cで2h加熱された場合に構造水の脱水反応が大分進み、結晶学的に非晶質に近い状態になる。この状態になると繊維状組織は破壊され、粉砕により容易に破壊できるようになる。アスベストのさらなる高温加熱により結晶相としてはフォルステライトが析出することになり、その繊維状組織の粉砕されやすい破壊状態は保持するものとみられる。以後の実験において、アスベストの脱水作用を十分に行う、仮想化させる理由から、600°Cでの保持時間は3hとした。

3.2 焼結体の作製

次に、アスベストを600°Cで3h加熱処理した試料を5min粉砕して得た粉末から成形体を作製し、その焼結状態について調べた。図7は、1000°Cから1400°Cの各温度で1h加熱保持した場合の試料の相対密度変化を示している。比較のために、未処理アスベストから成形体を作製し、それを加熱した場合の相対密度変化を示した。未処理アスベストから成形体を作製した場合には、すべての加熱温度で熱処理粉砕試料成形体から得られた焼き体に比べ、相対密度は低下した。熱処理粉砕試料成形体を1300°Cで加熱した場合、相対密度は90%の最高峰を示した。図8は熱処理・粉砕試料成形体を様々な温度で焼成し得た試料体。及び図9は未処理アスベスト成形体試料
Fig. 8. SEM microphotographs of the fractured surfaces of the compacts made by asbestos with grinding after heating at 600°C for 3 h, which were heated at 1100-1400°C for 1 h.

Fig. 9. SEM microphotographs of the fractured surface of the compact made by raw asbestos after heating 1300°C for 1 h.

Fig. 10. XRD patterns of the compacts made by asbestos with heat treatment and grinding after heating at 1100°C and 1400°C for 1 h.

を1300°Cで焼成して得た試料体の、断破面のSEM観察写真を示す。図9の未処理アスベストを焼成した場合には、加熱中の
脱水反応により試料体内に多孔の気孔を形成すること、及び繊維状の形状を高密度まで保持するため、繊維状粒子間の結晶反応が
進行し難いため相対密度は上がらなかったものと被えられる。
一方、図8中の焼結・粉碎試料成形体を焼成した場合、温度の
上昇とともに気孔は少なくなり、1300°Cで最も気孔は少なく
なかった。しかし1400°Cで焼成した場合には、数μmくらい大き
いものでは数mmに及ぶ結晶状に近い孔が多く観察さ
れるようになり、図7で示されたように相対密度は低下した。
図10には、焼結・粉碎試料成形体を1100°C及び1400°Cで加熱
した場合の、試料の粉末X線回折分析の結果を示す。加熱温
度による違いはみられず、主な結晶相はともにカルノスタナイト
であったが、クリノエンスタナイト（MgO·SiO₂）をわずかか
が検出された。最後に、焼結・粉碎試料成形体を1400°Cで加
熱した場合に気孔を多く形成し、相対密度が低下した理由につ
いて考える。MgO·SiO₂系2成分状態図におけるもので
は1543°C以下の温度では融液化は生成しない。ここで、表1に示
されているアスベストの化学組成において、主成分であるMgO
及びSiO₂以外で、Al₂O₃が存在が示されている。MgO·SiO₂-Al₂O₃系
3成分状態図において、Mixed比によっては1400°C以下の温
度でも融液化の生成が可能である。本試料体も1400°Cでの加熱に
おいて、Al₂O₃が存在するところではMgO·SiO₂-Al₂O₃系融液化が
生成したとみられる。さらにFe₂O₃やCaOの共存が試料体内
での部分的な反応を示している可能性も考えられる。このような
融液化の生成の後、引き続いて蒸気圧下の高い気相圧が生成し、
例えば表1から不純物として脱水存在すると示唆される硫酸塩
の脱水反応によってSO₃(g)が放出され、試料体内に球状に近
い気孔を多く形成することがわかったと考えられる。その結果、
試料体の相対密度は低下した。

4. まとめ
アスベストの繊維形状を消減させる基礎研究を行った。空気中600°Cで3h加熱することにより、ほぼアスベストの構成
の脱水反応が完了し、さらにアスベストは非晶質化する。そ
の非晶質化に伴ってアスベストは機械的に脆くなり、乳鉢によ
る粉碎で容易に繊維状結晶を破壊できるようになり、1μm以
下の微細な粉末にすることが可能である。得られた粉末を80MPa
で一輪加圧して成形体を作製し、1300°Cで1h熟成することで
相対密度90%の焼結体を得ることができ、その場合の主な結
晶相はカルノスタナイトであるが、若干のクリノエンスタナ
イトも含まれる。

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アスベスト含有セメント板中のアスベストの機械的粉砕

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Commination of Asbestos by a Mechanical Grinding in Asbestos-Containing Cement Board

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When 10–20 mass% of asbestos (chrysotile: Mg₃Si₂O₅(OH)₄) containing cement board of 5 mm thickness was heated at 600°C for 2 h, the asbestos lost the crystal structure due to its dehydration reaction in the cement board, changing to an amorphous phase. Further, the heated cement board could be easily ground to grains with several μm size using a mortar. Then the asbestos seemed to be ground to below the size at the same time, because the fiber shape of original asbestos was not found in the sample.

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Key-words: Asbestos, Chrysotile, Mechanical grinding, Heat treatment, Cement board

1. 緒 言

これまでにわが国に輸入されたアスベスト（石綿）の総量は、白石綿（クリソタイル）、青石綿（クロノサイト）、亜石綿（アモサイト）などの種類を区別しないで財務省輸入統計を単純積算した場合、およそ1700トンと推定される。そのうち90%を超える労働者に対する吹き付け板やセメント板などの建築材とし
て使用されてきた。労働安全衛生法関係省令等の改正により1995年に毒性の高い青石綿、亜石綿の使用が禁止とされてから、白石綿（クリソタイル: Mg₃Si₂O₅(OH)₄）のみがカナダから輸入され、2000年で10トン弱、ここ数年で毎年2～3トン、2004年には40トン超の輸入があった。2004年は大手建材メーカーのアスベスト使用禁止の自覚規制により輸入量が大幅に減った。その後労働安全衛生関係省令の一部改正により2004年10月には、アスベストの原則禁止が打ち出された。しか
しそれはこれまでにアスベスト含有量の特に高かった「繊維強化セメント板」や「プレーキパッド」など特定10品目に対し、1mass%以上含有してはならないというもので、それ以外の品目は除外されており、何よりクリソタイルの輸入そのものが禁止
されたわけではなかった。しかしながら今後、厚生労働省の方針による2008年以降は前例アスベスト全面使用禁止
になるものとみられる。

アスベストに関する規制として作業業者保護の立場から、1975
年の労働安全衛生法をもって早咲く「吹き付けアスベスト」の原
則禁止が打ち出された。1987年に、学校教育施設にその「吹
き付けアスベスト」が使われていることが分かり、いわゆる「学校バック」を含め社会問題化したが、その調査と撤
去という行政指導による対応により、アスベスト問題は一旦沈
静化したかにみえた。しかし2009年、肺、心、脳などの
細胞のがんの一種である「悪性中皮腫」の原因として，アスベストの吸
入による1という労災認定問題
が大きく取り上げられ、あたかも「公害」認定を視野に入れな
がら、再び社会の関心がアスベスト問題に向けられるようになった。この飛散性の高い「吹き付けアスベスト」の撤去及び
その処理に関しては、1988年の旧厚生省のガイドラインにより
撤去作業はマニュアル化され、特別管理産業廃棄物として管理
型廃棄物最終処分場で埋め立て処理されている。しかししながら
非飛散性のアスベスト含有セメント板に関しては、撤去の際に
アスベストを飛散させないことや、またその運搬や保管に際
しての保護や表示の義務がある程度である。廃棄物として処理する場
合には、セメントで固定化されており安全であるという理由か
ら、ほとんど一般廃棄物と同扱いとなっている。今後はセメ
ントの風化や破壊によるアスベストの露出や飛散など、アスベ
スト含有セメント板や廃棄物の安全性の問題が指摘さ
れ、管理型の廃棄処分が要求されるものとみられる。

著者らは最近、クリソタイルの呼吸に及ぼす気道経路と粉
砕処理により、健康障害の原因であるクリソタイルの繊維形
状態を、Stanonらの推奨した健康を害する危険サイズ: 長さ8μ
m以上、径0.2μm以下2より小さくできることが見たし報
告した3）。本研究では、実際にセメント板に強化材として加え
られているアスベスト（クリソタイル）が、同様な処理処理と粉
砕により、安全性が大きくまでに確保されるのか、また化学組
成の変化と併せて、それを検証することを目的とした。

2. 実験方法

実験に使用したアスベスト含有セメント板はJIS A5423適合
品で、アスベスト（クリソタイル）含有量は質量比で10～20%、
厚さ5mmの民間家庭の壁面に用いられていたスレートと呼ば
れる製品で、アスベスト製品であることを示す「a」の表示が
ある。以後、アスベストはクリソタイル自身を指す。本論
文中ではクリソタイルと記す。はじめにクリソタイルの微細形
態を知るために図1には代表的なカタナベッケ型産
のクリソタイルの走査型電子顕微鏡（SEM：JSM5200, JEOL
804
製）観察写真。本実験で使用したクリソタイル含有セメント板の観察、及びそのセメント板の破断面におけるSEM観察写真を示す。この写真のようにセメント板の破断面には、クリソタイルの繊維状結晶がむき出しになった状態が多く観察される。セメント板が繊維強化されている様子が伺えるとともに、破断すれば簡単にクリソタイルが露出してしまうことを示している。

そのセメント板から10×10 mm (厚さ 5 mm) の大きさに切り出し、実験に供する試料とした。試料を電気炉に入れ、600°Cの温度で0～3 h 加熱保持した。この600°Cという温度はクリソタイルのみの場合に効果のある温度である III。昇温速度は600°C/h とした。加熱後電源をOFFにして試料は室温まで自然放冷した。加熱後各試料の表面及び内部に分け、X線分析装置（XRD：島津製作所製、XD-D1）で構成結晶相の分析を行った。表面の分析では試料表面にX線を直線入射して回折パターンを測定し、内部の分析では粉末試料した粉末試料に対し回折パターンを測定した。比較のために非加熱処理試料についても表面及び内部についてXRD分析を行った。

粉末処理は、試料を熱処理した後、アルミナ製乳鉢に入れて粉碎した。軽く数秒叩いて粗粉碎し、その後クリソタイルを粉碎処理した場合と同様に、乳鉢と乳鉢には常時2～3 kg の荷重を掛けながら毎秒1～2 回転の速度で2～3 min、セメント成分をも含め粉碎した。粉碎された試料をSEMで観察することにより、その試料内部に繊維状粒子（残存クリソタイル）が存在するかを確認した。

3. 結果と考察

図2には、図1のカナダ産クリソタイル及び本実験で用いたセメント板の熱処理を施していない試料の粉末X線回折結果を示す。結果より、セメント板試料にクリソタイルが含まれていることが確認できた。また結晶相としては他に、SiO₂ (quartz) とCaCO₃ (calcite) が検出され、セメントの水和硬化体としての結晶相は結晶性が低いため回折面積強度が小さく、ほとんど同定できなかった。これはセメント板が長年に中性化（炭酸化）の作用を受けたことによると考えられる III。このクリソタイル結晶の回折線の有無が、化学組成としてクリソタイルの存在の有無の指標として捉えることができる。

図3に、600°Cでの保持時間を変えた試料を、粉碎せずその表面をそのままXRD分析した結果を示す。0 h 保持した場合とは、600°Cに到達後、その温度で保持せずすぐに冷却した試料であるが、その試料表面からはクリソタイルが検出された。一方、保持時間が1 h の試料表面からは、クリソタイルを示す回折線は検出されなかった。図4に、600°Cでの保持時間を変えた試料内部のXRD分析結果を示す。試料内部の場合、図
3の試料表面の場合には検出されなかったが、熟処理を示す回折線は検出された。しかしながら保
持時間が2hになると、クリソタイルを示す回折線は検出されなくなった。この600℃におけるクリソタイルの結晶相の消滅は。
クリソタイルの水素酸化による非晶質化に伴うものであると考えられる3)5)。

図5には、粉砕した非加熱処理試料と600℃で0h、1h及び
2h加熱処理後、その後粉砕処理した試料のSEM観察結果を示す。セメント硬化体（C-S-H）の比重は結晶相の種類によって
も違うが、おおよそ2.2～2.8 g/cm³の範囲にあり3)、これはクリソタイルの比重2.4～2.6 g/cm³7)とはほとんど同じ値である。
しかしクリソタイルは内部構造が中空を呈し3)、また図1(a)の
ように径が0.2～数μmの柔軟性をもった繊維状結晶でそれが束
になった形態をしている。そのため繊維間にはある程度の空間
空気）を含むためにかさ比重は小さくなり、クリソタイルの
実際のセメント板に占める体積割合は、重量に対する割合より
d大きくなることが考えられる。したがって重量で10～20%を
含める場合、クリソタイルが均一に分散していないならば、セメント
板の微細組織のどこを観察してもクリソタイルが発見できる量
であるといえる。実際に観察した図5の非加熱処理の試料の場
合では、多くの繊維状クリソタイル粒子が観察された。保持時
間を0hとした試料からは、ややその量は少なくなっているが
の繊維状の粒子は観察された。1h保持した試料からは、
繊維状の粒子はほとんどみられなくなった。ところどころに写真
のような比較的径の大きい繊維状粒子が観察された。図4の回

![XRD patterns](https://example.com/xrd1.png)

**Fig. 3. XRD patterns of the surfaces of the chrysotile-containing cement board after heating at 600℃ for 0-3 h.**

![XRD patterns](https://example.com/xrd2.png)

**Fig. 4. XRD patterns of the inside of the chrysotile-containing cement board after heating at 600℃ for 0-3 h.**

![SEM micrographs](https://example.com/sem1.png)

**Fig. 5. SEM micrographs of the ground powder of the chrysotile-containing cement board with and without heating at 600℃ for 0–2 h. (Arrow indicates asbestos.)**
折パターンからも、1h保持の条件ではクリソタイルの回折線がわずかに検出されており、この繊維状粒子がクリソタイルであるとみられた。一方、2h保持した試料からは、径の比較的小さなものまで含まれてほとんど繊維状の粒子はみられなくなっ
た。また、図4の回折パターンでも2h保持した条件ではクリ
ソタイルの結晶相は検出されなくなっており、上記の観察結果
と矛盾しない。以上の結果は、クリソタイル単体を対象とした
前報告の結論、すなわち、クリソタイルは600℃、2hの加熱
処理によりほぼ脱水反応が完了し非晶質化すること、及びその
場合に繊維状の形態を呈しているもののその粒子は非常に細
くなり、乳絨粉砕により容易に1μm以下に破壊できる、という
結果と一致する。加えて、クリソタイルがセメントなど他の
成分と共存すると、クリソタイル自身の反応性が活性化し、脱水反
応の促進、反応に伴う形態の消減や、残った針状を有する粒子
の脆化が促進した可能性も考えられる。
以上の結果から、クリソタイルを含有するセメント板を600
℃で2h加熱し、その後粉砕処理することで、内包されたクリ
ソタイルを組織的にも微細的にも破壊できることを明かに
とし、クリソタイルを無害化できる有効な技術となり得ることを
確認した。

4. まとめ
アスベスト単体での繊維状形状を消減させる研究結果を踏ま
え、本研究では、セメント板中に含まれるアスベストの無害化
への応用展開を図った。クリソタイル（白石綿）を質量比で10～20％含有する厚さ5mmのセメント板を600℃で2h加熱保
持することにより、セメント板中に内包された状態でもクリソ
タイルの発生は認められなかった。更にその後セメント成分もろとも粉砕することで、1μm以下という鍈状粒子が確認できない
までにクラソタイルの繊維状の形状は破壊された。

付記 この研国の株式会社技術研究所（山形県東根市）
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AlZrC₂ synthesis


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Abstract

AlZrC₂ was synthesized using a direct solid-state method. Various types of carbon were used as starting materials together with aluminum zirconium carbide powders. The effect of different carbon on the formation of Al–Zr–C compounds formation were investigated. The atomic arrangement of carbon affects the Al–Zr–C compounds formation, i.e., crystalline carbon facilitates Zr₂Al₃C₃ formation while glassy carbon facilitates AlZrC₂ formation. High purity AlZrC₂ was prepared from the appropriate mol ratio of Al/ZrC:glassy carbon by heating in vacuum at 1600 °C for 1 h. However, a little amount of Zr₂Al₃C₃ still formed due to graphitization of glassy carbon at high temperature. Glassy carbon from sugar showed a lower degree of crystallization (graphitization) than glassy carbon from phenolic resin. Finally, the obtained two phase specimen was ground and heat treated again using pulse electric current sintering to produce single AlZrC₂.

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Keywords: D. Carbide; D. Carbon; AlZrC₂; Graphitization

1. Introduction

Carbides are extensively used in various fields due to their excellent properties. For instance, SiC [1] is widely used as an engineering material because of its high-temperature fracture strength and creep resistance. The remarkable thermal stability and chemical inertness of B₄C make it well suited for applications requiring high stiffness or good wear resistance [2]. ZrC is an important structural material owing to its high strength and good corrosion resistance [3].

Several complex carbides have recently been synthesized and studied. For example, AlₓBₓC₇ [4] has remarkable antioxidant properties in carbon-containing refractory materials. Michalenko et al. found the AlZrC₂ phase in 1978 [5], but little has been reported about this material.

Hashimoto et al. [6] produced a composite material of AlZrC₂ and Al, and characterized its mechanical properties. They prepared the AlZrC₂ by heating a mixture of Al and ZrC, followed by leaching with HCl. After synthesizing, however, ZrC still remained in the sample.

We synthesized high purity AlZrC₂ using a direct solid-state method.

2. Experimental procedure

2.1. Starting materials

The starting materials we used were

(1) Al, 99.9% pure; 10-μm mean particle size (High Purity Chemicals Co., Ltd.).
(2) ZrC, 95% pure (High Purity Chemicals Co., Ltd.).
(3) Graphite, 99.7% pure; 5-μm mean particle size (High Purity Chemicals Co., Ltd.).
(4) Amorphous carbon. In this work, we used three kinds of amorphous carbon, i.e.,
(a) Prepared by heating phenolic resin in a muffle furnace at 400 °C for 30 min and grinding it into small pieces, reheating it at 400 °C for 5 min, then grinding it into a fine powder.
(b) Prepared by heating sugar in a porcelain crucible with Bunsen burner for 6 h and grinding it into small pieces, reheating it for 6 h, then grinding it into a fine powder.
(c) Carbon black, as received from industry (specific surface area, 125 m²/g).

2.2. Sample preparation and heating

The starting materials were mixed in acetone at various mol ratios as shown in Tables 1 and 2 and Fig. 1. The mixtures were pressed into pellets of ~1.8 g, CIPed at 100 MPa, and heated under two different conditions:

- Ar atmosphere: The samples were placed in a refractory block lined with carbon paper and covered with powder having the same composition to prevent surface oxidation [6]. They were heated from room temperature to 1600 °C for 1 h at a heating rate 10 °C/min.
- Vacuum: The samples were prefired in Ar atmosphere as described above at 900 °C for 1 h to prevent Al vapor from attacking the carbon lining of the vacuum chamber. After prefiring, the covered powder was removed. The samples were wrapped in carbon paper and placed in a carbon crucible before heating in vacuum at a heating rate 10 °C/min from room temperature to the maximum temperature for 1 h.

2.3. Characterization

Samples were crushed and ground into fine powder. Phase change was characterized by XRD (Shimadzu XD-XI). Thermal analysis was carried out by DTA/TG (Rikaku Thermoloop TG8120) from room temperature to 1200 °C in air to check the exothermic reaction of the residual ZrC around 500–600 °C [7]. After synthesis, fresh crack samples were investigated by SEM (JEOL JSM-6360LV).

3. Results and discussion

3.1. Effect of composition on phase formation

Al-ZrC–graphite mixtures with various mol ratios were heated in Ar atmosphere. Phases formed within the Al-ZrC–graphite pellets after firing at 1600 °C for 1 h are shown in Fig. 2. Phase formation depends on the ratio of the starting materials. Fig. 2a shows the phase formation for an Al:ZrC mol ratio of 1 at varying amounts of graphite. Fig. 2b shows phase formation for an Al:graphite mol ratio of 1 at varying amounts of ZrC. In the middle zone of the composition diagram (Fig. 1), Zr₂Al₅C₃ formed after firing. This formation did not depend on the Al:ZrC:graphite ratio, as shown by the XRD patterns of the compositions A, B and E in Fig. 2a and b. The phase formation after firing was completely different away from this middle zone, i.e., closer to the edges of the composition diagram. At a constant mol ratio of Al to ZrC with lower graphite content (compositions C and D in Fig. 2a), no Zr₂Al₅C₃ was found. At a constant mol ratio of Al to graphite with lower ZrC content (compositions F and G in Fig. 2b), no AlZrC₂ was found.
Fig. 2. Phase formation of Al–ZrC and graphite mixtures at various mol ratio after firing at 1600 °C in Ar for 1 h: (a) Al:ZrC = 1; (b) Al:ZrC = 1. (▼) ZrC; (●) graphite; (+) Al2C3.

After firing, from Fig. 2, we concluded that the Al2ZrC3 should be prepared from Al–ZrC–graphite mixture with very low graphite content, however, a very high residual ZrC still remained.

Although the diagram in Fig. 1 is similar to a phase diagram, and the composition axes have to be represented as elements (see Table 1), the carbon from graphite and from ZrC affects Al–ZrC compound formation differently. Graphite is a carbon compound with hcp structure [8], while carbon in ZrC is in octahedral interstices of Zr close-packed layer [9,10]. Hence, the reaction mechanism of carbon in graphite and the reaction mechanism of carbon in ZrC differ due to differences in the number and type of neighboring atoms or co-ordination number (C.N.). Schuster and Nowotny [5] presented the atomic arrangement of Al2ZrC3 and Zr2Al1C3. The interstitial carbon in both complex carbides shows some relation to the interstitial carbon in ZrC structure. Thus, we describe the mol ratio of the mixtures in terms of the starting compounds, rather than elemental components.

3.2. Effects of carbon phase

We prepared Al–ZrC–C mixtures with compositions A (molar composition equivalent to Al2ZrC3) and N (molar composition equivalent to Zr2Al1C3) with two types of carbon, i.e., graphite and amorphous carbon from phenolic resin, and heated in vacuum at various temperatures for 1 h.

The phase evolutions of the compositions A and N after heating are shown in Fig. 3, where A1, N1 and A2, N2 denote compositions with graphite and amorphous carbon, respectively. The results of thermal analysis of samples, which represent the residual ZrC in samples after firing as exothermic peak [7], are shown in Fig. 4. Based on the discussion in Section 3.1, composition N was expected to yield Zr2Al1C3 after heating regardless of the carbon type.

Fig. 3. Phase evolution of Al–ZrC–C mixtures containing different types of carbon upon firing at 1500–1700 °C in vacuum for 1 h; Al, composition A with graphite; A2, composition A with amorphous carbon; N1, composition N with graphite; N2, composition N with amorphous carbon. (▼) ZrC; (●) graphite; (♀) Zr2Al1C3; (+) Al2ZrC3; (?) unknown.
because this composition lies on the composition line of A–E–F–G (Fig. 1). Fig. 3a and b indicate that Zr2Al3C5 formed in the graphite-containing compositions A1 and N1, and AlZrC2 formed in the amorphous carbon-containing compositions A2 and N2. The amounts of Zr2Al3C5 and AlZrC2 were higher (Fig. 3) while the amount of ZrC decreased as firing temperature increased (Fig. 4). From Fig. 3, it is obvious that the formation of Zr2Al3C5 and AlZrC2 depends on the type of carbon in the composition, not the molar ratio of the starting materials. In other words, the atomic arrangement of carbon in graphite crystal facilitates Zr2Al3C5 formation, while the atomic arrangement of amorphous carbon from phenolic resin facilitates AlZrC2 formation.

AlZrC2 in the graphite-containing mixture and Zr2Al3C5 in the amorphous carbon-containing mixture heated at 1700 °C presumably came from evaporation during heating because there was weight loss in the samples after heating, and the losses increased as the heating temperature was increased.

Fig. 4b shows that there was no exothermic peak from the ZrC in composition N with both types of carbon after firing at 1600 °C. This means the phase of carbon does not affect the overall reaction between ZrC and other starting materials.

Although the firing atmosphere described in Section 3.1 and here differed, our previous study [7] and the results from studies of other compositions (not shown here) confirm that firing in Ar or in vacuum yields Zr2Al3C5 in case of graphite-containing mixtures, and AlZrC2 in case of (phenolic resin-derived) amorphous carbon-containing mixtures. The effects of the firing atmosphere (Ar versus vacuum) were discussed elsewhere [7].

Fig. 3 reveals an interesting fact about Al–Zr–C compound formation. Hashimoto et al. discussed the formation of AlZrC2 in an Al–Zr–C–C mixture with a high Al content [6]. After heating, the excess Al–Zr alloy was leached out by HCl. However, as shown in Fig. 3, no Al–Zr alloy was found in samples heated at 1500 °C or above. At 1600 °C, the amount of Al–Zr–C compound still increased. This indicates that there was an Al-containing intermediate phase reacted with ZrC and free carbon to form Al–Zr–C compound, however, this intermediate phase could not be detected. Though we fired the samples at 1600 °C for various short intervals, no Al-containing phase could be detected by XRD. It may be that this Al-containing phase exists only at high temperature. Due to the condition of the vacuum graphite arc furnace, it is impossible to remove the samples from the chamber during the hot stage to characterize this intermediate phase. Our previous study [7] on Zr2Al3C5 formation from Al–Zr–C–C mixture with a high Al content also confirmed that Al–Zr alloy formed upon firing up to 1400 °C. Thus, the reaction path of Al–Zr–C formation in this present study differs from that in Hashimoto’s Al-rich system.

3.3. Amorphism of amorphous carbon

The phenolic resin we used as an amorphous carbon source is widely used as binder in refractory industries [11]. However, carbon obtained from heating phenolic resin is too stiff for grinding. Thus, we used another kind of amorphous carbon, namely carbon black, because it is commercially available as powder. XRD patterns of carbon black, graphite and amorphous carbon from phenolic resin are compared in Fig. 5. Al–Zr–C–C mixtures of composition P (see Table 2) with amorphous carbon from phenolic resin and carbon black were fired in vacuum at 1600 °C for 1 h.

The resultant phases are shown in Fig. 6. The mixture with carbon from phenolic resin gave AlZrC2 as a main
amorphous. By contrast, under high TEM resolution [14],
carbon black showed very small primary particles
surrounded by concentrically deposited carbon layers.
The layers were nearly parallel to each other. But the
relative position of these layers was random, so that there
was no order as in the c direction of graphite. Therefore,
the carbon atoms arrangement in a carbon black primary particle
is non-well crystalline at the surface with an increasing order
at the core of the primary particle. For most carbon blacks,
these “crystalline” regions are 1.5–2.0 nm in length and
1.2–1.5 nm in height, corresponding to four to five layers.
With such small size of “crystalline” regions, carbon black
showed “amorphous” XRD pattern since the wavelength
of X-ray (Cu Kα, 1.54056 nm) is similar to the “crystalline
size” of carbon black.

Based on the results presented in Section 3.2, carbon
black in the Al–ZrC–C mixture gave a mixed product of
AlZrC3 and Zr2Al1C5 because of its mixed characteristic of
high reactivity from the non-well crystalline surface and
“crystalline” regions within carbon black primary particles.

As mentioned above, the diagram in Fig. 1 is related to
phase diagram. However, the results presented in Section 3.2
differ from those presented in Section 3.1. The Al–Zr–
graphite mixture gave the AlZrC3 phase when the main
carbon source was ZrC. This means the parent structure of
carbon affect the formation of the Al–Zr–C compound.
Nowotny et al. compared the crystal structure of Al–Zr–C
complex carbides with those of other complex carbides [15].
They found that the degree of filling of the voids by carbon
atoms is higher in Al–Zr–C complex carbides than in other
complex carbides. Though the mechanism of void filling
by carbon atoms in Zr2Al1C5 and AlZrC3 was not mentioned,
the difference in atomic size between Zr and Al affects this
mechanism. Carbon atoms in graphite and glassy carbon are
different in many ways, e.g., C.N., bond type between the
atom, and thermodynamic state. These factors affect the
mechanism of reaction between the Al-containing inter-
mediate phase, ZrC and carbon. The above results suggest
that the mechanism of void filling by glassy carbon atoms
may be similar to that of the interstitial carbon in ZrC. Thus,
at the same Al–ZrC–C composition, the glassy carbon-
containing mixture yielded a different Al–Zr–C phase from
the graphite-containing composition.

3.4. Composition line

We fired various compositions of Al–ZrC–amorphous
carbon in vacuum at 1600 °C for 1 h to find the zone in the
composition diagram yielding the lowest amount of
Zr2Al1C5 and ZrC. Phase analyses of a number of compositions
after firing are represented as composition line
in Figs. 7 and 8; the two figures show the XRD patterns of
Because the ZrC and Zr2Al1C5 peaks in the XRD
patterns overlap (at 2θ ≈ 33°), we conducted thermal
analysis of all samples in Figs. 7 and 8 to detect the
residual ZrC after firing (DTA diagrams of compositions not presented here). The compositions in Fig. 7 gave AlZrC₂ as the main product upon firing, with a small amount of Zr₂Al₃C₅ and trace amounts of ZrC. The compositions in Fig. 8, slightly richer in Al than those in Fig. 7, gave AlZrC₂ as the main product with a small amount of Zr₂Al₃C₅. These results indicate that during the AlZrC₂ formation, another phase of Al–Zr–C phase (Zr₂Al₃C₅) started to form although there was some ZrC left in the system.

3.5. Effect of excess aluminum

Schuster and Nowotny [5] studied Al–Zr–C phase diagram at 700 °C and 1000 °C and found that ZrC is very stable and still existed after very long annealing time (longer than 100 h). Gesing and Jeitschko [16] prepared Zr₂Al₃C₅ by melting the mixture of ZrC and Al at very high weight ratio of Al (1:5) under Ar for 2 days at 1500 °C to make sure that ZrC was completely reacted with Al and no ZrC was found. The phases of product after melting were ZrAl₃ and Zr₂Al₃C₅. It is believed that ZrC is very stable and need excessive amount of Al as flux. It is known that ZrC starts to oxidize even at low temperature (300 °C) under low oxygen partial pressure [3]. But no research had studied about the effect of oxygen amount on Al–Zr–C compound formation.

From our previous work, we proved that the significant amount of oxygen in Ar dissolved in ZrC and formed Zr–C–O solid solution which is stable and do not react with other starting materials. The Al–ZrC–graphite mixture of same composition after heating at 1600 °C for 1 h in vacuum and in Ar showed different XRD pattern and no ZrC phase was found in sample heated in vacuum. Therefore, the very excessive amount of Al is needed when the Al–Zr–C–C mixture is heated in Ar to form Al melt and cover ZrC grains to protect them from oxidation. However, Al evaporation occurred during heating in vacuum. The excess Al is necessary for Al–Zr–C compound formation, but at much less amount than heating in Ar.

From Section 3.2, the temperature which is suitable for Al–Zr–C compounds formation is 1600 °C. Aluminum has the lowest melting point (660 °C) in the Al–Zr–C system. Excess Al in the mixture may reduce the reaction
temperature so that ZrC might be completely consumed in the reaction. The excess-A1 composition (composition O) with amorphous carbon from phenolic resin was fired in vacuum at 1300–1600 °C to determine the effect of excess A1 on reaction temperature.

As shown in Fig. 9, although the main phase after firing was AlZrC2, A1-Zr alloy was found after firing at 1300 °C. Residual ZrC was found after firing up to 1500 °C, and Zr2Al1C3 was found from 1500 °C. Moreover, fracture surface of samples fired at 1500 °C revealed an inhomogeneous color pattern inside the sample, suggesting that the reaction between the starting materials was incomplete. Thus, excess A1 in the Al–ZrC–C mixture facilitates Zr2Al1C3 formation at lower temperatures. These results indicate that the optimal temperature for a complete reaction of the mixture (i.e., in which ZrC is completely reacted) is 1600 °C.

3.6. Graphitization

Composition Q, which lies between composition lines H–E—I–J–K and L–M–N–O, was selected because it gave only trace amounts of residual ZrC and lowest amount of Zr2Al1C3 after firing at 1600 °C for 1 h in vacuum. Mixtures of composition Q with amorphous carbon from phenolic resin and from sugar were fired in vacuum at 1600 °C for 1 h. As shown in Fig. 10, the sample with amorphous carbon from sugar gave AlZrC2 with a least amount of Zr2Al1C3. The fracture surface of Al–ZrC–amorphous carbon from sugar with composition Q heated in vacuum at 1600 °C for 1 h (Fig. 11), exhibited hexagonal platelets of AlZrC2. The true density of powder obtained from this sample using kerosene as medium is 4.91 g/cm³.

The results presented in Section 3.2 indicate that the phase formation of AlZrC2 and Zr2Al1C3 formed in the sample after firing depends on the carbon phase in the starting material. Glassy carbon can transform to a crystalline phase (graphite) at high temperature, so-called graphitization [17]. Graphitization of glassy carbon has been performed at high temperatures and high pressure [18], but the graphitization of glassy carbon in vacuum remains unproven. Thus, we performed a small test to confirm the graphitization of glassy carbons as starting materials. Glassy carbon powder from phenolic resin and glassy carbon powder from sugar were wrapped with clean carbon paper and fired in vacuum at 1600 °C for 1 h, i.e., under the same firing conditions used for our samples.

As evidenced by the high-intense peak in Fig. 12, graphitization occurred in amorphous carbon from phenolic resin while amorphous carbon from sugar showed a lower degree of graphitization. Thus, a small amount of Zr2Al1C3 formed spontaneously, and a sample with amorphous carbon from sugar yielded AlZrC2 with less Zr2Al1C3 compared with the sample with amorphous carbon from phenolic resin. In general, graphitization is an important step in the manufacture of carbon/carbon composite [17,19]. At this stage, carbon/carbon composites are heated up and disordered carbon transforms into well-ordered graphite structure. Although we prepared amorphous carbon from phenolic resin and sugar by heating in oxidizing atmosphere, a certain amount of organic functional group presumably remained as significant (ppm-level) impurities. Phenolic resin is viscous, high-molecular-weight hydrocarbon. There might be some functional groups left in amorphous carbon after heating phenolic resin at higher amount than heating sugar, which is lower molecular weight. There is a similar phase transformation in the silica glass, i.e., devitrification [20]. The significant amount of impurities in the glassy phase behaves as a mineralizer and initiate crystallization. Thus,
the graphitization of glassy carbon observed in this study resembles the devitrification in silica glass.

There are some foreign peaks in the XRD patterns of both amorphous carbon powders; they correspond to Al$_4$C$_3$. Although the amorphous carbon powders were wrapped with carbon paper, the samples still had to be placed in a small carbon crucible before being loaded into the carbon crucible of the vacuum furnace. Since all of the firing tests were done in the same crucible, Al$_4$C$_3$ from the reaction between Al vapor and the crucible may have accumulated on the inner surface of the crucible. Under vacuum, Al$_4$C$_3$ evaporated from the crucible surface at high temperature and diffused through the slit in the wrapping. Some of our results (not presented here) indicated that Al$_4$C$_3$ has some relation to AlZrC$_2$ and Zr$_2$Al$_4$C$_5$ formation. Therefore, Al$_4$C$_3$ as impurity during firing the samples does not have negative effect on Al–Zr–C compound formation.

Studies on graphitization of glassy carbon have generally been conducted without presence of other additives. In this work, however, there were other starting materials (Al and ZrC). Therefore, the graphitization of the amorphous carbon in our samples during heating was presumably stronger than graphitization of pure amorphous carbon powder because the other starting materials acted as mineralizer, reducing the graphitization temperature of the amorphous carbon, and hence, accelerating the graphitization process.

3.7. Effect of pressure

We incidentally found that high purity AlZrC$_2$ from composition Q (with amorphous carbon from sugar as source of carbon) shows only AlZrC$_2$ phase after a 5-min reheat under pressure with electric current by PECS [21]. Therefore, we prepared the mixture of composition Q from Al, ZrC and amorphous carbon from sugar, and heated it at 1600 °C in vacuum for 1 h. Subsequently, we ground it into a fine powder, heated it in PECS under high pressure (40 MPa) in vacuum from room temperature to 1700 °C, and then suddenly stopped. No Zr$_2$Al$_4$C$_5$ phase was found, as shown in Fig. 13. The pressure during sintering under PECS may suppress the formation of the Zr$_2$Al$_4$C$_5$ phase and rearrange the atomic packing. The effect of pressure on Zr$_2$Al$_4$C$_5$ after sintering by PECS [22] also showed the same phenomena.

