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Reactive Infiltration of Magnesium Vapor into Alumina Powder Compacts

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Abstract

The strengthening and densification of Al_2O_3 powder compacts were achieved by reacting powder compacts with Mg and N_2 vapors. The phases AlN, MgO, and $MgAl_2O_4$ appeared in the reacted region of the compact according to the following equation; $(1+\alpha)Al_2O_3(s) + 3Mg(g) + N_2(g) \rightarrow (3-\alpha)MgO(s) + \alpha MgAl_2O_4(s) + 2AlN(s)(0 \leqq \alpha \leqq 3)$. The weight of the compact increased with process time and temperature because of the incorporation of the vapors. This reaction was accompanied by the expansion and densification of the compact. The size of the Al_2O_3 powder particles affected the densification behavior of the compact. ⓒ 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Chemical vapor infiltration (CVI) is a process whereby ceramic materials can be deposited in the interior of ceramic preforms by vapor phase reaction.[1,2] Since the preform does not change in size during processing, this process has mainly been used to fabricate near net-shaped fiber-reinforced composites. SiC-fiber/SiC composites produced by CVI are candidate materials for fusion reactor applications.[3] The matrix SiC is deposited on the SiC-filament preform by the reaction $CH_3SiCl_3(g) \rightarrow SiC(s) + 3HCl(g)$. The disadvantage of the CVI process is that the filling up of the space in a thick preform requires considerable time. Also, care has to be exercised to avoid damage to the fiber reinforcement during the process.

In contrast, unique processes which positively utilize the reaction between preform and vapor have been developed. One is RBAO[4,5] process developed by Professor Claussen at the Technical University of Hamburg-Harburg. In this process, Al powder preform was reacted with oxygen, forming a dense Al_2O_3 body. Another process is Reactive Vapor Infiltration (RVI) process. Patibandla et al.[6] reacted a Mo powder compact with Si supplied from the vapor phase, forming $MoSi_2$. Although RVI has similar characteristics to the CVI process, it has the advantage of shortening the process time by utilizing the volume change accompanying the reaction.

This RVI-type reaction between Al_2O_3 powder compacts and Mg vapor was encountered by the authors while investigating the DIMOX process.[7] In this paper, the products obtained by this RVI-type reaction were characterized by changing the Al_2O_3, particle size, process time and temperature.
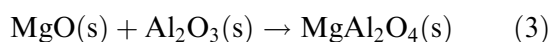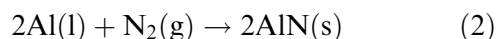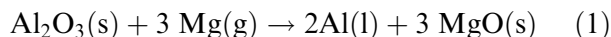
2 Experimental Procedure

The RVI process was conducted in an Al_2O_3 crucible [15 mm(W)×50 mm(L)×8 mm(H)] with an Al_2O_3 cover in order to enclose the Mg vapor inside the crucible. Al_2O_3 powders (Sumitomo Aluminum Co.) of 0·59, 1·23, and 5·7 μm in size were pressed into pellets of ϕ 10 mm×(3–4) mm at 100 MPa. After Mg powder (Rare Metallic Co., <147 μm) had been placed on the bottom of the crucible, the Al_2O_3 compact was put on it and covered with more Mg powder. The covered crucible was set in the center of a horizontal furnace. After replacing the atmosphere with N_2 (99·99%), the furnace was heated up to 1073, 1173, and 1273 K at 300 K h^{-1} under slight N_2 flow (<1 cm^3 min^{-1}). After keeping the crucible at the set temperature for 0–4 h, it was cooled down in the furnace. Although the process temperature was beyond the melting point of Mg (923 K),[8] the Mg particles kept

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their original shape. This must be due to the formation of a thin oxide film on them. Therefore, Mg did not infiltrate as a liquid, and the Mg powder can be easily removed from the compact after processing. Changes in the size and weight of the compact were evaluated.

The phases of the products were identified by X-ray diffraction (CuK_α) (XRD). The observation of the microstructure was conducted with a scanning electron microscope.

