

## Effect of particle size on the strength of a porous nickel aluminate fabricated by a polymer solution route

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Nickel aluminate ( $\text{NiAl}_2\text{O}_4$ ) powders were fabricated by a polymer solution route employing polyvinyl alcohol as a polymeric carrier in a mixed metal cation solution. The precursor gels were aerated and the calcined powders were also soft and porous. The crystalline development and microstructures of the synthesized powders were examined by X-ray diffractometry and scanning electron microscopy. The porous powders were ball-milled to sub-micron sized powders and their sintering behavior was examined.  $\text{NiAl}_2\text{O}_4$  porous samples were fabricated with the ball-milled powders and their microstructures and compressive strengths were also examined. The ball-milled, fine  $\text{NiAl}_2\text{O}_4$  powders were fully densified at a temperature of 1600 °C and the strength of the porous  $\text{NiAl}_2\text{O}_4$  was found to be affected by the sizes of the starting powder and internal pores.

**Key words:** Nickel aluminate, Porous body, Polymer, Ball milling, Compressive strength.

### Introduction

Oxide spinels have been investigated in the solid state sciences because of their usefulness as magnetic materials, semiconductors, pigments, catalysts, refractories, and as convenient model compounds to explore the relative stabilities of ions in octahedral and tetrahedral coordination [1]. In nickel aluminate spinel ( $\text{NiAl}_2\text{O}_4$ ), Al is located at octahedral sites and Ni is located at tetrahedral sites [2]. The nickel aluminate has excellent strength and good wettability with metals at high temperature, besides the general merits spinel materials have. In particular, the nickel aluminate having a porous structure can be used as a good ceramic skeleton for infiltration of metals at high temperature. This unique process can be applied as a new fabrication method for metal-ceramic composites. However, the study of the powder synthesis for the nickel aluminate has not been examined widely, but only in the limited field of solid state reaction or sol-gel synthesis [3, 4]. Also the porous, sintered nickel aluminate was not studied at all.

Chemical processing routes based on a steric entrapment route in soft solutions have recently been used to produce pure and homogeneous ceramic powders [5-10]. Various multi-element solutions yield solid-like gel precursors, which are stable and homogeneous. In this process, polymeric long chains prevent the segregation and/or precipitation of metal ions in the desired

solution system. Polyvinyl alcohol (PVA) is one of the polymeric carriers for the polymer solution process [6, 9]. The polymer surrounds and covers the cations or sol particles, which decreases their mobility and constrains the system to reduce premature agglomeration [9-11]. The PVA process also produces carbonaceous material that gives heat through its combustion, so that porous and single-phase powders can be formed from a homogeneous precursor solution at a relatively low external temperature [12-14].

In this study, nickel aluminate powders were synthesized by the polymer solution technique, and the characteristics of the synthesized powders were examined. In addition, the effect of particle size on the strength of porous nickel aluminate was examined. A simple ball milling process was used on the synthesized nickel aluminate powder and the milling effect on the soft and porous calcined powder is also studied.

### Experimental Procedure

#### Preparation of Powders and Porous Body

Nickel nitrate and aluminum nitrate were dissolved in stoichiometric proportions in de-ionized (D.I.) water. Once the nitrates were completely dissolved, the 5 wt% PVA polymer (78% hydrolyzed PVA) was dissolved in DI water and added to the solution. The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 4 times more positively charged valences from the cations than from the potentially negatively charged  $-(\text{OH})$  functional groups of the polymers [7, 8]. The polymeric long chains have hydroxyl groups in solution. Hence, one PVA monomer, which has one hydroxyl (OH) functional group,

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can be used as an unit for calculation of PVA content. The exact relative amount of PVA to cations in the solution can be calculated with reference to a monomeric unit of PVA.