4. Conclusions

1. The atomic arrangement of carbon in the starting materials affects the Al–Zr–C compound formation.
2. Excess Al does not accelerate the reaction between ZrC and other starting materials.
3. Graphitization of glassy carbon occurs spontaneously as it reacts with the other starting materials at high temperature and affects the Al–Zr–C compound formation.
4. AlZrC$_2$ can be prepared from a mixture of Al, ZrC, and amorphous carbon from sugar at a mol ratio of 21:14:15 by firing the mixture in vacuum at 1600 °C for 1 h and grinding the product into a fine powder, then reheating this powder up to 1700 °C under high pressure and applied electric current.
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References


Sintering and Characterization of Zr₂Al₃C₅ Monolith

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Keywords: Zr₂Al₃C₅, Pulse Electric Current Sintering (PECS), Complex carbide, Mechanical properties, Oxidation resistance, Hydration resistance

Abstract Zr₂Al₃C₅ has been successfully synthesized via solid state reaction between Al, ZrC and carbon powder at 1600°C in vacuum. This complex carbide has very strong bond between metal atoms and carbon atoms. Thus, this material has a potential to be utilized as structural materials. Some properties of Zr₂Al₃C₅ powder from solid-state reaction in vacuum had been tested. It was found that this powder was completely oxidized in air at 900°C 1 h, and can be hydrated in moist air. These drawbacks might come from the high reactivity of the powder due to synthesis in vacuum. Zr₂Al₃C₅ powder from solid state reaction in vacuum was sintered at various temperatures from 1500°C to 2000°C under vacuum with pulse electric current sintering (PECS) and pressureless sintering. Zr₂Al₃C₅ started to sinter at 1500°C and got partially dense from 1700°C. Physical properties and mechanical properties of this material were investigated and discussed.

Introduction

Many research works have been studied on properties of carbides and complex carbides. But no research on properties of Zr₂Al₃C₅ though this phase was found in 1980 [1]. Schuster and Nowotny found that this phase was always coexist with ZrC. This phase was successfully synthesized as single phase by Leela-adisorn and Yamaguchi [2]. The purpose of this work is to sinter and characterize the properties of this complex carbides.

Experimental procedure

The starting material of Al, ZrC, and graphite powders were mixed throughly at mol ratio 3:1:1. Then the mixture was pressed and sintered at 100 MPa as pellet before heating at 1600°C in vacuum for 1 h [2]. After heating, the pellet was ground to fine powder. About 3 g of powder was sintered in vacuum without pressure and with pressure (PECS) under various times and temperatures. After sintering, the samples were characterized by XRD. The density of samples was tested by Archimedes' method in kerosene. The mechanical properties, i.e., fracture strength and Vickers’ hardness were tested. The fracture surface of samples were observed by SEM. The oxidation test was done by heating small pieces of samples from room temperature to 1200°C in air. The hydration resistance was estimated by measuring the weight gain of the samples in a humid chamber at 70°C, 90 R.H.
Results and discussion
The phase change of samples after sintering at various conditions was shown in Figs. 1 and 2. The samples sintered in vacuum without pressure were gradually changed from Zr$_2$Al$_2$C$_7$ to ZrC at longer soaking time or higher sintering temperature due to loss of some components during sintering. Though the samples sintered with PECS did not show phase change but their XRD patterns reached to ideal XRD pattern calculated by Schuster and Nowotny (JCPDS No. 41-0814). Since the pressure of synthesis was not specified by Schuster and Nowotny, we assume that these work was done at normal atmosphere. Zr$_2$Al$_2$C$_7$ in this work was prepared in vacuum. Therefore, our starting material is a defect structure of Zr$_2$Al$_2$C$_7$ occurred at vacuum. The structure of carbide get closed to the ideal structure under high pressure from PECS.

![Fig. 1 Phase change of Zr$_2$Al$_2$C$_7$ after sinter by pressureless sintering in vacuum at different time and temperature.](image1)

![Fig. 2 XRD patterns of Zr$_2$Al$_2$C$_7$ after sinter at 1800℃ under different pressures compared with starting material](image2)

The density of samples after sintering at the same temperature and the same soaking time under different pressures as shown in Table 1 confirmed our assumption, i.e., the density of this carbide increased as the pressure of sintering increased.

Table 1 Density of Zr$_2$Al$_2$C$_7$ before and after sinter at 1800℃ for 5 min under various conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T. D. (JCPDS No. 41-0814)</td>
<td>4.983</td>
</tr>
<tr>
<td>Zr$_2$Al$_2$C$_7$ powder (as prepared)</td>
<td>4.49</td>
</tr>
<tr>
<td>Pressureless sintering in vacuum</td>
<td>2.42</td>
</tr>
<tr>
<td>20 MPa in vacuum (PECS)</td>
<td>3.92</td>
</tr>
<tr>
<td>40 MPa in vacuum (PECS)</td>
<td>4.45</td>
</tr>
</tbody>
</table>

The effects of sintering parameters on density of Zr$_2$Al$_2$C$_7$ monolith are shown in Fig. 3. This carbide can be sintered as dense monolith from 1800℃ under 20 MPa for 20 min and 40 MPa for 5 min. At 2000℃, the pressure and the soaking time had no effect on the density of monolith.

![Fig. 3 Relationship between density and sintering conditions.](image3)
Fracture strength and Vickers hardness of Zr₂Al₃C₅ monolith sintered by PECS under various parameters are illustrated in Figs. 4 and 5. At 1700°C for all parameters, the monolith showed very poor strength and hardness. The fracture strength and hardness were improved by sintering at higher temperature and higher pressure. This can be seen from monolith sintered at 1800°C at various sintering condition. At 2000°C the fracture strength and hardness of monolith under different sintering time and pressure are similar. The mechanical properties and density of monolith were compared in Table 2.

Table 2 Several properties of samples after sinter by PECS method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density g/cm³</th>
<th>Elastic Modulus GPa</th>
<th>Shear Modulus GPa</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700°C 40M5m</td>
<td>3.969</td>
<td>234.0</td>
<td>98.1</td>
<td>0.191</td>
</tr>
<tr>
<td>1800°C 40M5m</td>
<td>4.390</td>
<td>340.4</td>
<td>142.1</td>
<td>0.198</td>
</tr>
<tr>
<td>1900°C 40M5m</td>
<td>4.558</td>
<td>361.8</td>
<td>150.9</td>
<td>0.199</td>
</tr>
<tr>
<td>2000°C 40M5m</td>
<td>4.580</td>
<td>368.1</td>
<td>157.9</td>
<td>0.165</td>
</tr>
</tbody>
</table>

Fig. 6 Weight gain from oxidation of Zr₂Al₃C₅ after sintering at various temperatures by PECS under 20 MPa for 5 min.

Fig. 7 Weight change from hydration of Zr₂Al₃C₅ sintered at various temperatures by PECS under 20 MPa for 5 min.
The oxidation resistance of $\text{Zr}_2\text{Al}_3\text{C}_3$ monoliths was tested under DTA/TG (Fig. 6). The weight gain of monoliths after oxidation was compared and illustrated in Fig. 6. $\text{Zr}_2\text{Al}_3\text{C}_3$ after sintering by PECS at 1700°C and 1800°C under 20 MPa for 5 min show very poor oxidation resistance. The oxidation resistance of this carbide get improved by sinter at higher temperature. The small weight loss of samples sintered at 1700°C and 1800°C at the beginning of oxidation is due to the loss of moisture at the sample surface. The surface of sample is very easy to hydrated with moisture at ambient temperature. The result from hydration test in Fig.7 confirms this effect and shows the relation between oxidation resistance and hydration resistance of $\text{Zr}_2\text{Al}_3\text{C}_3$ monolith.

![Fig. 8 Microstructure of $\text{Zr}_2\text{Al}_3\text{C}_3$ monolith sintered at various temperatures by PECS under 20 MPa for 5 min; a) 1700°C, b) 1800°C, c) 1900°C, and d) 2000°C](image)

The microstructures of $\text{Zr}_2\text{Al}_3\text{C}_3$ monoliths shown in Fig. 8 indicate the porous structure of samples sinter at 1700°C and 1800°C as well as the dense structure of samples sintered at 1900°C and 2000°C, which confirmed the relation with other properties of monolith and sintering condition.

**Summary**
The sintering condition had effects on the properties of $\text{Zr}_2\text{Al}_3\text{C}_3$ monolith. The dense $\text{Zr}_2\text{Al}_3\text{C}_3$ monolith with good mechanical properties and better oxidation resistance as well as good hydration resistance were prepared by sintering at 2000°C under 20 MPa and 40 MPa.

**Acknowledgement**
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**References**
リン酸塩結合材を用いたパッチング耐火物の
作業性（可塑性）の低下機構

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Hardening Mechanism of Refractory Patching Materials with Phosphate Binder

by

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Tetsuhiro HAYASHI**** and Akira YAMAGUCHI*****

The hardening mechanism of refractory patching materials with a phosphate binder was investigated by means of $^{31}$P static and magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. Ten refractory patching materials were made of refractory powders of SiO$_2$ and fused alumina and five mixed solutions of phosphoric acid and aluminum biphosphate as phosphate binders. $^{31}$P static and MAS NMR spectra were measured of five phosphate binders and twenty soft and hard refractory patching materials, respectively, to reveal the local structure around P atoms. The $^{31}$P static and MAS NMR spectra revealed that PO$_4$ tetrahedra in the phosphate binders have no P–O–P linkage between PO$_4$ tetrahedra and that as the patching materials become hard, the ratio of PO$_4$ tetrahedra with bridging oxygens increases, respectively. This result suggests that the hardening of the patching materials is caused by the condensation of the phosphate binder. But the ratio of PO$_4$ tetrahedra with bridging oxygens was not enough to form the network by P–O–P linkage between PO$_4$ tetrahedra. On the basis of these results, the hardening mechanism of refractory patching materials with a phosphate binder is proposed.

Key words: Refractory patching material, Phosphate binder, SiO$_2$, Fused alumina, $^{31}$P MAS NMR spectroscopy, Local structure, Hardening mechanism

1 統 言

大量生産、大量消費、大量廃棄の仕組みの中で、狭い国土での高効率な土地活用および、最終処分場の延命化が求められている日本にとって、一般廃棄物の社会的コンセプトをもとにする処理方法は「焼却し、埋め立てる」という方法である。日本の一般廃棄物の量は、年間約500万トンであり、そのうち80％を焼却に頼っている。焼却処理に使用される焼却炉の材料としては大きく分け、耐火レンガなどの定形耐火物と、キャスタブル材、プラスチック材などの不定形耐火物の二種類がある。不定形耐火物は「粒状または薄板状の耐火物」としSDSで定義されており、耐熱構造物（耐火物の亀裂や割れに関する損傷への耐性）、気密性、低伝導性、吸湿性、不燃性、耐摩耗性、耐食性などの性能が求められている。しかし製造後、密封保存しても時間が経過するにつれて作業性（可塑性）の低下により硬化する性質がある。硬化速度が比較的速いため長期間の保存には耐えられないのが現状である。硬化速度が非常に悪いとみなされ、製造段階より数倍低くなり使用困難になる場合がある。従って、硬化速度を今まで以上に抑制することにより長期保存を可能にするような硬化速度の制御技術の確立が現在必要とされている。そこで本研究では硬化速度の制御の前段階としてまずリン酸塩結合材を用いたパッチング材中のリン原子の
3 結果と考察

3・1 リン酸（H₃PO₄）および重リン酸アルミニウム（Al₄(H₃PO₄)₃）中のリン原子の基本構造

リン酸および重リン酸アルミニウム中のリン原子は酸素四面体である。P₀四面体から成っている。一般的に P₀四面体の基本構造は架橋酸素の数によって分類し、架橋酸素数 n の基本構造を Qₙ と表記する。リン酸中の P₀四面体は、リン原子と結合した 4 つの酸素のうち 3 つが三重結合酸素で残り 1 つが一重結合酸素で、さらに水素を結合した Oₕ=P₀(=O)ₕ という構造をとおり、この四面体は脱水結合により P₀−P₀−P₀−結合の形成が可能である。従って、リン酸中の P₀四面体の基本構造は架橋酸素の数によって、Q₄、Q₃、Q₂、Q₁ の 4 種類に分類できる。Fig. 1 (a) にその基本構造 Q₄−Q₁ を示す。図中の BO は 2 個のリン原子と結合し P₀−P₀−P₀−結合を作る架橋酸素である。これ他、NBO は 1 個のリン原子とのみ結合し P₀−P₀−P₀−結合を作る非架橋酸素を示している。DBO は二重結合酸素である。P₀四面体によるネットワーク形成が可能な構造は、架橋酸素数の多い Q₄、Q₃ である。

重リン酸アルミニウム結晶は P₀四面体と Al₂O₃ 八面体が交互に頂点共有で結晶化することで直鎖を形成し、その直鎖間は P−O−H 基間の水素結合で互いに結合した構造をとる。この構造は非常に安定性が強い。大気中では普通の水を含んだ形で存在する。従って、重リン酸アルミニウム中の P₀四面体は、P₀四面体の 4 個の酸素のうち 2 個が別の Al₂O₃ 八面体と頂点共有して鎖を作るのによると考えられる（Fig. 1 (b)）。よって、脱水結合により P₀−P₀−P₀−結合形成可能な酸素は 2 個である。また、この P₀四面体はリン酸の場合は異なり三重結合がないので、リン酸の P₀四面体とは異なる結合状態をしてくると考えられる。そこで、リン酸の P₀四面体とは異なることを示すために、重リン酸アルミニウム中の P₀四面体の基本構造を Q₄' と表記した。従って、重リン酸アルミニウム中の P₀四面体の基本構造は架橋酸素数によって Q₄'、Q₃'、Q₂' の 3 種類に分類できる。Fig. 1 (b) にその基本構造 Q₄−Q₁ を示す。重リン酸アルミニウムの場合、元々 P₀四面体と Al₂O₃ 八面体から成る直鎖にによるネットワークがすでに形成されているが、架橋酸素数が増大するにつれてより複雑な絡み合ったネットワーク形成が可能となる。

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Basic structures of P₀ tetrahedra in phosphoric acid (H₃PO₄) (a) and aluminum biphosphate (Al₂(H₃PO₄)₃) (b).}
\end{figure}
3・2 $^{31}$P NMRにおけるPO₄四面体の基本構造と等方性化学シフトとの関係

Table 1にPO₄四面体の基本構造と等方性化学シフトδ(ppm)との関係を示す。Q₀(n=0~3), Q₁'(n=0~2)のいずれも架橋酸素数が増加するにつれて、等方性化学シフト値は小さくなっている。Q₀(n=0~3) およびQ₁' とQ₈'の等方性化学シフト範囲についてはすでに明らかにされているが、Q₈'の範囲については未だ明らかにされていない。しかし上記述べたように、架橋酸素数の増加と等方性化学シフト値が小さくなる傾向があるので、Q₀'の範囲はQ₀'とQ₂'の間にくるものと考えられる。従って、Q₀の範囲を-15~30ppmと考えて考察を行った。この関係に基づいて、本研究で測定した試料の$^{31}$P NMRスペクトルピックの帰属を行った。

3・3 バインダー溶液の$^{31}$P静止NMRスペクトル

Fig.2は、5種類のバインダー溶液の$^{31}$P静止NMRスペクトルを示している。同図の数値は等方性化学シフト値を示している。一番上のスペクトルがリン酸75%水溶液のものであり、下にいくにつれて重リン酸アルミニウム50%水溶液の割合が増加し、一番下が重リン酸アルミニウム50%水溶液のみのスペクトルである。いずれもシャープなピークが得られており、重リン酸アルミニウム50%水溶液の割合が増大するにつれて、ピークが高緯度側（右側）にシフトしていることが分かる。リン酸、重リン酸アルミニウム水溶液の等方性化学シフト値は0.1, -7.8ppmであり、これらはそれぞれO=P(O-H)₃, (Al-O)₂P(O-H)₂構造をとっているので、それぞれQ₀, Q₂構造に帰属できる。

混合溶液のピークはリン酸、重リン酸アルミニウム溶の間に出現している。これに、バインダー溶液等の混合だけではリン酸塩溶中的脱水縮合は起こらないことを示している。ピークの横幅は十分狭いので、混合溶液のピークはリン酸、重リン酸アルミニウムのそれぞれのピークが合成されてできたピークではなく、リン酸、重リン酸アルミニウムが溶中に十分に混ざり合って一本のシャープなピークになっていると考えられる。

Table 1 Isotropic chemical shift ranges of basic structures

<table>
<thead>
<tr>
<th>Q₀</th>
<th>δ (ppm)</th>
<th>Q₁'</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₀</td>
<td>+14~ -6</td>
<td>Q₀'</td>
<td>-15</td>
</tr>
<tr>
<td>Q₁</td>
<td>4~ -22</td>
<td>Q₁'</td>
<td>-15~ -30</td>
</tr>
<tr>
<td>Q₂</td>
<td>-16~ -27</td>
<td>Q₂'</td>
<td>-30~ -52</td>
</tr>
<tr>
<td>Q₃</td>
<td>-32~ -46</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Estimated range as the isotropic chemical shift range between Q₀' and Q₁' . The isotropic chemical shift range of Q₁' has not been reported so far.

3・4 パッチング材の$^{31}$P MAS NMRスペクトル

Fig.3はSiO₂原料のパッチング材の$^{31}$P MAS NMRスペクトルを示している。左図が柔らかい練り土状のパッチング材、右図が完全に硬化したパッチング材の$^{31}$P MAS NMRスペクトルを示している。同図の数値はピーク位置、*印はスピンシングサイドバンドを表している。一番上のスペクトルがリン酸75%水溶液のみのものであり、下にいくにつれて重リン酸アルミニウム50%水溶液の割合が増大し、一番下が重リン酸アルミニウム50%水溶液のみのスペクトルである。Table 1に基づいて各ピークの帰属を行った。また、リン酸75, 50, 25ω%のバインダー溶液の各ピークの帰属に関しては、Table 1の他に各ピークの強度比、バインダー溶液の体積比、リン酸100, 0ω%でのピーク位置も考慮した。その結果得られた各ピークに帰属できるPO₄四面体の基本構造を図中に示した。

左図のピークは0.1~11.7ppmの範囲で現れ、Fig.2の等方性化学シフト値に近いことから、水分をいくらか含む柔らかい練り土状のパッチング材中のピークはQ₀, Q₂構造に帰属でき、リン酸塩溶中の縮合は起こっていないと考えられる。

右図では、リン酸を50~100ω%含むパインダーでOpmp付近の鋭いピークと-13ppm付近の小さなピークが現れた。リン酸を25ω%含むパインダーでは、-0.8ppmの鋭いピークの他に-15.8ppm と-31.1ppmにピークが出現した。また、重リン酸アルミニウム溶液では-15.3ppmのブロードな1本のピークが得られた。

いずれのバインダー溶液でも、パッチング材の硬化とともにQ₀, Q₂構造のみがQ₀'構造が現れているので
で、バッティング材が硬化するに従って、架橋酸素をもつリン原子の割合が増加していることがわかる。このこととは、バッティング材の硬化により脱水結合が起こっていることを示している。しかし硬化したバッティング材では、いずれもネットワーク形成能をもたないQ0、Q1構造またはネットワーク形成能に乏しいQ0構造が主であり、比較的高いネットワーク形成能をもつQ1、Q2構造は少数であった。

Fig. 3 31P MAS NMR spectra of soft (left) and hard (right) refractory patching materials made by SiO2. Asterisks denote spinning side bands.

3.5 バッティング材の作業性（可塑性）の低下機構

バッティング材の31P MAS NMR測定結果から、バッティング材の作業性（可塑性）の低下に伴う硬化によりリン酸塩の一部が脱水結合していることを明らかにした。しかし、バッティング材中のリン原子はいずれもネットワーク形成しないQ0、Q1構造とネットワーク形成能に乏しいQ0構造が主であり、比較的高いネットワーク形成能をもつQ1、Q2構造は少数であった。つまり、脱水結合によるP-O-P-連結による形態はネットワーク構造の割合が小さいと考えられるので、リン酸塩の脱水結合によるネットワーク化のみで硬化するとは考えにくい。しかし実際には硬化している。これは、バッティング材の硬化に影響を及ぼす別の原因が存在することを示唆している。

リン酸塩結晶は無水相を含む無色の結晶であり、非常に吸湿性が強い。この結晶はPO4四面体のOH基同士がすべて水素結合で連結した層状構造をしている。したがって、無水の重リン酸アルミニウム結晶もPO4四面体とAlO6八面体から成る直鍵間はP-OH基間の水素結合で互いに連結した構造をしている。
におけるパッチング材は上記のリン酸（塩）を用いて
ているので、無水状態では上記の2つの結晶と類似的の
存在すると考えられる。即ち、パッチング材中の水分
の蒸発に伴うリン酸（塩）同士の水素結合による
増加が考えられる。

以上より、水分の減少によって引き起こされる水素結
合と脱水結合が、パッチング材の作業性（可塑性）の
低下の原因と考えられる。

4 結論

リン酸および重リン酸アルミニウム水溶液の混合溶液
から成るパッチング溶液、SiO₂および電解アルミニナ粉末
とリン酸塩パッチングから作製したパッチング材の乾燥
前後、乾燥後の試料について³¹P静止およびMAS NMR
測定を行い、パッチング材中のリン原子の局所構造を
明らかにするこことでパッチング材の作業性（可塑性）の
低下機構の解明を試みた結果、次の結論を得た。

(1) 硬化後の試料は乾燥前の試料に比べて脱水結合し
たリン原子の割合は多くなかったが、ネットワークを作
らないQₐ相、Q₁₈相とネットワーク形成能に乏しいQ₁₈相構
造が主であり、比較的高いネットワーク形成能をもつQ₁₉、
Q₂₁構造をもつリン原子は少なかった。

(2) 同じパッチングを用いた場合、原料の種類によっ
て脱水結合したリン原子の割合が変化し、電解アルミニ
ナ材質の方がSiO₂材質よりも脱水結合したリン原子の割合
が多くかった。

(3) パッチング材の作業性（可塑性）の低下の原因
は、水分の減少によって引き起こされる水素結合による
リン酸塩間の連結ならびにリン酸（塩）同士の脱水結合
によるネットワークの形成と考えられる。

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37
Investigation into Hydration Resistance of CaO-containing Materials

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Keywords: CaO, Al₂O₃, Fe₂O₃, SiO₂, TiO₂, ZrO₂, NiO, Hydration, Steel, Nozzle.

Abstract: In order to develop an ideal material for the nozzle used in steel continuous casting process, the hydration resistance of some CaO-containing complex oxides and CaO-NiO solid solutions were investigated systematically. The hydration resistance of the complex oxides was CT > CZ > CS > CF > C₆T₂ > C₂S > C₆F > C₆A > CA₂ > CaO. CT should be a promising material for the nozzle. A large number of fine secondary-NiOss particles were separated from the CaOss crystal grains in CaO-NiO solid solution and improved the hydration resistance.

I. Introduction

A submerged entry nozzle is used to introduce molten steel into a mold in steel continuous casting process. The refractory material of the nozzle is generally alumina-graphite. In this case, one problem frequently occurs, that is, an adhesion layer which causes nozzle clogging is produced on the inner wall of the nozzle during casting of Al-deoxidized steel. CaO has been considered to be an effective material to prevent the nozzle clogging according to some basic researches, but it is difficult to utilize CaO for the easy-hydration. So CaO-ZrO₂ material containing CaO of approximately 50 mol% is now applied in some nozzles. However, this material is not effective enough for prevention of the nozzle clogging and leads to ZrO₂ inclusions, which tend not to float out of molten steel due to the high density of ZrO₂.

In order to develop an ideal material for the nozzle, we systematically investigated the hydration resistance of CaO-containing materials in the present work. The effect of some added oxides, fluorides and chlorides on the hydration resistance of CaO has been reported in past literatures ¹ - ⁵). It can be known that free CaO remains in the sintered compacts if the amount of added components is small from the results. Once the sintered compacts are processed into grains of < 1 mm for the use to the nozzle as the raw material, the grains will be hydrated. Therefore, we paid attention to CaO-containing complex oxides and solid solutions, non-including free CaO.

CaO combines with many oxides to form the complex oxides as shown in Table 1. Taking into

<table>
<thead>
<tr>
<th>Table 1. Complex oxides in system containing CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Al₂O₃</td>
</tr>
<tr>
<td>2. B₂O₃</td>
</tr>
<tr>
<td>3. SiO₂</td>
</tr>
<tr>
<td>4. Cr₂O₃</td>
</tr>
<tr>
<td>5. Fe₂O₃</td>
</tr>
<tr>
<td>6. MnO</td>
</tr>
<tr>
<td>7. MgO</td>
</tr>
<tr>
<td>8. NiO</td>
</tr>
<tr>
<td>9. Na₂O</td>
</tr>
<tr>
<td>10. Na₂O</td>
</tr>
<tr>
<td>11. Nb₂O₅</td>
</tr>
<tr>
<td>12. P₂O₅</td>
</tr>
<tr>
<td>13. PbO</td>
</tr>
<tr>
<td>14. SiO₂</td>
</tr>
<tr>
<td>15. TiO₂</td>
</tr>
<tr>
<td>16. UO₂</td>
</tr>
<tr>
<td>17. V₂O₅</td>
</tr>
<tr>
<td>18. WO₃</td>
</tr>
<tr>
<td>19. ZrO₂</td>
</tr>
</tbody>
</table>
account the resource of oxides, we selected Al₂O₃, Fe₂O₃, SiO₂, TiO₂ and ZrO₂ as the second components in the complex oxides. In addition, CaO reacts with Ce₂O₃, FeO, La₂O₃, MgO, MnO, NiO, Pr₂O₃ and Y₂O₃ to produce the solid solutions. We took up CaO-NiO system in our experiment because the solid solubility of NiO in CaO is comparatively high and the hydration resistance of this system has never been studied.

II. Experimental Procedures

For promotion of the sintering, a light CaCO₃ obtained by blowing CO₂ gas into a Ca(OH)₂ aqueous solution was used as the starting raw material of CaO. The grain sizes were below about 1 μm, markedly smaller than the general CaCO₃ reagent, as seen in the microstructure shown in Fig.1. Al₂O₃, Fe₂O₃, SiO₂, TiO₂, ZrO₂ and NiO reagents were used as the second components.

In the case of the complex oxides, the proportion of the raw materials for the preparation of CaO·2Al₂O₃(CA₂), CaO·Fe₂O₃(CF), CaO·SiO₂(CS) and CaO·TiO₂(CT) specimens followed each stoichiometric ratio. While for the preparation of 3CaO·Al₂O₃(C₃A), 2CaO·Fe₂O₃(C₃F), 2CaO·SiO₂(C₂S), 3CaO·2TiO₂(C₃T₂) and CaO·ZrO₂(CZ) specimens, the amount of the second components was fixed to be 3 mol % higher than each stoichiometric ratio to completely prevent free CaO to remain in the sintered compacts, because these compounds adjoin free CaO on the phase diagrams. After the raw materials on the proportion were pulverized, mixed with ethanol in an agate mortar, the mixtures were dried in a rotating-vacuum processor. 2 g of each mixture was uniaxially pressed at 50 MPa and then sintered for 5 hr in atmosphere. The sintering temperature was set at 1100°C for CF specimen, 1300°C for C₂F, 1400°C for C₃A, 1500°C for C₂S, C₃S, C₃T₂ and CT, 1600°C for CaO and CZ depending on the fusion point of the complex oxides. The sintered C₂S compact powdered due to the phase transition during cooling. Each of the sintered compacts was pulverized immediately after taken out the electric furnace. A part of the powder was used for the phase identification analysis by X-ray diffraction (XRD), the other (0.5 g) being for the test of hydration resistance.

In the hydration test, the powdery specimen was put in a temperature-humidity chamber (70°C×90%-relative humidity) up to 48 hr. The hydrated specimen was weighed, and the mass-increasing percentage, α or β, was calculated by Eq. (1), (2).

\[
\alpha = \frac{\Delta M}{M_0} \times 100\% \quad \text{(1)}
\]

\[
\beta = \frac{\Delta M}{M_{\text{CaO}}} \times 100\% \quad \text{(2)}
\]

where, ΔM is the mass increase, M₀ and M_CaO are the total mass and the CaO mass of the specimen before the hydration test, respectively. For comparison, an Al₂O₃ regent powder was also tested.

In the case of CaO-NiO solid solutions, the sintered CaO-NiO compacts with NiO of 0, 10, 20, 30, 40, 50 and 60 mol% were prepared by the same method as mentioned above, the sintering temperature being 1600°C. The sintered compacts were directly used in the hydration test. XRD and EPMA analysis were conducted on the sintered compacts prepared under the same condition.
III. Results

(1) Case of complex oxides

The XRD results of the sintered specimens are shown in Fig.2. A small quantity of Ca(OH)$_2$ existed in CaO specimen due to the hydration of CaO upon pulverizing. The phases of 12CaO·7Al$_2$O$_3$, CaO·FeO$_2$, 3CaO·2SiO$_2$, 4CaO·3TiO$_2$ and ZrO$_2$ were included in C$_3$A, C$_2$F, C$_3$S, C$_3$T$_2$ and CZ specimens, respectively, because the added second components were higher than the stoichiometric ratios in them. Each of CA$_2$, CF, CS and CT specimens was composed of only the single phase.

Fig.2. XRD analysis of sintered complex oxide specimens.

The change of the mass-increasing percentage $\alpha$ of the specimens as a function of the hydration time is given in Fig.3. CaO, CF, CS, CZ and CT as well as Al$_2$O$_3$ specimens showed a similar change tendency, i.e., the mass increased rapidly in the time to 1 hr and then the increase rate became very slow, whereas the mass of the other specimens increased gradually over the whole period up to 48 hr.

The mass of CaO, CA$_2$, C$_3$A and C$_2$F specimens had a marked increase, reaching 10-45% at 48 hr hydration (Fig.3 (a)). C$_2$S, C$_3$T$_2$ and CF showed a relatively small increase, 1.5-2.5% (Fig.3 (b)). CS, CZ and CT were all below 1%; especially, CT increased only 0.45%, almost same as Al$_2$O$_3$ (Fig.3(c)).

Defining a hydration index $I_\alpha=\alpha/\alpha_{CaO}$, $I_\alpha$ of each specimen hydrated for 48 hr is presented in Fig.4. As can be seen in Fig.4, the order of the hydration resistance was

CT$>$CZ$>$CS$>$CF$>$C$_3$T$_2$$>$C$_2$S$>$C$_2$F$>$C$_3$A$>$CA$_2$$>$CaO

In addition, the mass-increasing percentage $\beta$ based on the mass of CaO ($M_{CaO}$) was calculated
Fig.3. Mass-increasing percentage α of complex oxide specimens.

by Eq.(2) and another hydration index defined as \( I_p = \beta / \alpha_{CaO} \) was obtained as shown in Fig.5 (values at 48hr hydration). This result indicates that TiO\(_2\), SiO\(_2\) and ZrO\(_2\) have large addition effect and the effect of Al\(_2\)O\(_3\) is small for improvement of CaO hydration resistance.

Moreover, all specimens hydrated for 48 hr were heated up to 1000°C in atmosphere. The mass-decreasing percentage of them is shown in Fig.6, which nearly agreed with the mass-increasing percentage α in the hydration test (Fig.3).

Fig. 4. Hydration index \( I_p \) on total mass of specimens (\( M_0 \)).

Fig. 5. Hydration index \( I_p \) on CaO mass of specimens (\( M_{CaO} \)).

Fig. 6. Mass-decreasing percentage of hydrated specimens with heating up to 1000°C.

(2) Case of CaO-NiO solid solutions

The sintered CaO-NiO compacts all had an apparent porosity of 0.8% or less. Fig.7 shows the
mass-increasing percentage $\beta$ of the compacts during the hydration test, which rose almost linearly with passage of the hydration time, but reduced with increase in NiO content of the compacts.

The average value of the hydration rate, equal to the ratio of the mass-increasing percentage $\beta$ to the hydration time, of the compacts is pointed in Fig.8. The hydration rate decreased sharply until NiO content of 20 mol% and then decreased slowly on further NiO increasing.

The microstructure of the sintered compacts is shown in Fig.9(a), which consists of white grains and a dark matrix. EPMA analysis indicated that the white grains are a NiO rich solid solution (primary-NiOss) containing around 7 mol% of CaO.

Fig.9(b) provides the microstructure of the matrix observed at a high magnification. A large number of fine particles (< 0.3 $\mu$m) were found to uniformly distribute in the matrix. According to EPMA analysis, the fine particles were also a NiO rich solid solution (secondary-NiOss), while the phase around secondary-NiOss was a CaO rich solid solution containing about 4 mol% NiO. As an example, the analysis result of NiO20 specimen is given in Fig.9(c).

Only a small amount of primary-NiOss existed in NiO10 (Fig.9(a)), so the hydration rate of NiO10 being 30% lower than CaO is considered to be mainly due to the action of secondary-NiOss.

**IV. Discussion**

(1) **Hydration mechanism**

Analyzing CaO specimens hydrated for 1 and 48 hr by XRD, Ca(OH)$_2$ was detected in the former and CaCO$_3$ besides Ca(OH)$_2$ in the latter. This signifies that the following reactions occurred in CaO on hydrating.

$$\text{CaO(s)} + \text{H}_2\text{O(g)} = \text{Ca(OH)}_2(s)$$ \hspace{0.5cm} (3)

$$\text{Ca(OH)}_2(s) + \text{CO}_2(g) = \text{CaCO}_3(s) + \text{H}_2\text{O(g)}$$ \hspace{0.5cm} (4)

The CO$_2$ gas mostly came from the distilled water used in the temperature-humidity chamber.

In C$_3$A specimen, the reaction expressed by Eq.(5) might have occurred, because Ca(OH)$_2$ and CaCO$_3$ were formed and the ratio of the XRD-peak intensity of C$_3$A to C$_{12}$A$_7$ became small after the hydration test.

$$7[3\text{CaO}\cdot\text{Al}_2\text{O}_3(s)] + 9\text{H}_2\text{O}(g) = 12\text{CaO}\cdot7\text{Al}_2\text{O}_3(s) + 9\text{Ca(OH)}_2(s)$$ \hspace{0.5cm} (5)

Al(OH)$_3$ was also identified in the hydrated CA$_2$ specimen, which suggests occurrence of the
reaction of Eq.(6).

\[
\text{CaO-2Al}_2\text{O}_3(s)+7\text{H}_2\text{O}(g)=\text{Ca(OH)}_2+4\text{Al(OH)}_3
\]  \hspace{1cm} (6)

There were some phases that cannot be judged definitely from the XRD charts of both C2F and C2S specimens hydrated. Perhaps, the phases were hydrates such as 2CaO-Fe$_2$O$_3$·xH$_2$O and 2CaO-SiO$_2$·xH$_2$O.

The reaction of Eq.(7) is thought to have happened in C$_3$T$_2$ specimen, based on existence of Ca(OH)$_2$ and CaCO$_3$ and decrease in the ratio of the XRD-peak intensity of C$_3$T$_2$ to C$_4$T$_3$.

\[
3[3\text{CaO-2TiO}_2(s)+\text{H}_2\text{O}(g)]=2[4\text{CaO-3TiO}_2(s)+\text{Ca(OH)}_2(s)
\]  \hspace{1cm} (7)
No difference was observed between the XRD chart of CF, CS, CT and CZ specimens before and after the hydration test, same as the case of Al₂O₃ specimen. However, since these specimens, particularly CF and CS showed a mass increase on hydrating (Fig.3), it is possible that the hydrates formed in these specimens were amorphous or of low crystallization degree.

In CaO-NiO system, the reactions of Eq.(3) and (4) occurred, like the case of CaO specimen.

(2) Formation mechanism of secondary-NiOss in CaO-NiO system

CaO-NiO phase diagram⁶ shows that the solid solubility of NiO in CaO decreases with temperature falling, for example, being 12.6 mol% at 1600°C and 3.7 mol% at 1200°C. Based on this point as well as the size, shape, number and distribution state of the secondary-NiOss particles (Fig.9), the particles can be judged to have been separated from the CaOss during the cooling stage in the heating process. This suggests that the cooling condition e.g. the cooling rate influences the separation behavior of secondary-NiOss (the cooling rate was 5°C/min from 1600 to 1200°C in our experiment). It is a future research subject to quantitatively clarify the relations among the cooling condition, the separation behavior of secondary-NiOss and the hydration resistance.