3 Results and Discussion

When Mg powder is heated in a N_2 atmosphere, Mg reacts with N_2 and both gaseous MgN and Mg vapors are formed. The vapor pressure of Mg is relatively high, 3·3 kPa (1073 K), 12 kPa (1173 K), and 36 kPa (1273 K),[8] but that of MgN is very low ($5·9 \times 10^{-3}$ Pa at 1273 K).[9] Therefore, only Mg could be considered as an active vapor phase in this process. The vaporized Mg reacted with the Al_2O_3 compacts, forming $MgAl_2O_4$, MgO, and AlN phases, as shown in Fig. 1. This XRD pattern was from the surface of an Al_2O_3 (0·59 μm) compact heated at 1273 K for 4 h with Mg powder. Elemental Mg was not observed in the product. According to these results, the following reactions occurred:

$$Al_2O_3(s) + 3\,Mg(g) \rightarrow 2Al(l) + 3\,MgO(s) \quad (1)$$

$$2Al(l) + N_2(g) \rightarrow 2AlN(s) \quad (2)$$

$$MgO(s) + Al_2O_3(s) \rightarrow MgAl_2O_4(s) \quad (3)$$

Al_2O_3 was reduced by Mg vapor [eqn (1)], forming Al and MgO. Since the products do not contain Al

metal, the resulting Al reacted immediately with the surrounding N_2 to form AlN [eqn (2)]. Also, MgO reacted partly with Al_2O_3, forming $MgAl_2O_4$ [eqn (3)]. The free energy changes of the reactions in eqn (1)–eqn (3) are -143, -359, and -29 kJ (at 1273 K),[9] respectively. The total reaction can be expressed as follows:

$$(1 + \alpha)Al_2O_3(s) + 3Mg(g) + N_2(g) \rightarrow \\ (3 - \alpha)MgO(s) + \alpha MgAl_2O_4(s) + 2AlN(s) \quad (4)$$
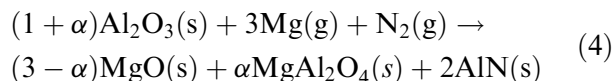
where α is the amount of reacted MgO with Al_2O_3 and where $0 \leq \alpha \leq 3$.
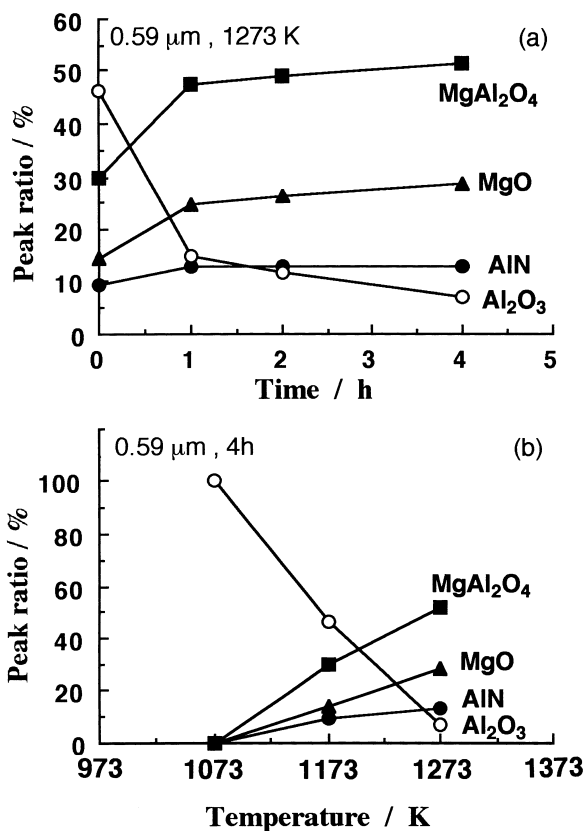
Fig. 2. Effects of process time and temperature on peak ratio in surface of Al_2O_3 (0·59 μm) compact.

Fig. 1. XRD pattern of surface of Al_2O_3 (0·59 μm) compact reacted at 1273 K for 4 h.
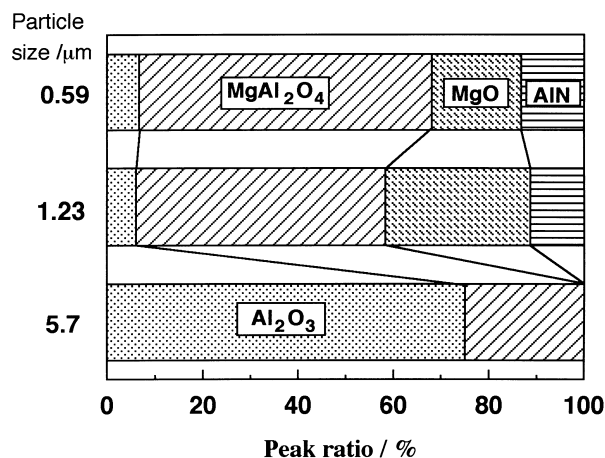

Fig. 3. Effect of particle size on peak ratio of surface product of Al_2O_3 compact.