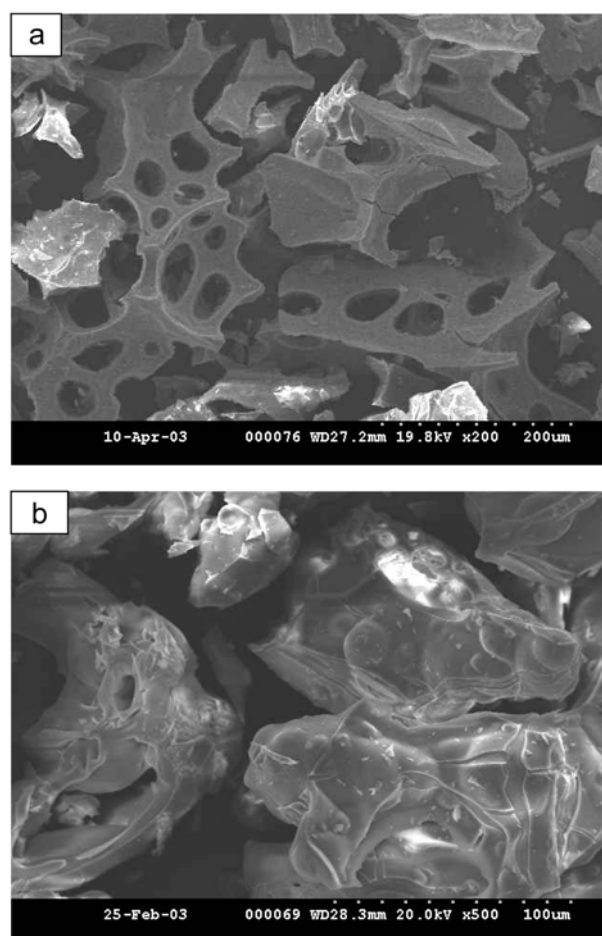
The D.I. water was evaporated by continuous stirring during heating at 150 °C on a hot plate. The resulting gel-type precursors were completely dried for several hours at 100 °C. The dried, organic/inorganic precursors were then ground and were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. The calcined powders were ball-milled with zirconia ball media for several hours. The charge included 20 g powder with zirconia balls having diameters of 5 mm. The jar volume was 250 ml and 100 ml isopropyl alcohol was used for wet milling. To make porous nickel aluminate, the ball-milled and dried powders were mixed with 1 wt% PVA solution by stirring. Polyurethane foams, which had different pore sizes, were dipped in the nickel aluminate slurry and were squeezed to remove the slurry from the sponge pores. Later, the wet polyurethane foams were dried and calcined at a slow heating rate for burn-out of the polyurethane skeleton. Finally, the calcined, porous nickel aluminate bodies were sintered at 1600 °C for 1h in an air atmosphere.

### Characterization

The crystallization behavior of the synthesized powders was determined with an X-ray diffractometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) using  $\text{CuK}\alpha$  radiation (40 kV, 40 mA). The measurements were made with a scanning speed of 10°/minute and a sampling interval of 0.02° at room temperature. The calcined powder and sintered porous bodies were examined by scanning electron microscopy (SEM, Hitachi S530, Hitachi, Japan). The specimens were mounted on an aluminum stub and Au-Pd sputtered at 15 mA for 40 s. The average particle sizes and their particle size distributions of the ball-milled powders were monitored by an electrophoretic light scattering spectrophotometer (ELS-8000, Photol, Tokyo, Japan) of the ultra-sonicated, powder dispersed slurry. Compressive tests with densified porous nickel aluminate were examined using an universal testing machine (model 4502, Instron Corp., Canton, MA). Mini-cubic specimens of 15 mm length on a side were tested.

### Results and Discussion

The green-colored, organic-inorganic precursors were formed through the development of foams during the stirring and drying process. The foams were generated by the evolution of  $\text{NO}_x$  gases caused by the decomposition of the nitrates in the high viscosity solution. The expansion of the precursors by the evolving  $\text{NO}_x$  gas continued until the precursors were dried completely, and finally turned to aerated gels. The gels were

