

# Preparation of Zirconium Powder Through $ZrCl_4$ Bubbling in Mg- $MgCl_2$ Bath

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An alternative process has been studied for zirconium production through chemical reaction between  $ZrCl_4$  bubbles and magnesium melt floating on molten  $MgCl_2$  salt. The preparation of pure zirconium in the form of powder was successfully accomplished by cleaning process consisting of washing with distilled water and pickling with hydrochloric acid solution. The purity of zirconium powder increased with dense concentration of hydrochloric acid solution and longer pickling time by removing residual magnesium,  $MgCl_2$  and other impurities except for zirconium. The sufficiently high level of purity was achieved by pickling for 6 hours using 3 mass% of hydrochloric acid solution. It was noteworthy that purity of zirconium powder was deteriorated with the formation of intermetallic compounds when alumina or iron was used for apparatus material. Meanwhile, a sound quality without any intermetallic compound and high purity were achieved when  $MgO$  material was used. It was found that there were no significant differences in purity and morphology of zirconium powder depending on reaction temperature. However, mean particle size was increased by increasing reaction temperature. [doi:10.2320/matertrans.M2015248]

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## 1. Introduction

Because of the attractive properties which are excellent corrosion resistance, great strength with ductility, thermal conductivity and biocompatible property, zirconium has been applied to various fields such as structural materials to aggressive environment, hardening agent to steel alloys, petrochemical industry and surgical appliances.<sup>1-4</sup> Notably, a considerable amount of zirconium has been used for fuel rod cladding tube because of a small cross section for the absorption of thermal neutron.<sup>5,6</sup>

The most well-known process to produce metallic zirconium is Kroll process.<sup>7,8</sup>  $ZrCl_4$  in the form of powder is fed into the reactor whose temperature is maintained in a range of 1073–1123 K. Then,  $ZrCl_4$  is vaporized, resulting in a reduction of  $ZrCl_4$  on the surface of magnesium melt. As a result, a zirconium consisting of agglomerated fine particles which is called zirconium sponge is formed. Thereafter, product is evaporated at 1273 K in a vacuum to remove residual magnesium and  $MgCl_2$  contained in the porosity of the sponge. Consequently, Kroll process produces pure zirconium sponge. However, quality is not uniform, and it has a limitation for productivity enhancement due to the batch-type operation for reduction and vacuum distillation which are costly and time-consuming.

In this study, a bubble reduction method, which had been studied for titanium powder production,<sup>9</sup> was investigated for a direct zirconium powder production from  $ZrCl_4$  as starting material. This method consists of two step; reduction and cleaning processes. Firstly, magnesium and  $MgCl_2$  are melted in the reactor. They are separated into two layers in which magnesium melt floats on  $MgCl_2$  salt due to the difference of specific gravity. Then, gaseous  $ZrCl_4$  is injected to  $MgCl_2$  salt through the lance, leading to a conversion into a bubble. This floats without a reaction in  $MgCl_2$  salt.

Subsequently, it is reduced in magnesium layer, resulting in formation of zirconium particles. They are settled in bath due to the greater specific gravity than the two melts, and piled up on bottom of the reactor. Next, the product is cleaned through washing and pickling with an acid solution to remove excess magnesium and  $MgCl_2$  existing within zirconium particles. As result of that, a metallic zirconium powder is produced. This method has many merits. The produced zirconium powder has a uniform quality and high purity because there is pure gaseous  $ZrCl_4$ /liquid magnesium reaction without contact with other phases. Cost-saving and less energy consumption are expected for zirconium powder production due to the simplified process compared to the conventional process which needs additional step such as HDH (Hydrogenation-dehydrogenation) process in that zirconium sponge is converted to  $ZrH_2$  by hydrogenation, and friable  $ZrH_2$  is milled for fine powder, in that order, they are converted to zirconium powder by dehydrogenation.<sup>10</sup>

This study was performed to verify an experimental preparation of zirconium powder through chemical reaction between  $ZrCl_4$  bubbles and magnesium melt. Also, cleaning process was investigated to purify zirconium powder. The effects of apparatus materials and reaction temperature were studied.