The effects of process conditions, such as temperature, time, and particle size of the Al_2O_3 on the phase contents of the products were investigated. The results are shown in Figs 2 and 3. Here, the peak ratio was expressed with $(I_{hkl}/It) \times 100$ (I; XRD intensity); $It = I_{311}^{MgAl_2O_4} + I_{200}^{MgO} + I_{100}^{AlN} + I_{116}^{Al_2O_3}$. In Fig. 2(a), $MgAl_2O_4$, MgO, and AlN had already been formed during heating up to the set temperature [time (t) = 0 h], and most of the Al_2O_3 had reacted at $t = 1$ h. Beyond 1 h, the quantity of each product increased slightly with time. The effect of process temperature was drastic [Fig. 2(b)]. No product was observed with the compact heated at 1073 K. This is perhaps due to the low Mg vapor pressure (3.3 kPa). As temperature increased, the Mg vapor pressure increased and the amount of products increased. Figure 3 depicts the effect of Al_2O_3 particle size on the peak ratio at the surface of Al_2O_3 compacts. The finer particle (0.59 and 1.23 μm) compacts showed almost the same ratio of products, but the Al_2O_3 (5.7 μm) compact showed only Al_2O_3 and $MgAl_2O_4$

phases. Reaction eqn (4) occurred from the surface of each Al_2O_3 particle towards the inside. Therefore, as the particle size became small, the specific surface area available to react with the vapor became large. As a consequence, the Al_2O_3 compact with the smaller particle size showed a higher content of the products. In the Al_2O_3 (5.7 μm) compact, all the resulting MgO reacted with Al_2O_3 [$\alpha = 3$ in eqn (4)]. However, why the sample did not include the AlN phase is still being investigated.