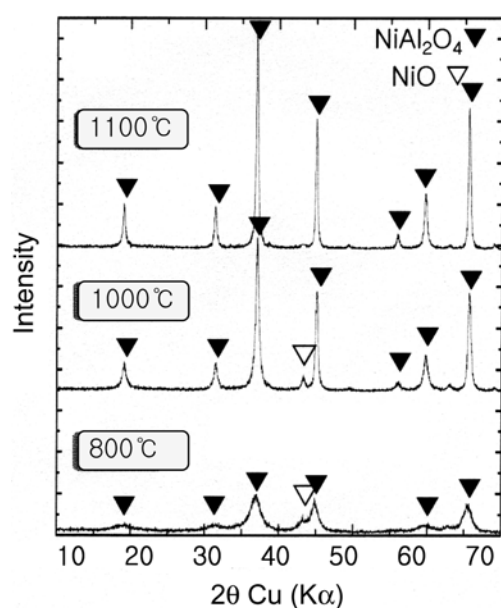


**Fig. 1.** Representative SEM micrographs of the calcined  $\text{NiAl}_2\text{O}_4$  powder prepared by PVA solution method, fired at 800 °C for 1h. (a) porous powder having sphere-type holes, and (b) porous powder having swollen particles.

white-colored and porous after calcination.

The calcined powder showed different morphologies at each observation point. Two representative morphologies of the calcined powder are shown in Fig. 1. The powder was quite soft and porous, and sphere-type holes were observed (Fig. 1(a)), and also some swollen particles were also observed (Fig. 1(b)). The morphological characteristic was produced by the trapped gases, such as  $\text{NO}_x$  gas, CO and  $\text{CO}_2$ , during the drying and calcination process. The swollen and agglomerated particles showed a wide size range of 10-200  $\mu\text{m}$ .

The results of XRD patterns of the calcined powders according to the heating temperature are presented in Fig. 2. At 1100 °C for 1h, the calcined powder was fully crystallized to  $\text{NiAl}_2\text{O}_4$ . NiO was observed at 1000 °C, however, it was not detected in the XRD pattern at 1100 °C. In a previous study of sol-gel method [3], NiO coexisted with  $\text{NiAl}_2\text{O}_4$  at 1100 °C and full crystallization of  $\text{NiAl}_2\text{O}_4$  occurred by heating for a long time at this temperature. This result means that the PVA solution route made the single-phase  $\text{NiAl}_2\text{O}_4$  at a relatively low external temperature. In this