## 2. Experimental Procedure

A schematic diagram of experimental apparatus for zirconium powder production is shown in Fig. 1.  $ZrCl_4$  vapor formed in the exterior chamber was injected through the lance made of alumina. Reduction reaction was occurred in the crucible (55 mm dia. and 150 mm h.) mounted on bottom of the cylindrical steel reactor (80 mm dia. and 480 mm h.) in the furnace. The chamber and the reactor were connected by steel tube whose temperature was maintained at 673 K with heating tape to prevent condensation of  $ZrCl_4$  vapor. All parts of the apparatus were covered by the insulating materials to block contact with air of room temperature.

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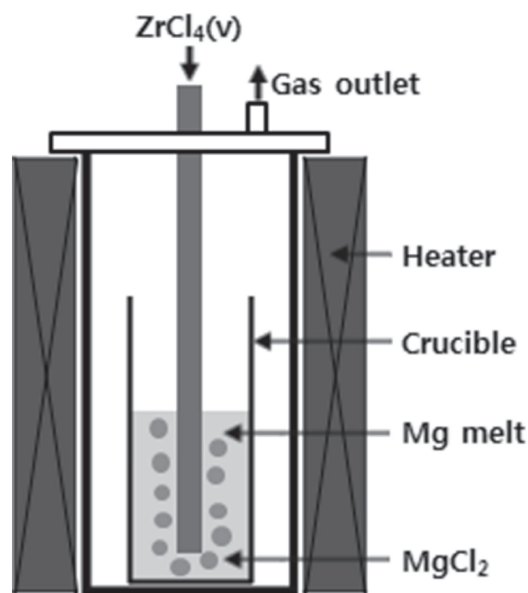


Fig. 1 Schematic of the reduction experiment.

30 g of  $ZrCl_4$  powder ( $\geq 99.5\%$ ) was prepared for vaporization as reactant, and metallic magnesium chips (99.98%) 105 g and  $MgCl_2$  powder (98.0%) 230 g were served in the crucible made of  $MgO$ . In some cases, for comparison, iron and alumina materials were used for the crucible. The experiments were conducted at 1023–1173 K under atmospheric pressure which was maintained by emission of gaseous phases including argon gas and unreacted  $ZrCl_4$  vapor through the outlet of the reactor.

Experiment was proceeded as follows. Firstly, the furnace was heated to the operating temperature to melt magnesium and  $MgCl_2$ , and they were stabilized in the crucible. The lance was immersed into the molten  $MgCl_2$  salt. Then,  $ZrCl_4$  vapor was injected with carrier argon gas whose flow rate was 100 ml/min regulated by flowmeter. This was continued for 90 min. After that, the lance was pulled off from the melts, and followed by a cooling-down of furnace to room temperature. The crucible was taken out from the reactor to separate the inner materials. They were washed with distilled water, and pickled with hydrochloric acid solution. In that order, ethyl alcohol and acetone were used to rinse the residue. Subsequently, it was dried.

The obtained powder was analyzed via scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS) for chemical composition and observation of microstructure. The phases were identified by X-ray diffractometer (XRD). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was applied to determine the concentration of metallic elements. The oxygen concentration was determined by inert gas fusion-infrared absorptiometry technique (LECO analysis).

### 3. Results and Discussion

#### 3.1 Zirconium powder preparation with cleaning process

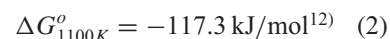
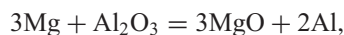
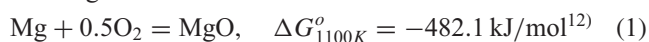
The Kroll reduction process produces zirconium sponge, and vacuum distillation is used to remove the residue and

impurities for purification of zirconium. This, however, is not proper in this study because the loss of zirconium powder could exist. Accordingly, a wet cleaning method was adopted to obtain pure zirconium powder.

The washing using distilled water was carried out for 6 h with two times to remove  $MgCl_2$  which is highly soluble in water.<sup>11)</sup> Then, precipitates were formed, and they were converted into the powder by drying. These were divided into four groups. Among them, three were pickled in hydrochloric acid solution of 1–5% for 12 h. The microstructures of the powders after drying are shown in Fig. 2.

Dust-like substances with small round particles were observed on the powder obtained by only washing. In EDS analysis, it was known that the powder contains oxygen, magnesium, aluminum and chlorine as well as zirconium. Meanwhile, a crowd of round particles was observed on the powder after pickling. In this case, impurities excepting for zirconium were hardly detected compared to the washed powder. In XRD analysis shown in Fig. 3, zirconium and magnesium compounds were found on the powder which was only washed. However, zirconium was mainly found after pickling. It means that pure zirconium powder was favorably achieved by cleaning process using distilled water and hydrochloric acid solution.