Based on eqns (1) and (2), the Al_2O_3 compact should increase in weight by 1.0 g for each 1.0 g of Al_2O_3 by the corporation of Mg and N_2 vapors. Figure 4 shows the effects of process time and Al_2O_3 particle size on the weight gain of each compact at (a) 1073 K, (b) 1173 K, and (c) 1273 K. The weight gain percentage was calculated by dividing the weight gain by the weight of Al_2O_3 compact. Then, this value corresponds to the reaction ratio of the Al_2O_3 compact. Before heating up to the set temperature, the Al_2O_3 compacts had already reacted with Mg and N_2, as described in
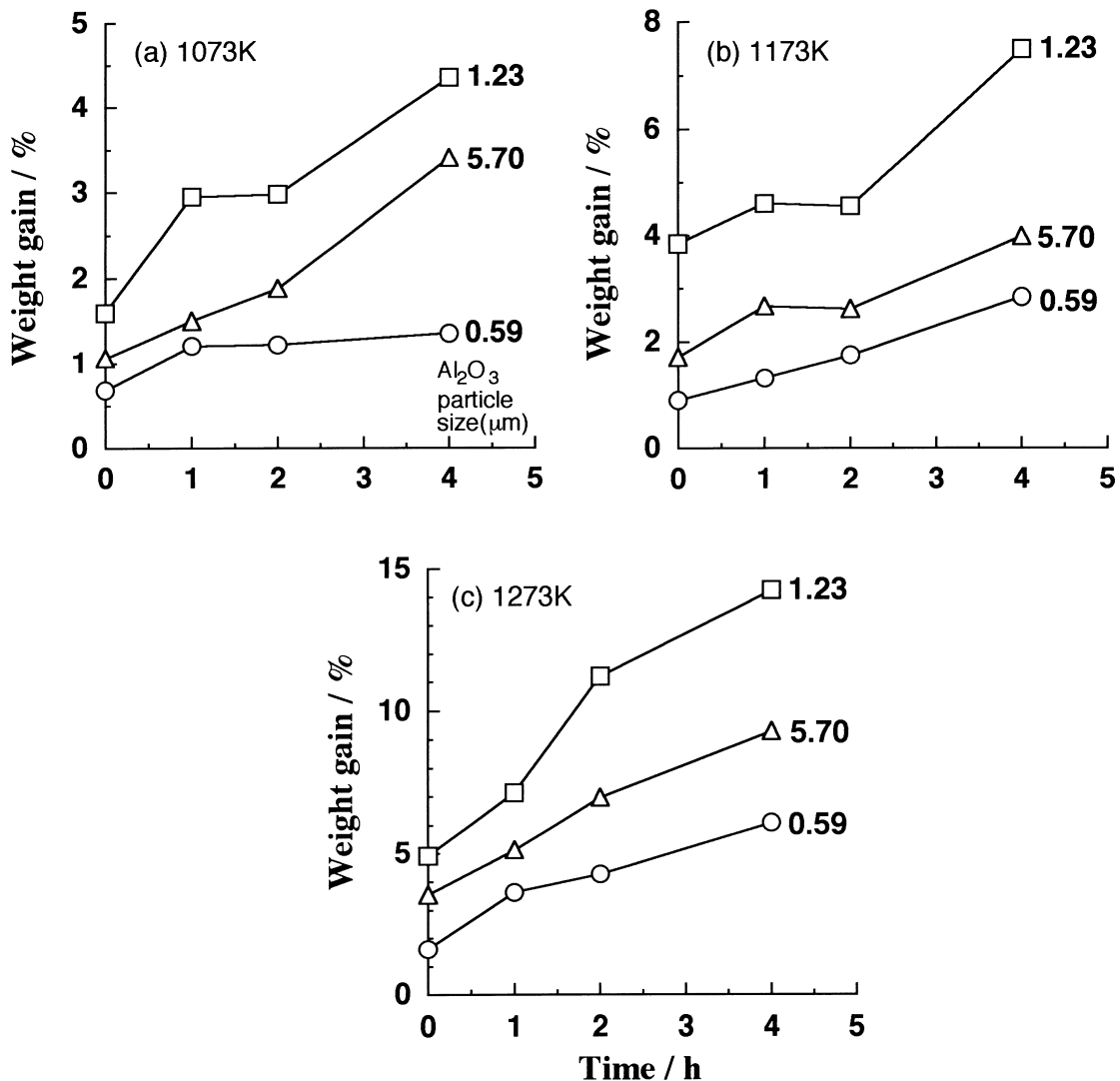

Fig. 4. Effects of process temperature and time on weight gain of Al_2O_3 compact.

Fig. 2(a), and increased their weight. The weight gain at $t = 0$ h increased with increasing process temperature. The actual weight gain from the value at $t = 0$ h increased almost linearly with time. The reaction ratio under these conditions was below 15%. In this work, the Al_2O_3 (0·59 μm) compact showed the smallest weight gain and the Al_2O_3 (1·23 μm) compact showed the largest one. The result in the Al_2O_3 (0·59 μm) compact is not consistent with Fig. 3, in which Al_2O_3 (0·59 μm) rather than Al_2O_3 (5·7 μm) reacted with the vapors. This result can be explained by the different microstructure of the reacted surface of the compacts, as shown in Fig. 5. The surface of the Al_2O_3 (0·59 μm) compact [Fig. 5(a)] became dense after reaction, but that of the reacted Al_2O_3 (5·7 μm) compact [Fig. 5(b)] kept a porous morphology. In the RVI process, Mg vapor diffuses into the compact through the pores according to the concentration gradient. Usually, the pore size of a powder compact is proportional to the particle size. Therefore, the Al_2O_3 (0·59 μm) compact is expected to have smaller pores than the Al_2O_3 (5·7 μm) compact. These can then be easily enclosed by the products in the early stage of the process, restricting the infiltration of Mg vapor. Therefore, this compact showed a small increase in weight although the surface reacted highly. On the other hand, in the Al_2O_3 (5·7 μm) compact, the

