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High-Pressure Combinatorial Process Integrating Hot Isostatic Pressing

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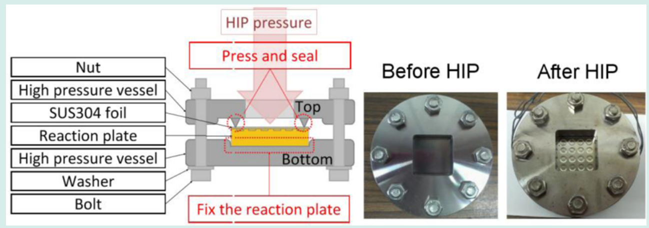
ABSTRACT: A high-pressure combinatorial process integrating hot isostatic pressing (HIP) was developed by providing a reaction vessel with a high-pressure tightness based on a commercial flange. The reaction vessel can be used up to 200 MPa and 500 °C under HIP processing condition. Preparation of spinel-type $MgAl_2O_4$ from $Mg(OH)_2$, $Al(OH)_3$ and AlOOH was performed using the reaction vessel under 200 MPa and 500 °C as demonstration. The entire powder library was characterized using powder X-ray diffraction patterns, and the single phase of spinel-type $MgAl_2O_4$ was obtained from $Mg(OH)_2$ + $Al(OH)_3$. These assessments corresponded with previously published data.



KEYWORDS: *high-pressure chemistry, combinatorial chemistry, hot isostatic pressing (HIP) method, spinel-type* $MgAl_2O_4$

1. INTRODUCTION

Present high-throughput materials preparation process derived from the solid-phase peptide synthesis by Merrifield et al.[1] and the multicomponents thin films preparation using sputtering technique by Kennedy et al.[2] and Hanak et al.[3] have been widely developed for exploring novel functional materials. And, since the 1990s, the field of inorganic and metal materials has actively been studied because of the development of various apparatus and software.[4,5] Incidentally, our research group have hitherto developed the high-throughput materials exploration apparatus "M-ist Combi" based on the electrostatic spray deposition method, which is one of solution processes for obtaining films or fine particles. The M-ist combi system consists of a mixture ratio control module for starting materials, such as liquid and slurry, a triaxial robot hand, a high-voltage power supply, a substrate heater for deposition of sprayed materials and a physical property evaluation module. And, by using the M-ist combi system, we have hitherto established various types of reaction phase diagrams and found candidate cathode materials for lithium ion secondary batteries.[6,7]

Including our in-house developed M-ist Combi system, previously reported combinatorial processes have been able to control chemical composition, heat-treatment temperature, atmosphere and pressure under less than atmospheric pressure. In conventional materials preparation processes, high pressure is important, and can be as critical as temperature control for synthesizing new materials. The hot isostatic pressing (HIP) method, which was invented in 1950s and is used for making sintered bodies, is one of these high-pressure processes .[8] We have found that spinel-type $MgAl_2O_4$ could be prepared from various hydroxides as starting materials by using the capsule HIP method. In conventional solid state-reaction methods, $MgAl_2O_4$ can be obtained from a mixture of MgO and Al_2O_3 and a heat-treatment condition above 1000 °C. In the capsule HIP method, however, it was found that the phase transition from the mixture of $Mg(OH)_2$ and $Al(OH)_3$ (or AlOOH) to spinel-type $MgAl_2O_4$ appeared at 400−500 °C with the application of 50 MPa.[9]

The capsule HIP process needs work time to obtain the product because the process consists of the weighing and mixing of starting materials and heat-treatment under the same high-pressure and temperature as the solid-state reaction process. Therefore, conventional materials exploration using the capsule HIP process takes much time.

In this study, we studied a system for reacting at the same time under high-pressure in a library which was obtained by the M-ist Combi system described above. In particular, we designed and fabricated a combinatorial high-pressure vessel for use with HIP apparatus and demonstrated the preparation of spinel-type $MgAl_2O_4$ powder using various starting materials.

