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 (MgAl2O4ss).

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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 (MgAl2O4ss) are detected in the oxidized product. The oxidation reaction of MgAlON proposed by Wang et al. is as fellows1)

\[ \text{MgAlON} + O_2 \rightarrow \text{MgAl}_2\text{O}_4\text{ss} + \text{Al}_2\text{O}_3 + \text{N}_2 \]  \(\text{(1)}\)

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 MgAl2O4ss forms MgAlON and the amount of dissolved materials has relatively wide ranges at high temperature.\(^2\) 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.\(^3\) 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 \(\mu\)m; purity, >99.9%), Al2O3 (\~0.1 \(\mu\)m; >99.99%), and AlN (\~0.7 \(\mu\)m; >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, Ehime, 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 \(\mu\)m 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 \(10 \times 10 \times 3.6\) 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, Tiba, Japan) (Pt crucible, 0.2 l, 0.01 \(\text{min}^{-1}\)) and a MoSi2 furnace (ventilating Pt net, 21 \(\text{min}^{-1}\)), respectively. The oxidation tests of powders were carried out with the heating rate at 5°C \(\text{min}^{-1}\) 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 1. Composition of Raw Materials in Molar Ratio and Mass Percent |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                             | S1                          |                             | S2                          |                             | S3                          |                             | S4                          |
|                             | Molar ratio                  | Mass%                      | Molar ratio                  | Mass%                      | Molar ratio                  | Mass%                      | Molar ratio                  | Mass%                      |
| MgO                         | 1                           | 3.38                       | 4                            | 17.49                      | 4                            | 9.94                       | 5.21                        | 12.57                      |
| Al2O3                       | 10                          | 86.22                      | 7                            | 78.03                      | 13                           | 82.41                      | 13                          | 80.01                      |
| AlN                         | 3                           | 10.40                      | 1                            | 4.48                       | 3                            | 7.64                       | 3                           | 7.42                       |
|                             |                             |                             |                             |                             |                             |                             |                             |                             |
| S5                          | Molar ratio                  | Mass%                      | Molar ratio                  | Mass%                      | Molar ratio                  | Mass%                      |                             |
|                             |                             |                             |                             |                             |                             |                             |                             |
|                             | S6                          |                             |                             |                             |                             |                             |                             |

* S4-S6 is 3 mass%, 6 mass%, and 9 mass% of additional MgO added into S3, respectively.
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. Results 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 density 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 MgAl₂O₄.⁴⁻⁵

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 (Wₘ) 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.

![Fig. 1. SE image of cross section of S1.](image)

![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.](image)

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<th>Table 2. Chemical Composition (mol%) and True Densities of the SPSed Samples as well as Some Results about Weight Change</th>
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Moreover, an EDS result of the material surrounding a big grain in the oxidized layer is illustrated in Fig. 4(f). As shown in Fig. 4(a), even the oxidized layer was very porous, only small amount of cracks and pores was in the un-oxidized layer. From Figs. 4(b)–(e), it was very interesting to found that N remained in the big grain and the content of Mg of the big grains was higher than that in the un-oxidized layer. So, the big grains were MgAlON with high content of Mg. Moreover, as shown in Fig. 4(f), only Al and O existed in the materials surrounding the big grains. Hence, during the oxidation of 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 MgAl₂O₄ (about 3.6 g cm⁻³) and MgAl₂O₃ (about 3.6 g cm⁻³) and much lower than that of α-Al₂O₃ (about 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 to 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 found 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: \[(\text{MgAlON})_{\text{low Mg}} + O_2 \rightarrow \text{MgAlON}_{\text{high Mg}} + \gamma\text{-Al}_2\text{O}_3 + N_2\] (2)
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Step 2: \((\text{MgAlON})_{(\text{high Mg})} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgAl}_2\text{O}_4\text{ss} + \gamma\text{-Al}_2\text{O}_3 + \frac{1}{2} \text{N}_2\) (3)

Step 1: \((\text{MgAlON})_{(\text{low Mg})} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgAlON}_{\text{high Mg}} + \gamma\text{-Al}_2\text{O}_3 + \frac{1}{2} \text{N}_2\) (4)

Step 2: \(\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3\) (5)

Step 3: \((\text{MgAlON})_{(\text{high Mg})} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgAl}_2\text{O}_4\text{ss} + \alpha\text{-Al}_2\text{O}_3 + \frac{1}{2} \text{N}_2\) (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

\[W_E = W_M - W_T\] (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,

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

with \([\text{Mg}]_{\text{vol}}\) in mol\% in the MgAlON phase. But, when the content of Mg was less than 5 mol\%, \(W_E\) had no 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.\(^6\) 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 weight change was obtained.\(^7\) In Eqs. (2)–(6), \(\gamma\text{-Al}_2\text{O}_3\) and \(\text{MgAl}_2\text{O}_4\text{ss}\) were the materials with lots of vacancies.\(^8\)–\(^10\) So, excess weight changes occurred during the oxidation of MgAlON.

Referring to relative diagram,\(^11\) the MgAlON with higher content of N and lower content of Mg led to more \(\gamma\text{-Al}_2\text{O}_3\) formation, and vice versa. In view of the law of phase transformation,\(^6\) 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 \(\text{MgAl}_2\text{O}_4\text{ss}\). As \(\text{MgAl}_2\text{O}_4\text{ss}\) 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 \(\text{MgAl}_2\text{O}_4\text{ss}\). 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.\(^12\) Thus, the excess weight change decreased with the content of Mg (Fig. 7). However, it was unknown until now why 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 (MgAl\(_2\)O\(_{4ss}\)).

References
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