The product of the reduction experiment is a mixture of zirconium, magnesium and  $MgCl_2$ . In addition,  $MgO$  was included in the product which was formed by oxidation of magnesium melt and reduction of the alumina lance as following reactions.



By washing,  $MgCl_2$  was removed by dissolving in water, and  $Mg(OH)_2$  was formed through the reaction (3).



The other impurities as well as  $Mg(OH)_2$  were removed by pickling with hydrochloric acid solution,<sup>13)</sup> resulting in obtaining pure metallic zirconium powder.

Elemental concentrations of the powder depending cleaning process are listed in Table 1. The concentrations of magnesium and oxygen were diminished with the dense concentration of hydrochloric acid solution. Accordingly, the purity of zirconium was enhanced due to the fact that zirconium is hardly removed in acid solution as noble metal.<sup>14)</sup> In other words, zirconium powder with high purity was achieved by pickling in hydrochloric acid solution of high concentration. However, no considerable difference in quality was found between the cases of 3% and 5% of hydrochloric acid solution. Thus, 3% of hydrochloric acid solution is needed at least for efficiently removing impurities of the zirconium powder.

Different pickling time was applied in 3% of hydrochloric acid solution. As a result, it was hard to find the relationship between pickling time and morphology of the powder. However, the purity of zirconium powder was changed as shown in Fig. 4. The maximum concentration of zirconium was reached to be 93.7 mass% by pickling for 6 hours, and it was hardly enhanced in 6–12 h. Oxygen concentration was

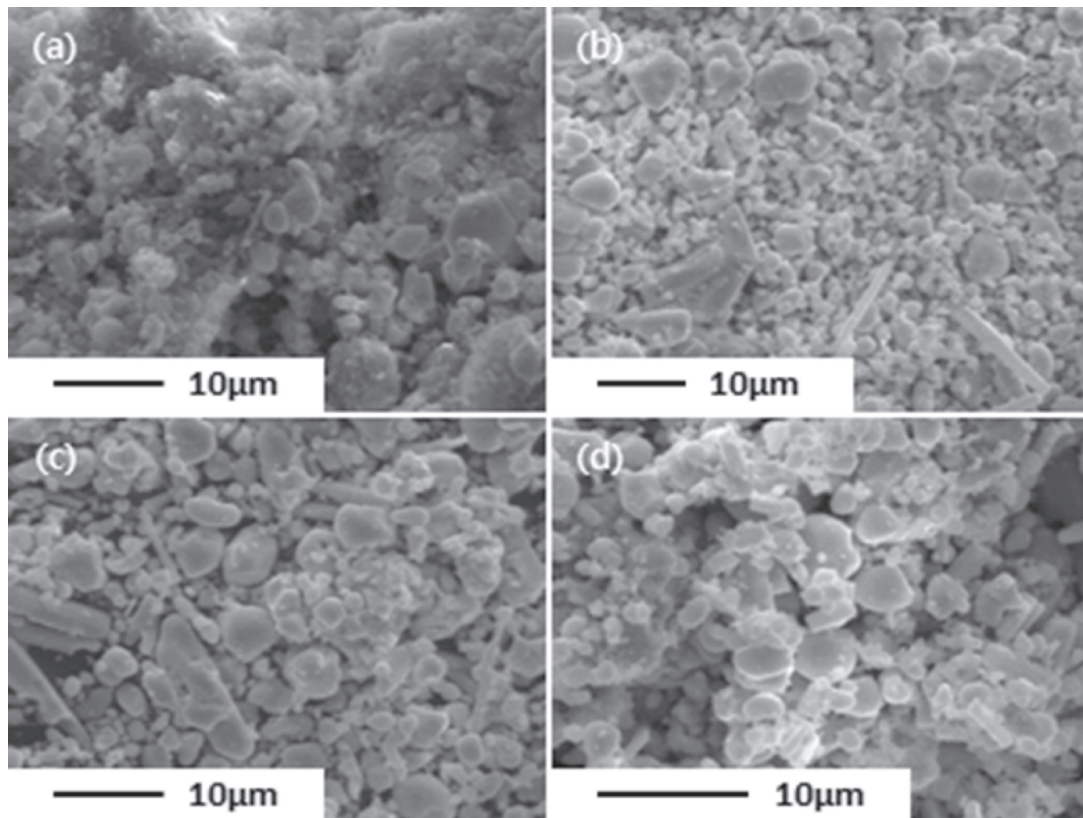


Fig. 2 SEM images of the powder obtained at 1073 K after (a) washing, and pickling with HCl of (b) 1%, (c) 3%, (d) 5%.