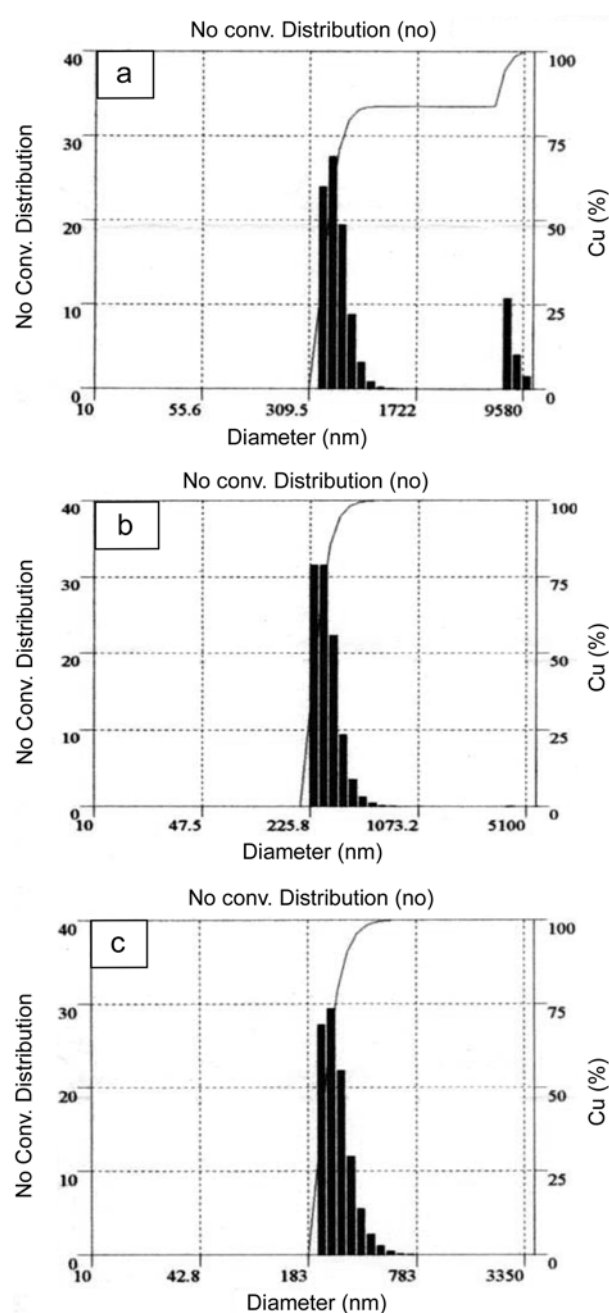


**Fig. 2.** XRD patterns of the fired  $\text{NiAl}_2\text{O}_4$  powders prepared by PVA solution method.

synthesis process, the PVA ensured the homogenous distribution of the Ni and Al ions in its polymeric network structure and contributed to the synthesis at a lower temperature [14].

Figure 3 shows the particle size distributions of the ball-milled, calcined  $\text{NiAl}_2\text{O}_4$  powders. At the beginning of 5 h milling, the powder size was significantly decreased to  $0.67\ \mu\text{m}$  in average particle size. However, some large particles of  $9\text{--}10\ \mu\text{m}$  in size were observed. The milling time of 5 hours should be not enough to obtain uniform particle size. As the milling time increased, the bi-modal particle size distribution gradually disappeared and the average particle size decreased. Finally, a fine powder of  $0.28\ \mu\text{m}$  in size was obtained with a narrow particle size distribution by ball milling for 15 h. (Fig. 3(c)). In the milling process with the porous  $\text{NiAl}_2\text{O}_4$  powders, the fine particles could be obtained in a relatively short milling time in comparison with the milling behavior of normal refractory ceramic powders. Such an excellent milling effect was already proved in the previous study of the milling behavior with porous cordierite powders [6]. In that study, nano-sized cordierite powder of  $30\ \text{nm}$  in size was fabricated by an effective attrition milling process with porous cordierite powders prepared by the PVA solution route.

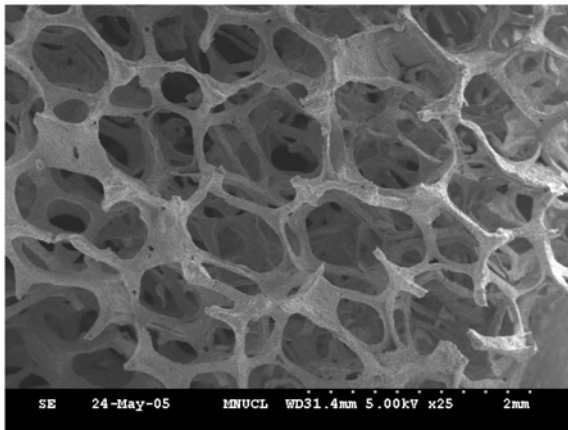
Porous  $\text{NiAl}_2\text{O}_4$  bodies were fabricated with the  $0.67\ \mu\text{m}$  sized  $\text{NiAl}_2\text{O}_4$  powder. The microstructure of the porous  $\text{NiAl}_2\text{O}_4$  is represented in Fig. 4. The pore distribution and skeleton thickness of the porous body were uniform throughout whole microstructure. Figure 5 shows the variation of strength of the porous  $\text{NiAl}_2\text{O}_4$  as a function of pore size. As expected on normal porous ceramics, the highest compressive strength of  $8.1\ \text{MPa}$  was obtained with the smallest pore size of