The solid solubility of CaO in NiO decreases also with temperature falling, 8.4 mol% at 1600°C and 1.2 mol% at 1200°C. However, no secondary-CaOss particles were observed in the primary-NiOss in the CaO-NiO specimens (Fig.9). This may signify that the diffusion rate of Ca²⁺ in NiO is slow, so that the formation of CaO nucleus is difficult.

(3) Possibility of suitable CaO-containing material for nozzles

The hydration test results mentioned above showed that CT material has the best hydration resistance. In addition, CT contains CaO of 41 mass%, 10 mass% higher than CZ, which is applied now in some nozzles, as listed in Table 2. The fusion point of CT is 1970°C, about 200°C higher than the temperature of molten steel and so the refractoriness is enough, although it is 370°C lower than CZ. Consequently, CT should be a more promising material for the nozzles.

<table>
<thead>
<tr>
<th></th>
<th>CT</th>
<th>CZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydration index I₉</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>CaO content, mass%</td>
<td>41</td>
<td>31</td>
</tr>
<tr>
<td>Fusion point, °C</td>
<td>1970</td>
<td>2340</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>4.03</td>
<td>4.62</td>
</tr>
</tbody>
</table>

V. Conclusion

1) The hydration resistance of the complex oxides in CaO-Al₂O₃, Fe₂O₃, SiO₂, TiO₂ and ZrO₂ systems was investigated on condition of 70°C and 90%-humidity, and the order of the hydration resistance was

CT > CZ > CS > CF > C₂T₂ > C₂S > C₂F > C₃A > CA1 > CaO

CT should be a more promising material than CZ for the submerged entry nozzle.

2) In the case of CaO-NiO solid solutions, a large number of fine secondary-NiOss particles were separated from the CaOss crystal grains during the cooling stage in the heating process and improved the hydration resistance.
References

Synthesis of Magnesium Aluminum Oxynitride by Carbothermal Reduction and Nitridation Process

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炭素熱還元窒化法によるMgAlONの合成

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Carbothermal reduction and nitridation (CRN) process was utilized to prepare magnesium aluminum oxynitride (MgAlON) and the influence of reaction variables, such as heating temperature, soaking time and the source of carbon, on the formation of MgAlON was investigated. In addition, the density of samples prepared under different route was compared. The results show that volatile gases, Mg (g) in chief, lead to variation in lattice constant and chemical composition at high temperature, and decrease the sintering effect. Since high temperature and low CO partial pressure are favorable to the CRN reaction in view of thermodynamic reason and high temperature also favors the transport of gases, the rate of CRN reaction increases with the increasing temperature. Due to the difference in reactivity between graphite and carbon black, CRN reaction may be the rate controlling step when graphite is used and solid solution of AlN may be the controlling step when carbon black is utilized. CRN reaction can increase surface energy of reaction materials and results in higher final density. However, gases in the system retard the densification effect.

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Key-words : Carbothermal reduction and nitridation (CRN), Magnesium aluminum oxynitride (MgAlON), Synthesis

1. Introduction

Magnesium aluminum oxynitride (MgAlON) is a cubic solid solution crystal material with excellent optical and mechanical properties and attracts lots of researchers’ interest after the introduction of Jack.[1,2] Moreover, since MgAlON and its oxidized material, magnesium aluminate spinel (MgAl2O4) and Al2O3, has high melting point and nitrogen in the material can increase the viscosity of slag to retard the further corrosion.[2,3] It can be considered as a promising superior refractory. To prepare this material, the following synthesis methods were utilized: (1) solid phase reaction of AlN, Al2O3 and MgO,[2,5,7] (2) reaction of Al, Al2O3 and MgO,[8] (3) carbothermal reduction and nitridation (CRN) of Carbon, Al2O3 and MgO.[9]

The MgAlON formation mechanism through solid phase reaction has been well investigated,[2,5,7] MgO reacts with Al2O3 to form MgAl2O4s above 1000°C. At higher temperatures, AlN and Al2O3 dissolve into MgAl2O4s to form MgAlON. The maximal amount of AlN and Al2O3 dissolved into MgAl2O4s increases with the heating temperature[7] and N diffusion is considered to be the rate controlling of MgAlON formation.[2]

From the viewpoint of the purity of product, preparation of the raw materials and potential for large-scale production, the CRN process is considered to have advantages. However, the synthetic process and other details on preparing MgAlON through CRN were seldom discussed except for few reports proposed that AlON, prepared through CRN process, could be stabilized at low temperature by adding MgO or MgAl2O4.[9]

Since density is probably the most important parameter in the study of sintering and it relates to the sintering kinetics and correlates with many properties of sintering materials,[10] the sintering characteristics of various routes could be surveyed by the comparison of the density of samples heated at the same condition.

In present investigation, CRN process was utilized to prepare MgAlON and the influence of reaction variables, such as heating temperature, soaking time and the source of carbon, on the formation of MgAlON was investigated. Moreover, density of the samples prepared by different route was compared. Based on the results, evaporation of MgAlON was analyzed, MgAlON formation mechanism through CRN process was discussed, and sintering characteristics of CRN process were surveyed.

2. Experimental procedure

2.1 Starting materials and synthesis procedure

Table 1 gives information about the starting materials used in present investigation. According to Table 2, the raw materials were meticulous weighted and then mixed by ball milling with alumina balls in ethyl alcohol. After evaporating the solvent in vacuum rotary, the mixtures were uniaxial pressed under 150 MPa. As described in Table 2, the green compacts were heated in a graphite furnace under various conditions. Gas pressure of the furnace was constant at 0.1 MPa and flowing rate of N2 gas (purity > 99.999%) was 1 L min-1.

2.2 Characterization

In present work, Bulk density and apparent porosity were measured by SGM–6 automatic gravimeter, true density was analyzed by IONICS multi pycnometer, and specific surface area was tested by IONICS monosorb. The phase composition
Table 1. Some Information of Staring Materials

<table>
<thead>
<tr>
<th></th>
<th>MgO(^1)</th>
<th>Al(_2)O(_3)</th>
<th>Carbon</th>
<th>AIN</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>AO1</td>
<td>AO2</td>
<td>Graphite</td>
</tr>
<tr>
<td>Purity (wt%)</td>
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<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
<td>99.4</td>
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<tr>
<td>Particle size (μm)</td>
<td>0.1</td>
<td>0.24</td>
<td>&lt;75</td>
<td>0.1</td>
<td>&lt;45</td>
</tr>
<tr>
<td>Specific surface area (m(^2)/g)</td>
<td>12</td>
<td>106</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(^1\) The materials for chemical analysis were preheated at 1000°C. The ignition loss of M1 and M2 was 3.6% and 8.2%, respectively, and it was considered during the weighting.

\(^2\) Amorphous

Table 2. Composition of the Compacts in Molar ratio and Heating Conditions

<table>
<thead>
<tr>
<th>Sample No</th>
<th>MgO</th>
<th>Al(_2)O(_3)</th>
<th>Carbon</th>
<th>AIN</th>
<th>Al</th>
<th>Heating conditions</th>
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<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>AO1</td>
<td>AO2</td>
<td>Graphite</td>
<td>Carbon black</td>
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<tr>
<td>A(_1)</td>
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<td>29</td>
<td>9</td>
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<tr>
<td>A(_2)</td>
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<td>9</td>
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<tr>
<td>A(_3)</td>
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<td>A(_4)</td>
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was identified by RINT2200 X-ray diffraction (XRD) and the relative intensity of the random i phase (\(R_i\)) was calculated according to the following equation,

\[
R_i = \frac{I_i}{I_1 + I_2 + \ldots + I_i + \ldots} \times 100\% \tag{1}
\]

where the subscripts represent the detected phases, \(I_i\) is the intensity of the strongest peak of i phase.

To analyze formation process in quantity, chemical composition of intermediate product should be concerned. However, it is difficult to determine composition of MgAl\(_2\)O\(_{4+}\) and MgAlON only by chemical analysis when Al\(_2\)O\(_3\) exists in the sample. In present work, chemical composition of MgAl\(_2\)O\(_{4+}\) and MgAlON is calculated by the combination of chemical composition and lattice constant. As lattice constant of MgAl\(_2\)O\(_{4+}\) and MgAlON, designated as \(\alpha_{\text{MgAl}_2\text{O}_{4+}}\) and \(\alpha_{\text{MgAlON}}\), can be calculated through the following equations,

\[
\alpha_{\text{MgAl}_2\text{O}_{4+}} = 0.7900 + 0.0375[MgO]_{\text{MgAl}_2\text{O}_{4+}} \% (\text{nm}) \tag{2}
\]

\[
\alpha_{\text{MgAlON}} = 0.7900 + 0.0375[MgO]_{\text{MgAlON}} \% + 0.0150[AIN]_{\text{MgAlON}} \% (\text{nm}) \tag{3}
\]

where the relative intensity of MgO and AlN in mole% of each component.
ture.
\[
[Mg]_{MgAI01.0\%} = \frac{(\alpha_{MgAI01.0\%} - 0.7900) \times 80}{(15 - (\alpha_{MgAI01.0\%} - 0.7900) \times 240)} \times 100\%
\]
\[
[Al]_{MgAI01.0\%} = \frac{6 - (\alpha_{MgAI01.0\%} - 0.7900) \times 160}{(15 - (\alpha_{MgAI01.0\%} - 0.7900) \times 240)} \times 100\%
\]
\[
[O]_{MgAI01.0\%} = 1 - [Mg]\% - [Al]\%
\]
When entire N and Mg exist in MgAlION structure, chemical composition of MgAlION can be figured out in the following equations:
\[
[Mg]_{MgAlION\%} = \frac{(\alpha_{MgAlION\%} - 0.7900) \times (Mg)\%}{(2.5575 \times (Mg)\% + 2.445 \times (N)\% - \alpha_{MgAlION\%} \times ((Mg)\% + (N)\% \times 3))} \times 100\%
\]
\[
[Al]_{MgAlION\%} = \frac{(1.655 \times (Mg)\% + 0.82 \times (N)\% - (Mg)\% \times 2 + (N)\% \times \alpha_{MgAlION\%})}{(2.5575 \times (Mg)\% + 2.445 \times (N)\% - \alpha_{MgAlION\%} \times ((Mg)\% + (N)\% \times 3))} \times 100\%
\]
\[
[N]_{MgAlION\%} = \frac{(\alpha_{MgAlION\%} - 0.7900) \times (N)\%}{(2.5575 \times (Mg)\% + 2.445 \times (N)\% - \alpha_{MgAlION\%} \times ((Mg)\% + (N)\% \times 3))} \times 100\%
\]
\[
[O]_{MgAlION\%} = 1 - [Mg]\% - [Al]\% - [N]\%
\]
where \([Mg], [Al] and [O]_{MgAI01.0\%}\) or \([Mg], [Al] and [O]_{MgAlION}\) are \(\%\) of elements in these two phases. \((Mg)\% and (N)\%\) are \(\%\) of Mg and N in the sintered sample. In present investigation, lattice constant of MgAl2O4 and MgAlION was determined by XRD by using high purity silicon (purity > 99.999 mass%) as internal standard material, and the content of Mg and Al was measured by Simultix12 X-ray fluorescence spectroscopy (XRF), O, N by EMGA650 oxygen and nitrogen analyzer, and Carbon by EMIA810 carbon analyzer.

3. Results and discussion

3.1 Influence of heating temperature

The content of residual carbon in the samples of A1-A10 is plotted in Fig. 1. At temperatures below 1300°C, the content of residual carbon in these samples (3.16 mass\%) approximated to that in the raw material (3.19 mass\%) and when above it, especially above 1400°C, the rate of graphite consumption increased with the increasing temperature.

Figure 2 reveals the relative intensities of detected phases in the samples of A1-A10. MgO could not be detected in samples even as low as 1100°C, because entire MgO reacted with Al2O3 to form MgAl2O4, in view of lattice constant of MgAl2O4, decreased from 0.8079 nm at 1100°C to 0.8080 nm at 1300°C, as shown in Fig. 3, chemical composition of MgAl2O4 calculated by equations (4) - (6) could be represented as Mg3Al1.76 O17.14 (1100°C) and Mg3Al1.6 O16.3 (1300°C), respectively. Since the amount of Al2O3 dissolved into MgAl2O4 increased with the increasing temperature and the molar weight of graphite and MgAl2O4 had not obvious change below 1300°C, the relative intensity of Al2O3 decreased, while that of graphite and MgAl2O4 increased from 1100°C to 1300°C. By making use of chemical analysis and XRD detection, it was confirmed that MgAlION was formed in the samples heated above 1350°C. Based on the result of lattice constant, as shown in Fig. 3 chemical composition of the synthesized MgAlION could be calculated by Eqs. (7) - (9) and some of them were Mg6Al13.41O23.68N1.11 (1350°C), Mg6Al17.41O29.06N1.76 (1450°C) and Mg6Al21.16O41.40O2.93 (1600°C). When over 1650°C, mono-

![Fig. 1. Content of residual carbon in the samples of A1-A10.](image)

![Fig. 2. Change of relative intensities of detected phases in the samples of A1-A10.](image)

![Fig. 3. Lattice constant of MgAl2O4, and MgAlION in the samples of A1-A10.](image)
bon was 0.09 mass%. The AlN provided by CRN reaction did not dissolve into MgAl₂O₄, entirely and it was different from the sample of A₁0, which was heated at 1500°C for 6 h, for that AlN could not be detect. As the amount of AlN dissolved into MgAl₂O₄ has a maximal value at a temperature, the AlN provided by CRN reaction in the sample of B₁ was excessive for MgAl₂O₄ at this temperature. Considering the phase composition of samples of A₁, A₁₀ heated at different temperature for 6 h, as mentioned in Section 3.1, it can be concluded that the generating rate of AlN by CRN of graphite is slower than the potential maximal solid solution rate of AlN before a critical point. In the samples of B₁-B₆, which were heated at 1700°C for different soaking time, the content of residual carbon was less than 0.03 mass% and only MgAl₄ON detected. According to the result of chemical analysis, their chemical composition could be expressed as Mg₃Al₈O₁₆N₂ (3 h), Mg₃Al₁₂O₂₄N₂ (6 h), and Mg₃Al₁₆O₃₂N₄ (9 h), respectively. It implies that Mg content decreased with the soaking time and the decrease caused variation in lattice constant (Fig. 4). Evaporation of MgAl₄ON at high temperature leads to it and the reason was further discussed in Section 3.5.

3.3 Effect of the source of carbon

In the sample of C₁, which was made from carbon black and heated at 1500°C for 6 h, AlN, Al₂O₃ and MgAl₄ON were detected and the content of residual carbon was 0.11 mass%. Its composition was close to the sample of B₁ which was made from graphite and heated at 1500°C for 6 h, and its residual carbon was much lower than that of the sample of A₁₀, which was made from graphite and heated at 1500°C for 6 h. Hence, the carbon consumption rate in the sample made from carbon black was much higher than that made from graphite. Since the amorphous carbon black used in this work has smaller size (about 0.023 μm) and higher surface area (106 m²·g⁻¹), the reactivity of it is much higher than that of graphite.

3.4 Density of samples prepared by different route

In present investigation, all the samples heated at 1700°C for 6 h were monophase MgAl₄ON and the chemical composition was close to each other. However, as shown in Fig. 5, the relative density was different with the synthesis route. Among the samples B₁, C₁, D, and E, which were made from coarser MgO and Al₂O₃, the sample of B₁, which was made from graphite by CRN process, had the highest density and that of C₁, which was made from carbon black, was the most porous one. As to the samples made of finer MgO and Al₂O₃ (F, G, H, and Y), the density was much higher than that of samples made from coarser materials. The density of samples F and G, which was prepared by CRN process, was lower than that of others and the sample of H, which was made from MgO, Al₂O₃, and AlN, had the highest density. However, due to volatile gases of MgAl₄ON at high temperature, which was discussed in Section 3.5, closed pores were formed in the matrix and full dense samples could not be obtained in present condition even the apparent porosity approximated to 0.

3.5 Evaporation of MgAl₄ON

Based on the thermodynamics data, equilibrium partial pressure of gases of Mg₃Al₁₂O₄N₃ at 1727°C in nitrogen atmosphere are calculated and plotted in Fig. 6. These gases, Mg (g) in chief, may be entrained by the flowing nitrogen gas and then evaporation occurs at high temperature. In this way, as mentioned in Sections 3.1 and 3.2, Mg content in the sample decreased and lattice constant was also decreased according to Eq. (3). Moreover, the volatile gases lead to closed pores formed in the matrix and it is difficult to obtain full dense MgAl₄ON sample in present condition without any auxiliary means, such as spark plasma.

3.6 MgAl₄ON formation mechanism by CRN process

As mentioned in Section 3.1, entire MgO react with Al₂O₃ to form MgAl₂O₄, below 1100°C. The reaction is considered as the first step and similar to solid phase reaction system. In the CRN process, it is certain that nitride, AlN, must be provided before its solid solution reaction. Hence, in the second step, AlN supplies by the following overall reaction.

\[
\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}
\]

Figure 7 shows the equilibrium partial pressure of CO of
CRN reaction when the partial pressure of nitrogen is given as 0.1 MPa. Obviously, high temperature and low CO partial pressure are favorable to the CRN reaction. In the inner of the sample, the partial pressure of CO would be increased and that of N₂ would be decreased when CRN reaction proceeds with, because of the consumption of N₂ and formation of CO. If the diffusivity of gases is too slow, CRN reaction would be retarded or even ceased. On the other hand, since the diffusivity of gases increases with the increasing temperature, high heating temperature is also favorable to the transport of gases and favors the CRN reaction. Hence, the rate of CRN reaction increases with the increasing temperature. In the third process, Al₂O₃ and AlN, which was provided by CRN reaction, dissolve into MgAl₂O₄ to form MgAlON. In the sample made from graphite, the reaction rate of the second step should be slower than the maximum potential rate of the third step considering that AlN could not be detected in the samples of Al₂O₃ with a high content of AlN. In the sample made from carbon black, the reaction rate of the second step is much faster for the higher reactivity of carbon black and the third step is assumed as the rate limiting steps.

3.7 Characteristics of CRN process

When CRN reaction occurs, the reaction of carbon and Al₂O₃ can increase the surface energy of Al₂O₃ and the product of CRN reaction, AlN, has high surface energy. Since raw materials with high surface energy always lead to higher final density, the CRN process is favorable for the densification of samples and the sample of B₃ which was made from graphite, has the highest density. On the other hand, being the reactivity of carbon black is higher than graphite, lots of gases might be generated from the sintering body at one time and the sinterability of C₂ would be decreased. So, the density of C₂ is lower than that of B₃. The densities of Al and AlN are 2.702 g·cm⁻³ and 3.26 g·cm⁻³, respectively, and the volume expansion caused by the nitridation of Al, which occurs at 600-800°C, is about 26%. Hence, the density of E is increased before the solid phase reaction of MgO-Al₂O₃-AlN system and the final density of E is higher than that of D, which was made from AlN.

When fine MgO and Al₂O₃ are used as raw materials, the materials themselves have high surface energy and the influence of the rise in the surface energy caused by CRN process could be neglected. Moreover, since CRN reaction is a kind of gas solid reaction and gases in the system are not favorable to the densification. Hence, the density of samples made from CRN process is lower than that of samples made from the other processes.

4. Conclusions

The process of carbothermal reduction and nitridation (CRN) on the synthesis of magnesium aluminum oxynitride (MgAlON) was investigated in present investigation. Being the volatile gases of MgAlON, Mg (g) in chief, there was variation in lattice constant and chemical composition at high temperature. In addition, these gases resulted in closed pores formed in the matrix and decreased the density of sample. Considering that high temperature and low CO partial pressure are favorable to the CRN reaction in view of thermodynamics reason and high temperature also favors the transport of gases, increasing the heating temperature is an efficient means to increase CRN reaction rate. Because of the difference in reactivity between graphite and carbon black, CRN reaction was the rate controlling step when graphite was used and solid solution of AlN was the controlling step when carbon black was utilized. CRN reaction could increase surface energy and lead to higher final density. However, gases in the system tended to decrease the final density.

Acknowledgments

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References

Oxidation Behavior of Magnesium Aluminum Oxynitride

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Oxidation behavior of spark plasma sintered (SPS) magnesium aluminum oxynitride (MgAlION) was investigated in this study. Monophasic MgAlION without pores was easily obtained and evaporation was sufficiently limited by the utilization of the SPS process. The MgAlION powder was oxidized above 750°C, and a detectable mass gain of the MgAlION plate could not be obtained below 1200°C, because the oxidation reaction was of a very low level and occurred only on the surface. High temperature was favorable to oxidation reaction. According to the isothermal mass gain and evolution of oxidized morphology of the plates oxidized at different temperature, it could be deduced that the oxidation of MgAlION was limited by interface reaction. To analyze more profoundly, an oxidation model was proposed.

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Key-words: Magnesium aluminum oxynitride (MgAlION), Oxidation behavior, Spark plasma sintering (SPS), Interface reaction, Controlling step

1. Introduction

Magnesium aluminum oxynitride (MgAlION), a solid solution material with high melting point, was proposed by Jack in 1976. And some relative studies, such as oxidation behavior, reactivity, and synthesis processes, have been carried out recently. As an oxynitride, oxidation behavior is one of the most important high-temperature properties and the overall oxidation reaction follows

\[ \text{MgAlION} + O_2 \rightarrow \text{MgAl}_2\text{O}_4 + \text{Al}_2\text{O}_3 + N_2 \]  (1)

Wang et al. have investigated some properties of hot pressed MgAlION and proposed that the oxidation of MgAlION would be limited by gas diffusion because of the protective of oxidized layer. However, as shown in Fig. 1, the oxidized layer of MgAlION is porous though the tested sample is in full density. Obviously, gas diffusion in the oxidized layer may not be the controlling steps during the oxidation of MgAlION. So the oxidation behavior of MgAlION needs further research.

On the other hand, according to the thermodynamic analysis, it is known that evaporation occurs at high temperature and rapid heating process might be favor to decrease the effect. Though some efforts have been taken to decrease the evaporation of MgAlION, they are not so efficient because of their long soaking time at high temperature. Moreover, to decrease the effect of impurity and pores on the investigation of oxidation behavior, dense samples in high purity are required. Fortunately, a newly developed sintering technical, spark plasma sintering (SPS), with application of mechanical pressure and an on-off DC current, is an efficient means to prepare dense samples in short time. That’s why SPS is used to prepare MgAlION in our present experiment.

Raw materials with the composition same as Wang et al. are utilized and our objective here is to further study the oxidation behavior of MgAlION and find a more reasonable oxidation model.

2. Experimental procedure

2.1 Sample preparation

High purity starting materials in small size, MgO (0.24 μm, >99.9%), Al₂O₃ (0.1 μm, >99.9%), and AlN (0.7 μm, >99.2%), with molar proportions of 4:13:3 were meetilcous weighed before milled in pet with alumina balls by using ethanol as dispersion. Subsequently, the slurry was vacuum dried in rotary evaporator (Model BUCHI R-134 rotavapor, SIBATA, Tokyo, Japan) and then the dried powders were placed in a graphite die and then set in SPS system (Model DR. SINTER 820S, Sumitomo Heavy Industries, Ehime, Japan). After the chamber was evacuated to less than 5 Pa and flushed with nitrogen (purity >99.999%), repeatedly, the green samples were heated to 1700°C in 20 min and then held at 1700°C for 10 min under the pressure of 30 MPa.

The plates for oxidation test were cut from SPSed samples by using a conventional mechanical cutting procedure. After ground with a diamond wheel to 10×10×3.6 mm, the plates were rough polished and the edges were chamfered at 45°. On the other hand, some SPSed samples were pulverized into less than 10 μm in an agate mortar to prepare powders for oxidation test.

2.2 Oxidation test

Oxidation tests of the powders and plates prepared by SPS were conducted under dry air flowing on thermo-gravimeter (TG, Model TG/DTA 6300, Seiko Instruments, Tiba, Japan) (_Pt crucible, 0.21 min⁻¹_) and MoSi₂ furnace (ventilating _Pt net, 2 l min⁻¹_), respectively. Moreover, the mixed raw powders after drying were also tested by TG. The non-isothermal tests of powders and plates were conducted with the warming

Fig. 1. Morphology of MgAlION oxidized at 1400°C for 14.5 h, black areas are pores or cracks.
up rate at 5°C min⁻¹. As to the isothermal oxidation of plates, they were placed into the furnace later after that had arrived the setting temperature for 30 min. The oxidized plates were cut parallel and about 5 mm to the edge and the cross sections were polished up to 0.5 μm. All the polished plates were ultrasonically cleaned in ethanol and then kept in desiccators before characterization.

2.3 Characterization
Microstructure and element distribution were characterized by field emission scanning electron microscope (FE-SEM, Model JSM6340F, JEOL, Tokyo, Japan) equipped with energy-dispersive X-ray spectrocope (EDAX). Phase composition was determined by X-ray diffraction (XRD, Model RINT2200, Rigaku, Tokyo, Japan). The content of Mg and Al was measured by X-ray fluorescence spectroscope (XRFs, Model Simultix12, Rigaku, Tokyo, Japan), and O, N by oxygen and nitrogen analyzer (Model EMGA650, HORIBA, Kyoto, Japan). Bulk density was measured by automatic gravimeter (Model SGM-6, Mettler-Toledo International, Ohio, USA) and true density was analyzed by multi pycnometer (Model MVP-1, YUASA IONICS, Massachusetts, USA).

3. Results and discussion
3.1 Phase composition and structure of prepared sample
As shown in Fig. 2, monophase MgAlON was obtained by SPS in a rapid heating process. Excitingly, as listed in Table 1, the difference of chemical composition between raw materials and prepared MgAlON was so small that the evaporation was sufficiently limited in present work. Moreover, as shown in Fig. 3, the synthesized sample was so dense that pores could not be seen in the matrix, and by the further testing, the density of sample was higher than 99.9% and it was denser than the ever reported. So, SPS process should be a better choice to prepare MgAlON than other processes.

3.2 Oxidation behavior of powders
Figure 4 shows the weight change of mixed raw powders and SPSed MgAlON powders. As the grain size of the raw powders was so small, it was inevitable that some water was attached, which may be reasonable to explain why the weight loss below 700°C. Oxidation of MgAlON powders and raw powders almost started at about 750°C and maximum weight change of raw powders caused by oxidation reaction was about 1.8% while that of prepared MgAlON powders was about 4.0%. As the chemical composition of raw powders had not obvious difference to the MgAlON powders (Table 1), there was an abnormal weight change during the oxidation MgAlON according to Eq. (1). The possible reason for the abnormal weight change was still unknown and it need further study.

3.3 Oxidation behavior of plates
Isothermal mass gain of plates oxidized at different temperature is shown in Fig. 5. Mass gain of plates oxidized at 1200°C followed a parabolic law and that of plates oxidized at higher temperature close obeyed linear laws. As mass gain would obey a parabolic rate law when the reaction was limited by gas diffusion and follow a linear law when controlled by interface reaction, interface reaction might be the controlling step during the oxidation of MgAlON. However, Wang et al. considered that the gas diffusion would be the controlling step from 1200°C–1500°C except for the short initial surface oxidation reaction. On the other hand, since lots of pores and cracks existed in the oxidized region (Fig. 1), the resistance of gas diffusion was in low level. So, there were some flaws in the proposition of Wang et al. To clarify the oxidation behavior, the evolution of morphology of oxidized plates was dis-
Fig. 5. Isothermal mass gain \( \alpha = W/S, S \) is geometrical surface exposed to oxidation) of MgAION plates oxidized at different temperature.

Fig. 6. Mass gain of MgAION plates with respect to temperature.

cussed in Section 3.4. Figure 6 illustrates the oxidation behavior of plates with respect to temperature. Detectable mass gain could not be obtained lower than 1200°C even the powder could be oxidized as low as 750°C (Fig. 5). Over 1200°C, the oxidation rate increased with the increasing of temperature and it got to a high speed at 1600°C.

3.4 Morphology of oxidized plates

Figure 7 shows the morphology of plate oxidized at 1200°C for 26 h. Since grain-boundary/surface intersections in single-phase ceramics were the most active centers for oxidation, stress concentrations might occur at these areas and pores or cracks would be formed. In Fig. 7(a), cracks were recognized and micron-sized grains were discontinuously distributed on the surface of the oxidized plate, which implied that oxidation reaction had occurred and stress was generated during the oxidation process. According to the change of elemental distribution plotted in Fig. 7(c), an interface about 40 µm below the surface could be identified and the region with some change of element distributions was considered as oxidized layer and the region without obvious changes was un-oxidized layer. In the oxidized layer, cracks propagated along the grain boundaries, which implied that the stress caused by oxidation reaction was not so strong to crack the big grains. As cracks were formed on the surface and in the oxidized layer, the gas diffusivity would be in high level and the gas partial pressures near the surface and the interface should not have big difference. Hence, oxidation reaction could not be prevented by the oxidized layer and gas diffusion should not be the con-

Fig. 7. Morphology of MgAION plates oxidized at 1200°C (a) Surface, the arrow shows one of cracks on the surface, (b) polished cross section, and (c) magnified microstructure showing in (b) with the pattern of elemental distribution.
trolling step, though the mass gain followed a parabolic law (Fig. 5). Even oxidized at 1200°C for 26 h, the oxidation of MgAlON was kept in low level. Consequently, detectable mass gain could not be obtained below 1200°C during non-isothermal testing (Fig. 6). As stress was generated during oxidation process, the stability of grain boundary was decreased and some stresses would transfer to un-oxidized layer. Consequently, areas with residual stress, which was formed during sintering process, were very active and cracks were favor to be formed in these areas. Hence, as shown in Fig. 7(c), cracks along the grain boundary could be observed even about 70 µm below the interface. Figures 8(a) and (b) show the surface and inner morphology of plate oxidized at 1400°C. An interface between oxidized layer and un-oxidized layer could be distinguished easily. The morphology was very different to that of plate oxidized at 1200°C and lots of pores and cracks existed in the oxidized layer. Elemental distributions of Mg and Al near the surface and the interface are plotted in Figs. 8(c) and (d). The dense thin surface layer (about 1 µm) and reticular materials around big grains were made of Al₂O₃. As the big grains were surrounded by Al₂O₃ and the content of Mg of the big grains in oxidized layer was higher than that in the un-oxidized layer, it could be deduced that Al₂O₃ were precipitated from big grains during oxidation reaction. If the oxidation of MgAlON was controlled by the gas diffusion, gradient of gas partial pressure should exist, and the morphology near the surface would be different to that near the interface. However, the morphology near the surface (Fig. 8(c)) was very similar to that near the interface (Fig. 8(d)). Moreover, as lots of pores and cracks were formed in the oxidized layer, the resistance of gas diffusion by oxidized layer should in low level. In addition, as described in Fig. 5, the mass gain behavior of plates oxidized at 1400°C followed a linear law. Hence, gas diffusion would not be the controlling step during oxidation of MgAlON and interface reaction should be the case. In samples oxidized at 1400°C, the stress yielded by oxidation reaction was so stronger that that big grain could not withstand and cracks of big grain were

Fig. 8. Morphology of MgAlON plates oxidized at 1400°C (a) surface, (b) low magnified cross section, (c, d) high magnified cross sections near the surface and the interface with the pattern of elemental distribution, arrows show cracks of grains.
observed. Consequently, the amount of stress transferred from oxidized layer to un-oxidized layer was increased and the cracks in the inner of the interface were more obvious. Hence, the resistance of interface was decreased and the oxidation reaction was in high rate. As to the MgAlON plate oxidized at 1200°C, the stress caused by oxidation was in low level and the interface could not be damaged easily. Hence, the oxidation rate was low and mass gain followed a parabolic law. But, the oxidation of MgAlON at 1200°C would also be controlled by interface reaction. The morphology of plate oxidized at 1500°C is shown in Fig. 9. Because of the increasing of oxidation temperature, the precipitated Al₂O₃ grains on the dense thin surface were more homogenous. Considering that the width of precipitated Al₂O₃ between big grains was thicker and the original big grains became smaller and smoother with the increasing of oxidation degree, it could be deduced that the big grains in oxidized region should be MgAlON. The oxidation interface became more illegible than that of plate oxidized at 1400°C and the amount of cracks in the inner of the interface was increased, which implied that the stress was increased with temperature. Hence, it was reasonable to assume that at 1600°C, the stress was much higher than 1500°C and as a result, the oxidation rate was very high (Fig. 6).

3.5 Oxidation model

According to the above discussion, an oxidation model could be schematically drawn in Fig. 10. When lower than 1200°C, the stress caused by oxidation was in low level, the interface could not be damaged easily and the further oxidation reaction was retarded. At higher temperature, stress caused by oxidation reaction was increased and even over the critical values that MgAlON grain could resist, the interface could not withstand the stress then oxidation proceeded on from surface to inside step by step in relative high rate.

4. Conclusions

Monophase magnesium aluminum oxynitride (MgAlON) without pores was obtained by spark plasma sintering (SPS) process and utilized to further investigate the oxidation behavior. Oxidation reaction of MgAlON powder started at about 750°C, and detectable mass gain of MgAlON plate could not observed below 1200°C because oxidation reaction was in very low level and occurred only on the surface. Higher temperature was favor to oxidation reaction and the reaction continued on from surface to inside step by step because the interface could not withstand the stress caused by oxidation reaction. From this work, it was clear that the oxidation of
MgAlON was limited by interface reaction and not by gas diffusion, which was proposed before. According to the evolution of morphology, a model for oxidation of MgAlON was proposed.

References
Oxidation Behavior of Magnesium Aluminum Oxynitride with Different Composition

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Oxidation behavior of spark plasma sintered (SPS) magnesium aluminum oxynitride (MgAlON) with different composition was investigated in present work. Results showed that the variation in composition had not obvious effect on the density of MgAlON, but had some effect on excess weight change. Also found that the oxidation behavior of MgAlON was different with oxidation temperature, which was attributed to the transformation from γ-Al2O3 to α-Al2O3. Moreover, the excess weight change was ascribed to the existence of lots of vacancies in γ-Al2O3 and magnesium aluminate spinel (MgAl2O4).

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Key-words: Magnesium aluminum oxynitride (MgAlON), Oxidation, Composition, Weight change

1. Introduction

As known, MgAlON can be inevitably oxidized under oxidation atmosphere at high temperature and the oxidation behavior is one of its most important properties. When MgAlON is oxidized under certain condition, α-Al2O3 and magnesium aluminate spinel (MgAl2O4) are detected in the oxidized product. The reaction oxidation of MgAlON proposed by Wang et al. is as fellows:\footnote{11}

\[
\text{MgAlON} + \text{O}_2 \rightarrow \text{MgAl}_{2}\text{O}_{4} + \text{Al}_2\text{O}_3 + \text{N}_2
\]

In their report, no intermediate oxidized products have been obtained. On the other hand, it has been reported that the solid solution of Al2O3 and AlN into MgAl2O4 forms MgAlON and the amount of dissolved materials has relatively wide ranges at high temperature.\footnote{21} So, oxidation behavior and density of MgAlON might change with the composition. In addition, we have obtained an excess weight change during the oxidation of MgAlON powder in the previous study.\footnote{21} But, the effect of chemical composition on density and oxidation behavior has not been mentioned in the earlier reports.

Our objective here is to investigate the influence of chemical composition of MgAlON on its density and excess weight change, and to further discuss the oxidation mechanism of MgAlON at elevated temperature.

2. Experimental procedure

2.1 Preparation of MgAlON

The raw materials of MgO (particle size, ~0.24 μm; purity, >99.9%), Al2O3 (~0.1 μm; >99.99%), and AlN (~0.7 μm; >99.2%) were meticulously weighed according to Table 1, and milled with alumina balls by using ethanol as dispersion. Subsequently, the slurry was dried in a vacuum rotary evaporator (Model BUCHI R-134 rotavapor, SIBATA, Tokyo, Japan) and then the dried powders were placed in a graphite die and set in a SPS machine (Model DR. SINTER 820S, Sumitomo Heavy Industries, Eihime, Japan). After the chamber was repeatedly evacuated to less than 5 Pa and flushed with nitrogen (purity >99.999%), the samples were heated to 1700°C in 20 min and then held at 1700°C for 10 min under the pressure of 30 MPa.

2.2 Oxidation test

In present work, the oxidation behavior of MgAlON powders and plates was integrally surveyed. The powders less than 10 μm were pulverized from the SPSed samples in an agate mortar. The plates were cut from the SPSed samples by using a conventional mechanical cutting procedure. After ground with a diamond wheel to 10×10×3.6 mm, the plates were roughly polished with the edges chamfered at 45°. The oxidation tests of the powders and plates were conducted under flowing dry air by a thermo-gravimetry (TG, Model TG/DTA 6300, Seiko Instruments, Thiba, Japan) (Pt crucible, 0.21 min\(^{-1}\)) and a MoSi2 furnace (ventilating Pt net, 2.1 min\(^{-1}\)), respectively. The oxidation tests of powders were carried out with the heating rate at 5°C min\(^{-1}\) and then soaked at different temperature for presetting time. The plates were placed into the furnace later after the furnace had arrived the setting temperature for 30 min. Then, the oxidized plates were cut along the middle lines and the cross sections were well polished. All the polished plates were ultrasonically cleaned in an ethanol and then kept in a desiccate before characterization.