2. EXPERIMENTAL SECTION

2.1. Design and Fabrication of a Reaction Vessel That Has High-Pressure Tightness. To develop a high-pressure vessel that can withstand pressures such as 200 MPa, we made a reaction vessel that has high-pressure tightness. We aimed at fabricating a vessel that would fulfill the condition of being able to be put into HIP apparatus and set to the reaction plate (35 mm ×35 mm ×5 mm^t) used in the M-ist Combi system. The reaction plate has 36 hollows and a separate function of the HIP capsule for each hollow. Furthermore, we explored candidate metal films for the top of the reaction plate that

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would allow the vessel to be used for the same function as HIP multiple capsules.

In this study, we focused on the commercial flanges (ICF standard flunge, ICF70 (70 mm$^{\varphi}$)) used in vacuum equipment. Figure 1 shows a schematic diagram of the reaction vessel. The underside of the reaction vessel had a recess for fixing the reaction plate. And, the upper side had through-hole for applying high-pressure to the prepared library.

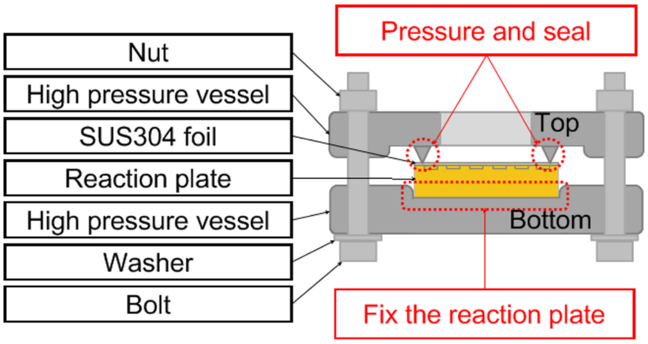

Figure 1. Schematic image of the combinatorial high-pressure reaction vessel.

As mentioned above, the most suitable metal cover for achieving the same reaction in the developed vessel as in conventional capsule HIP processing was explored. The metal foils used were SUS304 (0.01−0.08 mm thickness), Ni (0.01 mm), Mo (0.01 mm), and Cu (0.1 and 0.3 mm). These metal foils were superimposed on the reaction plate, and an overlap was set to the vessel. Then 200 MPa was applied to the vessel using the cold isostatic press (CIP) method under ambient temperature, and it was checked whether each metal foil hollowed along the form of the reaction plate without cutting.

2.2. Preparation of Spinel-Type $MgAl_2O_4$ Using the Combinatorial High-Pressure Vessel. In this study, spinel-type $MgAl_2O_4$ was prepared to demonstrate the performance of the new reaction vessel. The starting materials used were $Mg(OH)_2$ (99.9%, Wako Pure Chemical Industries, Ltd.), $Al(OH)_3$ (99.99%, Kojundo Chemical Lab. Co., Ltd.) and AlOOH (Wako Pure Chemical Industries, Ltd.). Mixture of $Mg(OH)_2/Al(OH)_3$ = 1:2 and $Mg(OH)_2$/AlOOH = 1:2 were mounted in the hollows on the reaction plate.

The reaction plate was covered by the metal foil and set on the reaction vessel. Then 200 MPa was applied to the reaction vessel in HIP apparatus (NIKKISO Co., Ltd., 30M3.2−05.5GU200). Heat-treatment under 500 °C was performed for 1 h.

After HIP processing, the obtained powder library was characterized using powder X-ray diffraction with CoKα radiation (λ = 0.17889 nm) using a RIGAKU RINT2550/PC-K system with RINT-2000 software.[10]

3. RESULTS AND DISCUSSION

3.1. Exploration of the Metal Cover to Cover to the Reaction Vessel. Figure 2 shows the actual image of the reaction vessel (75.6 mm$^{\varphi}$, 12.7 mm^{t}). Size of the reaction vessel was adjusted for fitting nearly into the inside diameter of HIP apparatus. SUS304 was used as the material of the reaction vessel because, conventionally, we use it in capsule HIP processing. The upside the reaction vessel has edges for imposing on the metal cover to the reaction plate. And screw holes were used to allow the upper side and underside of the reaction vessel to be fastened with bolts.

Table 1 shows the exploration results for the optimal metal cover. The reason the CIP process was used in this experiment was that water could be used as the pressure medium and the pressure leakage between the metal cover and the reaction vessel checked. Figure 3 shows the image of a broken metal cover after the CIP process. From these results, the most suitable metal cover was found to be SUS304 with a 0.08 mm thickness.