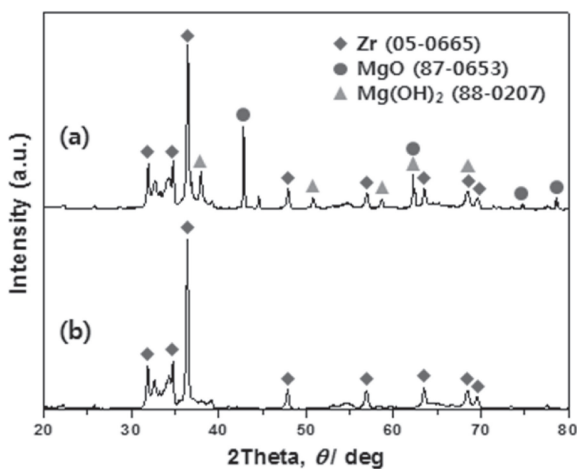


Fig. 3 X-ray diffraction patterns after (a) washing, (b) pickling (with HCl 5%).

Table 1 Effect of cleaning process on the purity of zirconium powder.

#	Treatment	Liquid solution	Concentration/mass%			
			Zr	Mg	Al	O
1	Washing	Distilled water	47.8	19.88	2.33	5.18
2	Pickling	HCl 1%	92.1	0.51	3.18	2.41
3	Pickling	HCl 3%	93.7	0.52	3.07	2.33
4	Pickling	HCl 5%	93.6	0.51	3.09	2.31

minimized by pickling for 4 h and it slightly increased with more pickling time. This is because oxygen, which is soluble in the solution, might be adsorbed on the surface of

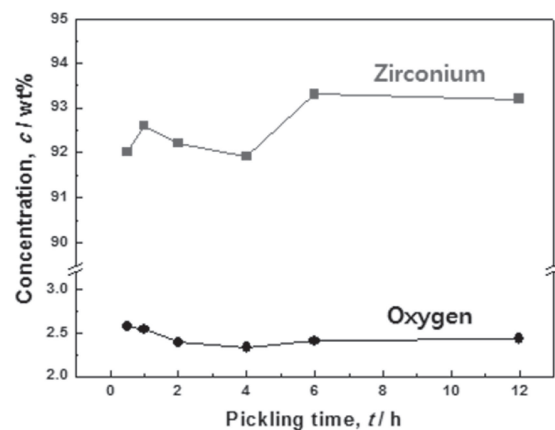


Fig. 4 Effect of cleaning time with HCl 3%.

zirconium particles. However, oxygen concentration was hardly changed after 6 h. Consequently, it needs at least 6 h to achieve a successful pickling with hydrochloric acid solution of 3% for production of zirconium powder with a high level of purity.

### 3.2 Effect of materials

Figure 5 shows the powders obtained in the experiments using the crucible made of alumina and iron. When alumina crucible was used, the particle shape of the powder is angular and rugged. It was confirmed by EDS analysis that zirconium and aluminum were contained in the powder, which led to the formation of not only zirconium but also  $Al_3Zr_4$  and  $AlZr_3$  as shown in Fig. 6. In Ellingham diagram, magnesium is more



Table 2 Zirconium powder obtained in the different experimental conditions.

Crucible	Lance	Temperature (K)	Concentration/mass%					Morphology
			Zr	Mg	Al	Fe	O	
Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	1073	84.0	0.35	14.07	—	1.84	granular
Fe	Al <sub>2</sub> O <sub>3</sub>	1073	72.3	0.29	3.17	21.39	2.98	agglomerated
MgO	Al <sub>2</sub> O <sub>3</sub>	1073	93.7	0.52	3.07	—	2.33	granular
MgO	MgO	1073	95.6	0.43	0.77	—	2.80	granular
MgO	Al <sub>2</sub> O <sub>3</sub>	1023	93.5	0.45	2.80	—	2.42	granular
MgO	Al <sub>2</sub> O <sub>3</sub>	1123	93.7	0.45	3.43	—	2.21	granular
MgO	Al <sub>2</sub> O <sub>3</sub>	1173	93.4	0.50	3.54	—	2.13	granular