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4*</th>
<th>S5*</th>
<th>S6*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio</td>
<td>Mass%</td>
<td>Molar ratio</td>
<td>Mass%</td>
<td>Molar ratio</td>
<td>Mass%</td>
<td>Molar ratio</td>
</tr>
<tr>
<td>MgO</td>
<td>1</td>
<td>3.38</td>
<td>4</td>
<td>17.49</td>
<td>4</td>
<td>9.94</td>
</tr>
<tr>
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<td>10</td>
<td>86.22</td>
<td>7</td>
<td>78.03</td>
<td>13</td>
<td>82.41</td>
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<tr>
<td>AlN</td>
<td>3</td>
<td>10.40</td>
<td>1</td>
<td>4.48</td>
<td>3</td>
<td>7.64</td>
</tr>
</tbody>
</table>

* S4-S6 is 3 mass%, 6 mass%, and 9 mass% of additional MgO added into S3, respectively.

409
2.3 Characterization
Microstructures and elemental distributions were observed by field emission scanning electron microscope (FE-SEM, Model JSM-6340F, JEOL, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDAX) and SEM (Model JXA-8621MX, JEOL, Tokyo, Japan) equipped with wavelength dispersion spectrometer (WDS). Phases were identified by X-ray diffraction (XRD, Model RINT2200, Rigaku, Tokyo, Japan) by using Si (purity >99.999 mass%) powders as internal standard material. The contents of Mg and Al were measured by X-ray fluorescence spectroscopy (XRFS, Model Simultix12, Rigaku, Tokyo, Japan), and those of O and N were tested by oxygen and nitrogen analyzer (Model EMGA650, HORIBA, Kyoto, Japan). The bulk density was measured by an automatic gravimetry (Model SGM-6, Mettler-Toledo International, Ohio, USA) and the true density was analyzed by a multi pycnometer (Model MVP-1, YUASA IONICS, Massachusetts, USA).

3. Result and discussion
3.1 Properties of prepared samples
All the SPsed samples were identified by XRD as monophase MgAlON. The relative densities were higher than 99.9%, and as shown in Fig. 1, pores were seldom in these samples.

As listed in Table 2, though the samples had some difference in chemical composition, the deviation of the true densities was very small. So, the influence of the amount of dissolved Al₂O₃ and AlN could be neglected. The conclusion expanded the viewpoint on the solid solution of cubic spinel, for Nakagawa has proposed that the amount of dissolved Al₂O₃ has a minor influence on the density of MgAl₂O₄.⁴

3.2 Effect of oxidation conditions on weight change and product
Figures 2 and 3 show XRD patterns of S3 oxidized at variation conditions and their maximum weight changes (Wₚ) during oxidation process, respectively. The oxidation rate was very slow below 1000°C. When above it, the oxidation rate dramatically increased. Worth to note that though the weight changes were obtained in the samples oxidized as low as 900°C, the XRD patterns of their products were still similar to that of MgAlON until to 1100°C. When oxidized at 1200°C, α-Al₂O₃ was detected in the oxidized products besides the cubic spinel crystalline.

3.3 Effect of oxidation conditions on the microstructure of plates
Figures 4(a)-(d) show the BSE image and X-ray dot maps for Mg, Al, and O obtained from an area beside the interface of oxidized layer and un-oxidized layer of S1 oxidized at 1400°C for 14.5 h. Figure 4(e) shows the distribution of N of a big grain in the oxidized layer approaching to the interface.

---

Table 2. Chemical Composition (mol%) and True Densities of the SPsed Samples as well as Some Results about Weight Change

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
</tr>
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<tbody>
<tr>
<td>Mg</td>
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<td>8.68</td>
<td>5.10</td>
<td>6.28</td>
<td>7.54</td>
<td>8.68</td>
</tr>
<tr>
<td>Al</td>
<td>39.82</td>
<td>33.74</td>
<td>36.80</td>
<td>35.82</td>
<td>34.91</td>
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<td>O</td>
<td>53.85</td>
<td>56.09</td>
<td>54.90</td>
<td>54.83</td>
<td>54.65</td>
<td>54.55</td>
</tr>
<tr>
<td>N</td>
<td>4.66</td>
<td>1.49</td>
<td>3.20</td>
<td>3.08</td>
<td>2.90</td>
<td>2.75</td>
</tr>
<tr>
<td>True density (g cm⁻³)</td>
<td>3.67</td>
<td>3.62</td>
<td>3.65</td>
<td>3.64</td>
<td>3.64</td>
<td>3.63</td>
</tr>
<tr>
<td>Theoretical weight change (Wₚ)</td>
<td>2.28</td>
<td>0.73</td>
<td>1.56</td>
<td>1.51</td>
<td>1.42</td>
<td>1.35</td>
</tr>
<tr>
<td>maximum weight change (Wₚ)</td>
<td>4.77</td>
<td>2.13</td>
<td>4.01</td>
<td>3.59</td>
<td>3.33</td>
<td>2.76</td>
</tr>
<tr>
<td>Excess weight change (Wₚ)</td>
<td>2.49</td>
<td>1.40</td>
<td>2.45</td>
<td>2.08</td>
<td>1.91</td>
<td>1.41</td>
</tr>
</tbody>
</table>

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Fig. 1. SE image of cross section of S1.

Fig. 2. XRD patterns of the oxidized products of S3 oxidized at different condition. (A) synthesized SPsed sample, (B) oxidized at 900°C for 12 h, (C) oxidized at 1000°C for 12 h, (D) oxidized at 1100°C for 6 h, (E) oxidized at 1200°C for 3 h, and (F) oxidized at 1300°C for 3 h.
Fig. 3. Maximum weight change of S3 oxidized at different conditions. (A) oxidized at 900°C for 12 h, (B) oxidized at 1000°C for 12 h, (C) oxidized at 1100°C for 6 h, (D) oxidized at 1200°C for 3 h, and (E) oxidized at 1300°C for 3 h.

Fig. 5. (a) BSE image and X-ray dot maps for (b) Mg, (c) Al, and (d) O obtained from a polished cross section of S1 oxidized at 1200°C.

MgAlON, the precipitation of Al2O3 caused the enrichment of Mg of MgAlON grains in the oxidized layer.

Figures 5(a)–(d) illustrate BSE image and X-ray dot maps for Mg, Al, and O obtained from S1 oxidized at 1200°C for 26 h. Worth to note that though lots of Al2O3 were precipitated in the oxidized layer, the amount of pores and cracks was small. In addition, the size of MgAlON grains in the oxidized layer was much bigger than that in the S1 oxidized at 1400°C.

3.4 Oxidation mechanism of MgAlON

During the oxidation of single phase ceramics, stress always concentrated at grain-boundary/surface intersections. When the stress exceeded a critical value, pores and cracks were formed in the structure. In respect that the densities of MgAlON (Table 2) approximated to those of γ-Al2O3 (~3.5 g cm⁻³) and MgAl2O4 (~3.6 g cm⁻³) and much lower than that of α-Al2O3 (~3.97 g cm⁻³), stress aroused from the oxidation of MgAlON was much lower when γ-Al2O3 was the oxidation product rather than α-Al2O3. Thus, the amount of formed pores and cracks was small when γ-Al2O3 was the main phase in the precipitated Al2O3. When α-Al2O3 was the main phase, lots of pores and cracks were formed. On the other hand, even γ-Al2O3 could transfer to α-Al2O3 as low as 1000°C, the rate of conversion was very low until 1200°C. At higher temperatures, the rate of the phase transformation increased with temperature.

Figure 5 revealed that the microstructure of the plate oxidized at 1200°C kept dense with lots of Al2O3 precipitation. So, γ-Al2O3 must form during the oxidation of MgAlON and it was the main product of the precipitated Al2O3 at this condition. Because of phase transformation, stress was intense when oxidized at 1400°C. As shown in Fig. 4, lots of pores and cracks were formed in the oxidized layer. In addition, in view of the similarity of XRD patterns among γ-Al2O3, MgAl2O4, and MgAlON, the formation of γ-Al2O3 was not observable by XRD pattern of necessity (Fig. 2). So, Wang et al. did not find the intermediate oxidation product.

According to the above discussion, the oxidation reaction of MgAlON could be divided into two regimes:

(1) 750°C < T ≤ 1200°C

Step1: (MgAlON) (low Mg) + O₂ → MgAlON (high Mg) + γ-Al₂O₃ + N₂

(2)
Oxidation Behavior of Magnesium Aluminum Oxynitride with Different Composition

Fig. 6. Weight changes \(W = \Delta m/m, \Delta m\) is the weightness before testing, \(\Delta m\) is the change of weightiness of prepared samples with different composition with respect to the oxidation temperature and soaking time.

\[
\text{Step 2: (MgAlON)}_{(\text{high Mg})} + O_2 \\
\rightarrow \text{MgAl}_2\text{O}_4 + \gamma-\text{Al}_2\text{O}_3 + N_2 \tag{3}
\]

\(1200^\circ C < T\)

\[
\text{Step 1: (MgAlON)}_{(\text{low Mg})} + O_2 \\
\rightarrow \text{MgAlON}_{(\text{high Mg})} + \gamma-\text{Al}_2\text{O}_3 + N_2 \tag{4}
\]

\[
\text{Step 2: } \gamma-\text{Al}_2\text{O}_3 \\
\rightarrow \alpha-\text{Al}_2\text{O}_3 \tag{5}
\]

\[
\text{Step 3: (MgAlON)}_{(\text{high Mg})} + O_2 \\
\rightarrow \text{MgAl}_2\text{O}_4 + \alpha-\text{Al}_2\text{O}_3 + N_2 \tag{6}
\]

3.5 Effect of composition on excess weight change
Weight changes of the MgAlON powders with different composition versus oxidation temperature and soaking time are shown in Fig. 6. All the samples were oxidized above 750°C, and the weight changes of S1 and S3 had a decrease with the prolonging soaking time. According to Eq. (1), the theoretical weight changes \(W_T\) were calculated and shown in Fig. 7 and Table 2. But, all of them were lower than \(W_M\) obtained from TG analysis. In present work, the excess weight changes \(W_E\) were defined as

\[W_E = W_M - W_T\tag{7}\]

and shown in Fig. 7 and Table 2. From Fig. 7, it was very interesting to observe that \(W_E\) decreased almost in linear according to the equation,

\[W_E = -29.07 \times [\text{Mg}]\% + 3.9285 \quad (5< [\text{Mg}] < 9) \tag{8}\]

with \([\text{Mg}]\%\) in mol\% in the MgAlON phase. But, when the content of Mg was less than 5 mol\%, \(W_E\) had not obvious change.

It was reported that the oxidation of oxynitride was the substitution of N by O, and the discharged N was in atomic state. In addition, if oxidized product had vacancies, the N and other elements had chance to occupy the vacancies when the elements diffused through the material. Thus, excess weights change was obtained. In Eqs. (2)-(6), \(\gamma-\text{Al}_2\text{O}_3\) and \(\text{MgAl}_2\text{O}_4\) were the materials with lots of vacancies. So, excess weight changes occurred during the oxidation of MgAlON.

Referring to relative diagram, the MgAlON with higher content of N and lower content of Mg led to more \(\gamma-\text{Al}_2\text{O}_3\) forma-

tion, and vice versa. In view of the law of phase transformation, it was known that the amount of remained \(\gamma-\text{Al}_2\text{O}_3\) could be neglected when the samples with high content of Mg and low content of N oxidized at 1300°C. Hence, the excess weight changes of these samples were solely ascribed to the dissolution of elements into \(\text{MgAl}_2\text{O}_4\). As \(\text{MgAl}_2\text{O}_4\) was stable at this condition, the weight changes were constant with the prolonging soaking time (Fig. 6). On the contrary, some \(\gamma-\text{Al}_2\text{O}_3\) might remain initially when the samples with high content of N and low content of Mg oxidized at 1300°C. So, the excess weight changes were caused by the dissolution of elements into \(\gamma-\text{Al}_2\text{O}_3\) and \(\text{MgAl}_2\text{O}_4\). Since \(\alpha-\text{Al}_2\text{O}_3\) was the crystal with fewer vacancies, the dissolved elements in \(\gamma-\text{Al}_2\text{O}_3\) in the initial stage were discharged with the prolonging soaking time. Thus, as shown in Fig. 6, the weight change of S1 and S3 had a decrease.

In addition, due to the decrease of the Mg site to accept the excess Al ion, the solubility of elements increased with the decreasing of the content of Mg. Thus, the excess weight change decreased with the content of Mg (Fig. 7). However, it was unknown until now how the excess weight change had not obvious change when the content of Mg was less than 5 mol\%.

4. Conclusions
The present work mainly investigated the oxidation behavior of spark plasma sintered (SPS) magnesium aluminum oxynitride (MgAlON) with different composition. The variation of composition almost no affect on density but had some effects on excess weight change. Because of the transformation from \(\gamma-\text{Al}_2\text{O}_3\) to \(\alpha-\text{Al}_2\text{O}_3\) at high temperature, the oxidation behavior of MgAlON was different with oxidation temperature. Moreover, the excess weight change was ascribed to the vacancies of \(\gamma-\text{Al}_2\text{O}_3\) and magnesium aluminate spinel (\(\text{MgAl}_2\text{O}_4\)).

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Preparation of slaking resistant CaO aggregate from lightweight CaCO₃ with oxide addition

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Abstract

CaO aggregate was sintered from reagent-grade lightweight CaCO₃ powder by the addition of 0–20% (molar ratio) MgO and ZrO₂, respectively. The results showed that the CaO derived from lightweight CaCO₃ was highly sinterable and compact CaO aggregate with relative density above 90% was obtained after sintering at 1400 °C for 2 h, but further increase of compactness was restrained due to the occurrence of abnormal grain growth. The densification of the aggregate was promoted due to the behavior of oxide addition on restraining the grain growth of CaO. With increasing the amount of oxide addition, the microstructure of CaO aggregate underwent a restructuring process. Homogeneous microstructure, with well growing MgO grains occupying most of the boundary triple points of CaO grain, formed by the addition of 20% MgO. Especially when 20% ZrO₂ was added, CaZrO₃ layer formed around CaO grains. The slaking resistance of the aggregate was appreciably improved due to the promotion of densification, the formation of CaO solid solution (while MgO added) and the modification of microstructure.

Keywords: Lime refractories; Lightweight CaCO₃; MgO; ZrO₂; Sintering; Slaking resistance

1. Introduction

Lime has the properties of high melting temperature, low vapor pressure, and thermodynamic stability in the presence of carbon as well as high alkalinity, thus it has long been considered to be used as the raw materials for high temperature ceramics (such as crucible and ceramic filter), refractories and metallurgical accessories (such as refining slag and tundish covering powder) [1–5]. With the development of high temperature technology, lime containing materials are acting more and more important roles [6–11]. It is considered that application of CaO containing refractories is one of the essential directions for the development of metallurgical industries and other high temperature fields [12]. However, the application of CaO containing materials has been inhibited due to their drawback of poor slaking resistance, and many studies have been carried out on this subject [13–15].

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Oftentimes, the slaking resistance of lime aggregate is improved by increasing its compactness, and the traditional manufacture technology to produce lime aggregate is by two steps: firstly lightburnt lime is derived from limestone, and then the deadburnt lime aggregate is obtained by heating lightburnt lime at temperature above 1700 °C which leads to high energy consumption. Therefore, it is essential to develop a new technology to produce compact slaking resistant lime aggregate.

It is reported that CaO derived directly from the decomposition of lightweight CaCO₃ is very reactive and highly sinterable [16,17]. In the present work, the sintering property and effect of oxide addition on densification and slaking resistance were studied using synthetic lightweight CaCO₃ as raw materials. The purpose of this work is to find a new economic way for producing dense slaking resistant lime aggregate.

2. Experimental procedure

The starting materials were lightweight CaCO₃ powder and oxide additives. The lightweight CaCO₃ powder was reagent
grade with average diameter of 0.9 μm that was prepared from reagent grade CaCO₃ by precipitation reaction (details as described in a previous work [16]). Oxide additives were MgO and ZrO₂ powders. The former, MgO powder, was derived from heating reagent-grade Mg(OH)₂ powder at 600 °C, while the later, ZrO₂ powder, was from Sumidono Ltd, with average diameter of 0.046 μm and purity of 99.7%.

The two kinds of oxide powders were added to lightweight CaCO₃ respectively and wet-mixed with acetone using a ball mill in the molar proportion of CaO/oxide additive = (100−x)/x (x = 0−20). After being dried completely, the mixed powder was shaped into a 20 mm by 20 mm by 7 mm sized compact by using a cold isostatic press (CIP) under a pressure of 100 MPa. The compacts were then heated to 1300−1600 °C at a rate of 10 °C/min in an electric furnace. After soaking at different temperatures, the sample was cooled at the same rate as that of heating.

The sintered samples were characterized by carrying out bulk density, phase composition, and microstructural analyses as well as a slaking test. Bulk density was measured by liquid displacement using Archimedes’ principle in kerosene. Phase compositions were analyzed by X-ray powder diffraction (Cu target, 30 kV and 30 mA). Lattice parameter of the sintered CaO was calculated by program according to the d values of the 4 strongest diffraction lines of (111), (200), (220) and (311) detected by X-ray diffraction. The microstructure was observed by SEM (scanning electron microscopy) attached with EPMA (electric probe micro analysis) on the polished surface after etching. The slaking resistance of CaO aggregates was evaluated by measuring the mass gain after soaking the sintered bodies under the conditions of 70 °C and 90% humidity.

3. Results and discussion

3.1. Densification

Fig. 1 shows the relative density of the CaO aggregate without oxide addition. It is observed that the relative density abruptly increased with temperature increasing from 1300 to 1400 °C when the relative density was 96.9%. This result shows that the lightweight CaCO₃ had considerable highly sintering activity, and the sintering temperature was much lower than that of the traditional one. But when further increasing temperature from 1400 to 1600 °C, there was only a slight increase in compactness.

Fig. 2 shows the relative density of aggregate with different amounts of oxide addition sintered at 1500 °C for 2 h. The relative density was appreciably increased by addition of MgO and ZrO₂. The relative density was 96.9% for the sample without addition, which
increased to 98.5% and 99.0% when 3% MgO and 3% ZrO₂ were added respectively. It is also observed that the densification was very sensitive to a small amount of additions (below 3%), and ZrO₂ addition was more effective than MgO on promotion of densification.

The changes of relative density with soaking time at 1500 °C are shown in Fig. 3. It is observed that for the sample without addition, the densification process was still in progress after soaking at 1500 °C for 2 h. By addition of oxides, the time necessary for completion of sintering was effectively shortened. Thus, it is considered that the shrinkage of the compact, or the full densification of compacts, was promoted by addition of oxides. In addition, it is also observed that the values of the line with 1% ZrO₂ is almost equal to that of 5% MgO added, indicating that the effect of 1% ZrO₂ addition was equivalent to 5% MgO addition on promotion of densification.

3.2. Phase composition and microstructure

XRD patterns showed that the added ZrO₂ reacted with CaO to form CaZrO₃, but there was not any new phase formed when MgO was added. The lattice parameter of CaO is shown in Fig. 4. It was 0.4811 nm (theoretical value is 0.4813 nm) for the sample sintered without MgO, which decreased to 0.4795 nm with increasing the addition of MgO to 3%, and no change was found with further increasing the content of MgO. From this result it is considered that the added MgO had formed solid solution with CaO and the solubility limit of MgO in CaO was around 2% under the present sintering conditions. But when ZrO₂ was added, there is no change in the value of lattice parameter, indicating that the added ZrO₂ did not form solid solution with CaO.

Microstructure observation shows that coarse CaO grains (53 μm), with irregular grain boundaries and most of pores within the individual grains, were observed for the aggregate without oxide addition, indicating the occurrence of discontinuous or abnormal grain growth (Fig. 5). While MgO was added, the grain size of CaO was sharply decreased (Fig. 6), with the elimination of most pores, and the fine MgO particles were found within CaO grains (Fig. 7a). This result shows that the densification of CaO compact was promoted by inhibiting grain growth when MgO was added. With increasing MgO content, the grain size of CaO decreased further, and the added MgO grew up and preferred to gather between CaO grains, often at grain-boundary triple points (Fig. 7b). Homogeneous microstructure, with well growing MgO grains occupying most of the grain-boundary triple points, formed when 20% MgO was added (Fig. 7c). When ZrO₂ was added, it was more effective on inhibiting grain growth of CaO (Fig. 7d–f), and a homogeneous microstructure with CaZrO₃ layers around CaO grains formed when 20% ZrO₂ was added.

3.3. Slaking resistance

Fig. 8 illustrates the dependence of oxide content on mass gains after the CaO aggregates were slacked under the conditions of 70 °C and 90% humidity for 96 h. The mass change was expressed by mass gain percent to the original mass of the samples. It is observed that the slaking resistance was effectively improved by oxide addition, and the addition of less than 5% was more effective. The mass gain after 96 h was 10% for the sample without MgO, and it decreased to 3.5% and 2.1% by addition of 5% MgO and 20% MgO, respectively. It is also observed that the addition of ZrO₂ was more effective on improving the slaking resistance of CaO aggregate. The mass gain was 1.9% when 5% ZrO₂ was added, and it decreased to merely 0.6% by addition of 20% ZrO₂.

4. Discussion

4.1. Effect of oxide addition on densification and microstructure

Discontinuous grain growth or secondary recrystallization is a common phenomenon that occurs on the sintering of oxide ceramics, giving rise to non-uniform microstructures. Due to the high sintering activity of the CaO derived from lightweight CaCO₃, discontinuous grain growth preferred to happen in the present work, with formation of coarse CaO grains containing many pores. With increasing the sintering temperature, the grain growth was promoted and the escaping of pores was inhibited, thus it is observed that there was only a slight increase in relative density when the temperature was increased from 1400 to 1600 °C (Fig. 1).

When oxides were added, these fine particles dispersed in the structure and inhibit the discontinuous growth by increasing the energy necessary for the movement of grain boundaries [18]. Thus, the movement of CaO grain boundaries was slowed down and the escaping of pores was promoted. When a small amount of oxides was added, these oxide particles were so small that the
grain boundaries of CaO were easily passed over, with the fine oxide particles inside CaO grains (Fig. 7a and d). When these oxide particles were so big with their content increasing that the grain boundaries would not pass over, thus these additives were observed at the grain boundaries, often at boundary triple points.

Since a part of the added MgO formed solid solution with CaO, only a part of it acted as inhibitor of grain growth. But when ZrO₂ was added, it did not form solid solution with CaO, and all of the added ZrO₂ reacted with CaO by solid phase reaction and acted as inhibitor of grain growth. Thus it was observed that the addition of a small amount ZrO₂ was more effective on restraining grain growth of CaO. Owing to the solid phase reaction happening, the microstructure was modified, with protective CaZrO₃ layer formed around CaO grains.

4.2. Improvement of slaking resistance

It is known that the slaking resistance of CaO aggregate is dependent on the reaction specific surface area that is related to the microstructure, including the relative density, pore distribution as well as grain size, etc. The CaO aggregate with high compactness and large CaO grains is considered to be more slaking resistant. In the present work, when MgO and ZrO₂ were added, the slaking resistance of CaO aggregate was improved due to the following reasons.

First, CaO solid solution was formed when MgO was added. Since the radius of Mg²⁺ cation (0.76 × 10⁻¹⁰ m) is smaller than that of Ca²⁺ cation (1.14 × 10⁻¹⁰ m) [19], the substitution of Ca²⁺ cation by Mg²⁺ cation contributed to the shrinkage of the lattice of CaO crystal, resulting in enhancement of the electrostatic
force among the ions in CaO lattice [20]. Thus the slaking resistance of CaO was improved by the formation of solid solution when MgO was added.

Second, the CaO grain was stabilized due to the promotion of densification by addition of MgO and ZrO₂, which effectively decreased the reaction specific surface area of the CaO aggregate.

Lastly, the slaking resistance was improved due to the modification of microstructure when the addition of MgO and ZrO₂ increased. It is well known that the slaking reaction always begins from the sites with crystal defects. Thus, the grain boundaries, especially the boundary triple points, are the poor slaking resistant sites. While enough MgO was added, and the well growing MgO grains occupying these sites, the slaking resistance of CaO aggregate could be effectively improved. Especially when CaZrO₃ layer formed by addition of enough ZrO₂, CaO grains were effectively isolated to circumstance, thus the slaking reaction was retarded and the slaking resistance was improved.

5. Conclusions

Based on the above results, the following conclusions were drawn when CaO aggregate was sintered from lightweight CaCO₃ by addition of MgO and ZrO₂.

1) The lightweight CaCO₃ was highly sinterable, and compact CaO aggregate with relative density above 96% was obtained after soaking at 1400 °C that was much lower than the present commercial sintering temperature. However, further increase of compactness was restrained due to the occurrence of abnormal grain growth.

2) The densification of CaO aggregate was promoted by addition of MgO and ZrO₂ due to their effect on restraining grain growth. In addition, the microstructure was modified by addition of MgO and ZrO₂. Homogeneous microstructure, with well growing MgO grains occupying most of the boundary triple points of CaO grain, formed by the addition of 20% MgO. Especially when 20% ZrO₂ was added, homogeneous CaZrO₃ layer formed around CaO grains.

3) The slaking resistance of CaO aggregate was improved due to the promotion of densification, the formation of CaO solid solution (while MgO was added) and the modification of microstructure. Especially when 20% ZrO₂ was added and CaZrO₃ layer formed around CaO grains, the slaking resistance of CaO aggregate was appreciably improved.

References

アルミナと黒鉛を出発原料とした$\text{Al}_4\text{O}_4\text{C}$の合成

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Synthesis of $\text{Al}_4\text{O}_4\text{C}$ from Starting Raw Materials of Alumina and Graphite

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Abstract: $\text{Al}_4\text{O}_4\text{C}$ has been reported to be a good additive for carbon-containing refractories. The present study investigated various factors influencing the synthesis of $\text{Al}_4\text{O}_4\text{C}$ by heating mixtures of $\text{Al}_2\text{O}_3$ and graphite in an argon atmosphere. The reactions in the powder mixtures were faster than those in the pressed compacts. The formation of $\text{Al}_4\text{O}_4\text{C}$ began from a temperature between 1500 and 1550°C. The optimum molar ratio of graphite to $\text{Al}_2\text{O}_3$ was 1.5 for the synthesis of $\text{Al}_4\text{O}_4\text{C}$. The quantity of $\text{Al}_4\text{O}_4\text{C}$ was decreased and $\text{Al}_2\text{O}_3$ remained more when the ratio was below 1.5, contrastively, $\text{Al}_2\text{C}_3$ was formed with a decrease of $\text{Al}_4\text{O}_4\text{C}$ when above 1.5. As the heating time was extended, $\text{Al}_4\text{O}_4\text{C}$ was increased gradually in cases of $C/\text{Al}_2\text{O}_3 \leq 1.5$, but $\text{Al}_4\text{O}_4\text{C}$ was decreased after an increase and at the same time $\text{Al}_2\text{C}_3$ was increased in cases of $C/\text{Al}_2\text{O}_3 > 1.5$. The formation mechanism of $\text{Al}_4\text{O}_4\text{C}$ was also discussed.

Key words: $\text{Al}_4\text{O}_4\text{C}$, Synthesis, $\text{Al}_2\text{O}_3$, Graphite, Carbon-containing refractories.

要 旨: $\text{Al}_4\text{O}_4\text{C}$は、炭素含有耐火物に対して良い添加剤であると報告されている。本研究では、$\text{Al}_2\text{O}_3$と黒鉛の混合物をAr雰囲気で加熱することによる$\text{Al}_4\text{O}_4\text{C}$の合成に及ぼす影響因子について検討した。空気率の大きい粉体での反応は、空気率の小さい成形体に比べて速かった。$\text{Al}_4\text{O}_4\text{C}$の生成は1500〜1550°Cの間から始まった。$\text{Al}_4\text{O}_4\text{C}$の合成に適した黒鉛と$\text{Al}_2\text{O}_3$のモル比は1.5であった。1.5より小さくなると、$\text{Al}_4\text{O}_4\text{C}$の量が少なくなり、残留$\text{Al}_2\text{O}_3$の量が増加することから、1.5を超えると、$\text{Al}_4\text{O}_4\text{C}$の量が減少することを同時に、$\text{Al}_2\text{C}_3$が生成した。加熱時間が長くなるにつれて、$C/\text{Al}_2\text{O}_3 \leq 1.5$では$\text{Al}_4\text{O}_4\text{C}$の量が徐々に増加したが、$C/\text{Al}_2\text{O}_3 > 1.5$では$\text{Al}_4\text{O}_4\text{C}$の量が始めのうち増加し、その後$\text{Al}_2\text{C}_3$の生成に伴って減少した。$\text{Al}_2\text{O}_3$と黒鉛の反応メカニズムについても考察を行った。

キーワード: $\text{Al}_4\text{O}_4\text{C}$, 合成, $\text{Al}_2\text{O}_3$, 黒鉛, 炭素含有耐火物

1 結言

$\text{Al}_2\text{O}_3$系や$\text{MgO}$系などの炭素含有耐火物において、炭素の酸化を防止し、耐火物の熱間特性を改善するなどの目的で、添加剤として金属アルミニウム(Al)が広く用いられているが、いくつかの問題がある。これら、金属Alは高温で耐火物中の炭素を反応して炭化アルミニウム($\text{Al}_4\text{C}_3$)を生成し、この$\text{Al}_4\text{C}_3$が冷却時に大気中の水と反応を起こすため、再昇温の際に耐火物の崩壊をもたらすこと4)。また、これが水と反応しやすいため、水系結合剤を用いる不定形耐火物に使用することはできないこと5)。さらに、微細な金属Al粉末が燃焼し易いので、その取り扱いに従間が伴うことである。

図1に$\text{Al}_2\text{O}_3$-$\text{Al}_4\text{C}_3$系相平衡の状態図6)を示す。この系には、常温から1890°Cまで安定である化合物$\text{Al}_4\text{O}_4\text{C}$が存在する。この化合物は、$P_{\text{CO}} = 0.101325 \text{MPa} (= 1 \text{atm})$のCO雰囲気において約800°CからCOガスと反応して$\text{Al}_4\text{C}_3$の生成を経由せずに$\text{Al}_2\text{O}_3$と炭素へ変化

平成18年11月10日受理、平成19年2月14日受理
し、また水和しない特徴を有するため、金属Al粉末よりも良い耐火物の添加剤であると報告されている。そのため、Al_{2}O_{3}C原料を多量に合成する方法についての研究が必要となっている。

Al_{2}O_{3}C耐火物での金属Alの挙動に関して、ZhangとYamaguchiは、Al_{2}O_{3}C、金属Alおよび黒鉛からなる混合物をAr雰囲気中で加熱して結晶相の変化を調べている。その結果、900℃でAl_{4}C_{3}、1300℃でAl_{4}O_{4}Cが生成し、1700℃まで昇温するとAl_{4}C_{3}の消失に伴ってAl_{4}OCが主相となることを示し、その反応機構として、金属Alと黒鉛の反応で先に生じたAl_{4}C_{3}は、さらにAl_{2}O_{3}と反応しAl_{4}OCを生成することを説明した。

一方、金属Alの製鍊分野において、Al_{2}O_{3}Cの炭素不揮発元による溶融金属Alの製鍊方法についての研究が報告されている。それによると、金属Alの生成には高い加熱温度が必要であり、またAl_{4}O_{4}C、Al_{4}OCおよびAl_{4}C_{3}の経路間の生成が伴う。例えば、Waiらは2300-2550KでのプラズマによるAl_{2}O_{3}の炭素不揮発元について検討し、Katkobらは2600K以上の不揮発温度が必要であることを述べた。また、KibbyらはAl_{4}O_{4}CおよびAl_{4}C_{3}を経て金属Alを生成する反応モデルを構築し、QiuらおよびLihrmannらはAl_{4}O_{4}Cの標準生成自由エネルギーを求めた。

本研究では、Al_{4}O_{4}C合成プロセスの開発に基礎的な知見を提供するため、金属Alを使用せず、Al_{2}O_{3}と黒鉛のみを出発原料としたAl_{4}O_{4}Cの合成方法について検討した。Ar雰囲気においてAl_{2}O_{3}と黒鉛との混合物を加熱し、生成物の結晶相に及ぼす炭素とAl_{2}O_{3}の混合比、混合物の状態（粉体および成形体）、加熱温度および加熱時間などの因子の影響を実験的に調査し、反応の機構を考察した。

2 実験方法

純度99.99mass%以上のアルミナ（大明化学工業㈱）および純度99mass%以上の黒鉛試薬（光薬純薬工業㈱）を出発原料とした。前者の平均粒径は0.1μmであり、後者の粒径は45μm以下と称されているが、顕微鏡の観察によると、大部分は20〜30μmであった。

所定比例の黒鉛とアルミナ（C/Al_{2}O_{3}モル比は0.5、1、1.5、2および3）にエタノールを加え、メノウ乳鉱で混合した後、真空回転式乾燥装置で混合物を乾燥した。次に、混合物の粉体（2g）を高純度の黒鉛つぼに入れ、電気炉（発熱体は黒鉛）の中に設置し、炉内を真空にした後、Arガスを送入した（Arガスは純度99.999%以上の超純度ものので、1700℃での酸素分圧をZrO_{2}酸素センサーで測定した結果、その分圧は10^{-28}MPaである）。Arガスの流量を1L/minと一定にし、10℃/minの速度で1500〜1700℃まで昇温してから、3〜9時間保持した。その後、電源を切って試料を炉内で冷却した（1700℃から1000℃までの平均冷却速度は64℃/min）。室温まで冷却した試料からサンプルを採取し、X線回折（XRD）により結晶相を同定した。また、微構造の観察およびEPMA分析を行った。

混合物の状態（粉体または成形体）の加熱後試料の結晶相に及ぼす影響を明確にするため、予備実験として、混合物の粉体を予め100MPaで加圧成形して得られた成形体を用いた実験を行った。

3 結果

3.1 混合物の状態の影響

C/Al_{2}O_{3}=1.5の混合物の粉体および成形体の1700℃、9時間加熱後各試料のXRDパターンを図2（a）、（b）に示す。加熱前の粉体試料中の空隙率は75%、成形体は39%であった。各結晶相のXRD最大強度を図3（a）にまとめた。いずれの場合もAl_{4}O_{4}Cが生成していたが、粉体でのAl_{4}O_{4}Cの生成量は成形体の場合より多かった。

また、C/Al_{2}O_{3}=3の混合物の粉体（空隙率：80%）および成形体（空隙率：37%）を1600℃で3時間加熱した場合の各結晶相の最大強度を図3（b）に示す。成形体の場合は、新しい相は生成せず、加熱前の結晶相と同じ
Fig. 2 XRD patterns of C/Al₂O₃=1.5 samples heated at 1700°C for 9h.

Fig. 3 Phases of powder samples and pressed compact samples heated.