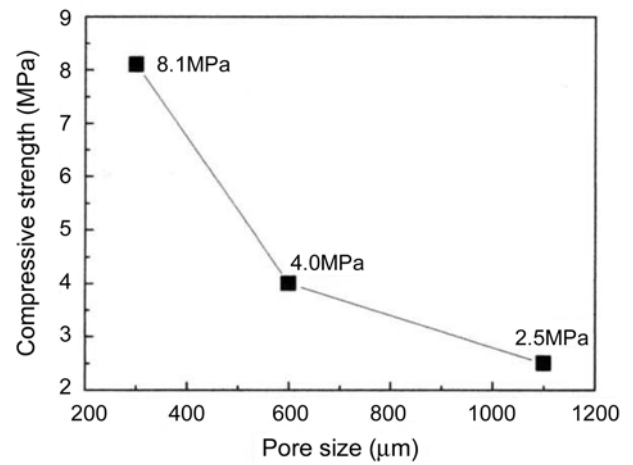
**Fig. 3.** Particle size distributions of the ball-milled, calcined  $\text{NiAl}_2\text{O}_4$  powders at different milling times of (a) 5 h, (b) 10 h and (c) 15 h.

$300\ \mu\text{m}$ .

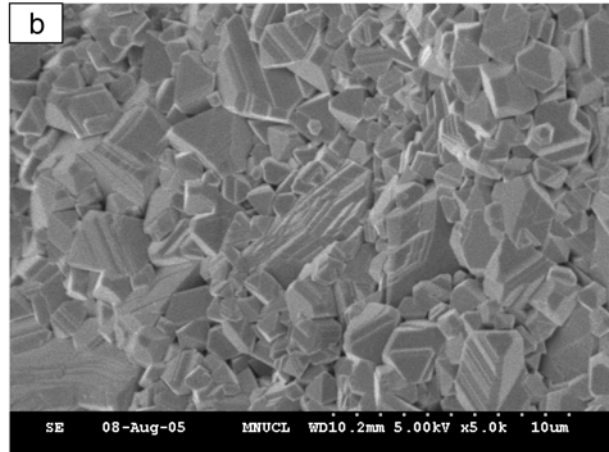
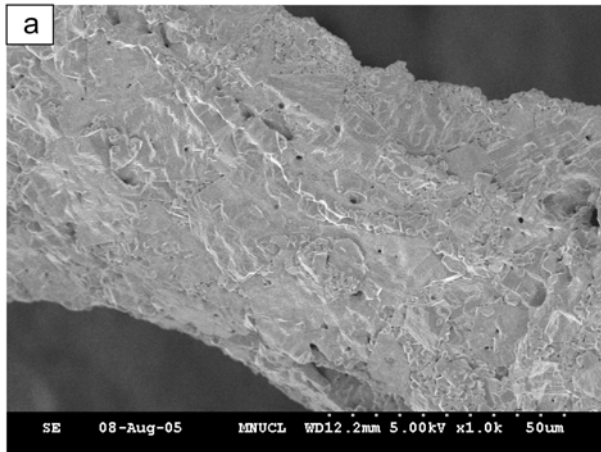
Two differently sized powders were used for the fabrication of porous  $\text{NiAl}_2\text{O}_4$  bodies. Figures 6 and 7 represent the SEM photographs of the skeletons of the porous  $\text{NiAl}_2\text{O}_4$  and their densified microstructures. In the porous  $\text{NiAl}_2\text{O}_4$  fabricated with the  $0.67\ \mu\text{m}$  powder (Fig. 6), the microstructures of skeleton and grains were coarser than the microstructures of Fig. 7. In particular, the sintered  $\text{NiAl}_2\text{O}_4$  grains were faceted having a wide grain size distribution. By contrast, the porous  $\text{NiAl}_2\text{O}_4$  fabricated with the  $0.28\ \mu\text{m}$  powder (Fig. 7) showed more dense microstructures.