Table 1. Exploration of Optimum Materials and Thickness of Metal Foil on the Reaction Plate (after CIP ×, broken; ○, not broken; −, not tested)

material	thickness	material condition after CIPping	sealing condition of the lid
SUS304	0.01 mm	×	−
	0.01 min × 2 sheets	×	−
	0.01 mm × 3 sheets	×	−
	0.04 mm	×	−
	0.06 mm	×	−
	0.08 mm	○	○
Ni	0.01 mm	×	−
Mo	0.01 mm	×	−
Cu	0.1 mm	○	×
	0.3 mm	○	×

3.2. Preparation Spinel-Type $MgAl_2O_4$ under High Pressure. Figure 4 shows the image of the unbroken optimal metal cover after 200 MPa had been applied simultaneously with heat-treatment at 500 °C for 1 h, in the HIP process.

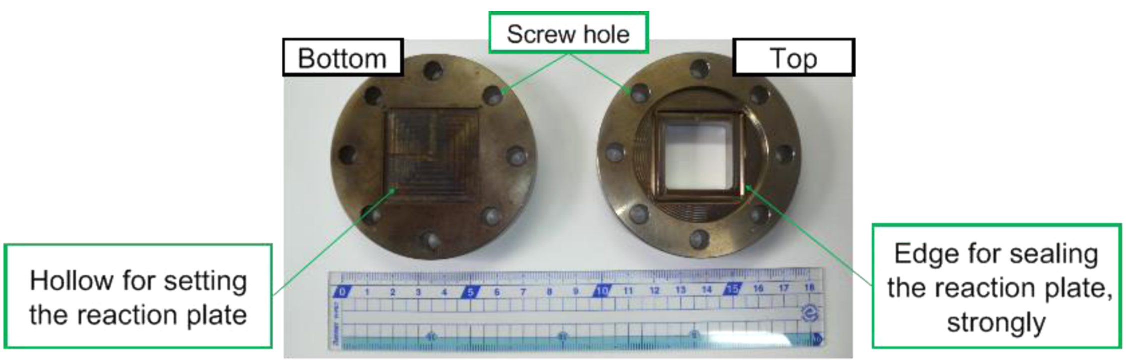

Figure 2. Actual image of the combinatorial high-pressure reaction vessel (size of the reaction vessel = 75.6 mm$^{\varphi}$, 12.7 mm^{t}).

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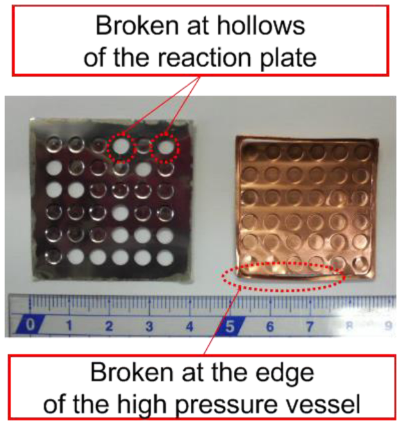

Figure 3. Metal foil images after CIPping (left, SUS304 0.04 mm[t]; right, Cu 0.1 mm[t]).

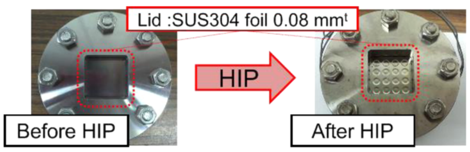

Figure 4. Images of the reaction vessel before and after HIP processing.

Powder library after HIP treatment was evaluated using combinatorial X-ray diffraction apparatus. To check whether the high-pressure had been applied uniformly, the starting materials for 18 samples were $Mg(OH)_2/Al(OH)_3$ = 1:2, and the remaining 18 samples were $Mg(OH)_2/AlOOH$ = 1:2. Figure 5 shows the X-ray diffraction patterns of the powder library. Single phase of spinel-type $MgAl_2O_4$ was obtained when the mixture of $Mg(OH)_2/Al(OH)_3$ = 1:2 used as starting materials. On the other hand, the high-pressure preparation by using the mixture of $Mg(OH)_2/AlOOH$ = 1:2 showed the presence of unreacted starting materials. These results were similar to the previous report of the capsule HIP method.[9] As mentioned above, it was found that the new reaction vessel with 36 hollows had functioned as the HIP capsule.