であるのに対して、著体の場合は、Al₂O₃および黒鉛の量が低減し、Al₂O₃Cが生成していた。

以上の結果は、成形体よりも粉末の反応性の方が速いことを意味している。したがって、以下の実験では、すべて混合物の粉末を用いた。

3.2 加熱温度の影響

C/Al₂O₃ = 1.5および3の混合物をそれぞれ1500、1550、1600、1650および1700°Cで3時間加熱した。加熱後試料の結晶相の最大強度変化を図4（a）、（b）に示す。

いずれの場合も、1550°C以上で加熱した試料からAl₂O₃Cに検出され、加熱温度が高くなるにつれてAl₂O₃Cの生成量が増加し、同時にAl₂O₃および黒鉛の量が減少していた。1500°Cで加熱した試料からはAl₂O₃Cは検出されなかった。このことは、Al₂O₃Cの生成開始温度が1500〜1550°Cの間にあることを示している。ただ

し、C/Al₂O₃ = 1.5のときは、1600°CまでではAl₂O₃Cの生成量が少なく、1600°Cを超えるとその量は多くなった。C/Al₂O₃ = 3のときは、Al₂O₃Cの生成量は加熱温度の増加にしたがって徐々に増加し、1600〜1650°Cの間からAl₂O₃CおよびAl₂C₃も少量ながら生成しはじめた。

3.3 C/Al₂O₃の影響

1700°CでC/Al₂O₃ = 0.5、1、1.5、2および3の混合物をそれぞれ3と9時間加熱した。加熱後各試料中の各結晶相の最大強度変化を図5（a）、（b）に示す。

いずれの場合も、Al₂O₃Cの生成量は当初C/Al₂O₃の増加にしたがって増加し、C/Al₂O₃ = 1.5で最大値となった。C/Al₂O₃がさらに増すと、Al₂O₃Cの量が減少すると同時に、Al₂O₃およびAl₂C₃が生成した。9時間加熱の時はAl₂O₃Cは生成せず、Al₂C₃が生成し、その量はC/Al₂O₃の増加につれて大幅に増加した。

290
この結果から、C/Al₂O₃ = 1.5のときはAl₄C₃の生成量が最も多く、またAl₂OCおよびAl₄C₃が生じないため、Al₄C₃の合成には最も良い桑田比であると判断される。ただし、本実験において、Al₂O₃および黒鉛を含まない純粋なAl₄C₃は得られなかった。

3.4 加熱時間の影響

1700℃でC/Al₂O₃ = 1.5および3の混合物をそれぞれ3, 5, 7および9時間加熱し、加熱後試料の時における結晶相の最大強度変化を図6(a), (b)に示す。

C/Al₂O₃ = 1.5のときは、Al₄C₃のみが生成し、加熱時間が長くなるに従って、Al₄C₃の量が徐々に増加し、Al₂O₃および黒鉛の量が减少していた。

C/Al₂O₃ = 3のときは、Al₄C₃のほかAl₂OCおよびAl₄C₃も生成した。Al₂OCの量は5時間までは増加の傾向、その以後は減少の傾向を示した。Al₂OCは5時間まで

Fig. 4 Phases of samples heated at different temperatures for 3h.

Fig. 5 Phases of heated samples with different C/Al₂O₃ ratios.

では少量生成したが、7時間になると消失した。Al₄C₃は、加熱時間が長くなるにしたがって増加した。この結果から、この混合比ではAl₄C₃を最大限に生成すると同時に、Al₂OCおよびAl₄C₃量を抑制するには適した加熱時間があり、この場合は5時間であった。

3.5 合成物の微細構造

C/Al₂O₃ = 1.5の混合物の1700℃、9時間加熱試料を樹脂に埋め込み研磨し微細構造観察を行った。研磨面のSEM写真を図7(a), EPMA分析結果の一例を図7(b)に示す。粒径は10～100μm程度で、30～50μmのものが多かった。また、粒の内部には気孔がなく、緻密になっていた。EPMA面分析による粒の構成元素はAl、OおよびCであり、図2(a)に示したXRD分析結果と合わせると、その結晶相はAl₄C₃であると判断される。ただし、少数の粒の内部には、小さな鱗状の黒鉛が存在していることが観察された。それは、未反応で残留していた黒鉛と考えられる。
Fig. 6 Phases of samples heated at 1700°C for different times.

XRD分析結果によれば、この試料には少量のAI₂O₃も含まれていたが、その量は少なく、またサイズが小さすぎるためか、EPMA分析では検出されなかった。

4 考察

4.1 AI₂O₃Cの生成およびAI₄C₃への変化の反応

C/Al₂O₃が1.5以下で結晶相としての生成物がAI₂O₃Cのみであった結果（図5）から、この場合は次のような反応が生じたと考えられる。すなわち、AI₂O₃と黒鉛の粒が接触している最初の段階では、固相－固相間の反応

\[ 2AI₂O₃(s) + 3C(s) = AI₂O₃C(s) + 2CO(g) \]  

が起こった。粒の間が接触しなくなると、固相－COガス間の反応

\[ 2AI₂O₃(s) + 4CO(g) = AI₂O₃C(s) + 3CO₂(g) \]  
\[ CO₂(g) + C(s) = 2CO(g) \]

が生じた。反応(2)と(3)の全反応は反応(1)と同じ形になるが、AI₂O₃C(s)生成の主反応になったと推定される。

Fig. 7 SEM photograph and EPMA analysis of C/Al₂O₃=1.5 sample heated at 1700°C for 9h.

C/Al₂O₃が1.5を超えると、AI₄C₃も生成し、また加熱時間の延長によってAI₂O₃Cの生成量は増加の後AI₄C₃の生成に伴って減少した結果（図5、6（b））から、反応(1)に対してCが過剰なので、反応(1)～(3)で生成したAI₂O₃CはさらにCOと反応してAI₄C₃へ変化したと考えられる。すなわち、

\[ AI₂O₃C(s) + 8CO(g) = AI₄C₃(s) + 6CO₂(g) \]  

反応(3)と(4)の全反応は、

\[ AI₂O₃C(s) + 6C(s) = AI₄C₃(s) + 4CO(g) \]

になる。

AI₂O₃C、AI₂O₃CがAI₄C₃へ変化している過程で不安定な中间相として生成した後、AI₄C₃へ変わったと考えられる。すなわち、

\[ AI₂O₃C(s) + 4CO(g) = 2AI₂O₃C(s) + 3CO₂(g) \]
2Al₂O₃(C)+4CO(g)=Al₄C₃(s)+3CO₂(g)  (7)

全反応を表す反応(1)、(5)にしたがい、各化合物の標準生成自由エネルギー(Δ_fG°)から、本実験の加熱温度における炭素共存下でのAl₂O₃、Al₄O₉CおよびAl₄C₃の安定領域とCOガス分圧(P_CO)の関係を求めた。本実験の最高加熱温度の1700℃(1973K)での結果を図8に示す。実験④により、1715℃以下ではAl₂O₃が不安定なので、本計算にAl₂O₃-C系を入れなかった。計算に用いたAl₄O₉CのΔ_fG°(1)2)の示した式から算出し、Al₂O₃、Al₄O₉CおよびCOのそれは"JANAF熱力学データ"3)のデータを基に回帰解析で得られたものである。基準圧力(P°)は、いずれも0.101325MPa (=1atm)とした。

図8により、炭素共存下の1700℃において、Al₂O₃がAl₄O₉Cへ変化する臨界CO分圧P_CO(Al₂O₃→Al₄O₉C)は5.685×10⁻³MPa(logP_CO/P°)=1.251)、Al₄O₉CのAl₄C₃へ変化するそれP_CO(Al₄O₉C→Al₄C₃)は4.099×10⁻⁶MPa(logP_CO/P°)=1.393)であり、すなわち、Al₄O₉Cの安定領域は、P_CO=(4.099~5.685)×10⁻³MPaである。言い換えれば、実際のCO分圧が4.099×10⁻³MPa以下で、また炭素が共存している条件では、結晶相の生成物はAl₄O₉Cとなると、Al₄C₃となる。

前述したように、本実験においては、酸素分圧P_O₂が10⁻²⁰MPaの超常純度のArガスを1L/minの流量で流していた。Arガス中の酸素は発熱体のカーボンと反応し(1/2O₂+C(s)=CO(g))COガスを発生するとすれば、そのCOガス分圧は、1500~1700℃で約0.5×10⁻²⁰MPaとなる。これにより、本実験の加熱温度において、試料の上部にあるCO分圧は4.099×10⁻⁶MPaの臨界値より顕著に小さかったと推定される。C/Al₄O₉C比1.5の場合にAl₄C₃が生成せずAl₄O₉Cのみが生成した理由としては、Al₄O₉Cが生じた後黒鉬はほぼなく、Al₄C₃と共存する状態にはななかったことが推測される。

また、求められた各温度での臨界CO分圧P_CO(Al₂O₃→Al₄O₉C)、P_CO(Al₄O₉C→Al₄C₃)を図9に示す。これによると、熱力学上では、Al₄O₉CおよびAl₄C₃生成の開始温度は、いずれも雰囲気中COガス分圧の増大につれて高くなるが、P_CO=0.5×10⁻³MPaより顕著に高い10⁻⁶MPaであってもそれぞれ1180℃と1200℃になる。これらに比べ、図4に示したように、実際のAl₄O₉C生成の開始温度は1500~1550℃、Al₄C₃のそれは1600~1650℃と300~500℃高かった。これは、Al₄O₉CおよびAl₄C₃の生成にはその温度差に応じる活性炭化エネルギーが必要であること示唆していると考えられる。

なお、上述したことから、炭素共存下でAl₄O₉Cが安定となるCO分圧および温度の範囲はいずれも狭いことがわかる。この例によれば、1700℃でのP_CO(Al₂O₃→Al₄O₉C)/P_CO(Al₂O₃→Al₄C₃)の比は0.72であり、P_CO=10⁻⁶MPaでの温度範囲は20℃である。したがって、将来Al₄O₉C原料を大量に合成する場合には、雰囲気および温度を精密に制御することが必要であることが示された。

4.2 Al-O系気相の生成反応

加熱実験後、炉の内壁およびガス出口の付近には付着物が付着していることが観察された。この付着物は、SEM観察によるとナノサイズの粒子の凝集物であり、XRD分析によると、C、Al₂O₃、Al₄O₉CおよびAl₄C₃からなっていることが判明した。これらの生成、加熱中に試料から
発生した気相の揮発に起因したものと推定される。気相種としては、(1)～(7)式に示したCO、CO₂ガス以外に、Al₂O₃(g)、Al₃C₃(g)、Al₃O₃(g)およびAl₂O₃(g)などの気相も考えられる。

図8には、一例として1700℃でのAl₂O₃-C、Al₃C₃-CおよびAl₃O₃-C系におけるAl₂O₃、Al₃C₃の気相種の平衡圧力も示されている。これによると、いずれの系でも、ほかの気相よりAl₂O₃およびAl₂O₃(g)の圧力が高い。例えば、Al₂O₃-Al₃C₃-Cの平衡位置において、P(Al₂O₃) = 5.685×10⁻³MPaを1とすれば、P₂O₅, PAl₂O₃, P₃Al₂O₇, およびPAl₅O₁₂はそれぞれ2.237×10⁻², 1.943×10⁻², 5.529×10⁻², 2.018×10⁻⁷, 1.323×10⁻¹²となる。本実験の最低加熱温度の1500℃においても、同じ傾向がある。それゆえ、Alを含む気相は、主にAl₂O₃およびAl₂O₃(g)と推定される。これらの生成の反応として、(8)～(11)の反応が考えられるが、全反応は(8)、(10)の反応となる。

\[
\begin{align*}
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) &= 2\text{Al}(g) + 3\text{CO}(g) \\
\text{Al}_2\text{O}_3(s) + 3\text{C}(g) &= 2\text{Al}(g) + 3\text{CO}_2(g) \\
\text{Al}_2\text{O}_3(s) + 2\text{C}(s) &= \text{Al}_2\text{O}_3(g) + 2\text{CO}(g) \\
\text{Al}_2\text{O}_3(s) + 2\text{CO}(g) &= \text{Al}_2\text{O}_3(g) + 2\text{CO}_2(g)
\end{align*}
\]

生じた気相は、さらにAl₂O₃(s)と反応するとAl₃C₃、Al₃O₃を生成する。例えば、

\[
\begin{align*}
\text{Al}_2\text{O}_3(s) + 2\text{Al}(g) + \text{CO}(g) &= \text{Al}_3\text{C}_3(s) \\
\text{Al}_2\text{O}_3(s) + 3\text{Al}_2\text{O}_3(g) + 2\text{CO}(g) &= 2\text{Al}_2\text{O}_3C_3(s)
\end{align*}
\]

となるが、(8)+(12) = (1), (8)+(10) + 0.5×(13) = (1)となるので、気相を介しての反応も(1)式と同じ式で示される。

一部の気相は、温度の低い炉の上部へ揮発し、観察された付着物を生成したと考えられる。例えば、

\[
\begin{align*}
2\text{CO}(g) &= \text{C}(s) + \text{CO}_2(g) \\
4\text{Al}(g) + 3\text{CO}_2(g) &= 2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \\
4\text{Al}(g) + 3\text{C}(s) &= \text{Al}_3\text{C}_3(s) \\
2\text{Al}_2\text{O}_3(g) + \text{CO}_2(g) &= \text{Al}_2\text{O}_3C_3(s)
\end{align*}
\]

である。将来Al₂O₃-Cを多量に合成する場合は、原料のロスを減らすため、付着物回収の必要性が生じると考えられる。

4.3 微構造の形成機構

本実験に用いたAl₂O₃原料は平均粒径が0.1μmと微細なものであり、黒鉛粉末は平均粒径が20～30μmと比較的大きなものである。加熱前の2種類の原料の分布状態を示すモデルを図10(a)に示す。すなわち、Al₂O₃の粒は黒鉛粒子を被覆している状態である。以下C/Al₂O₃ = 1.5の場合について微構造形成機構の推定を行う。

最初は、黒鉛とAl₂O₃の界面で反応(1)、および反応(8)、(10)のような反応が起こり、結晶粒のAl₂O₃が生成すると同時に、CO、Al₂O₃などの気相が生じる。生じた気相は、空気を通じて界面から離れているAl₂O₃粒子の間へ拡散し、Al₂O₃と反応(2)、および反応(8)、(11)～(13)のような反応を起こし、続いてAl₂O₃を生成す
 Apartmenta and Al₂O₃ と黒鉛から純粋な Al₂O₃ と黒鉛の混合物を合体することは困難であるが、その Al₂O₃ と黒鉛を少量に含んでいる Al₂O₃ 合成原料でも、炭素含有耐火物の添加材として用いることができると考えられる。

文献
Sintering of Al$_2$O$_3$-Cr$_2$O$_3$ Powder Prepared by Sol-Gel Process

by

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The sol-gel method was applied to create Al$_2$O$_3$-Cr$_2$O$_3$ ceramics using aluminum ethylacetoacetate diisopropylate and chromium (III) chloride hexahydrate as starting materials. In the calcination at 600-1200°C it was found that the grains of Cr$_2$O$_3$-rich solid solution grew when they were exposed to the surrounding Al$_2$O$_3$-rich amorphous particles. The composition of the powders obtained by the sol-gel process changed with calcining temperature. Cr$_2$O$_3$-rich solid solutions firstly crystallize at low temperature and the composition of the crystallites changes as the crystals grow and react with the surrounding Al$_2$O$_3$-rich phases. The final sintered bodies fired under an Ar atmosphere showed higher relative densities as compared with those fired in air. A dense sintered body was not obtained when abnormal grains grew when calcining occurred.

Key words: Al$_2$O$_3$, Cr$_2$O$_3$, Solid solution, Sol-gel process, Sintering

1 Introduction

The amount of municipal wastes in Japan is about 50 million tons/year. About 80% of waste disposal relies on incineration. In this case, however, endocrine disruptors such as dioxin are present in the gas and fly ash exhausted from the incineration facilities. This problem has become serious social issues. Melting type incinerators such as gasification melting furnaces have been developed as a solution to this problem. In high temperature melting type incinerators the wastes are burnt and melted above 1300°C. Generally Al$_2$O$_3$-Cr$_2$O$_3$ refractories are used in such conditions.\(^1\!,\,2\!\)\(^2\!\)

The alkali and alkali-earth elements such as Na, K and Ca are present in the municipal wastes and corrode furnace lining refractories. Porous microstructure refractories are attacked so a dense body is used to avoid damage. Hirata et al. investigated densification and corrosion of Al$_2$O$_3$-Cr$_2$O$_3$ by addition of TiO$_2$.\(^3\!\!,\,4\!\)

Aluminium organometallic compounds\(^5\!\!,\,6\!\!,\,7\!\!) starting materials were used to obtain dense ceramics. The powders obtained from the starting material contained uniformly dispered fine particles. The sintered Al$_2$O$_3$-Cr$_2$O$_3$ body seemed to have corrosion resistance when the material was used in the same way.

Al$_2$O$_3$-Cr$_2$O$_3$ ceramic is a solid solution of Al$_2$O$_3$ and Cr$_2$O$_3$ has high chemical stability even at high temperatures and hence it is used as a refractory brick in gasification melting furnaces. Both Al$_2$O$_3$ and Cr$_2$O$_3$ are chemically stable at high temperature and take a corundum crystal structure forming a solid solution (Al$_{1-x}$Cr$_x$)$_2$O$_3$ in the entire composition region at high temperature (Fig. 1). At relatively low temperatures a miscibility gap is present in which two crystalline phases of Al$_2$O$_3$-rich and Cr$_2$O$_3$-rich solid solutions are present. As shown in Fig. 1, the critical temperature Tc depends on the surrounding pressure.\(^8\!\!,\,9\!\!,\,10\!\!\) A thermodynamically stable solid solution is necessary to obtain, and some conditions of the metastability are being researched now. Murakami et al.\(^11\!\!) confirmed a metastable two-phase region at around 1300°C. Bondioi\(^12\!\!) investi-

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gated two metastable phase by solid phases reaction and coprecipitation. When the different phases were observed in the heat-treated powder, reactivity was thought to influence sintering behavior.

Moreover, the vapor pressure of CrO₃ and Cr₂O₃ is high so that the sintered body of Cr₂O₃ becomes porous due to the evaporation of Cr-compounds when fired in air.

We prepared uniform precursor powder mixed at a molecular level, and then got Al₂O₃-Cr₂O₃ dense ceramics. In this paper we investigated the mechanism for the formation of solid solution. The effects of powder size and sintering atmosphere on sintering were investigated.

2 Experimental Procedures

The raw materials used were aluminum ethylacetacetae diisopropylate (ALCH, Kawaken Fine Chemicals Co., Ltd.) and CrCl₃·6H₂O (Wako Pure Chemical Industries Ltd.). ALCH and CrCl₃·6H₂O were dissolved in a 10 times the amount of raw material mole ratio of ethanol and were stirred and mixed with a homogenizer for 30 minutes and a supersonic homogenizer for 5 minutes. 30 times mole ratio of ion exchange water was slowly dropped with stirring and was mixed for 30 minutes with a magnetic stirrer to obtain gels at room temperature. The gels were dried in a rotary evaporator and calcined at 600–1200°C for 1h in air. After the calcinations the powders were mixed with a ball mill for 10h using an ethanol solvent and pressed into pellets of about 25mm in diameter. The green bodies were sintered at 1600°C for 1h in an atmosphere of air or Ar. Fig. 2 shows the sample preparation procedures.

For comparison Al₂O₃-Cr₂O₃ ceramics were also prepared by a conventional solid phase reaction. The starting powders of Cr₂O₃ (Kanto Chemical Co., Inc.) and α-Al₂O₃ (AES-12 Sumitomo Chemical Co., Ltd.) were mixed with a ball mill for 10h using an ethanol solvent.

The bulk densities of the sintered bodies were measured and the relative densities were also estimated from the experimental values and the theoretical densities calculated from the compositions. The crystalline phases were identified by X-ray diffraction (XRD ; Rigaku RINT2200VHF + /PC) with CuKα radiation. The microstructures of the specimens were observed by optical microscope and scanning electron microscope (SEM ; JEOL JSM-6340F).

3 Results and Discussion

3.1 Formation of solid solution

Fig. 3 shows the XRD patterns of the sol-gel derived powders of 10, 30 and 50 mol% Cr₂O₃ calcined at 600–1200°C. A/C = 50/50 implies an equimolar ratio of Al₂O₃ and Cr₂O₃. Two phases in the A/C = 50/50 sample calcined at 600°C with a Cr₂O₃ content richer than the nominal composition, were observed. The double peak turned into a single peak above 700°C. In the A/C = 70/30 sample, no peak appeared when calcined at 600°C, and a phase was found when calcined above 800°C. In A/C = 90/10 sample no peak appeared when calcined at 800°C, and a crystalline phase was found as calcined above 900°C. In all the compositions as the calcination temperature increased the peak shifted to the higher diffraction angle side (Al₂O₃-rich side). These results indicate that Cr₂O₃-rich solid solutions firstly crystallize at low temperature and the composition of the crystallites changes.

![Fig. 2 Sample preparation procedures.](image)

![Fig. 3 XRD patterns of the sol-gel derived powders of A/C = 90/10, A/C = 70/30 and A/C = 50/50 calcined at 600–1200°C. Solid lines indicate the position of respective (012) plane in pure Cr₂O₃ and Al₂O₃.](image)
as they grow and react with the surrounding \( \text{Al}_2\text{O}_3 \)-rich phases. When \( \text{Cr}_2\text{O}_3 \)-rich phase was formed, the remained composition must be more excessive about \( \text{Al}_2\text{O}_3 \) content than the mixed composition. However, no \( \text{Al}_2\text{O}_3 \) excessive XRD peaks were seen. Hence \( \text{Al}_2\text{O}_3 \)-rich phases are considered to be amorphous.

Fig. 4 shows the SEM micrographs of the A/C = 50/50 sol-gel derived powders calcined at 1000° and 1200°C. There was one peak in the sample of A/C = 50/50 whose critical temperature is reported to be 1250°C\(^{10}\) even when calcined at 700° and 800°C. These powders, which were calcined at 1000° and 1200°C, are thought to be metastable. At 1000°C fine particles adhere to the larger particles however at 1200°C the fine particles disappear and hexagonal plates with smooth surfaces are observed. This suggests that the fine particles which vanish at 1200°C are the \( \text{Al}_2\text{O}_3 \)-rich amorphous phases.

Fig. 5 shows the lattice constants of the sol-gel derived \( \text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3 \) powders calcined at 1000°C for 1h. The straight line of Fig. 5 is the theoretical line of the solid solution, which is a line drawn between the lattice constants\(^{14},15\) of corundum (a = 0.476nm, c = 1.295nm) and eskolite (a = 0.496nm, c = 1.369nm). As the results in Fig. 3 show, the XRD peak of A/C = 70/30 and A/C = 50/50 were broader than A/C = 90/10. It is thought that, with a high \( \text{Cr}_2\text{O}_3 \) content, the particles are divided into \( \text{Cr}_2\text{O}_3 \)-rich crystalline and \( \text{Al}_2\text{O}_3 \)-rich amorphous phases which resist unification into theoretical composition.

### 3.2 Sintering behavior of \( \text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3 \) system

Fig. 6 shows the relative density of \( \text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3 \) ceramics sintered at 1600°C in Ar and air atmospheres. As for the sample in Ar with A/C = 70/30 and with A/C = 50/50 prepared by the sol-gel method, the relative density increases up to 95% at all calcining temperatures. When the calcining temperature was high, relative density was low at A/C = 90/10. In the sintered bodies that were made from the powder prepared by a solid state reaction, the relative density was about 92% at all the content levels. As for the sintering atmospheres the samples sintered in air show lower density and the samples with higher \( \text{Cr}_2\text{O}_3 \) content have loosely packed structures. When the powder prepared by sol-gel method was used and calcined at 1000°C, the relative density of the sintered bodies was about 60% at all the \( \text{Cr}_2\text{O}_3 \) content levels.

Fig. 7 shows the vapor pressure diagrams of the compounds of Al-O and Cr-O at 1900K. Pressure is shown...
without the dimension standardized under the standard-state pressure (10^5 Pa). None of the sample heated in air were dense. This results can be explained as follows, based on the Fig. 7. CrO\textsubscript{3} (g) and CrO\textsubscript{2} (g), which partial pressure is the highest in Cr-O system, undergo high pressure increase under O\textsubscript{2} partial pressure. In air atmosphere, CrO\textsubscript{2} (g) partial pressure has logP\textsubscript{CrO\textsubscript{2}} = -5. Therefore, the powder was sintered without shrinkage because of the vaporization and condensation mechanism.

Although Cr\textsubscript{2}O\textsubscript{3} may discharge Cr (g) under low P\textsubscript{O\textsubscript{2}} conditions, the sintered bodies did not loses weight in an Ar atmosphere nor did the metal Cr (s) separate. This suggests that the evaporation speed was very slow. Therefore dense sintered bodies were obtained in an Ar atmosphere.

Fig. 8 shows the SEM micrographs of the A/C = 90/10 samples after calcination at 1000°C and 600°C in air and after sintering at 1600°C for 1h in Ar. The particle diameter of powder calcined at 600°C was 0.1\mu m, and grain growth to 5\mu m was confirmed when sintered at 1600°C. The powder calcined at 1000°C had a 5\mu m particle diameter which grew to 10\mu m when sintered. When calcining temperature was changed to 1000°C from 600°C, grain diameter also changed from 5\mu m from 0.1\mu m. This is the result of unusual grain growth during calcination. In the A/C = 90/10 samples the relative density of the final products decreased with an increase in calcination temperature.

Fig. 9 shows the microstructure of the sol-gel derived Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} ceramics sintered at 1600°C in Ar after the calcination at 600°C. The particle size increases with increasing Cr\textsubscript{2}O\textsubscript{3} content. This tendency was also seen in the sintered bodies made from the powder prepared by the solid state reaction.

Fig. 10 shows a relation between the grain size of the calcined powder and the relative density of the sintered body at 1600°C in Ar by the sol-gel method. For the A/C = 50/50 samples, the relative density was 95% and the
grain size of the powder calcined at 1000°C was 1μm. For the A/C = 70/30 samples, the relative density was 95% and the grain size of the powder calcined at 1000°C was 1μm and at 800°C was 0.2μm. In the A/C = 90/10 sample, the relative density increased in inverse proportion to the logarithmic grain size. This tendency was very different from that for A/C = 30/70 and 50/50. The separated phase state of the calcined powder was divided into Cr₂O₃-rich crystalline and Al₂O₃-rich amorphous phases. This is considered to be the cause for dense sintering to proceed.

4 Conclusions

Al₂O₃-Cr₂O₃ ceramics were prepared by the sol-gel method and the formation mechanism of solid solution and the sintering process were examined.

(1) The composition of the crystallized phases changes with the calcined temperature.
(2) Cr₂O₃-rich solid solution firstly crystallize at low temperature and the composition of the crystallites changes as they grow and react with the surrounding Al₂O₃-rich phase.
(3) Al₂O₃-Cr₂O₃ precursor becomes much denser when sintered at 1600°C in Ar.
(4) A dense sintered body was obtained when abnormal grains did not grow when calcining occurred.

REFERENCE

Al-Si-C-N 系組成物の焼結に及ぼす炭素の影響

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Influence of Carbon on Sintering of the Al-Si-C-N System Composite
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The composite in Al_{x}Si_{y}C_{z}-AIN and Al_{x}Si_{y}C_{z}-AIN-C system were sintered by a spark plasma sintering method. The powders of metal Al, Si and carbon black and AIN as starting materials were mixed. The mixture was calcined at 1300°C and sintered at 1600°C to 1800°C by spark plasma sintering. Shrinkage during sintering, density, microstructure and phase of sintered bodies were measured. X-ray diffraction analysis gave Al_{x}Si_{y}C_{z}N (15R) and AIN (2H) phases in the bodies sintered at 1750°C. Densification did not occur in some composition in 50 to 80% AIN of the system Al_{x}Si_{y}C_{z}-AIN, but their densification was accelerated by addition of carbon. By the analysis of shrinkage during sintering and SEM observation of microstructure, the grain of Al_{x}Si_{y}C_{z}N (15R) and AIN (2H) grew, and pore exclusion was obstructed in the system Al_{x}Si_{y}C_{z}-AIN, though the grain did not grow, and pore exclusion was accelerated in the system Al_{x}Si_{y}C_{z}-AIN-C.

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Key-words: Al_{x}Si_{y}C_{z}, AIN, Spark plasma sintering, Pore exclusion, Reaction sintering

1. 統 言

Al と Si の複合炭化物である Al_{x}Si_{y}C_{z}N は SiC よりも高温での耐熱性に優れる性質が見出されている(1,2). Al_{x}Si_{y}C_{z}N の微密焼結体が放電プラズマ焼結で助剤無添加で1700°C程度の比較的低温から得られており(3-5), 電気伝導率(6), 熱膨張率(7)及び熱伝導率(8)が計られており, 新たな高密度材料としての可能性も見出されている。(9)

Al-Si 系の炭化物,窒化物の複合は,AIN-C 系(9-11), SiC-AIN 系(12-17), Al_{x}C_{y}-SiC-AIN 系(18-20)などのいくつかの系で検討され,新たな研究の発展が期待されている.しかし, Al_{x}Si_{y}C_{z}N に添加物を混合した場合の報告例は少ない.このため,本研究では Al_{x}Si_{y}C_{z}N に AIN を混合した場合,焼結挙動について検討した.複合の形態を Al_{x}Si_{y}C_{z}-AIN 系及び Al_{x}Si_{y}C_{z}-AIN-C 系とし,焼結条件を放電プラズマ焼結で作製し,焼結性の評価を行った. AIN が Al_{x}Si_{y}C_{z}N を添加することにより,焼結温度が低下する範囲が認められ,この焼結性変化を防ぐ方法として炭素を若干過剰とする方法で蒸発性が可能となったことについて報告する.

2. 実験

Al_{x}Si_{y}C_{z}N のみ及びこれに少量の適正 C を含む組成に対して AIN を加えた Al_{x}Si_{y}C_{z}-AIN 系と Al_{x}Si_{y}C_{z}-AIN-C 系について検討した. 出発原料には Al 粉末 (試薬, 99.99% - 200 mesh, 三ツ化和), Si 粉末 (試薬, 99.99% - 200 mesh, 三ツ化和), C 粉末 (カプトン), SiC (東洋カーボンTOKABLACK7350)及びAIN粉末 (試薬, 99% 8.85 μm, 三ツ化和)を使用し, Al_{x}Si_{y}C_{z}-AIN 系組成物を作製した.また, Al_{x}Si_{y}C_{z}N に対して C を過剰に外掛で2.7%添加した組成に AIN を加えることにより, Al_{x}Si_{y}C_{z}-AIN-C 系組成物を作製した. 図 1 に作製試料の組成を Al-Si-C-N 系図上に示す.

全量100 gになるように所定量を混合した粉末をアルミナ質ボールミルで粉砕し, 28 gの粉末をφ50 mmの塩化タイダイに装荷し, 0.03 MPaのN2雰囲気で昇温速度60～80°C min^{-1}で1600°Cから1800°Cまで昇温し20 min保持の条件で,放電プラズマ焼結装置 (SPS シンテックス製, SPS-8205)を用い, 焼結させた.得られた焼結体の上下面を切断して,アルギニシス材で密度測定を行い, 破断面を SEM (電解放電型走査電子顕微鏡: 日本電子 JSM-6340F)で観察した. 残った試片を粉砕し,乾式型ピクノメータ (液体アイオニクス: マルチピクノメータ)で試料の真密度を測定した. 焼結体の相対密度は密接度に対するあらかじめ密度の値である. また,
Table 1. Phase Present and Densities in Calcined Powder at 1300°C for 3 h and Sintered Bodies by SPS at 1750°C for 20 min

<table>
<thead>
<tr>
<th>Al₂SiC₆ / mass%</th>
<th>Al₂Al₆C₂ / mass%</th>
<th>C / mass%</th>
<th>Al₂SiC₆</th>
<th>Al₂Al₆C₂</th>
<th>C</th>
<th>Sintered Al₂SiC₆ (g/cm³)</th>
<th>Sintered Al₂Al₆C₂ (g/cm³)</th>
<th>Sintered C (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>1.28 (42.9)</td>
<td>3.01</td>
<td>Al₂SiC₆</td>
<td>3.01 (99.96)</td>
<td>3.01</td>
<td>1.28 (42.9)</td>
</tr>
<tr>
<td>95</td>
<td>5</td>
<td>0</td>
<td>1.40 (46.3)</td>
<td>3.02</td>
<td>Al₂Al₆C₂</td>
<td>2.97 (99.2)</td>
<td>2.99</td>
<td>1.40 (46.3)</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>0</td>
<td>1.28 (42.2)</td>
<td>3.03</td>
<td>Al₂SiC₆</td>
<td>2.74 (91.6)</td>
<td>2.99</td>
<td>1.28 (42.2)</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0</td>
<td>1.31 (42.7)</td>
<td>3.06</td>
<td>Al₂Al₆C₂</td>
<td>2.94 (97.0)</td>
<td>3.03</td>
<td>1.31 (42.7)</td>
</tr>
<tr>
<td>67</td>
<td>33</td>
<td>0</td>
<td>1.25 (40.5)</td>
<td>3.09</td>
<td>Al₂SiC₆</td>
<td>2.76 (92.3)</td>
<td>2.99</td>
<td>1.25 (40.5)</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0</td>
<td>1.27 (40.6)</td>
<td>3.13</td>
<td>Al₂Al₆C₂</td>
<td>2.72 (89.6)</td>
<td>3.03</td>
<td>1.27 (40.6)</td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>0</td>
<td>1.44 (45.4)</td>
<td>3.17</td>
<td>Al₂Al₆C₂</td>
<td>2.40 (75.3)</td>
<td>3.18</td>
<td>1.44 (45.4)</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0</td>
<td>1.52 (47.4)</td>
<td>3.20</td>
<td>Al₂Al₆C₂</td>
<td>2.33 (73.1)</td>
<td>3.19</td>
<td>1.52 (47.4)</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>1.85 (57.2)</td>
<td>3.24</td>
<td>Al₂Al₆C₂</td>
<td>2.88 (88.7)</td>
<td>3.24</td>
<td>1.85 (57.2)</td>
</tr>
</tbody>
</table>

Al₂SiC₆ | Al₂Al₆C₂ | C | Al₂SiC₆ | Al₂Al₆C₂ | C | Al₂SiC₆ | Al₂Al₆C₂ | C |

XRD (理学電機; RINT 2200 VHF +/PC) で結晶相を同定した。

3. 結果
3.1 仮焼粉末の相と成形体密度
表1に1300℃で仮焼した粉末と1750℃で焼結した焼結体のXRD結果及び粉末成形体の充填密度、焼結体の焼結密度を示す。
1300℃で仮焼した粉末ではAl₂SiC₆組成（AIN 0%）でAl₂SiC₆（8H相）単相、AIN 100%ではウルル鉱AIN（2H相）の単相に変わった。
Al₂SiC₆－AIN系のは5%ではAl₂SiC₆（8H相）のみが観察され、AIN 10%ではAl₂SiC₆（8H）とAl₂SiC₆（15R）の共存相でAl₂SiC₆（8H）が主相であった。
AIN 20%ではAl₂SiC₆（15R）とAl₂SiC₆（8H）の共存相でAl₂SiC₆（15R）が主相であった。
AIN 33%ではAIN（2H）、Al₂SiC₆（8H）とAl₂SiC₆（15R）の三つの共存相でAIN（2H）が主相であった。
AIN 50%以上ではAIN（2H）、Al₂SiC₆（8H）の共存相でAIN（2H）が主相となった。
Al₂SiC₆－AIN系ではAIN 0%ではAl₂SiC₆（8H）、AIN 33%ではAIN（2H）、Al₂SiC₆（8H）とAl₂SiC₆（15R）の三つの共存相でAIN 67%ではAIN（2H）とAl₂SiC₆（8H）の共存相。AIN 100%にCと混合した場合にはAIN（2H）となった。いずれも各Al₂SiC₆/AIN比に対する生成相はAl₂SiC₆－AIN系の場合とAl₂SiC₆－AIN系の場合と変わりはない結果であった。

3.2 Al₂SiC₆－AIN系及びAl₂SiC₆－AIN－C系の緻密化焼結
図2にAl₂SiC₆－AIN系焼結体の焼結温度と相対密度の関係を示す。AIN 0%、33%、67%及び100%いずれの組成も焼結温度が上昇すると相対密度は高くなった。
AIN 0%では1675°Cで1750°C。AIN 33%では1600°Cでの焼結温度で、相対密度は98%以上に達しているが、AIN 67%及び100%では1800°Cの焼結温度でも相対密度は80%と92%にとどまった。

図3にAl₂SiC₆－AIN系及びAl₂SiC₆－AIN－C系の1750°Cでの加熱によって得られた焼結体について、AIN含有量に対する観察孔率及び全気孔率の関係を示す。Al₂SiC₆－AIN系ではAIN 50%以下では観察孔率がほぼ0%程度であり、気孔の形態は

Fig. 2. Relation between sintering temperature and relative density of Al₂SiC₆－AIN bodies sintered by spark plasma sintering.

Fig. 3. Relation between sintering temperature and relative density of Al₂SiC₆－AIN bodies sintered by spark plasma sintering.