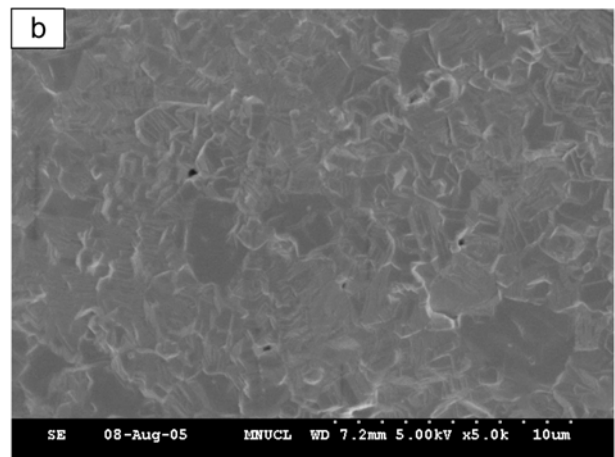
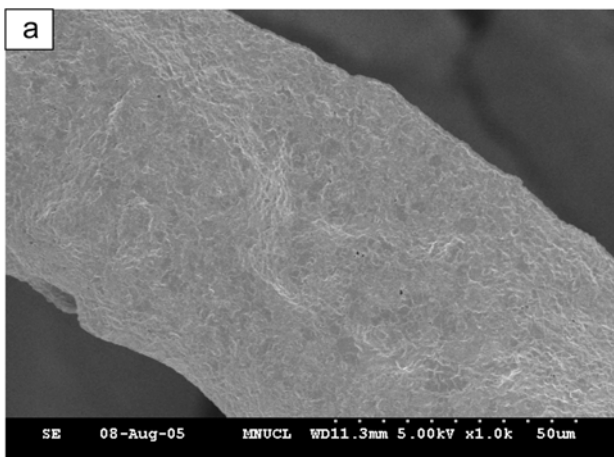
**Fig. 4.** SEM microstructure of the porous  $\text{NiAl}_2\text{O}_4$  fabricated with  $0.67\ \mu\text{m}$  sized  $\text{NiAl}_2\text{O}_4$  powder and  $600\ \mu\text{m}$  pore-sized polyurethane foam.



**Fig. 5.** Variation of compressive strengths of the porous  $\text{NiAl}_2\text{O}_4$ , fabricated with the powder of  $0.67\ \mu\text{m}$ , as a function of pore size.



**Fig. 6.** SEM micrographs of porous  $\text{NiAl}_2\text{O}_4$  fabricated with the powder of  $0.67\ \mu\text{m}$ . (a) skeleton and (b) sintered surface.



**Fig. 7.** SEM micrographs of porous  $\text{NiAl}_2\text{O}_4$  fabricated with the powder of  $0.28\ \mu\text{m}$ . (a) skeleton and (b) sintered surface.

The compressive strengths of the porous  $\text{NiAl}_2\text{O}_4$  fabricated with the two powders are listed in Table 1 which should be compared with the results in Fig. 5.

The strengths of the porous bodies fabricated with the smaller sized starting powder showed almost two times increased strength at each pore size.

**Table 1.** Variation of compressive strengths of porous  $\text{NiAl}_2\text{O}_4$  as the functions of particle size of starting powder and pore size

| Particle size of starting powder ( $\mu\text{m}$ ) | 0.67 |     |     | 0.28 |     |      |
|----------------------------------------------------|------|-----|-----|------|-----|------|
| Pore size ( $\mu\text{m}$ )                        | 1100 | 600 | 300 | 1100 | 600 | 300  |
| Compressive strength (MPa)                         | 2.5  | 4.0 | 8.1 | 4.2  | 7.8 | 13.0 |

### Conclusions

Fully densified, porous  $\text{NiAl}_2\text{O}_4$  was successfully fabricated with ball-milled, fine powders, which were synthesized by a PVA solution route. The ball milling process with the porous  $\text{NiAl}_2\text{O}_4$  powders was quite effective in grinding the particles to sub-micron sizes. The porous  $\text{NiAl}_2\text{O}_4$  powders could be obtained by a polymer addition to the normal chemical solution method. Finally, the porous  $\text{NiAl}_2\text{O}_4$  fabricated with the 0.28  $\mu\text{m}$  sized powder showed a reasonable strength of 13 MPa with the conditions of 70  $\mu\text{m}$  thickness of the skeleton and 300  $\mu\text{m}$  internal pore size.

### Acknowledgement

This work was supported by Korea Research Foundation Grant (KRF-2003-041-D20288).

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