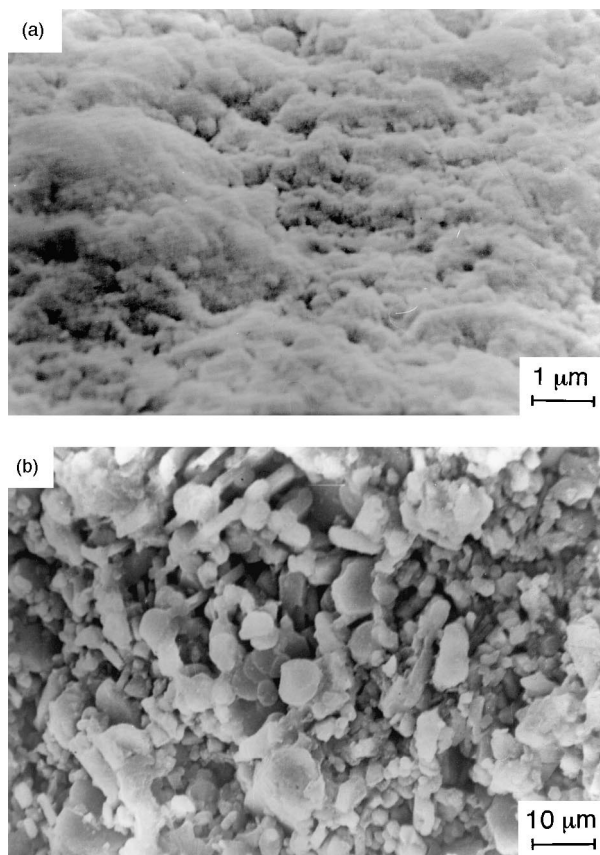relatively large pores remained open during the process, and Mg infiltration occurred continuously, producing a relatively large increase in weight although the surface only slightly reacted. In order to confirm these considerations, the phase change through the compact was examined with XRD, as shown in Fig. 6. The content of unreacted Al_2O_3 phase in the Al_2O_3 (0·59 μm) compact increased abruptly at regions deeper than 0.05 mm [Fig. 6(a)]. On the other hand, the Al_2O_3 (5·7 μm) compact showed almost constant contents of Al_2O_3 and $MgAl_2O_4$ phases through the compact [Fig. 6(c)]. Furthermore, the Al_2O_3 (1·23 μm) compact showed intermediate behavior between them [Fig. 6(b)]. These results support the interpretation given above. Additionally, the unreacted region of the Al_2O_3 (0·59 μm) compact was fragile, but the reacted Al_2O_3 (5·7 μm) compact was extremely strong.

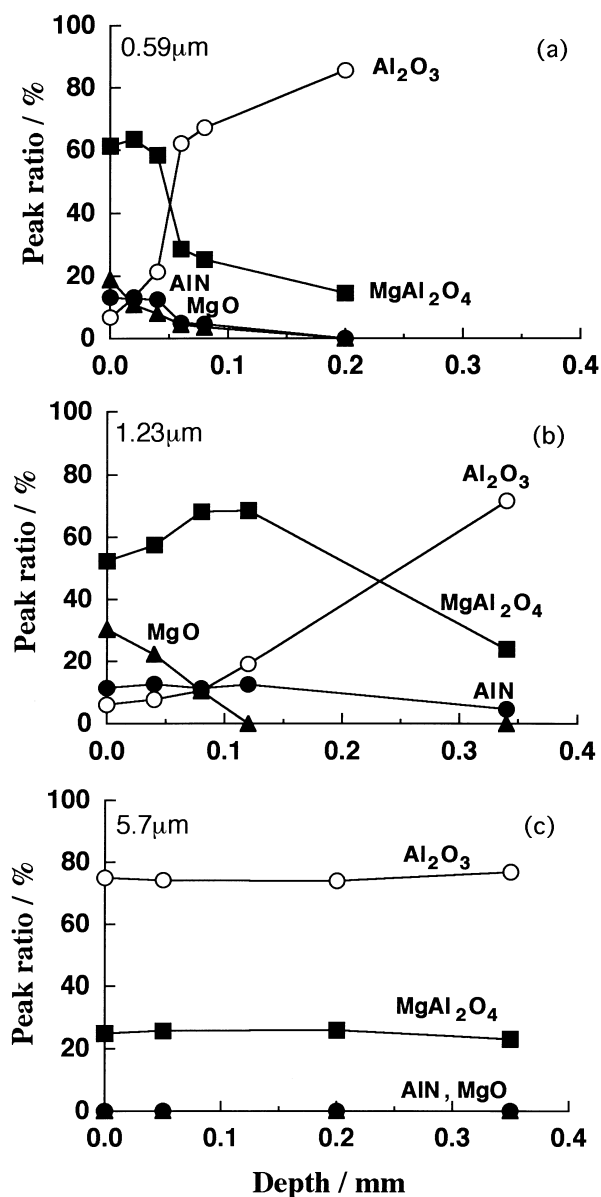**Fig. 5.** Microstructures of surface of Al_2O_3 compact reacted at 1273 K for 4 h: (a) 0·59 μm; (b) 5·7 μm.