81
ほとんどの密閉気孔であった。AIN 67〜80％では25％程度の開放気孔であった。AIN 100％では10％弱の開放気孔があった。Al2SiC2-AlN 系では開放気孔はほとんどなく、AIN 67％で見掛け気孔率はもっとも高く、約 2％であった。なお、いずれの試料も重量減少はなかった。

図4 に1750℃及び1800℃で焼結させた焼結体の相対密度を出発原材料のAIN含有量に対して示す。Al2SiC2の理論組成通りの原料組み合わせ（AIN無添加）では100％近くまで緻密化した。他方 AINのみでも若干の気孔があるが相対密度90％にまで緻密化した。Al2SiC2-AlN系では1750℃の場合、AIN 3％以下では98％以上の相対密度であるが、AIN の増加とともに低下し、AIN 67％及び80％では約75％であった。しかし、AIN 100％では90％と上昇した。焼結温度を1800℃に上げると AIN 33％では98％、AIN 67％では約80％、AIN 100％で92％まで相対密度が上昇した。

これに対し、1750℃でのAl2SiC2-AlN-C系ではAIN33％で98％、AIN 67％では90％、AIN 100％では95％の相対密度であった。Al2SiC2-AlN系のAIN 67％〜100％の範囲で焼結温度を上昇させた場合より炭素を添加した方が緻密化の促進が見られた。

図5に1750℃で作製した焼結体の破断面のSEM像を示す。
ALSiC₁₋₁⁻AIN と ALSiC₂⁻AIN-C 組成では AIN 0%、5% では気孔はほとんど見られず、緻密化していた。AIN 10% では、2 μm 程度の気孔が少
量に存在していた。AIN 10% 及び 33% では若干の開閉気孔が見られ
た。また、AIN 67% では多くの気孔が観察された。 ALSiC₁⁻⁻AIN-C 組成では、AIN 0% では気孔はなく、破壊面の組織は
ALSiC₁⁻⁻AIN-C 組成よりも粒が小さく観察された。AIN 33% でも
気孔はなく、緻密化された。AIN 67% では気孔は存在するが
ALSiC₁⁻⁻AIN-C 組成のものよりも気孔径は小さく、しかも量的に
少なかった。

緻密化に差異のあった ALSiC₁⁻⁻AIN 系と ALSiC₂⁻⁻AIN-C 系 の
AIN67%の焼結体について、より拡大した組織を観察した。
図 6 に研磨面を熱エッチングした表面の SEM 像を示す。 ALSiC₁⁻⁻AIN 系では粒の境界が明瞭に見られなかった。これに対
して、ALSiC₂⁻⁻AIN-C 系では粒の境界が明瞭である。

3.3 ALSiC₁⁻⁻AIN 系及び ALSiC₂⁻⁻AIN-C 系の焼結体の相と収
縮挙動

表 1 に 1750℃で処理した焼結体の XRD 結果を示す。ALSiC₁⁻⁻AIN 系では ALSiC₁⁻⁻AIN (AIN 0%) で ALSiC₁⁻⁻AIN (8H) 単相、AIN
100% ではウルトラ plein AIN (2H) の単相になった。AIN 10% 以下
では ALSiC₁⁻⁻AIN (8H) と ALSiC₁⁻⁻AIN (15R) の 2 相である。AIN 10% で
ALSiC₁⁻⁻AIN とわずかな ALSiC₁⁻⁻AIN 的 2 相になった。これに対し
て ALSiC₂⁻⁻AIN-C 系では AIN 33%、AIN 67% でいずれも AIN
(2H) と ALSiC₁⁻⁻AIN (15R) の混相であったが、AIN (2H) の回折
図形上では同一反射面に対して二つのピークが観察された。ま
た、過剰に添加した C については、黒鉛として検出されなかっ
た。

図 7 に ALSiC₁⁻⁻AIN 系及び ALSiC₂⁻⁻AIN-C 系試料での AIN
67% の仮焼粉末と焼結体の XRD ビークを示す。仮焼粉末で
はどちらの系でも生成相は AIN (2H) と ALSiC₁⁻⁻AIN (8H) で大き
な差はなかった。焼結体では、仮焼粉末で生成していない
ALSiC₁⁻⁻AIN (15R) 相が、いずれも生成していた。ALSiC₂⁻⁻AIN 系
では仮焼粉末と焼結体で AIN (2H) のピーク位置が異な
ており、焼結体では仮焼粉末の AIN (2H) よりも低角側にシ
フトしていた。これに対して C を 2.7 mass% 外掛け添加した
ALSiC₁⁻⁻AIN-C 系の焼結体では AIN のピークは二つに分か
れた。一つは仮焼粉末の AIN (2H) と同様の位置のピークで
他の一つは仮焼粉末よりも低角側にシフトしていた。C の有無
により AIN (2H) 相の構造の変化がみられる結果となった。

図 8 に 1750℃、20 min の放電プラズマ焼結での処理後の加圧
方向の試料の変位を温度に対して及び一定温度に保持した後は
時間に対して示す。ALSiC₁⁻⁻AIN 系の AIN 0% では 1300℃付近
で収縮が開始し、その後直線的に収縮量が増加した。この後、
1750℃での保持後に数分で、収縮は止まった。AIN 5 〜 33% で
は収縮の開始温度は約 1300℃からで AIN 0% とあまり変わらな
かったが、1600℃以上の高温域で収縮曲線の傾きは AIN 0% と
比べると若干低下した。このうち AIN 10% 以上では 1750℃で
保持中に収縮が継続された。AIN 量が多いものほど収縮が継続
される傾向が強い。AIN 50% 以上では収縮開始の温度が低くな
り、その後の収縮量が小さくなる。AIN 50%、67% 及び AIN
80% の順に収縮量が小さかった。AIN 100% では、収縮開始温
度は高かった。

ALSiC₁⁻⁻AIN-C 系では、各試料ともに約 1300℃で収縮が開始し,
AIN の含有量が異なることに収縮曲線の傾きが変化した。AIN
67% が収縮曲線の傾きが小さいが、ALSiC₁⁻⁻AIN-C 系ではいず
れのものでも収縮量は AIN 0% 系よりも大きかった。ALSiC₁⁻⁻AIN
系と ALSiC₂⁻⁻AIN-C 系の緻密化的度合いの差は大きく、
AIN 67% の組成で比較すると、収縮開始前の収縮量が
ALSiC₁⁻⁻AIN-C 系の方が大きくなっていた。

4. 考 察

4.1 生成相と緻密化について

図 4 で示したように ALSiC₁⁻⁻AIN 系と ALSiC₂⁻⁻AIN-C 系の焼
結体に差異が認められ、C が存在する系で緻密化が促進され
た。この理由は次のように考えられ、表 1 の結果から ALSiC₁⁻⁻AIN
Fig. 8. Shrinkage curves of the samples during spark plasma sintering with composition a) Al₂SiC₆-AIN and b) Al₂SiC₆-AIN-C.

系ではAIN 50～80％のとき1300°Cでの仮焼粉末の結晶相はAIN (2H) とAl₂SiC₆ (8H) である。焼結体は両者が反応して新たにAl₂SiC₆N (15R) を生成して, AIN (2H) との2相となっている。また, 図7に示される焼結体のAIN (2H) は, 仮焼粉末で現れたAIN (2H) のピークより低角度側にずれていた。このAIN (2H) は, SiやCが固溶して生成したものであると考えられる。これによって、ピークのずれが生じたと考えられる。また、焼結体はAINおよびAINが粒成長し、気孔を囲むことになると考えられる。それぞれの粒は成長し、気孔を排除できず、緻密化が進行しなかったと考えられる。AIN 10～33％ではAl₂SiC₆Nが主相であるが、同様に粒が成長し、気孔内のガスは排除されにくくなり、密閉気孔となったと考えられる。

一方、Al₂SiC₆-AIN-C系では、1750°Cで加熱された焼結体はAl₂SiC₆N (15R) とAIN (2H) が検出され、そのAIN (2H) は図7dの(100)面、(002)面及び(101)面のピークが300°Cに分かれていた。一つは出力1750°C加熱によって現れたAINのピークと一致している。他方は仮焼粉末に現れるAINのピークと一致している。このようにCの含有により、生成相に変化が認められたのは次のように考えられる。共存するCはAl₂SiC₆やAINと化合物をつくるのでき、Al₂SiC₆NやAINの気孔の周辺で点在しAl₂SiC₆とAINの結晶を塞げたと考えられる。その結果としてAl₂SiC₆-AINの粒界面を通じた気孔内のガス排出を容易にした結果であると考えられる。

4.2 焼結時の密度と組織について
Al₂SiC₆-AIN-C系で緻密化が進むした理由について図6の結果からみると次のように考えられる。Al₂SiC₆-AIN系においては強固な結合で、気孔を取り囲んでおり、気孔の排除が進行しないようにみられるが、これに対し、Al₂SiC₆-AIN-C系では形成する粒の境界がはっきりしている。この境界は過剰なCの分散により形成された粒界であったと考えられる。粒界が多く存在することにより、粒は成長せず、強固に結合して形成させずに気孔排除が可能となり、緻密化が進行したと考えられる。Cの介在によって、粒界が多く存在することにより自己調滑特性が付加され、気孔排除が容易になり、緻密化が進行したと考えられる。

AIN 67％のAl₂SiC₆-AIN系とAl₂SiC₆-AIN-C系の焼結体について、緻密化の進行度合いと相対密度の変化として見られる。図9は放電プラズマ焼結での加熱及び加圧時における相対密度変化である。この図は、図8の試料厚みの変化とダイの断面率（焼結体試料の厚さは焼結時に一定である）を示した粉末重量から試料密度を算出し、それより求めた相対密度である。仮焼粉末と焼結体の粉末粉末の真密度はほぼ同じであるので、後の値を用いて示出した。Al₂SiC₆-AIN系とAl₂SiC₆-AIN-C系とも、成形体の相対密度は45％程度で、ほぼ同じである。1750℃で20min保持した後の試料の相対密度は、Al₂SiC₆-AIN系では75％、Al₂SiC₆-AIN-C系では90％で、大きな差が生じていた。両者とも約1300℃から収縮を始めているが、約1450℃からAl₂SiC₆-AIN系の相対密度増加が著しく、差異が生じ始めている。この変異が生じたのは、Cの介在によっ

4.2 焼結時の密度と組織について
Al₂SiC₆-AIN-C系で緻密化が進むした理由について図6の結果からみると次のように考えられる。Al₂SiC₆-AIN系においては強固な結合で、気孔を取り囲んでおり、気孔の排除が進行しないようにみられるが、これに対し、Al₂SiC₆-AIN-C系では形成する粒の境界がはっきりしている。この境界は過剰なCの分散により形成された粒界であったと考えられる。粒界が多く存在することにより、粒は成長せず、強固に結合して形成させずに気孔排除が可能となり、緻密化が進行したと考えられる。Cの介在によって、粒界が多く存在することにより自己調滑特性が付加され、気孔排除が容易になり、緻密化が進行したと考えられる。

5. 結論
Al₂SiC₆とAINの組成に注目し、Al₂SiC₆-AIN系及びAl₂SiC₆-AIN-C系の焼結特性を金属Al粉末、Si粉末、カーボンプラック粉末及びAIN粉末を混合して放電プラズマ焼結により焼結体を作製し、緻密化に及ぼす炭素の影響を調べ、以下の結論を得た。

(1) Al₂SiC₆-AIN系の焼結においてAINの量比が50～80％の組成範囲で、Cの添加によって緻密化が促進される。
(2) C添加により、粒界はより多く形成し、気孔排除は容易となり、緻密化は促進される。

References
Oxidation protection of CaO–ZrO\textsubscript{2}–C refractories by addition of SiC

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Abstract

The effect of SiC used as antioxidant in carbon-containing CaO–ZrO\textsubscript{2} refractories and the behaviour of SiC in CO gas were studied. SiC was found to react initially with CO to form SiO\textsubscript{2}(s) and C(s) at $\sim$1200 °C, and then the formed SiO\textsubscript{2} reacted with CaO in the refractories to form belite (2CaO·SiO\textsubscript{2}). The refractory microstructure was modified by addition of SiC. Due to the deposition of SiO\textsubscript{2} in the large (2–10 μm) pores of the refractory through the reaction of SiO\textsubscript{2} with CO, the percentage of large pores decreased and a dense layer, mainly consisting of belite, was formed near the surface of the refractory after it was heated at high temperature (1500 °C). The oxidation resistance of CaO–ZrO\textsubscript{2}–C refractories was improved by reaction of SiC with CO to deposit C(s) and decrease the size of the large pores. The oxidation resistance of such refractories can be improved significantly when such a dense layer is formed near their surfaces.

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Keywords: CaO–ZrO\textsubscript{2}–C refractories; Oxidation resistance; Oxidation; Antioxidant

1. Introduction

Carbon possesses excellent thermal shock and slag resistance properties, and it has become an important component of commercial refractories, however, carbon suffers the drawback of poor oxidation resistance [1]. To improve the oxidation resistance of carbon-containing refractories, antioxidants, such as metals (Mg, Al, Si), alloys (Mg–Al) and carbides (B\textsubscript{4}C, SiC) are often added to them. The antioxidant selected varies according to the matrix type of the carbon-containing refractories. For example, Mg and Al are often added to MgO–C refractories, whereas SiC is often added to Al\textsubscript{2}O\textsubscript{3}–C refractories [2,3].

Lime has the advantages of being abundant, having a high melting temperature, a low vapour pressure and thermodynamic stability in the presence of carbon. Accordingly, CaO–C refractories have long been regarded as potentially attractive for applications in the metallurgical industries [4,5]. In recent years, lime-containing refractories have shown great advantages in dephosphorization and desulphurization of molten steel [6]. Nevertheless, the application of CaO refractories has been inhibited owing to its poor hydration resistance, and the main attention of lime refractories research has been in this area [7,8]. The present authors have also studied this topic and prepared hydration resistant CaO–ZrO\textsubscript{2} composites through the formation of a protective CaZrO\textsubscript{3} layer around CaO grains [9]. Little attention has been paid to improve the oxidation resistance of CaO–C refractories [10,11].

In the present work, the behaviour of SiC antioxidant in CO gas and the mechanism of improved oxidation resistance of CaO–ZrO\textsubscript{2}–C refractories were studied.

2. Experimental procedures

2.1. Starting materials

The starting materials in the present work were CaO–ZrO\textsubscript{2} grain prepared by grinding CaO–ZrO\textsubscript{2} clinker (sintered from a mixture of reagent grade CaCO\textsubscript{3} and ZrO\textsubscript{2} in the molar proportion CaO:ZrO\textsubscript{2} = 80:20, with relative density of over 99%) [9] to pass 90 μm, carbon (graphite flake, with purity of over 99.7% and average size of less than 0.5 μm) and SiC (with purity of over 99% and average grain diameter of 2–3 μm).
2.2. Sample preparation

Two batches of powder were prepared by wet-mixing (in acetone) CaO–ZrO$_2$ grain, carbon and SiC in the proportions shown in Table 1. Then the mixed powders were shaped to cylindrical compacts of $D15$ mm × $\sim15$ mm and plate compacts of $20$ mm × $20$ mm × $\sim12$ mm by using CIP (cold isostatic pressing) under 100 MPa with 4 mass% phenolic resin as a binder. Cylindrical compacts were pre-treated at 800 °C for 5 h in a carbon powder bed for the carbonization of resin before the oxidation test.

2.3. High temperature behaviour of SiC added to CaO–ZrO$_2$–C refractories

Approximately 1.5 g of the mixture with SiC addition (with composition of sample 2) was heated in a tube furnace at a heating rate of 10 °C/min. After soaking at different temperatures for 2 h and at 1500 °C for 2–6 h, the heated sample was cooled in the furnace to room temperature at a rate of 10 °C/min. CO gas was bled into the furnace at a flow rate of 0.2 L/min for the duration of the heat treatment. The phase composition of the heat treated mixture was analyzed by using powder XRD (X-ray diffraction, Cu target, 20 kV, 20 mA) and the mass change was measured using an electric balance.

2.4. High temperatures oxidation testing

The oxidation test was carried out by heating the cylindrical bricks in a TG (thermogravimetric) furnace in air (Fig. 1a), with the same heating and cooling rate of 10 °C/min. The pore size distribution of the bricks was examined using mercury porosimetry, and the phase composition of the samples after heating was analyzed using XRD. Cross sections of the heated samples were observed under optical microscopy and SEM (scanning electron microscopy).

Because of the low pressure used, the relative density of the brick was so poor that the cylindrical compact was completely oxidized before it reached the higher temperature (1500 °C). To investigate the oxidation behaviour of the refractory with SiC addition at a higher temperature, the oxidation test was also carried out in another electric furnace by embedding most of a plate compact in carbon powder while keeping its top surface exposed to air, as shown in Fig. 1b. The sample was heated to 1500 °C at a rate of 10 °C/min and kept at this temperature for 4 h. After heating, the microstructure was observed under optical microscopy and the composition near the surface was obtained by spot analyses with interval of 200 μm using EPMA (Electron Probe Micro Analysis).

3. Results and discussion

3.1. Behaviour of SiC added to CaO–ZrO$_2$–C refractories

It is known that the main gaseous species in the refractories is CO when the oxides coexist with condensed carbon. Therefore, the present work investigated the behaviour of SiC added to the refractories in CO gas. Fig. 2 shows the phase change of the CaO–ZrO$_2$–C refractories with SiC addition after heating at different temperatures for 2 h and at 1500 °C for 2–6 h in CO gas. The intensity of SiC began to decrease significantly above 1200 °C, and, simultaneously, the intensity of CaO decreased and belite (Ca$_2$SiO$_4$) began to be detected. This indicates that the SiC reacted with CO to form SiO$_2$(s) and C(s) according to reaction (1) from $\sim$1200 °C. The identification of belite indicates that the formed SiO$_2$ reacted further with CaO. For CaZrO$_3$, no change of its intensity after heating at different temperatures confirmed that it was stable in these
atmospheres and temperature conditions. The intensities of CaO and belite reached a constant value when the sample was heated at 1500 °C for 6 h, indicating the completion of the reaction in the refractories.

\[ \text{SiC(s)} + 2\text{CO(g)} = \text{SiO}_2(s) + 3\text{C(s)} \]  

(1)

Fig. 3 shows the mass change of the mixture with SiC addition (with composition of sample 2) after heating at different temperatures for 2 h and at 1500 °C for 2–6 h in CO gas. The abrupt increase of mass gain from 1200 °C also confirmed the occurrence of reaction (1) from this temperature. As previously reported, it is considered that the occurrence of reaction (1) proceeded in the following two steps [2]:

\[ \text{SiC(s)} + \text{CO(g)} = \text{SiO(g)} + 2\text{C(s)} \]  

(2)

\[ \text{SiO(g)} + \text{CO(g)} = \text{SiO}_2(s) + \text{C(s)} \]  

(3)

Because a part of the SiO(g) volatilized to the atmosphere, it did not completely condense as SiO₂ within the refractories. As a result, after the refractory was heated in CO gas for 6 h, the mass gain of the refractory was only 5.8 mass%, which was less than the theoretical value of 7.0 mass%.

3.2. Improved oxidation resistance of the CaO–ZrO₂–C refractories

Fig. 4 shows the mass changes of the CaO–ZrO₂–C refractories heated to 1300 °C and kept at this temperature for 2 h in air at a heating rate of 10 °C/min. Mass decrease in a similar manner for both samples at lower temperatures, but from 1200 °C, the mass decrease was obviously suppressed and a plateau was found for samples with SiC addition. For samples without SiC, the mass reached a constant value after 11 min at 1300 °C, whereas it was 32 min for samples with SiC. These results indicate that the oxidation of carbon was effectively suppressed by the deposition of C(s) when SiC was added.

![Fig. 3. Mass change of the CaO–ZrO₂–C refractories with SiC addition heated at various temperatures for 2 h and at 1500 °C for different time.](image)

![Fig. 5. XRD of the SiC added CaO–ZrO₂–C refractories heated to (a) 1200 °C and (b) kept at 1300 °C for 10 min.](image)
without SiC, the refractories were almost completely oxidized (the central black zone is the unoxidized core). But for the sample with SiC, a large unoxidized zone was still observed. This result also confirmed that the addition of SiC effectively improved the oxidation resistance of the refractories.

3.3. Modification of microstructure

Fig. 7 shows the pore size distribution of the refractories with and without SiC heated at 1300 °C for 2 h. It is observed that although there was no obvious change in apparent porosity (it was 50% and 49% for the sample without and with SiC addition, respectively), the percentage of large pores (2–10 μm) was decreased when SiC was added. The microstructure observation also identified that the amount of large pores decreased when SiC was added, as shown in Fig. 8.

The modification of microstructure was considered to occur by the reaction of SiC turning to SiO₂. Because of diffusion of SiO(g) at high temperature, SiO(g) was considered likely to condense as SiO₂(s) in the pores. As a result, the pores were filled with SiO₂ (which further reacted with CaO to form belite) and the pore size decreased.

It is known that the partial pressure of \( P_{\text{SiO}_2(g)} \) is strongly dependent on temperature. For example, it is calculated that \( P_{\text{SiO}_2(g)} \) is 270 Pa at 1300 °C, increasing to 535 Pa when the temperature is elevated to 1500 °C. Because of the low \( P_{\text{SiO}_2(g)} \) and limited time of SiC coexisting with carbon due to the complete oxidation of carbon at 1300 °C, SiO(g) would be expected to diffuse only a short distance. As a result, SiO(g) reacted with CO gas to condense as SiO₂ (reaction (3)) just at the original SiC site or the pores nearby.

---

**Fig. 6.** Section of (a) SiC free and (b) SiC added CaO–ZrO₂–C refractories heated at 1300 °C for 10 min in air.

---

**Fig. 7.** Pore size distribution of the CaO–ZrO₂–C bricks after 2 h at 1300 °C.

**Fig. 8.** SEM photographs of the fractured surface of CaO–ZrO₂–C bricks (a) without and (b) with SiC addition after heating at 1300 °C for 2 h.
4. Conclusions

Based on the above results, the following conclusions were drawn when SiC was added as an antioxidant to the CaO–ZrO$_2$–C refractories:

1. SiC begins to react with CO gas at ~1200 °C, forming C(s) and SiO$_2$(s). The latter further reacts with CaO to form belite. Due to the diffusion and condensation of SiO(g), the microstructure was modified. The percentage of large pores (2–10 μm) is decreased and a dense protective layer is formed when SiC coexists with condensed carbon in the refractory at higher temperature (1500 °C) for enough time.

2. The addition of SiC improves the oxidation resistance of CaO–ZrO$_2$–C refractories by reaction of SiC with CO gas to deposit carbon and modification of the microstructure. In particular, a dense protective layer formed near the refractories surface is effective in improving the oxidation resistance.

References

Preparation and Properties of Spark Plasma Sintered Magnesium Aluminum Oxynitride

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In this paper, the effects of heating temperature and soaking time on the synthesis of magnesium aluminum oxynitride (MgAlON) by spark plasma sintering (SPS) were investigated. Results showed that the content of N decreased while that of O increased with the increasing of temperature, because of the reaction between MgN2 and H2O when the sample heated below 1500°C. Owing to the rapid warming up rate and the reaction between graphite and H2O, the variation of chemical composition was lowered in the sample heated at higher temperature. During the heating process, shrinkage started above 1000°C and expansion was observed above 1600°C. Moreover, open pores were not detected in the sample heated at 1500°C for 1 min and single phase MgAlON without pores could be obtained when heated at 1700°C for 10 min. With the increasing of the content of Mg and the decreasing of N, all the thermal characteristics were increased and the cold bending strength was decreased, which may provide a standard data about the cold bending strength and the thermal characteristics of MgAlON with different composition.

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Key-words: Magnesium aluminum oxynitride (MgAlON), Spark plasma sintering (SPS), Preparation, Property

1. Introduction

Magnesium aluminum oxynitride (MgAlON) is a solid solution material with high melting point and considered as a promising superior refractory. Investigations on its oxidation behavior and synthesis processes have been carried out and lots of meaningful results have been achieved. Up to now, three methods about the preparation of MgAlON have been proposed: (1) solid phase reaction of AlN, Al2O3, and MgO; (2) reaction of Al, Al2O3, and MgO; and (3) carbothermal reduction and nitridation of carbon, Al2O3, and MgO. Among these methods, the first one has more advantages to prepare high density MgAlON with small sized starting materials, and its reaction sequences can be described as following: MgO reacts with Al2O3 above 1000°C and magnesium aluminate spinel (MgAl2O4) is formed at first. Then, with the solid solution of AlN and Al2O3 into MgAl2O4, above 1350°C, MgAlON is formed, and the potential of the solution of AlN and Al2O3 increases with the increasing of temperature.

As a material to utilize at high temperature, it is necessary to investigate the thermal characteristics, such as thermal expansion, thermal diffusivity, thermal capacitance, and thermal conductivity. To obtain standard data of MgAlON with respect to thermal characteristics and strength, single phase samples without pores need to be prepared. In addition, since MgAlON is a solid solution material and its chemical composition has a relatively wide range, the properties of MgAlON with different composition should be explored.

Considering the advantages of spark plasma sintering (SPS) (schematically shown in Fig. 1), it is used to prepare high density MgAlON in this work, and we have successfully prepared single phase MgAlON without pores in very short process by SPS process through solid phase reaction of MgO, Al2O3 and AlN. However, the process has not been systematically investigated.

In this paper, our objective is to investigate the effect of syntactical parameters, such as heating temperature and soaking time, on the preparation of MgAlON by SPS process and to obtain the standard data about the cold bending strength and thermal characteristics of single phase MgAlON without pores in different composition.

2. Experimental procedure

2.1 Preparation of MgAlON

High purity and small sized starting powders, MgO (0.24 μm, >99.9%), Al2O3 (0.1 μm, >99.9%), and AlN (0.7 μm, >99.2%), were meticulously weighed according to the proportion listed in Table 1, and milled with alumina balls by using ethanol as dispersion. Subsequently, the slurry was vacuum dried in rotary evaporator (Model BUCHI R–134 rotovapor, SIBATA, Tokyo, Japan) and then the dried powders were placed in a graphite die and set in SPS system (Model DR. SINTER 820S, Sumitomo Heavy Industries, Ehime, Japan). After the chamber was evacuated to less than 5 Pa and flushed with nitrogen (purity >99.999%), repeatedly, the samples were heated following the patterns listed in

![Fig. 1. Schematic of SPS system.](image_url)
Table 1. Chemical Composition of Raw Materials and Heating Conditions

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Heating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Warming up conditions</td>
</tr>
<tr>
<td></td>
<td>Just mixed</td>
</tr>
<tr>
<td>MgO Al₂O₃ AlN MgO Al₂O₃ AlN</td>
<td>T0</td>
</tr>
</tbody>
</table>
| MgO Al₂O₃ AlN | T1 | 4 | 13 | 3 | 9.94 | 82.41 | 7.64 | \begin{align*}
\text{Just mixed} & \quad \text{R.T.-1100 °C in 12 min} \\
& \quad 1100 °C \text{ for 1 min} \\
\text{T1} & \quad \text{R.T.-1500 °C in 16 min} \\
& \quad 1500 °C \text{ for 1 min} \\
\text{T2} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 1 min} \\
\text{T3} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{H1} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C1} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C2} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C3} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C4} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C5} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\text{C6} & \quad \text{R.T.-1700 °C in 20 min} \\
& \quad 1700 °C \text{ for 10 min} \\
\end{align*}

3. Results and discussion

3.1 Effect of heating conditions on composition

Chemical composition of SPSeD samples and that of green compact (T0) are listed in Table 2. In these samples, the content of Mg and Al had not obvious variation. When lower than 1500°C, the content of O had a minor increase and that of N had a tiny decrease with the increasing of temperature. However, the difference of the content of O and N between the heated samples and green compact had not obvious change higher than 1500°C.

Phase composition of T0-T3 and H1 is shown in Fig. 2. In T1, the reaction of MgO and Al₂O₃ generated Mg₄Al₅O₁₄, but due to the short heating process, the MgO was not completely consumed. The accurate chemical composition of Mg₄Al₅O₁₄ could be calculated from the following equations:

\[ [\text{Mg}]_{\text{Mg} \text{Al} \text{O} \text{O}} \times 100\% = \frac{\text{O}_{\text{Mg} \text{Al} \text{O} \text{O}} - 0.7900}{15 - \text{O}_{\text{Mg} \text{Al} \text{O} \text{O}}} \times 100\% \]

\[ [\text{Al}]_{\text{Mg} \text{Al} \text{O} \text{O}} \times 100\% = \frac{6 - \text{O}_{\text{Mg} \text{Al} \text{O} \text{O}} - 0.7900}{15 - \text{O}_{\text{Mg} \text{Al} \text{O} \text{O}}} \times 100\% \]

\[ [\text{O}]_{\text{Mg} \text{Al} \text{O} \text{O}} = 1 - [\text{Mg}] - [\text{Al}] \]

when the lattice constant of the determined Mg₄Al₅O₁₄ in T1 was 0.80826 nm, its chemical composition was Mg₄Al₅O₁₄.

From the XRD result of T2, the MgO was entirely consumed and MgAlON was obtained. Combined with the result of Fig. 3, where the excess weight change (\( W\% \) of T2 was 1.45%, the content of Mg of MgAlON in T2 calculated from Eq. (4) was 8.52 mol%.

\[ W\% = 29.07 \times [\text{Mg}] \times 3.9285 \]

However, the content of Mg in T2 was 5.11 mol% (Table 2). So, it could be deduced that only about three quarters of Al₂O₃ dissolved into the MgAlON in T2. In T3 and H1, single phase MgAlON was obtained. According to Table 2, the chemical composition of MgAlON of T3 and H1 could be represented as Mg₄Al₅O₁₄ and Mg₄Al₇O₁₄N₂, respectively.

Figure 3 shows the weight change of SPSeD samples and that of mixed raw materials. The sizes of starting powders...
Table 2. Chemical Composition of Samples T0–T3 and Sample H1 (mol%) \[
\begin{array}{cccccc}
\text{Soaking conditions} & \text{ Chemical composition} \\
\text{T0} & \text{Mixed raw materials} & 5.08 & 36.71 & 54.78 & 3.42 \\
\text{T1} & 1100^\circ C \text{ for 1 min} & 5.10 & 36.76 & 54.88 & 3.26 \\
\text{T2} & 1500^\circ C \text{ for 1 min} & 5.10 & 36.79 & 55.01 & 3.10 \\
\text{T3} & 1700^\circ C \text{ for 1 min} & 5.10 & 36.79 & 54.90 & 3.20 \\
\text{H1} & 1700^\circ C \text{ for 10 min} & 5.10 & 36.80 & 54.90 & 3.20 \\
\end{array}
\]

![XRD patterns of T0–T3 and sample H1.](image)

![Weight change of T0–T2, and H1.](image)

were very small, and inevitably, some attached water existed in the mixed raw materials. Hence, the weight decrease of T0 below 700°C was ascribed to the evaporation of attached water. Above 750°C, all the samples were oxidized, however, their oxidation behavior had some difference: T0 and T1 had an obvious oxidation, while T2 and H1 had not obvious oxidation until to 1000°C, though AIN was detected in T1 and T2. Considering that the Al₂O₃ used in present work was very sinterable, un-reacted AIN in T2 might be surrounded by MgAlON and Al₂O₃ grains. Moreover, the oxidation of MgAlON was slow below 1000°C. As a result, the oxidation of AIN was retarded and T2 had not obvious oxidation until 1000°C.

From Fig. 3, it can be also found that the total weight change of T0 had minor difference to that of T1 but obviously lower than that of T2 and H1, even though the chemical composition of these samples had not big difference (Table 2). Considering the overall oxidation reaction of MgAlON and AIN:

\[
\begin{align*}
\text{MgAlON} + \text{O}_2 & \rightarrow \text{MgAl}_2\text{O}_4 + \text{Al}_2\text{O}_3 + \text{N}_2 \\
\text{AlN} + \text{O}_2 & \rightarrow \text{Al}_2\text{O}_3 + \text{N}_2 
\end{align*}
\]

The oxidation reaction of the above two nitrides can be represented as,

\[
4\text{N}^3^- + 3\text{O}_2 = 2\text{N}_2 + 6\text{O}^2^- 
\]

By using Eq. (7), the theoretical weight change (\(W_T\)) could be calculated. Compared with Table 2, the chemical composition of all samples was similar, and the difference of \(W_T\) among these samples could be neglected. However, it should be noted that there existed some obvious differences in weight changes achieved by TG analysis. \(W_E\) was determined by the equation,

\[
W_E = W_M - W_T 
\]

where, \(W_M\) is the maximum weight changes shown in Fig. 3. In present work, \(W_M\) of T2 was 1.45% and that of H1 was 2.45%. In ref 4), Dai et al. had proposed that during the oxidation of MgAlON, there was an excess weight change and it related to the content of the content of Mg of the MgAlON phase (Eq. (4)). So, the oxidation behavior of samples agreed well with the proposition.

In the following, a possible reason for the change of the chemical composition at different heating condition (Table 2) was discussed. During the preparation of MgAlON by solid phase reaction, Mg₂N₂ as a volatile material with the vaporizing temperature at 700°C formed through the reaction between MgO and AIN:

\[
\text{MgO} + \text{AlN} \rightarrow \text{Al}_2\text{O}_3 + \text{Mg}_2\text{N}_2 
\]

In addition, as attached water remained in the green compact, the Mg₂N₂ was favorable to react with H₂O as follows:

\[
\begin{align*}
\text{Mg}_2\text{N}_2 + \text{H}_2\text{O} & \rightarrow \text{MgO} + \text{H}_2 + \text{N}_2 \\
\text{Mg}_2\text{N}_2 + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{MgAl}_2\text{O}_4 + \text{H}_2 + \text{N}_2 \\
\text{Mg}_2\text{N}_2 + \text{MgAl}_2\text{O}_4 + \text{H}_2\text{O} & \rightarrow \text{MgAlON} + \text{H}_2 + \text{N}_2 
\end{align*}
\]

Taking into account the graphite die as heater, the reaction between H₂O and graphite could also occur according to,

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 
\]

With the proceeding of the reaction between Mg₂N₂ and H₂O as reactions (10)–(12), the content of N would decrease and
that of O would increase, and the occurrence of reaction (13) had not effect on the chemical composition of heated sample. As Mg₃N₂ reacts with H₂O at low temperatures and graphite reacts with H₂O only at high temperature, obviously, the change of chemical composition in the samples heated lower than 1500°C mainly caused by the reactions (10)–(12). With the temperature increasing, the solid phase reaction rate among MgO, AIN and Al₂O₃ was increased and the formation of Mg₃N₂ was lowered. Oppositely, with the increasing of temperature, the reactivity between graphite and H₂O increased, thus, lots of H₂O were consumed by the graphite. Hence, the difference of the content O and N between T3 and T0 was lower than that between T2 and T0.

3.2 Effect of heating conditions on microstructure

Pore distributions of samples heated at different temperature are plotted in Fig. 4. The volume of pore was about 0.16 ml g⁻¹ and mean diameter was less than 100 nm in T1. In T2 and T3, the amount of mercury accessed in the samples could be neglected. Furthermore, the measurement of the bulk density and porosity of T2 and T3 by Archimedes method implied that their apparent porosity almost to zero. Moreover, as shown in Fig. 5, the relative densities of T1, T2, and T3 were 59.6%, 92.4%, and 99.5%, respectively. So, some closed pores were remained in T2 and T3.

Figure 6 illustrates the microstructures of samples heated at different condition. With the increasing of temperature, the pores became smaller and the grains got coarser. T1 was very porous and its grains were very small; For T2, the grains and pores were about 1 μm, and pores were distributed around dense grains; For T3, the grains were about 5 μm and few pores were involved in the grain. Especially, the grain size of H1 was about 10 μm and as twice as that of T3, and no pores existed in the inner of grains. Since the sample was heated under vacuum condition, pores involved in the grains were in negative pressure and they could migrate to the grain boundaries and out of the sintering body easily at higher temperature. In this case, the pores were efficiently removed through SPS process. Therefore, SPS process was an effective means to prepare full density sample.

3.3 Shrinkage behavior during heating process

Figure 7 shows the shrinkage behavior of H1 during the heating process. The shrinkage behavior had not obvious change until 1000°C because the raw materials kept stable at low temperature. It could be found that the shrinkage rate was rapidly increased from about 1100°C to 1400°C and became slower from 1400°C to 1600°C. As the densities of raw materials were 3.97 g cm⁻³ (Al₂O₃), 3.26 g cm⁻³ (AlN), 3.58 g cm⁻³ (MgO), and the formed Mg₃Al₂O₆ and MgAlON
were about 3.6 g cm$^{-3}$ and 3.65 g cm$^{-3}$, respectively, expansion would occur during the solid solution of Al$_2$O$_3$ into MgAl$_2$O$_4$s and MgAl$_2$ION. At the beginning of shrinkage (1100°C–1400°C), as the sample was very porous, the expansion caused by the solid phase reaction had minor effect on the dimensional change of sample compared to the shrinkage induced by the elimination of pores. In the succeeding stage (1400°C–1600°C), as the density of the sample was increased, the effect of the shrinkage caused by elimination of pores was lowered. On the other hand, since the rate of the solid solution of Al$_2$O$_3$ was increased at higher temperature, the influence of the expansion aroused from the solid solution reaction increased. When higher than 1600°C, an expansion was obtained. As some residual Al$_2$O$_3$ were existed and the density was about 92.4% in T2, it could be deduced that in the sample heated at 1600°C without holding process, some un-reacted Al$_2$O$_3$ should remain and the density was relatively high. Since about 8% of volume expansion was generated during the solid solution of Al$_2$O$_3$ into MgAl$_2$O$_4$ and MgAl$_2$O$_4$ s, the solution of Al$_2$O$_3$ should be the reason for the expansion higher than 1600°C. As the densities of T3 and H1 were about 99.5% and 100%, respectively, the variation of the dimension of sample could be neglected and the sample soaked at 1700°C had not obvious change.