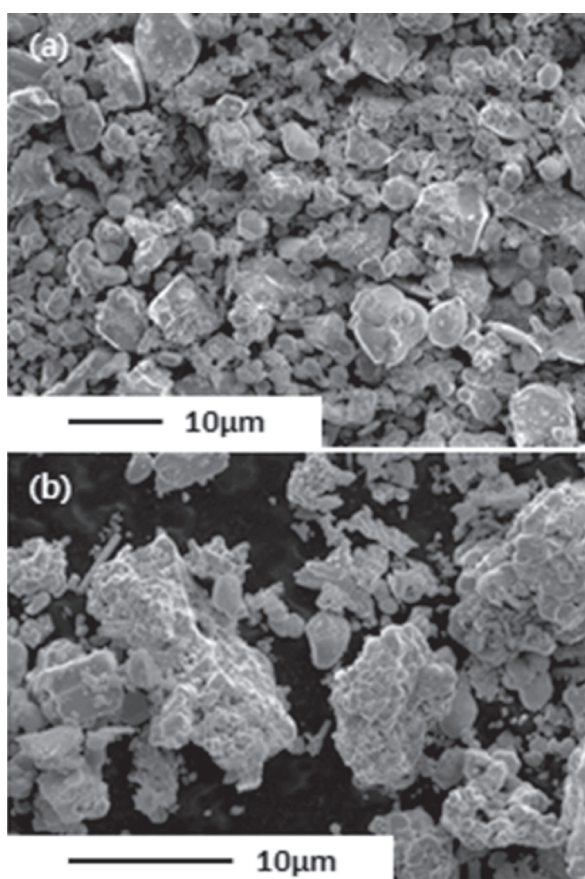


Fig. 5 SEM images of the powder manufactured at 1073 K by using the crucible made of (a) alumina, (b) iron.

oxidized than aluminum.<sup>15)</sup> For that reason, metallic aluminum is reduced from Al<sub>2</sub>O<sub>3</sub> by strong reducing ability of magnesium melt. Subsequently, aluminum component is combined with zirconium, and then various compounds in Al-Zr phase diagram are formed.<sup>16)</sup> When iron crucible was used, agglomerated particles were shown on SEM observation, and iron was detected as impurity. XRD analysis showed FeZr<sub>2</sub> as well as zirconium for stable phases in the powder. It might be caused by iron diffusing from the surface of iron crucible.<sup>17)</sup>

Elemental concentrations depending on experimental conditions, which are determined by ICP-AES and LECO, are listed in Table 2. The powder obtained in alumina crucible has relatively high aluminum concentration. Likewise, an iron concentration is relatively high in the case of

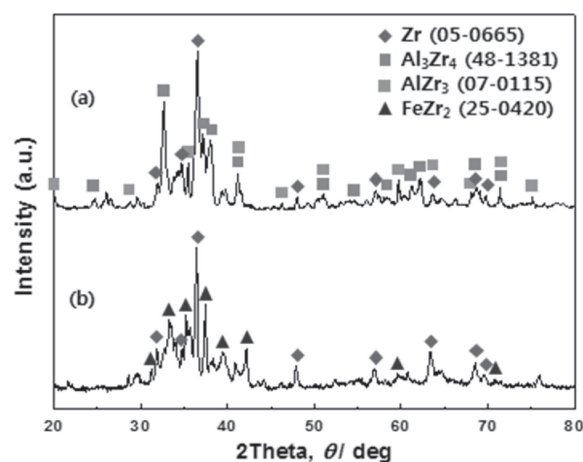


Fig. 6 X-ray diffraction patterns of the powders obtained in the crucible made of (a) alumina, (b) iron.