Fig. 6. Changes of peak ratio in Al_2O_3 compacts reacted at 1273 K for 4 h with depth: (a) 0·59 μm; (b) 1·23 μm; (c) 5·7 μm.

The densification of the surface area of the Al_2O_3 (0.59 μm) compact is instructive. The usual CVI process needs considerable time to fill out the pores of the preform because all pore-filling materials are supplied from the vapor phase. On the other hand, the reaction between preform and vapor in the RVI process itself increases the solid volume within the preform, as the product starts to fill the pores. This characteristic of the RVI process is critically different from CVI. Figure 7 shows the linear expansion of each reacted Al_2O_3 compact with process time. All compacts expanded during the reaction, and the degree of the expansion increased in the order of 5.70, 0.59, and 1.23 μm. The theoretical volume increase due to eqn (4) can be estimated as 1.43 ($\alpha = 3$)–2.33 ($\alpha = 0$) by ignoring the gas phase volume on the basis of the following densities: 3.97 (Al_2O_3), 3.65 (MgO), 3.55 ($MgAl_2O_4$), and 3.05 g cm^{-3} (AlN).[8] This value corresponds to 13–33% linear expansion. The observed expansions, 1–2.5% (at 4 h), are much smaller than this calculated value. One reason is incomplete reaction. The estimated expansion based on the reaction ratio in Fig. 4 are 0.13–4.6%. Another reason is the fill-out of the pores of the preform by small particles broken from the reacted particles due to stresses associated with the volume increase. Figure 5(b) shows the existence of smaller particles than are found in the original. Furthermore, the real temperature of the surface must be higher than the set temperature because of the exothermic reaction of eqn (4) [−1184 ($\alpha = 0$), −1249 ($\alpha = 3$) kJ at 1273 K].[9] Assuming an adiabatic reaction, the temperature increase due to eqn (4) is estimated as 4600 K ($\alpha = 0$) and 1660 K ($\alpha = 3$) on the basis of the
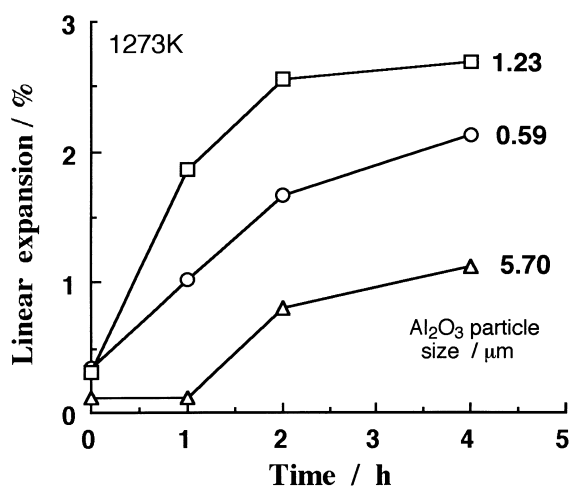
following specific heat: 53 (MgO),[8] 185 ($MgAl_2O_4$),[8] and 49 J mol^{-1} K^{-1} (AlN).[10] Therefore, the higher temperature in the reaction zone is expected to accelerate the sintering of the submicron powders.

4 Conclusions

Al_2O_3 powder compacts were reacted with Mg and N_2 vapors, forming $MgAl_2O_4$, MgO, and AlN. The weight gain and linear expansion of the compacts were observed after reaction.

1. The surface layer ($\sim$0.05 mm) of the Al_2O_3 (0.59 μm) compact reacted strongly with the vapors and was densified at 1273 K after 4 h. The reacted layer was mechanically strong, but the unreacted interior of the compact was fragile.
2. The reaction of the Al_2O_3 (5.7 μm) compact occurred throughout the compact (3–4 mm thickness). The reacted compact was porous but strong enough to handle. An AlN phase could not be detected with XRD.

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Fig. 7. Effects of Al_2O_3 particle size and process time on linear expansion of Al_2O_3 compact reacted at 1273 K.