3.4 Effect of composition on the properties of SPSed MgAlION

All the SPSed samples for the measurement of the properties were confirmed to be single phase MgAlION without pores (density $>$99.9%) by the determination of phase composition and density. According to the properties of SPSed MgAlION listed in Table 3, the difference of thermal diffusivity, thermal capacitance, and thermal conductivity at room temperature was greater than that at 500°C and the thermal capacitance had not obvious change with the variation of chemical composition. With the increasing of the content of Mg and the decreasing of N, all the thermal characteristics, thermal expansion, thermal diffusivity, thermal capacitance, and thermal conductivity, were increased and the cold bending strength was decreased. The reason of the relationship between the properties and the composition of MgAlION was still unknown and it need further study.

4. Conclusions

During the synthesis of magnesium aluminum oxynitride (MgAlION) by spark plasma sintering (SPS) process, a minor variation of the content of N and O at temperatures lower than 1500°C was caused by the reaction between Mg$_3$N$_2$ and H$_2$O. At higher temperature, the change of the chemical composition was decreased, because of the high efficiency of the SPS process and the reaction between graphite heater and H$_2$O. In the course of the heating process, the shrinkage rate was very fast from about 1100°C to 1400°C, and slowed down from 1400°C to 1600°C. When above 1600°C, an expansion was obtained. In addition, Open pores were not existed in the sample heated at 1500°C for 1 min and single phase MgAlION without pores were obtained when heated at 1700°C for 10 min. With the increasing of the content of Mg and the decreasing of N, the cold bending strength was decreased and all the thermal characteristics were increased.

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References
Influence of Heating Temperature, Keeping Time and Raw Materials Grain Size on 
\(Al_4O_3C\) Synthesis in Carbothermal Reduction Process and Oxidation of \(Al_4O_3C\)

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Several factors, influencing synthesis of \(Al_4O_3C\) in carbothermal reduction process from \(Al_2O_3\) and C starting raw materials in argon atmosphere, and oxidation characteristics of \(Al_4O_3C\) were investigated. The formed \(Al_4O_3C\) in heated specimens was increased and \(Al_2O_3\) and C were decreased with increase of heating temperature and extension of keeping time. Grain size of \(Al_2O_3\) had obvious influence on synthesis of \(Al_4O_3C\) and fine \(Al_2O_3\) was more advantageous. The activation energy of the reduction reaction from \(Al_2O_3\) and graphite to form \(Al_4O_3C\) was calculated as 358.0 kJ/mol basing on experimental data. \(Al_4O_3C\) was observed to be oxidized from about 820°C in air. \(Al_4O_3C\), buried in graphite powder and heated in air, was converted into \(Al_2O_3\) and C.

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**Key-words**: \(Al_4O_3C\), Synthesis, \(Al_2O_3\), 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 \(Al_4C_3\), which may lead the refractories to collapse for the poor hydration resistance of \(Al_4C_3\).

\(Al_4O_3C\) that is stable until 1890°C exists in \(Al_2O_3-\)\(Al_4C_3\) system. This compound has been confirmed to have good hydration resistance and be transformed into \(Al_2O_3\) and C at \(P_{CO_2}=0.1\) MPa (1 atm). So \(Al_4O_3C\) may be a better additive than metal Al for carbon-containing refractories.

The authors have proceeded some research works about synthesis of \(Al_4O_3C\) from \(Al_2O_3\) and graphite starting raw materials in argon atmosphere and it was known that the formation of \(Al_4O_3C\) started at a temperature of 1500–1550°C.

However, more factors influencing synthesis of \(Al_4O_3C\) are necessary to be investigated for comprehending synthesis of \(Al_4O_3C\) in detail, and characteristics of formed \(Al_4O_3C\) are also necessary to be investigated for probable utilization in the future.

In the present work, several factors, influencing synthesis of \(Al_4O_3C\), such as heating temperature, keeping time and grain size of \(Al_2O_3\), and oxidation characteristics of formed \(Al_4O_3C\) were investigated.

2. Experimental procedure

2.1 Investigation on factors influencing synthesis of \(Al_4O_3C\)

\(Al_2O_3\) (average grain size: 0.1 µm, 30 µm, 60 µm and 1 mm, purity: ++ 99.0 mass%), and graphite (average grain size: 30 µm, purity: ++ 99.0 mass%) were used as starting raw materials. They were weighed in proportions of \(C/Al_2O_3 = 1.5\) (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 \(10^{-8}\) MPa (by a ZrO₂ 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 \(Al_4O_3C\)

1) Oxidation of \(Al_4O_3C\) in air

The specimen from mixture with \(C/Al_2O_3 = 1.5\) heated at 1700°C for 9 h, with the highest \(Al_4O_3C\) content and a little of \(Al_2O_3\) and graphite, was grounded into grain size of approx. 10 µm and was named \(Al_4O_3C\) 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 Al₂O₃C buried in graphite powder and heated in air

Since Al₂O₃C is probable to be used as an additive into carbon-containing refractories, oxidation characteristic of Al₂O₃C coexisting with C is necessary to be determined. So oxidation characteristic of formed Al₂O₃C, buried in graphite powder and heated in air, was also investigated.

The Al₂O₃C product stated above was mixed with graphite powder in molar ratio of Al₂O₃C : graphite = 1 : 6 (Al₂O₃C product was calculated as 100% Al₂O₃C). This (Al₂O₃C 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 Al₂O₃C

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, Al₂O₃C 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, Al₂O₃C and graphite in heated specimens, which were calculated from Table 1 and according to equations as

\[
[\text{Al}] = \left[\text{[Al₂O₃]} \times 54/102 + [\text{Al₂O₃C}] \times 108/184\right]
\]

\[
[\text{O}] = \left[\text{Al₂O₃]} \times 48/102 + [\text{Al₂O₃C}] \times 64/184\right]
\]

\[
[\text{C}] = [\text{graphite}] + [\text{Al₂O₃C}] \times 12/184
\]

Where [Al], [O], [C], [Al₂O₃], [Al₂O₃C] and [graphite] are the mass contents of Al element, O element, C element, Al₂O₃ phase, Al₂O₃C phase and graphite phase in the heated specimens.

As temperature was raised, increase of Al₂O₃C and decrease of Al₂O₃ and graphite were turned into more quick. At the same time, proportion of Al₂O₃C 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](image)

![Figure 3. Mass contents of the phases of Al₂O₃, Al₂O₃C and graphite in specimens from mixtures with C/Al₂O₃ = 1.5 heated at various temperatures for different times](image)
Influence of Heating Temperature, Keeping Time and Raw Materials Grain Size on
\(\text{Al}_2\text{O}_3\text{C}\) Synthesis in Carbothermal Reduction Process and Oxidation of \(\text{Al}_2\text{O}_3\text{C}\)

![Graph showing changes in intensity of Al2O3C](image)

Fig. 4. Phases in specimens from mixtures with various \(\text{Al}_2\text{O}_3\) grain sizes and \(\text{C}/\text{Al}_2\text{O}_3 = 1.5\) heated at 1700°C for 9 h. \((h k l)\) of the highest peak of each phase: \(C = (003); \text{Al}_2\text{O}_3 = (104); \text{Al}_2\text{O}_3\text{C} = (111); \text{Al}_2\text{C}_3 = (012)\).

![Graph showing TG patterns](image)

Fig. 5. TG patterns of \(\text{Al}_2\text{O}_3\text{C}\) product, reheated powder and graphite (air: 200 ml/min; temperature rising: 5°C/min).

The increased and those of \(\text{Al}_2\text{O}_3\) and graphite were decreased for same keeping time. It was assumed that increase of heating temperature would increase reaction speed of \(\text{Al}_2\text{O}_3\) and graphite to form \(\text{Al}_2\text{O}_3\text{C}\).

As keeping time was extended, proportion of \(\text{Al}_2\text{O}_3\text{C}\) in the heated specimens was gradually increased and those of \(\text{Al}_2\text{O}_3\) and graphite were gradually decreased at each temperature. The conclusion was gained that extension of keeping time would increase reaction extend of \(\text{Al}_2\text{O}_3\) and graphite to form \(\text{Al}_2\text{O}_3\text{C}\).

The highest \(\text{Al}_2\text{O}_3\text{C}\) proportion was obtained at 1700°C for 9 h. In this specimen, mass content of \(\text{Al}_2\text{O}_3\text{C}\) was 91.3% and those of \(\text{Al}_2\text{O}_3\) and graphite were 6.2% and 2.5%, respectively. According to SEM observations on this specimen, the formed \(\text{Al}_2\text{O}_3\text{C}\) 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 \(\text{Al}_2\text{O}_3\text{C}\) grains.

2) Influence of grain size of \(\text{Al}_2\text{O}_3\)

The powder mixtures with \(\text{C}/\text{Al}_2\text{O}_3 = 1.5\) (\(\text{Al}_2\text{O}_3\): 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 \(\text{Al}_2\text{O}_3\) was advantageous for synthesis of \(\text{Al}_2\text{O}_3\text{C}\). Increasing grain size of \(\text{Al}_2\text{O}_3\), the reduction rate of \(\text{Al}_2\text{O}_3\) was decreased and at the same time, \(\text{Al}_2\text{C}_3\) was increased with \(\text{Al}_2\text{O}_3\text{C}\) decreased. It was assumed that enough fine \(\text{Al}_2\text{O}_3\) as starting raw material is necessary for synthesis of \(\text{Al}_2\text{O}_3\text{C}\) and in this research the best grain size of \(\text{Al}_2\text{O}_3\) was 0.1 μm.

3.2 Oxidation characteristics of \(\text{Al}_2\text{O}_3\text{C}\)

1) Oxidation of \(\text{Al}_2\text{O}_3\text{C}\) in air

The reheated powder was analyzed by using XRD and it was known that all residual graphite was oxidized; only \(\text{Al}_2\text{O}_3\text{C}\) and \(\text{Al}_2\text{O}_3\) existed (Fig. 10(a)).

TG patterns of the \(\text{Al}_2\text{O}_3\text{C}\) product, the reheated powder and the graphite used in this research are shown in Fig. 5.

From Fig. 5, the mass of the \(\text{Al}_2\text{O}_3\text{C}\) 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 \(\text{Al}_2\text{O}_3\text{C}\) was oxidized.

2) Oxidation of \(\text{Al}_2\text{O}_3\text{C}\) buried in graphite powder and heated in air

Phases of specimens from (\(\text{Al}_2\text{O}_3\text{C}\) 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, \(\text{Al}_2\text{O}_3\text{C}\) was decreased, simultaneously that of \(\text{Al}_2\text{O}_3\) was increased. \(\text{Al}_2\text{O}_3\text{C}\) was converted into \(\text{Al}_2\text{O}_3\) from about 600°C × 1 h and the conversion was finished at 1500°C × 3 h.

4. Discussion

1) \(\text{Al}_2\text{O}_3\text{C}\)’s formation and conversion into \(\text{Al}_2\text{C}_3\)

Figure 7 presents change of condensed phases for various partial pressures of \(\text{CO}\) (g) in the \(\text{Al}-\text{O}-\text{C}\) system, which was calculated thermodynamically (Since \(\text{Al}_2\text{O}_3\text{C}\) is unstable below 1715°C, \(\text{Al}_2\text{OC}\) is not included.). The formation free energy of \(\text{Al}_2\text{O}_3\text{C}\) reported by Lihrmann et al. was used in the calculation. Those of \(\text{Al}_2\text{O}_3\), \(\text{C}\), \(\text{Al}_2\text{C}_3\) and \(\text{CO}\) were from NIST-JANAF Thermo-chemical Tables. The standard pressure \((P^0)\) was 0.1 MPa (1 atm).

The critical \(P_{\text{CO}}/P^0\) of \(\text{Al}_2\text{O}_3\text{C}\) and \(\text{Al}_2\text{C}_3\) formation increases with rise of temperature from Fig. 7. Since the con-
version critical temperature of Al₂O₃—the Al₂O₃C is less than that of Al₂O₃C—the Al₂C₃ at same partial pressure of CO(g). Al₂O₃C would be formed firstly according to Re. (1) and then be converted into Al₂C₃ according to Re. (2) as temperature was raised.

\[
\begin{align*}
2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) &\rightarrow \text{Al}_2\text{O}_3\text{C}(s) + 2\text{CO}(g) \quad \text{(1)} \\
\text{Al}_2\text{O}_3\text{C}(s) + 6\text{C}(s) &\rightarrow \text{Al}_2\text{C}_3(s) + 4\text{CO}(g) \quad \text{(2)}
\end{align*}
\]

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

\[
\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al}_2\text{O}_3\text{C} + \text{C} \rightarrow \text{Al}_2\text{C}_3 + \text{C}
\]

In addition, since the stable area of Al₂O₃C is very narrow, the formed Al₂O₃C would quickly be reduced by C to form Al₂C₃ as temperature was raised.

Re. (1) should only occur in the reaction-starting period of Al₂O₃ and C, after Al₂O₃ was separated from C by formed Al₂O₃C, Al₂O₃C would be formed mainly according to Re. (3) and (4). Similarly, Re. (2) should also only happen in the reaction-starting period of Al₂O₃C and C, as long as Al₂O₃C was separated from C by formed Al₂C₃, Al₂C₃ would be formed mainly according to Re. (5) and (4). Overall reaction of Re. (3) and Re. (4) is same with Re. (1) \((3) \times 3 \times 4 = (1)\). Overall reaction of Re. (5) and Re. (4) is same with Re. (2) \((5) + 6 \times 4 = (2)\).

\[
\begin{align*}
2\text{Al}_2\text{O}_3(s) + 4\text{CO}(g) &\rightarrow \text{Al}_2\text{O}_3\text{C}(s) + 3\text{CO}_2(g) \quad \text{(3)} \\
\text{CO}_2(g) + \text{C}(s) &\rightarrow 2\text{CO}(g) \quad \text{(4)} \\
\text{Al}_2\text{O}_3\text{C}(s) + 8\text{CO}(g) &\rightarrow \text{Al}_2\text{C}_3(s) + 6\text{CO}_2(g) \quad \text{(5)}
\end{align*}
\]

Since this research was proceeded in argon atmosphere with partial pressure of O₂ as \(10^{-20}\) MPa as statement, O₂ should have reacted with the graphite heater, the graphite crucible and the graphite in mixtures into CO \((1/2\text{O}_2(g) + \text{C}(s) \rightarrow \text{CO}(g))\) with a partial pressure as approximately \(2 \times 10^{-20}\) MPa. But, even if \(P_{\text{CO}}\) is \(10^{-8}\) MPa, very higher than \(2 \times 10^{-20}\) MPa, the starting temperature of Al₂O₃C formation is 1180°C \((1453\, \text{K})\) 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 Al₂O₃ grain size on Al₂O₃C synthesis

The change of Al₂O₃ 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 Al₂O₃ with 0.1 μm in grain size and that from Al₂O₃ 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 Al₂O₃ was 0.1 μm and graphite was 30 μm, Al₂O₃C grains were adhering on the surface of graphite grains modeled in Fig. 8 (a), and when Al₂O₃ was 1 mm and graphite was 30 μm, graphite grains were adhering on the surface of Al₂O₃ grains, modeled in Fig. 9 (a).

As temperature was increased, Al₂O₃ reacted with graphite to form Al₂O₃C. When Al₂O₃ was 0.1 μm, Al₂O₃C would be formed in the contacting area of Al₂O₃ and graphite according to Re. (1) and in the Al₂O₃ grains area according to Re. (3) and (4) due to the diffusion of CO(g) and CO₂(g). Even if a part of formed Al₂O₃C reacted with C or CO(g) to form Al₂C₃, the formed Al₂C₃ would react with Al₂O₃ again to form Al₂O₃C according to Re. (6).
procedure was modeled in Fig. 8(b). The formed Al$_2$O$_3$C was dense grains as former statement. Since dense Al$_2$O$_3$C grains packed the residual graphite and so no gas was allowed to diffuse, the residual graphite could not further react with Al$_2$O$_3$C to form Al$_4$C$_3$. And because the formed Al$_2$O$_3$C estranged the residual graphite and the residual Al$_2$O$_3$, the residual graphite and Al$_2$O$_3$ also could not react with each other and so were remained in the last product, as modeled in Fig. 8(c).

When Al$_2$O$_3$ was 1 mm, the reduction of Al$_2$O$_3$ was slow and difficult and even a part of Al$_2$O$_3$ could not be reduced at last. Al$_2$O$_3$C would be formed on the surface of Al$_2$O$_3$ grains as modeled in Fig. 9(b). Since the formed Al$_2$O$_3$C and C or CO(g) coexisted for a long time, C was excessive for the formed Al$_2$O$_3$C, the formed Al$_2$O$_3$C would further be reduced to form Al$_4$C$_3$ according to Re. (2), (5) and (4). The formed Al$_4$C$_3$ was packing the grains of Al$_2$O$_3$ from observation of the heated product. From Fig. 4, besides Al$_2$O$_3$ and Al$_2$C$_3$, there are a little of residual Al$_2$O$_3$C and C in the heated specimen. The residual Al$_2$O$_3$C is considered a part of the formed Al$_2$O$_3$C that was near the unreacted Al$_2$O$_3$ and was not reduced into Al$_4$C$_3$. Another probability is the residual Al$_2$O$_3$C is the result of the reaction between the formed Al$_2$O$_3$C and the unreacted Al$_2$O$_3$ according to Re. (6). The residual Al$_2$O$_3$C should locate between unreacted Al$_2$O$_3$ grain and formed Al$_4$C$_3$. The reason that residual C existed is considered that, because the formed Al$_4$C$_3$ had estranged C from Al$_2$O$_3$ and Al$_2$O$_3$C, C could not react with Al$_2$O$_3$ or Al$_2$O$_3$C and was remained on the surface of grains as modeled in Fig. 9(c). When Al$_2$O$_3$ was 30 μm and 60 μm, the reaction tendencies were between the two states as discussed above.

3) Oxidation mechanism of Al$_2$O$_3$C

When Al$_2$O$_3$C product was oxidized in air by using TG-DTA method, since the sample was little and the flowing rate of air was high, Al$_2$O$_3$C should be sufficiently oxidized from about 820°C by O$_2$ in air to form Al$_2$O$_3$ and CO$_2$ according to Re. (7).

$$\text{Al}_2\text{O}_3\text{C}(s) + 2\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s) + \text{CO}_2(g) \quad (7)$$

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$_2$O$_3$C 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$_2$O$_3$C product buried in graphite powder was heated in air, Al$_2$O$_3$C should be oxidized according to Re. (8) to form Al$_2$O$_3$ and C, because the main gas is CO(g) in carbon-containing refractories at high temperature.\(^{11}\)

$$\text{Al}_2\text{O}_3\text{C}(s) + 2\text{CO}(g) \rightarrow 2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \quad (8)$$

$$2\text{C}(s) + \text{O}_2(g) \rightarrow 2\text{CO}(g) \quad (9)$$

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

$$\text{Al}_2\text{O}_3\text{C}(s) + \text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s) + \text{C}(s) \quad (10)$$

4) Advantage of Al$_2$O$_3$C 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$_2$O$_3$ → Al$_2$O$_3$C, Al$_2$O$_3$C(s) exists stably. It means that Re. (1) happens. When partial
into CO. Al$_2$O$_3$C’s role of oxidation resistance is concluded. The formed Al$_2$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.

$$2\text{Al}(s) + 3\text{CO}(g) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{C}(s) \quad (11)$$

The spalling is one of the main factors of carbon-containing refractories damage. Particularly for MgO-C refractories, the formed Al$_2$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. Al$_2$O$_3$C additive can slightly decrease the affection of expansion of spinel formation. So Al$_2$O$_3$C additive is considered better than Al additive on spalling resistance of refractories.

Furthermore, since Al$_2$O$_3$C will not be transformed into Al$_2$C$_3$, Al$_2$O$_3$C as an additive in carbon-containing refractories will not lead the refractories to collapse. Al$_2$O$_3$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 Al$_2$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 Al$_2$C$_3$. This process is complex and time-consuming. Using Al$_2$O$_3$C additive, this problem does not exist.

Moreover, Although Al$_2$O$_3$C started to be oxidized from about 820°C by O$_2$ later than graphite (from about 610°C by O$_2$), Al$_2$O$_3$C started to be oxidized at almost the same temperature with graphite when buried in graphite powder and heated in air. This indicates that Al$_2$O$_3$C can play a role of decreasing the oxidation of graphite in the carbon-containing refractories. Al$_2$O$_3$C, even if milled to very fine, has no combustible danger and so does not involve risks in utilization.

From the discussion above, Al$_2$O$_3$C is considered a promising additive for carbon-containing refractories.

5. Conclusions

Several dynamics factors influencing synthesis of Al$_2$O$_3$C and oxidation characteristics of Al$_2$O$_3$C were investigated and results are concluded as the following.

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

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

(3) Al$_2$O$_3$C started to be oxidized from about 820°C when heated in air.

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

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Influence of Heating Temperature, Keeping Time and Raw Materials Grain Size on 
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Synthesis of Al₄SiC₄ from Alumina, Silica and Graphite

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Al₄SiC₄ has been reported to be a good additive for carbon-containing refractories. The present study investigated various factors influencing the synthesis of Al₄SiC₄ by heating mixtures of Al₂O₃, SiO₂ and graphite in an argon atmosphere. The formation of Al₄SiC₄ began from a temperature between 1450°C and 1500°C. The formed quantity of Al₄SiC₄ increased as the heating temperature was raised. As the heating time was extended, the Al₄SiC₄ increased to its greatest amount and then it hardly changed. SiC and Al₂O₃ were also formed as mediums and were decreased as the heating time was extended. The optimum molar ratio of C, Al₂O₃ and SiO₂ was 8:2:0.8 and at that time pure Al₄SiC₄ was formed. The formation mechanism of Al₄SiC₄ was also discussed.

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Key-words: Al₄SiC₄, Synthesis, Al₂O₃, SiO₂, Graphite, Al₄O₆C, SiC, Carbon-containing refractories

1. Introduction

Metal Al, Si and SiC are frequently used in carbon-containing refractories as additives to improve the oxidation resistance and thermal properties, but they also cause some problems. For example, Al reacts with C in the refractories to form Al₄C₃, which may lead the refractories to collapse due to the poor hydration resistance of Al₄C₃. Al cannot be used in unshaped refractories containing water because it reacts with water. Fine Al powder is combustible, so its utilization involves risks. When Si or SiC is added into refractories, SiO₂ with a low melting point is formed due to oxidation.

In Al₄C₃-SiC₄ system (Fig. 1), there is a compound, Al₄SiC₄, that is stable until 2080°C and has good hydration resistance. A protective film composed of Al₂O₃ and mullite will be formed on the surface when Al₄SiC₄ is oxidized, which prevents the further oxidation. The Al₄SiC₄ added into MgO-C and Al₂O₃-C refractories will minimize the pores and improve the oxidation resistance and rupture modulus, because it reacts with CO gas to convert into Al₂O₃, Al₅Si₇O₁₆ and C. So, Al₄SiC₄ has been considered to be a promising additive for carbon-containing refractories.

Several methods for synthesis of Al₄SiC₄ have been investigated by using metals (Al, Si) and carbides (Al₄C₃, SiC) as starting raw materials on a laboratory scale. Yamaguchi et al. obtained Al₄SiC₄ by heating a mixture of Al, Si and C in an argon atmosphere at 1700°C. Yamamoto et al. synthesized Al₄SiC₄ at a low temperature of 1450°C by adding N(CH₃)₂OH into the powder of Al, Si and C. Wills et al. used SiC and Al₄C₃ raw materials and hot-press process at 1750-1800°C in an argon atmosphere for the synthesis of Al₄SiC₄. Hasegawa et al. prepared Al₄SiC₄ at a low temperature of 1600°C utilizing superfine SiC and Al₄C₃ powders. Yamaguchi et al. gained Al₄SiC₄ by heating a mixture of Al, Si and C containing 3% Al₂O₃ at 1700°C, and Inoue et al. synthesized Al₄SiC₄ by heating a mixture of Al, kaolin and C at 1700°C in a vacuum.

In order to obtain some fundamental information on the development of an industrial scale synthesis process of Al₄SiC₄, Al₂O₃, SiO₂ and graphite were used as starting raw materials, without metals and carbides, and influence factors on the synthesis, such as the condition of the mixture (powder or pressed compact), heating temperature, heating time and ratios of the raw materials, were investigated in the present study.

2. Experimental procedure

Common Al₂O₃ (average grain size: 0.1 μm, purity: ≥99.99 mass%), SiO₂ (average grain size: 100 μm, purity: ≥99 mass%) and graphite (average grain size: 30 μm, purity: ≥99 mass%) were used as starting raw materials. They were weighted in proportions of C:Al₄O₃:SiO₂ = 12:2:1, 8:2:0.8, 8:2:0.85, 8:2:0.9, 8:2:1.1, 8:2:1:0.5, 8:2:1:1, 4:2:1 (molar ratio), mixed with alcohol and dried in a vacuum-rotary evaporator. 2 g of the mixture in a high purity graphite crucible was set into an electric furnace with a graphite heater (Fig. 2). Arg gas (purity: ≥99.9999 mass%) was poured into the furnace after the vacuum. The mixture was heated to a temperature of 1450-1700°C at a rate of 10°C/min and maintained for 3-9 h under flowing Ar (1 L/min). Finally, the specimens were cooled to room temperature within the furnace through shutting off the power supply, where the average cooling rate was 64°C/min from 1700 to 1000°C. Phases in the specimens were identified by using X-ray diffraction (XRD, RINT 2200, Rigaku, Japan), and the microstructure was observed using field emission scanning electron microscope (FE-SEM, JSM-6340F, JEOL, Japan).
3. Results

3.1 Influence of mixture's condition

A powder mixture with C:Al$_2$O$_3$:SiO$_2$ = 8:2:1 and pressed compact mixture with C:Al$_2$O$_3$:SiO$_2$ = 8:2:1 and 20 mm diameter pressed at 100 MPa were heated at 1700°C for 9 h. The voidage of the powder mixture was 78% and that of the pressed compact was 31% before heating. The intensity of the strongest XRD peak of each phase in the heated specimens is shown in Fig. 3. From Fig. 3, it is known that there are not significant differences on the formed phases when using the powder mixture or the pressed compact mixture. Considering the fact that the product from the pressed compact mixture is porous, similar with that from the powder mixture, the powder mixtures were used in the following tests for convenience.

3.2 Influence of heating temperature

The results of the powder mixtures with C:Al$_2$O$_3$:SiO$_2$ = 12:2:1 and 8:2:1 heated at 1450, 1500, 1550, 1600, 1650 and 1700°C for 9 h are shown in Figs. 4(a) and (b). Al$_2$SiC$_4$ was detected in the specimens heated at 1500°C and above, and the quantity of Al$_2$SiC$_4$ increased by increasing the temperature. All SiO$_2$ has been reduced into SiC at the lowest heating temperature, 1450°C, and the quantity of SiC slowly decreased as the temperature was raised from 1450 to 1700°C. The Al$_2$O$_3$C was observed from 1550°C and the quantity of Al$_2$O$_3$C increased by increasing the temperature up to 1600°C, but disappeared at 1700°C.

3.3 Influence of heating time

The results of the mixtures with C:Al$_2$O$_3$:SiO$_2$ = 12:2:1 and 8:2:1 heated at 1700°C for 3, 5, 7 and 9 h are shown in Figs. 5(a) and (b). In the former ratio, the quantity of Al$_2$SiC$_4$ increased until 5 h and hardly changed after 5 h. Al$_2$O$_3$C has been formed at 3 h and disappeared at 5 h. In the later ratio, the changing tendency of each phase was the same as that in the former case, but the change was slower. In the specimen from the mixture with C:Al$_2$O$_3$:SiO$_2$ = 8:2:1 heated at 1700°C for 9 h, the phases were only Al$_2$SiC$_4$ and SiC.

3.4 Influence of SiO$_2$ content in the mixture

The results of the mixtures with C:Al$_2$O$_3$:SiO$_2$ = 8:2:x (x = 0.8, 0.85, 0.9, 1, 1.05, 1.1) heated at 1700°C for 9 h are shown in Fig. 6.

The quantity of SiC in the heated specimens dropped by decreasing the SiO$_2$ content in the mixtures. When x = 0.8, SiC disappeared and only Al$_2$SiC$_4$ existed in the specimen. XRD pattern and SEM micrograph of this specimen (x = 0.8) were shown in Figs. 7 and 8, respectively. The formed Al$_2$SiC$_4$ appeared to be powder consisting of plate-like crystals with about 1 μm thickness, 3-5 μm width and 6-8 μm in length.
4. Discussion

4.1 Formation mechanism of Al$_2$SiC$_4$

Figure 9 shows the SEM micrograph of the powder mixture with C:Al$_2$O$_3$:SiO$_2$ = 8:2:1. Since the starting raw materials are Al$_2$O$_3$ (average grain size: 0.1 μm), SiO$_2$ (average grain size: 100 μm), and graphite (average grain size: 30 μm), it was known that the great grains (Marked as S) with about 100 μm size are SiO$_2$ grains with fine Al$_2$O$_3$ on the surface and the flakes with about 30 μm size are graphite grains with fine Al$_2$O$_3$ on the surface. This condition of the unheated powder mixture was modeled as Fig. 10(a).

Figure 11 presents change of condensed phases for various partial pressures of CO(g) in the Al–Si–C–O system, calculated thermodynamically. The formation free energy of Al$_2$SiC$_4$ and Al$_2$O$_3$C reported by Yokokawa et al. and Lihrmann et al., respectively, were used in the calculation. Those of Al$_2$O$_3$, SiO$_2$, SiC and CO were from NIST-JANAF Thermochemical Tables. The standard pressure (P°) is 0.101325
Fig. 10. Models of formation process of Al$_2$SiC$_4$ (a)→b→c→d).

Fig. 11. Stable relation among the condensed phases in Al-Si-C-O system for temperature and partial pressure of CO(g).

From Fig. 11, it can be known that the change of condensed phases is according to the following when coexisting with C(s) as decreasing partial pressure of CO(g).

\[
\text{(Al}_2\text{O}_3 + \text{SiO}_2) \rightarrow (\text{Al}_2\text{O}_3 + \text{SiC}) \rightarrow (\text{Al}_4\text{O}_6\text{C} + \text{SiC}) \rightarrow (\text{Al}_2\text{SiC}_4)
\]

Since the conversion starting temperature of SiO$_2$→SiC is much lower than that of Al$_2$O$_3$→Al$_2$O$_3$C and that of Al$_2$O$_3$C→Al$_2$SiC$_4$, this was verified by the fact that all SiO$_2$ was converted to SiC at 1450°C, while Al$_2$O$_3$C and Al$_2$SiC$_4$ had not been observed at that temperature (Fig. 4(a) (b)).

**Figure 12** presents the micrograph of the specimen from the mixture with C:Al$_2$O$_3$:SiO$_2$=8:2:1 heated at 1450°C for 9 h. It was observed that fine powders packed the grains. In the grains, grain A seems that its surface was partly damaged. The grain A was analyzed by using EDAX. Since the phases in this specimen are only graphite, Al$_2$O$_3$ and SiC (Fig. 4(b)), it can be assumed that grain A is graphite, the powders adhered on the surface of grain A were Al$_2$O$_3$ and SiC. The formed SiC was a fine powder and adhered on the surface of the graphite grains and the Al$_2$O$_3$ powder. This existing condition of SiC suggests that SiC was formed mainly by gas reactions. The probable reaction process was stated below.

As the temperature was raised, firstly, SiO$_2$(s) would react with C(s) according to Re. (1).

\[
\text{SiO}_2(g) + C(s) = \text{SiO}(g) + \text{CO}(g)
\]

(1)

CO(g) would also reduce SiO$_2$ into SiO(g) according to Re. (2) and Re. (3).

\[
\begin{align*}
\text{SiO}_2(g) + \text{CO}(g) &= \text{SiO}(g) + \text{CO}_2(g) \\
\text{CO}_2(g) + C(s) &= 2\text{CO}(g)
\end{align*}
\]

(2) \hspace{1cm} (3)

Reaction. (1) is the same with the overall reaction of Re. (2) and Re. (3) \((2 + 3 = 1)\).

SiC was considered formed by Re. (4) from SiO(g) and CO(g). The formed SiC powder accumulated on the surface of the graphite grains and the Al$_2$O$_3$ powder as modeled in Fig. 10(b) (The graphite grain was enlarged for easier looking.), which is advantageous to the next reactions to form Al$_2$SiC$_4$.

\[
\text{SiO}(g) + 3\text{CO}(g) = \text{SiC}(s) + 2\text{CO}_2(g)
\]

(4)

The overall reaction of SiO$_2$ and C translating into SiC is Re. (5) \((1 + (4) + 2 \times (3))\).

\[
\text{SiO}_2(g) + 3\text{C}(s) = \text{SiC}(s) + 2\text{CO}_2(g)
\]

(5)
When the temperature was raised further, the Al₂O₃ would react with C to form Al₄O₆C according to Re. (6).

\[ 2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Al}_4\text{O}_6\text{C}(s) + 2\text{CO}(g) \]  \hspace{1cm} (6)

Once the Al₂O₃ was separated from C by the formed Al₄O₆C, it should react with CO(g) following Res. (7) and (3) to form Al₄O₆C.

\[ 2\text{Al}_2\text{O}_3(s) + 4\text{CO}(g) = 2\text{Al}_4\text{O}_6\text{C}(s) + 3\text{CO}_2(g) \]  \hspace{1cm} (7)

The overall reaction of Res. (7) and (3) is same with Re. (6). The formed Al₄O₆C contacted well with SiC powder as modeled in Fig. 10(c).

The stable area of Al₂O₃C is very narrow From Fig. 11, so the formed Al₂O₃C would be rapidly converted to Al₄SiC₄ during heating according to Re. (8) and Re. (9). Re. (8) is the same with the overall reaction of Re. (9) and Re. (3). The reaction result was modeled in Fig. 10(d). It was considered that Re.(8) was proceeded only in the starting period of the Al₂SiC₄ formation at the contacting points of Al₂O₃C, SiC and C. The main reaction for Al₂SiC₄ formation is Re. (9) and (3).

\[ \text{Al}_4\text{O}_6\text{C}(s) + 6\text{SiC}(s) = 3\text{Al}_2\text{SiC}_4(s) + 4\text{CO}(g) \]  \hspace{1cm} (8)

\[ \text{Al}_4\text{O}_6\text{C}(s) + 8\text{CO}(g) = 3\text{Al}_2\text{SiC}_4(s) + 6\text{CO}_2(g) \]  \hspace{1cm} (9)

The reason why Al₂SiC₄ was observed at 1500°C, but Al₂O₃C was not observed until 1550°C, is probably due to the rapid conversion from Al₂O₃C and SiC into Al₂SiC₄ after a little Al₂O₃C formed at 1500°C.

The overall reaction of Al₂SiC₄ formation from Al₂O₃, SiO₂ and C is Re. (10) \((= (5) + (6) + (8))\).

\[ 2\text{Al}_2\text{O}_3(s) + \text{SiO}_2(s) + 12\text{C}(s) = 3\text{Al}_2\text{SiC}_4(s) + 8\text{CO}(g) \]  \hspace{1cm} (10)

4.2 Volatile gases in Al-Si-C-O system

Deposit was observed on the upper metal inwall of the furnace after heating. The deposit was collected after the furnace was cooled into room temperature and analyzed by using XRD. The result is shown in Fig. 13. It is seen that the main crystal phases are Al₄C₃, Al₂O₃ and SiC and a amorphous phase also exists. These substances in the deposit are considered to be formed by the reactions of volatile gases of the Al-Si-C-O system.