iron crucible. These impurities could lower the purity of zirconium powder due to the formation of intermetallic compounds by combining with zirconium.<sup>16,18)</sup> Meanwhile, a significant amount of impurity was not detected in the case of MgO crucible. In addition, no impure phase was observed. This is because magnesium and zirconium coexist without intermetallic compound formation in the range of 2.7–99.9 mass%Zr.<sup>19)</sup> Thus, a higher purity of zirconium powder could be achieved when MgO is used for apparatus material. Furthermore, MgO material was used for not only the crucible but also the lance. As a result, a purity of zirconium powder was improved with the decrease of aluminum concentration. However, oxygen concentration is higher than commercial zirconium sponge with oxygen of thousands ppm.<sup>20)</sup> Powder type of zirconium has a large specific surface area compared to the bulk type like zirconium sponge. Namely, comparatively a large amount of oxygen could be absorbed on zirconium powder due to the wide surface area to contact with oxygen. Also, soluble oxygen in MgCl<sub>2</sub> salt which is used for stable formation of ZrCl<sub>4</sub> bubbles could be an origin to increase oxygen concentration of the powder. Therefore, the utilization of the purified argon gas and MgCl<sub>2</sub> salt whose oxygen concentration is very low could be a way to reduce oxygen concentration in the zirconium powder.

### 3.3 Effect of reaction temperature

Using the alumina lance and the MgO crucible, the experiments were conducted at temperature range of 1023–

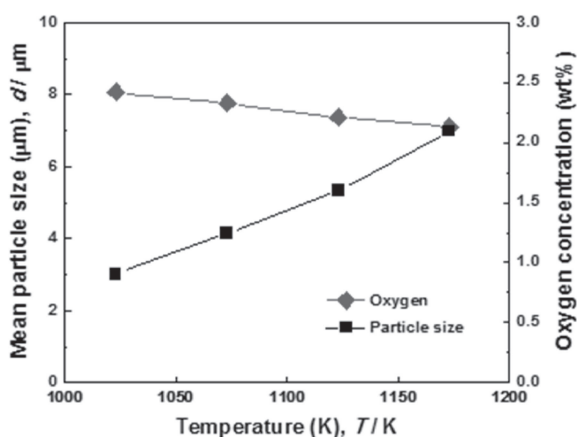


Fig. 7 Mean particle size and oxygen concentration of the zirconium powder as a function of reaction temperature.

1173 K. Regardless of reaction temperature, round particles were observed in the most powders without a significant difference in shape. The chemical composition and the purity of the zirconium powder were hardly changed depending on reaction temperature. However, the considerable change was found in particle size. Figure 7 shows mean particle size as a function of reaction temperature, where the particle size was obtained from the SEM images by assistance of the software of Image Pro Plus v4.5.<sup>21)</sup> It was observed to be about 3 μm at 1023 K and 7 μm at 1173 K. The mean value in particle size of the zirconium powder increased by increasing reaction temperature, and then the oxygen concentration decreased. Oxygen might exist in the form of  $ZrO_2$  film on the surface of zirconium particles piled on the crucible bottom.<sup>13)</sup> The particles grow with increasing temperature due to the increase of the rate of coalescence,<sup>22)</sup> thereby narrowing the spaces between the particles, in which oxygen could be trapped. This is why oxygen concentration decreased at higher temperature. In addition, smaller amount of oxygen could be absorbed on the surface of zirconium particles due to the larger particle size causing smaller specific surface area. Thus, zirconium powder with lower oxygen concentration is produced when the reaction temperature increased. Meanwhile, the mass of magnesium melt would be reduced at high reaction temperature leading to the vaporization. For this reason, a very high reaction temperature has to be avoided for stable zirconium powder production.

#### 4. Conclusions

The reduction reaction of  $ZrCl_4$  bubbles was verified for zirconium powder production by the experiments with  $ZrCl_4$  bubbling in Mg-MgCl<sub>2</sub> bath. Subsequently, pure zirconium powder was achieved through the cleaning process consisting

of washing and pickling. Then, pickling with hydrochloric acid solution of 3% for 6 h was effective to remove efficiently impurities of the zirconium powder. The purity of zirconium powder reached to 95.6 mass% in the experiment using MgO materials for both the crucible and the lance at 1073 K. Meanwhile, alumina and iron materials caused the purity decrease with the formation of intermetallic compounds. The higher reaction temperature induced the increase of mean zirconium particle size, leading to the lower concentration of oxygen.

The zirconium powder produced in this study is appropriate for pyrotechnic areas which require the purity more than 95.0 mass%. However, it is too low for highly effective getter which needs zirconium powder more than 98.0 mass%. Also, comparing the produced mass of zirconium powder and the consumed  $ZrCl_4$  mass, the yield is about 50–70%. A scaled-up the process is subjected to further study for improvement of purity and yield.

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