4. CONCLUSION

In this study, a reaction vessel with high-pressure tightness was designed and fabricated in order to integrate the conventional combinatorial materials preparation process and high-pressure technology. The developed reaction vessel consists of an upper part and under part, the reaction plate (35 mm ×35 mm ×5 mm[t]) used in the M-ist Combi system and a metal film on the top of the reaction plate to use the vessel for the same function as HIP multiple capsules. The developed reaction vessel could be used up to 200 MPa and 500 °C.

Spinel-type $MgAl_2O_4$ powders were prepared from $Mg(OH)_2$, $Al(OH)_3$, and AlOOH using the reaction vessel under 200 MPa and 500 °C. The entire powder library was characterized using powder X-ray diffraction patterns, and single phase of spinel-type $MgAl_2O_4$ was obtained from $Mg(OH)_2$ + $Al(OH)_3$. The results corresponded with previously published data those of the previous report. From this demonstration, the reaction vessel is promising for use in combinatorial high-pressure processes (~200 MPa).

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Notes

The authors declare no competing financial interest.

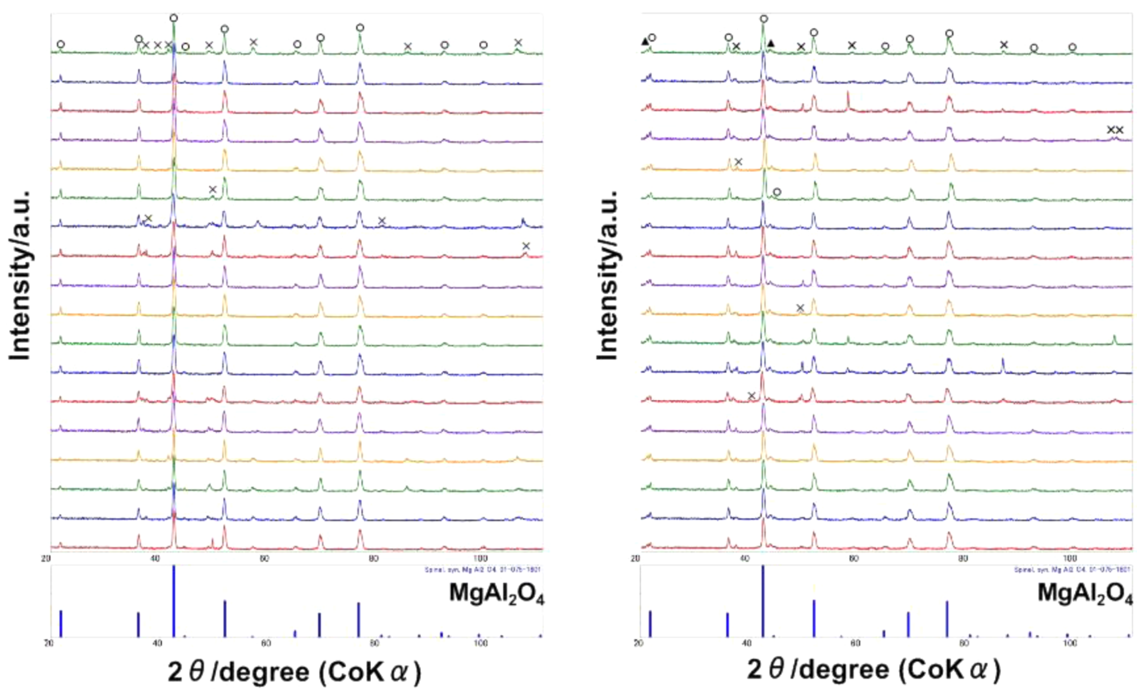

Figure 5. Powder X-ray diffraction patterns of heat-treated powder library at 500 °C under 200 MPa. Mixture ratio of starting materials: left, $Mg(OH)_2/Al(OH)_3$ = 1:2, right, $Mg(OH)_2/AlOOH$ = 1:2. ○: $MgAl_2O_4$. ▲: unreacted. ×: reaction plate.

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Due to a production error, the author names were transposed in the version of this article published November 20, 2013. The correct version published December 9, 2013.