**Figure 14** shows the equilibrium partial pressure of gases formed in the Al-Si-C-O system at 1973K (1700°C) calculated thermodynamically. There are many kinds of gases in the system, while Al₂O₃, SiO₂ and CO gases have a relatively high partial pressure, being the main gases. The formation reactions of the main gases are listed in Res. (1), (11) and (12) as examples.

\[ \text{Al}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Al}(g) + 3\text{CO}(g) \]  \hspace{1cm} (11)

\[ \text{Al}_2\text{O}_3(s) + 2\text{C}(s) = \text{Al}(g) + 2\text{CO}(g) \]  \hspace{1cm} (12)

The main gases may be also participating in the formation reactions of Al₂O₃C and Al₂SiC₄ in the powder mixtures. For example,

\[ 4\text{Al}(g) + 4\text{CO}(g) = 2\text{Al}_2\text{O}_3C(s) + 3\text{C}(s) \]  \hspace{1cm} (13)

\[ 2\text{Al}_2\text{O}_3(g) + 2\text{CO}(g) = \text{Al}_2\text{O}_3C(s) + \text{C}(s) \]  \hspace{1cm} (14)

\[ 4\text{Al}(g) + \text{SiO}_2(g) + 5\text{C}(s) = \text{Al}_2\text{SiC}_4(s) + 2\text{CO}(g) \]  \hspace{1cm} (15)

\[ 2\text{Al}_2\text{O}_3(g) + \text{SiO}_2(g) + 7\text{C}(s) = 2\text{Al}_2\text{SiC}_4(s) + 3\text{CO}(g) \]  \hspace{1cm} (16)

The overall reaction of \((11) + (13)) \) and \((12) + (14))\) is the same as Re. (6). The overall reaction of \((1) + 2 \times (11) + (15)) \) and \((1) + 2 \times (12) + (16))\) is Re. (10).

The deposit was considered to be formed by the Al, Al₂O₃, SiO₂ and CO gases according to Res. (17)-(20).

\[ 2\text{Al}(g) + 3\text{CO}(g) = \text{Al}_2\text{O}_3(s) + 3\text{C}(s) \]  \hspace{1cm} (17)

\[ \text{Al}_2\text{O}_3(g) + 2\text{CO}(g) = \text{Al}_2\text{O}_3(s) + 2\text{C}(s) \]  \hspace{1cm} (18)

\[ 2\text{Al}_2\text{O}_3(g) + 8\text{CO}(g) = 4\text{Al}_2\text{SiC}_4(s) + 5\text{CO}_2(g) \]  \hspace{1cm} (19)

\[ \text{SiO}_2(g) + 3\text{CO}(g) = \text{SiC}(s) + 2\text{CO}_2(g) \]  \hspace{1cm} (20)

No Al₂SiC₄ crystal was detected in the deposit. The reason may be that Al₂SiC₄ was not formed because the temperature was low on the upper metal inwall of the furnace (In the heating period, the temperature at this site was estimated as no higher than 1000°C, because the furnace was cooled by flowing water in the metal wall.) or that Al₂SiC₄ was formed, but was in an amorphous phase.

On the other hand, the best ratio for the synthesis of pure Al₂SiC₄ phase is 8:2:0.8, different with the ratio of 12:2:1 in theory (Re. (10)). This indicates that the volatilized quantities of Al₂O₃ and SiO₂ are comparatively more than that of C and the volatilized quantity of Al₂O₃ is comparatively more than that of SiO₂ in this research.
5. Conclusions

Synthesis of AlSiC₄ by heating the mixture of Al₂O₃, SiO₂ and graphite in an argon atmosphere was investigated. The following results were obtained.

(1) The formation of Al₅SiC₄ began from a temperature between 1450°C and 1500°C. The formed quantity of Al₅SiC₄ was increased as the heating temperature was raised.

(2) As the heating time was extended, Al₅SiC₄ increased into its greatest amount and then hardly changed. SiC and Al₂O₃C were also formed as mediums and were decreased as the heating time was extended.

(3) The optimum molar ratio of C, Al₂O₃ and SiO₂ was 8:2:0.8 and at that time the pure Al₅SiC₄ was formed.

(4) The formed Al₅SiC₄ was powder consisting of plate-like crystals with about 1 μm thickness, 3-5 μm width and 6-8 μm in length.

References

Effect of porosity on carbonation and hydration resistance of CaO materials

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Abstract

CaO pellets with different porosity were carbonated at 700 °C in CO2 atmosphere. The carbonation rate was controlled by the diffusion of CO2, regardless of the difference in porosities. For the low-porosity pellet, carbonation reaction only occurred on the surface, with a dense CaCO3 film thus formed, which combined well with the substrate material; while for the pellet of high-porosity, the carbonation reaction occurred simultaneously both on surface and inside pores, and each CaO grain was surrounded by CaCO3 film that contained microfissures. Hydration test results showed that carbonation treatment could effectively improve the hydration resistance of CaO materials regardless of porosity, but the carbonated high-porosity pellet was prone to breakage due to poor combination between the carbonated CaO grains. Therefore, for the purpose to improve the hydration resistance by carbonation treatment, it is recommended that the CaO materials should be either with less appreciable apparent porosity or with a limited carbonation ratio for the high-porosity CaO material.

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Keywords: A. CaO materials; B. Porosity; C. Carbonation treatment; D. CaCO3 film; E. Hydration resistance

1. Introduction

Lime has the properties of high melting temperature, low vapor pressure, and thermodynamic stability in the presence of carbon as well as high alkalinity, thus it has long been considered to use as the raw materials for high temperature ceramics (such as crucible and ceramic filter), refractory and metallurgical accessories (such as refining slag and tundish covering powder).1–6 With the development of clean steel production, free lime containing materials have been becoming more and more important for increasing the service life and removing inclusions from molten steel.7–11 It is considered that application of CaO containing materials is an essential direction for the development of metallurgical industries and other high temperature field.12 However, the application of CaO containing materials have been inhibited due to their drawback of poor hydration resistance, and many studies on this subject had been carried out from quite a long time ago.13–15

Among all of the methods to improve the hydration resistance of CaO materials, carbonation treatment is considered to be “green”, since no impurities are added into CaO materials so that their advantages are kept after CaCO3 decomposes at high temperature. Another reason for calling this method “green” is that carbonation process can consume CO2 which is friendly to environment. Therefore, the studies on improving hydration resistance of CaO materials by carbonation treatment have been conducted since 1970s.16–19 However, most of these works focused on the carbonation conditions by using deadburned CaO clinker as starting material, and it has been concluded that the optimum carbonation temperature is around 700 °C.16,17 In fact, besides the deadburned CaO clinker with high compactness used for refractory materials, there are also porous CaO materials, such as CaO filter and lightburned CaO for tundish covering powder, and it is more difficult to prevent these porous CaO materials from hydrating.5 It is necessary to confirm the feasibility to improve these CaO materials by carbonation treatment. Therefore, the present work investigated the carbonation of CaO materials with different porosities. The influence of porosity on carbonation behavior and microstructure of CaO pellets as well as their hydration properties were discussed.

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2. Experimental

Reagent CaCO₃ powder (99.5% purity and average size of 10 μm) and lightweight CaCO₃ powder were used as starting materials. The lightweight CaCO₃ powder was prepared from precipitation reaction by bubbling CO₂ gas to aqueous solution of CaO (that was derived from heating reagent CaCO₃ powder at 900°C), with average size less than 1 μm. The two kinds of powders were pressed to pellet sized of 20 mm × 20 mm × ~5 mm by CIP under pressure of 100 MPa, and then fired at 1500°C for 4 h in an electric furnace to obtain CaO pellets with low- and high-porosities. To obtain the sintered CaO pellets with different porosities, the pellets pressed from lightweight CaCO₃ powder were also fired at 1250–1400°C (with the temperature interval of 50°C) for 4 h.

Then the obtained CaO pellets were led into a vertical alumina tube furnace kept at 700°C, with mass change recorded continuously. CO₂ gas flowed into the tube furnace at the bottom and exited at the top with a rate of 0.4 L/min during the whole heating and cooling process. The flow of CO₂ was so slow that it did not disturb the measurement of mass change in the present experiment conditions.

The samples were characterized by bulk density and apparent porosity, X-ray diffraction (XRD, Cu target, 20 kV and 20 mA), scanning electron microscopy (SEM), and hydration resistance. The bulk density and apparent porosity of samples before and after carbonation were measured by immersion method in kerosene under vacuum using Archimedes’ principle and calculated according to Eqs. (1) and (2):

\[ \text{Bulk density} = \frac{m_1 d}{m_3 - m_2} \text{ (g/cm}^3) \]  
\[ \text{Apparent porosity} = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \]  

where \( m_1 \) is the mass of dried sample in air (g), \( m_2 \) is the mass of a sample in kerosene (g), \( m_3 \) is the mass of a sample with free bubbles on the surface (g), and \( d \) is the density of kerosene (g/cm³).

The hydration resistance of the sample was evaluated by measuring the mass gain after soaking the pellets in a chamber kept at 70°C and 90% relative humidity.

3. Results

3.1. Carbonation properties

Table 1 shows the porosity and relative density of the CaO pellets before and after carbonation treatment. After firing at 1500°C for 4 h, the relative density of CaO pellet sintered from reagent CaCO₃ was 70% and its apparent porosity was 27% (hereafter called high-porosity pellet). The relative density was calculated by comparing bulk density of the pellet as the fraction of its theoretical density that was calculated from a fractional summation of the theoretical densities of cubic CaO (3.346 g/cm³) and hexagonal CaCO₃ (2.710 g/cm³) according to Eq. (3):

\[ \text{Theoretical density} = \frac{m_{\text{CaO}} + m_{\text{CaCO}_3}}{m_{\text{CaO}}/3.346 + m_{\text{CaCO}_3}/2.710} \]  

where \( m_{\text{CaO}} \) and \( m_{\text{CaCO}_3} \) are the mass of CaO and CaCO₃ in the pellet, respectively.

After carbonation treatment, the relative density of the high-porosity sample increased obviously, and almost all of the open pores turned to the closed ones. The relative density increased to 86% and the apparent porosity decreased significantly to 0.2%. But for the pellet sintered from lightweight CaCO₃, its relative density was 95% and the apparent porosity was 0.2% (hereafter called low-porosity pellet). After carbonation treatment, there was little change in relative density and the apparent porosity disappeared.

Fig. 1 shows the mass change of the low- and high-porosity pellets against carbonation time. The mass change was expressed by the percentage of mass gain to the original mass. The mass gain increased gradually and reached a plateau indicating completion of the carbonation process. The mass gain was only 2% for the low-porosity pellet, whereas it was about 14% for the high-porosity one. For both samples, a parabolic relationship between mass gain and carbonation time is observed. This result indicates that for both the low- and high-porosity CaO pellets, the carbonation reactions were controlled by the diffusion process.

Fig. 2 shows the changes of relative density and apparent porosity of CaO pellets sintered at 1250–1400°C for 4 h and subsequently carbonated at 700°C for 24 h. It is observed that the relative density increased and apparent porosity decreased with increase of firing temperature. After carbonation treatment, the relative density of all samples increased appreciably, with the disappearance of the apparent porosity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative density (%)</th>
<th>Apparent porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>High-porosity</td>
<td>70</td>
<td>86</td>
</tr>
<tr>
<td>Low-porosity</td>
<td>95</td>
<td>95</td>
</tr>
</tbody>
</table>

Fig. 1. Values of mass gain against carbonation time kept at 700°C. M is the original mass of the sample and \( \Delta M \) is the mass gain after carbonation treatment.
3.2. Phase composition and microstructure

Fig. 3 shows XRD patterns of the low- and high-porosity CaO pellets after carbonation treatment. CaCO₃ (calcite) was identified in both samples, indicating the formation of CaCO₃ after carbonation treatment. The intensity of the formed CaCO₃ in the high-porosity sample was much stronger than that in the low-porosity one, indicating the amount of the formed CaCO₃ in the high-porosity sample was more than that in the low-porosity one. For both the low- and high-porosity pellets, CaO was still the main phase after carbonation treatment.

Fig. 4 illustrates the microstructure of the low-porosity pellet before and after carbonation treatment. It is observed that the low-porosity pellet was only carbonated on the surface, with a dense CaCO₃ film about 2 µm in thickness formed. It is also observed that the CaCO₃ film combined well with the substrate CaO material. This result is correspondent to the previous works.¹⁶,¹⁷ But different from the low-porosity sample, the high-porosity pellet was carbonated both on the surface and in the pores, with each CaO grain being encompassed by the formed CaCO₃ film. In addition, microsisses were observed in the formed CaCO₃ film (Fig. 5).

3.3. Hydration properties

Fig. 6 illustrates the relationship between mass change and hydration time kept at 70 °C and 90% relative humidity for both the low- and high-porosity pellets with and without carbonation treatment. The mass gain was expressed by the percentage of mass gain to the original mass of CaO pellets. The arrows represent the time when the pellets broke during hydration process. It shows that carbonation treatment significantly improved the hydration resistance of both the low- and high-porosity samples, with the formation of an induction period (during which there was no appreciable mass change).¹⁸ For the low-porosity pellet, the hydration reaction proceeded from surface to inside gradu-
ally, with appreciable interface between the hydrated and unhydrated part. For the orientated growth of the formed Ca(OH)$_2$ and anisotropic volume expansion when CaO was hydrated, cracks were observed at the corner (Fig. 7). After carbonation treatment, a long induction period of 7 days formed and the sample did not break after soaking for 21 days, with mass gain of about 22% that was a little more than that of the uncarbonated one (20%).

![Fig. 5. Fractured surfaces of the high-porosity pellet: (a) before and (b) after carbonation treatment.](image)

Fig. 6. Mass gains of: (a) the low- and (b) the high-porosity CaO pellets with time soaking at 70 °C and 90% RH. $M$ is the original mass of the sample before hydration test and $\Delta M$ is the mass change after hydration test.

![Fig. 7. Microstructures of CaO pellet after soaking at 70 °C and 90% humidity for 96 h.](image)

But for the carbonated high-porosity pellet, there was only a short induction period of about 12 h. The interesting result was that the pellet broke to several pieces after hydration test for only 6 h. This time was within the induction period. Even after the induction period, the hydration reaction still proceeded at a low rate, and the mass gain was only about 2.5% after 24 h. Then with hydration time increasing, the broken pieces further turned to much smaller size gradually, and finally turned to fine powders. From these results, it is considered that the carbonated low- and high-porosity pellets were hydrated in different mechanisms.

Fig. 8 shows the hydration test result of the carbonated CaO pellets with different apparent porosity. It is found that although there was little apparent porosity for all the carbonated pellets, the time of the carbonated CaO pellet to break was abruptly decreased with increase of the apparent porosity of the original CaO pellet, even with a very limited mass gain. From this result, it is considered that the breakage of the carbonated CaO pellet was closely dependent to apparent porosity or compactness of the sintered original CaO pellet.

4. Discussion

4.1. Carbonation properties and microstructure

From the curves of mass gain and microstructure observation, it is considered that the CaO materials with different porosity...
Fig. 8. The dependence of apparent porosity on the time of the carbonated CaO pellets to break and its mass gain during hydration process.

were carbonated in different mechanisms, as shown in Fig. 9. For the pellet without apparent porosity, CO₂ gas could not flow into the sample and thus the carbonation reaction only occurred on the surface, with a thin and dense CaCO₃ film formed on the surface. It is calculated that the molar volume of CaCO₃ (36.9 cm³/mol) is larger than that of CaO (16.7 cm³/mol), and there is a large volume expansion when CaO converts to CaCO₃, with the generation of stress between the formed CaCO₃ and the uncarbonated CaO grains. But for the amount of the formed CaCO₃ was limited when the low-porosity pellet was carbonated, the stress between the formed CaCO₃ and the substrate CaO grains was not so severe to form microfissures. Therefore, there was no microfissures were observed in the CaCO₃ film which combined well with the substrate CaO materials. It is unnecessary to concern for the formation of microfissure when the CaO materials of low-porosity were carbonated.

But for the pellet with apparent porosity, the CO₂ gas could easily flow to the inside of the sample, and thus carbonation reaction occurred in all open pores, with each CaO grain surrounded by CaCO₃ films. When the CaCO₃ films formed inside the pores, CO₂ gas had to pass through these films to maintain the reaction proceeding. Thus, though the carbonation reaction occurred inside all pores, the carbonation rate was still controlled by the diffusion of CO₂ through these formed CaCO₃ films around CaO grains. With increase of the thickness of the formed CaCO₃ film and decrease of apparent porosity, the diffusion of CO₂ became so difficult that the carbonation reaction tended to cease. Since the reaction specific area of the high-porosity pellet was much larger than that of the low-porosity one, its carbonation rate was much fast than that of the low-porosity one, with a much more mass gain (Fig. 1). With the formation of the large amount CaCO₃ and the volume expansion, the stress between the formed CaCO₃ film and CaO grains was so severe that microfissures would form (Fig. 4). It is considered that the formation of these microfissures degraded the combining strength between the carbonated CaO grains.

Therefore, in order to prevent microfissure forming when the CaO materials is carbonated, the following two ways are recommended: one is that the pellet should be without appreciable apparent porosity and thus to ensure the carbonation reaction occurring on the surface; the other is to control the formed CaCO₃ amount, in another words, to control the carbonation ratio when the CaO materials with high-porosity is carbonated.

4.2. Hydration properties

Since the diameter of H₂O molecule (0.151 nm) is smaller than that of CO₂ molecule (0.232 nm), water vapor could still pass through CaCO₃ film although the carbonation reaction ceased owing to CO₂ diffusion. Therefore, carbonation treatment could effectively improve hydration resistance of CaO materials, but it could not inhibit CaO hydrating completely. For the low-porosity pellet, a long induction period of 7 days formed owing to the formation of dense CaCO₃ film after carbonation treatment. The time of the induction period is considered to be dependent to the thickness and the compactness of the formed CaCO₃ film. In fact, since the hydration reaction was conducted under the condition of 70 °C and 90% relative humidity, the hydration rate was several decade times to normal climate condition. Thus an induction period of 7 days means that the carbonated CaO materials could be safely stored for more than 1 year. Therefore, it is considered that carbonation treatment could almost completely prevent CaO materials from hydrating during storage period. In addition, whether carbonated or not, the hydration process of the low-porosity pellet proceeded from surface to inside. The breakage of the pellet was due to the volume expansion with the hydration reaction proceeding, and thus the mass gains were equivalent when the carbonated and uncarbonated samples broke. Therefore, it is considered that carbonation treatment is suitable for improving hydration resistance of compact CaO materials, without concerning for the materials over carbonated.

For the uncarbonated CaO pellet with high apparent porosity, the water vapor easily flowed to the inside of the pellet, thus the hydration reaction occurred in the whole sample at the same time and a high hydration rate was obtained, which led to the pellet soon breaking to fine powder due to the abruptly volume expansion caused by hydration reaction. Similar to the low-porosity sample, the formation of dense CaCO₃ film after carbonation treatment effectively retarded occurrence of the hydration reaction, with the formation of an appreciable induction period.
As described above, the combination between the carbonated CaO grains was very weak due to the formation of microfissures when the carbonation ratio is too large, and it became much weaker when the pellet hydrated. Therefore, for the carbonated pellet of high-porosity, the breakage was so sensitive to the apparent porosity that the carbonated pellet would break even with a very small amount of CaO hydrated (Fig. 8). After the carbonated pellet broke, the CaCO₃ films around CaO grains still effectively inhibited the hydration reaction, so that the time of the pellet to break was shorter than the induction period (Fig. 6). Therefore, it is considered, for the carbonated high-porosity pellet, its breakage was not for the volume expansion with hydration proceeding, but mainly for the poor combination between the carbonated CaO grains. For this reason, compared with the low-porosity pellet, the carbonated high-porosity one was hydrated in a different mechanism, as shown in Fig. 10. A more stage formed during hydration process. It firstly broke to several pieces, and further turned to much smaller size gradually with hydration time increasing. Thus, it is considered, the following two ways to prevent the carbonated CaO materials easily break are recommended: one is that the original CaO pellet should be with less appreciable apparent porosity and thus to ensure the carbonation reaction occurring on the surface; the other is to control the formed CaCO₃ amount, in another words, to control the carbonation ratio to avoid "over carbonated" when the high-porosity CaO materials are carbonated.

5. Conclusion

Based on the above results, in order to improve the hydration resistance of CaO materials by carbonation treatment, the followings are concluded:

1. The high-porosity CaO materials were carbonated with a higher rate compared to the low-porosity one. The carbonation processes were controlled by the diffusion of CO₂ through the formed CaCO₃ film, regardless of the porosity.

2. The high-porosity CaO materials was carbonated both on the surface and in the pores, with each CaO grain being encompassed by CaCO₃ film containing microfissures; whereas the low-porosity one was only carbonated on the surface, with the formation of a dense CaCO₃ film that combined well with the uncarbonated CaO materials.

3. The breakage of carbonated low-porosity pellets was due to the volume expansion caused by hydration reaction, whereas it was mainly due to the poor combination between the carbonated CaO grains for the high-porosity one.

4. Carbonation treatment effectively improved the hydration resistance of CaO materials, with formation of appreciable induction period, regardless of porosity. For the low-porosity pellet, the induction period reached to 7 days. However, since the carbonated CaO materials of high-porosity would easily break due to the poor combination between the carbonated CaO grains caused by formation of microfissures, it is necessary to control the carbonation ratio to avoid "over carbonated".

References


BEHAVIOR OF $\text{Al}_4\text{SiC}_4$ ADDED TO THE CARBON CONTAINING REFRactories

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Okayama Ceramics Research Foundation, Okayama, Japan

INTRODUCTION
Authors are researching new materials in the Al-Si-C system for the refractories\(^1\)\(^2\)\(^3\)\(^4\). The Al-Si-C system includes five compounds of $\text{Al}_4\text{SiC}_4$, $\text{Al}_4\text{Si}_2\text{C}_3$, $\text{Al}_4\text{Si}_2\text{C}_7$, $\text{Al}_4\text{Si}_2\text{C}_6$ and $\text{Al}_4\text{SiC}_7$. In these compounds, $\text{Al}_4\text{SiC}_4$ is most expected to be a new material for refractories, because it is stable in a wide range of temperature and has high melting point (2037°C\(^4\)) and high slaking resistance\(^4\). In this study, in order to clarify the behavior and the effect of $\text{Al}_4\text{SiC}_4$ on the carbon containing refractories, the properties and phase changes of the MgO-C brick containing $\text{Al}_4\text{SiC}_4$ powder were investigated comparing with the MgO-C brick containing aluminum powder.

EXPERIMENTAL PROCEDURE
$\text{Al}_4\text{SiC}_4$ powder was prepared by the following methods. Aluminum powder, silicon powder and carbon black were weighted in a theoretical composition and dry-mixed by using a ball mill for 10 hours. The mixed powder were placed in a carbon crucible and heated at 1300°C for 3 hours in argon atmosphere. The composition of the heated powder was a single-phase of $\text{Al}_4\text{SiC}_4$, and its average particle diameter was 8μm after ball milling for 10 hours. $\text{Al}_4\text{SiC}_4$ powder prepared in this method was used for the following investigation.

Table 1 indicates the composition of the MgO-C brick samples. Electric fused magnesia of purity 99% and flake graphite of purity 99% were used. $\text{Al}_4\text{SiC}_4$ powder was added instead of aluminum powder. Sample number 4 and 5 had same molar ratio of aluminum and silicon. Novolac type phenol resin was used as a binder and hexamethylenetetramine were added as a hardening agent. Brick samples were prepared with heating at 200°C for 6 hours after mixing and pressing.

The brick samples were cut off to 25×25×25mm size and put into the crucible which was filled by carbon powder, and then heated at various temperatures for 3 hours using an air atmosphere electric furnace. After heating, mass change, porosity, density and crushing strength of the samples were measured. The compositions of the heated samples were investigated by a powder X-ray diffraction method.

The samples with 25×25×25mm size were heated at 1400°C for 3 hours in air atmosphere in order to evaluate an oxidation resistance of the brick samples. The oxidation test was carried out with rapid heating and rapid cooling method. After heating, the decarbonized layer thickness of the samples was determined. In addition, in order to estimate a slaking resistance of the bricks after heating, the samples were heated at 1400°C for 3 hours in carbon powder using the air atmosphere furnace, and then the degree of their structure deterioration was monitored during putting them in the room.

**Table 1. Composition of the MgO-C brick samples.**

<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused MgO (&lt;1mm)</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Flake graphite (&lt;0.15mm)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Al powder (&lt;75μm)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Si powder (&lt;45μm)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\text{Al}_4\text{SiC}_4$ powder</td>
<td>3</td>
<td>3</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Phenol resin</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Hexamethylenetetramine</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

RESULTS
The mass changes of the samples during heating at various temperatures in the reducing atmosphere are shown in **Figure 2**. The mass decrease at 800°C depends on the thermal decomposition of the phenol resin. Based on the data at 800°C, the rapidly mass gains are observed at 1000°C in the No.2 and No.4 samples which include the aluminum powder. The reaction with mass increase is considered to occur rapidly between 800°C and 1000°C. In the case of No.3 and No.5 which include $\text{Al}_4\text{SiC}_4$ powder, the mass gain is observed at 1200°C and continues to 1400°C. Therefore, the reaction with mass increase is considered
to occur gradually between 1000°C and 1400°C. After heating at 1400°C and 1500°C, the mass gain of No.3 and 5 is larger than that of No.2 and 4. It follows that Al₂SiC₄ causes large mass increase more than aluminum at high temperature.

Figure 3 shows the apparent porosity of the samples after heating at various temperatures in the reducing atmosphere. The porosity increase at 800°C depends on the thermal decomposition of the phenol resin. The porosity of No.1 sample which does not include any additives increases with rising of temperature. That of No.2 and No.4 which contain aluminum powder hardly increases above 800°C. In contrast, the porosity of No.3 and No.5 which contain Al₂SiC₄ powder decreases linearly above 800°C, then the porosity after heating at 1500°C is 2% lower than that after heating at 800°C. From this, it is understood that Al₂SiC₄ powder densifies the MgO-C brick texture efficiently with the mass increasing reaction shown in Fig.2.

Figure 4 shows the cold crushing strength of the samples after heating at various temperatures in the reducing atmosphere. The strength decreases by the thermal decomposition of the phenol resin in the low temperature. The strength of No.2 and No.4 which include aluminum powder increases markedly between 800 and 1000°C. That of No.4 including silicon powder increases slightly above 1000°C. In contrast, the strength of the sample containing Al₂SiC₄ powder increases gradually with rising of temperature. In the case of No.3 which contains 3 mass% of Al₂SiC₄ powder, it occurs above 1200°C, and in the case of No.5 containing 5.1 mass% of Al₂SiC₄ powder, it occurs above 1000°C. The strength increase of No.3 and No.5 is characterized to be not rapid and be gradual. This phenomenon is interesting from the viewpoint of a spalling resistance improvement, because of the gradual change of the mechanical property with changing of temperature.
The mineral phase of the samples after heating in the reducing atmosphere is indicated in **Figure 5**. In the case of No.2, aluminum disappears and then Al$_2$C$_3$, AlN and MgAl$_2$O$_4$ (spinel) are formed at 1000°C. In the case of No.3, Al$_5$SiC$_4$ does not change below 1000°C. The reaction products are observed above 1200°C. Spinel and SiC are formed at 1200°C and the spinel increases with increasing of temperature. In addition, Mg$_2$SiO$_4$ (forsterite) is formed above 1400°C. Unlike No.2, the formation of Al$_2$C$_3$ and AlN are not observed. Al$_5$SiC$_4$ decreases at 1200°C and disappears at 1400°C. It follows that the reaction start temperature of Al$_5$SiC$_4$ powder in the MgO-C brick is understood to be high in comparison with aluminum powder. This tendency agrees with the results that the physical properties change gradually above 1200°C as shown in Fig.2 – Fig.4.

**Figure 6** shows the results of the oxidation test. The bar in the figure indicates the decarbonized layer thickness of the sample after heating at 1400°C in the air. The oxidized layer thicknesses of the samples containing additives are thinner than that of the sample without additive. Comparing No.2 and No.3, the decarbonized layer thicknesses are almost same. In addition, comparing No.4 and No.5, they are almost same too. Therefore, the oxidation resistance of the MgO-C bricks is recognized to be improved by Al$_5$SiC$_4$ powder as well as by aluminum powder.

The slaking test results are indicated in **Figure 7**. The photographs show the appearance of the samples which were kept in a room atmosphere for two weeks after the reducing atmosphere heating at 1400°C. No.2 sample added aluminum powder only is destroyed and became powder by the hydration reaction with the volume expansion. No.4 sample added aluminum and silicon powder has a smaller degree of deterioration than No.2. But many cracks are formed in the sample and its strength decreases by the hydration reaction. In comparison, in the case of No.3 and No.5 which were added Al$_5$SiC$_4$ powder, the crack is not observed at all. In the sample containing Al$_5$SiC$_4$ powder, Al$_2$C$_3$ and AlN which cause hydration reaction don’t form during heating as indicated in Fig.5. That is thought to be a reason of the high slaking resistance.

**DISCUSSION**

The behavior of Al$_5$SiC$_4$ in the brick is discussed as follows. When the reactions of Al$_5$SiC$_4$ in the carbon containing refractories are considered, the gas phase existing in the pore of the texture is important. Since an actual furnace is usually used in the air atmosphere, the surface of the refractory is exposed to the air. In this case, if the temperature is above 1000°C, the inner pore of the carbon containing refractory is filled by CO gas, and then the partial pressure of CO gas is approximated to 1.013×10$^5$Pa (1atm, P$_{CO}$=1). Al$_5$SiC$_4$ react mainly with CO gas under this condition, which means the solid–gas reaction occurs. The condition of the reducing atmosphere in this study is similar, the atmosphere in pores of the sample is considered to be near to P$_{CO}$=1.

Al$_5$SiC$_4$ powder added to the MgO-C brick begins to change into MgAl$_2$O$_4$ and SiC at 1200°C as shown in Fig.5, that is, Al$_5$SiC$_4$ reacts with CO gas to form Al$_2$O$_3$ and SiC, and then Al$_2$O$_3$ react with MgO to form MgAl$_2$O$_4$. SiC react with CO gas and MgO to form Mg$_2$SiO$_4$ at 1400°C. These reactions are indicated as the following equations.

1st stage reaction;

\[
\text{Al}_5\text{SiC}_4(s)+6\text{CO(g)}=2\text{Al}_2\text{O}_3(s)+\text{SiC(s)}+9\text{C(s)} \quad (1)
\]

\[
\text{Al}_2\text{O}_3(s)+\text{MgO}=\text{MgAl}_2\text{O}_4(s) \quad (2)
\]

\[
\text{Al}_5\text{SiC}_4(s)+2\text{MgO}+6\text{CO(g)}
\quad =2\text{MgAl}_2\text{O}_4(s)+\text{SiC(s)}+9\text{C(s)} \quad (3)
\]

2nd stage reaction;

\[
\text{SiC(s)}+2\text{CO(g)}=\text{SiO}_2(s)+3\text{C(s)} \quad (4)
\]

\[
\text{SiO}_2(s)+2\text{MgO}=\text{Mg}_2\text{SiO}_4(s) \quad (5)
\]

\[
(\text{SiC(s)}+2\text{MgO}+2\text{CO(g)}=\text{Mg}_2\text{SiO}_4(s)+3\text{C(s)} \quad (6)
\]

**Table 2** indicates mass and volume change in the above reactions. It shows that these reactions (equation 3 and 6) involve the large increase of mass and volume.
In addition, the large increase is recognized to be mainly influenced by the reactions with CO gas (equation 1 and 4). The carbon precipitated in the equation 1 or 4 is considered to influences remarkably to the volume expansion and to causes the texture densification as shown in Fig.3.

**Tab. 2. Calculated mass and volume increases.**

<table>
<thead>
<tr>
<th>Equation No.</th>
<th>Mass change /%</th>
<th>Volume change /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+91.3</td>
<td>+199.2</td>
</tr>
<tr>
<td>2</td>
<td>+63.5</td>
<td>+137.0</td>
</tr>
<tr>
<td>3</td>
<td>+139.7</td>
<td>+397.7</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>-3.4</td>
</tr>
<tr>
<td>5</td>
<td>+46.4</td>
<td>+136.8</td>
</tr>
</tbody>
</table>

*Following values were used as density [×10³ kg·m⁻³]*

\[
\begin{align*}
\text{Al}_4\text{SiC}_4(s) & : 3.03 \\
\text{Al}_2\text{O}_3(s) & : 3.99 \\
\text{SiC(s)} & : 3.22 \\
\text{SiO}_2(s) & : 2.66 \\
\text{MgAl}_2\text{O}_4(s) & : 3.58 \\
\text{Mg}_2\text{SiO}_4(s) & : 3.22 \\
\text{C(s)} & : 1.60 \\
\end{align*}
\]

**Fig. 8. Equilibrium partial pressures of the gases in the Al-Si-C-O system.**

Figure 8 shows the stable condensed phases and the equilibrium partial pressures of the gases in the Al-Si-O-C system at 1700K under coexistence of the solid carbon. It indicates that \(\text{Al}_4\text{SiC}_4(s)\), \(\text{Al}_2\text{O}_3(s)\)+\(\text{SiC(s)}\) and \(\text{Al}_2\text{O}_3(s)+\text{Al}_3\text{Si}_{2}\text{O}_{11}(s)\) are stable in the condition of \(\text{P}_{\text{CO}}<10³\), \(10²<\text{P}_{\text{CO}}<0.2\) and \(\text{P}_{\text{CO}}>0.2\), respectively. Since the added \(\text{Al}_4\text{SiC}_4\) is not stable in \(\text{P}_{\text{CO}}=1\), \(\text{Al}_4\text{SiC}_4\) first changes into \(\text{Al}_2\text{O}_3\) and \(\text{SiC}\), and next \(\text{SiC}\) changes into \(\text{SiO}_2\). These relations agree with the results shown in Fig.5 and the equations described above. In addition, the equilibrium partial pressures of \(\text{Al(g)}\) and \(\text{SiO(g)}\) are elevated in the high temperature shown in Fig.8. Therefore, these gases are estimated to be involved in the reactions. From the figure, it is considered that \(\text{Al(g)}\) forms under existence of \(\text{Al}_4\text{SiC}_4(s)\), and \(\text{SiO(g)}\) forms under existence of \(\text{SiC(s)}\) (equation 7 and 10). These gases are assumed to disperse in the texture and condense in the pore according to equation 8 and 11 when the gases move to the high \(\text{P}_{\text{CO}}\) area.

\[
\begin{align*}
\text{Al}_4\text{SiC}_4(s) & = 4\text{Al(g)} + \text{SiC(s)} + 3\text{C(s)} \quad (7) \\
2\text{Al(g)} + 3\text{CO(g)} & = \text{Al}_2\text{O}_3(s) + 3\text{C(s)} \quad (8) \\
(\text{MgO(s)} + 2\text{Al(g)} + 3\text{CO(g)} = \text{MgAl}_2\text{O}_4(s) + 3\text{C(s)}) \quad (9) \\
\text{SiC(s)} + \text{CO(g)} & = \text{SiO(g)} + 2\text{C(s)} \quad (10) \\
\text{SiO(g)} + \text{CO(g)} & = \text{SiO}_2(s) + \text{C(s)} \quad (11) \\
(2\text{MgO(s)} + \text{SiO(g)} + \text{CO(g)} = \text{Mg}_2\text{SiO}_4(s) + \text{C(s)}) \quad (12)
\end{align*}
\]

These condensed phases are considered to fill the pore, and that is assumed to be the reason of the more densification of the texture is provided.

**CONCLUSIONS**

The behavior and effect of \(\text{Al}_4\text{SiC}_4\) powder added to the \(\text{MgO-C}\) bricks have been investigated and discussed. The conclusions are as follows.

1. The mass increases and the porosity decreases in the \(\text{MgO-C}\) brick which was added \(\text{Al}_4\text{SiC}_4\) powder above 1000°C. The apparent porosity after heating at 1500°C is 2% lower than that after heating at 800°C.
2. The brick strength increases gradually above 1000°C by the addition of \(\text{Al}_4\text{SiC}_4\) powder.
3. \(\text{Al}_4\text{SiC}_4\) powder improves the oxidation resistance of the bricks as well as aluminum powder. The bricks containing \(\text{Al}_4\text{SiC}_4\) has high slaking resistance after heating.
4. \(\text{Al}_4\text{SiC}_4\) reacts with \(\text{CO}\) gas to form spinel(\(\text{MgAl}_2\text{O}_4\)) and \(\text{SiC}\) above 1200°C. The formed \(\text{SiC}\) also reacts with \(\text{CO}\) gas and \(\text{MgO}\) to form forsterite(\(\text{Mg}_2\text{SiO}_4\)) above 1400°C. \(\text{Al}_4\text{C}_3\) and \(\text{AlN}\) are not formed in these reaction processes.
5. The increase of mass and volume are caused by the reaction of \(\text{Al}_4\text{SiC}_4\) and \(\text{CO}\) gas, the more densification of the texture is provided.

**REFERENCES**