

# Formation of zirconia films by the aerosol gas deposition method

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Recently, zirconia films have attracted considerable attention because of their potential applications in solid oxide fuel cells and as thermal barrier coatings and oxygen sensors. Herein, we report that high-density zirconia films can be formed at room temperature by using the aerosol gas deposition (AGD) technique and discuss the conditions required for film formation. The experimental results indicate that the particle size and specific surface area of the zirconia powder used determine the success of film fabrication by AGD. Films are successfully formed when the mean particle size and specific surface area of the powder are in the range 2.1–3.5  $\mu\text{m}$  and 4.4–6.5  $\text{m}^2/\text{g}$ , respectively.

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## 1. Introduction

One of the authors (E. Fuchita) has been involved in the development of two new film formation techniques: a gas deposition method (GD)<sup>1),2)</sup> for film formation from nanoparticles and an aerosol gas deposition (AGD) method<sup>3),4)</sup> for film formation from conventional powders. He has been involved in the development of the former method since 1970 and in that of the latter since 1981. The advantage of these two methods is that they can be used to produce thin films at room temperature. The films produced by these two methods have several promising applications because these methods involve dry and low-temperature processes, and hence, substrate degradation does not occur. For example, metal films formed from nanoparticles by GD are used as conducting wires for electric fields<sup>5)</sup> since the use of this method helps prevent the degradation of the base materials. Ceramic films fabricated by AGD can be used as thermal barrier coatings and oxygen sensors, as well as in solid oxide fuel cells.<sup>6)–11)</sup> The use of AGD for the fabrication of various types of ceramics has been investigated. For example, films from oxides such as aluminum oxide, titanium oxide, silicon oxide, yttrium oxide,  $(\text{Ba}_{0.6}, \text{Sr}_{0.4})\text{TiO}_3$ , and lead titanate zirconate (PZT), as well as those from aluminum nitride and magnesium boride, can be easily obtained by this method.<sup>12)–15)</sup> The diameter of the particles in the source powders used for the fabrication of the abovementioned films is less than 1  $\mu\text{m}$ . However, while several patents<sup>16),17)</sup> on zirconia film formation have been filed, there are very few research papers on the formation of zirconia films. Zirconia films have several promising industrial applications. On the basis of the limited information available for zirconia film formation by AGD, it is speculated that the formation of zirconia films is difficult. Hence, we attempted to fabricate zirconia films by AGD while carefully monitoring the film formation conditions such as powder particle size and dryness of the source material. On the basis of the obtained results, we successfully determined the optimum conditions for zirconia film formation.

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## 2. Experimental procedure

### 2.1 Materials used

Commercially available zirconia powders (Daiichi Kigenso Kagaku Kogyo Co., Ltd.) were used as the starting materials. Eleven different powders were used for examining the effect of particle size and specific surface area on film formation. Powder no. 1 has been patented because of its potential application in zirconia film formation by AGD. **Table 1** shows the characteristics of the powders chosen for this study.

### 2.2 Experimental procedure

A photograph of the AGD facility designed by Fuchita Nanotechnology, Ltd. (Type GD-AE04/SS) is shown in **Fig. 1**. The prototype has a height of 2 m and a floor space of 2 m  $\times$  1.5 m. **Figure 2** shows a schematic representation of the AGD apparatus, which comprises an aerosol container, a deposition chamber, and a transfer pipe. The chamber can be evacuated to a pressure of 10 Pa by using a root blower pump and a rotary pump. The deposition chamber is equipped with a nozzle and an X–Y moving stage to be used during the fabrication of the films. The nozzle is linked to a container holding the source powder by means of a transfer pipe. The chamber is first evacuated, and then, nitrogen gas is introduced into the chamber from the bottom of the aerosol container. Subsequently, the gas is transported to the deposition chamber through the transfer pipe. The rate of gas supply is maintained between 3 and 20 L/min. The zirconia powder encased in the aerosol container is entrained by the supply gas and ejected from the nozzle into the deposition chamber, where it is deposited onto a substrate for film formation. Two types of nozzles with widths of 5 mm and 30 mm are used; each nozzle has a 0.3-mm-wide slit. Plates made of glass, alumina, and a nickel-based alloy are used as substrates for the aforementioned deposition. The dimensions of each substrate are 70 mm (length)  $\times$  50 mm (width)  $\times$  1 mm (thickness). The substrate holder can be scanned in the X and Y directions with the help of a digital programmable controller. The scanning speed is maintained at 1 mm/s or 5 mm/s for a 30-mm-long film, and scanning is performed 5 to 150 times in the X direction to obtain the final product.

Table 1. Characteristics of high-purity zirconia powders

No.	Mean particle size $D_{50}$ $\mu\text{m}$	Specific surface area $\text{m}^2/\text{g}$	$\text{ZrO}_2 + \text{HfO}_2$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	$\text{CaO}$	Product
			—	%	%	%	%	
1	0.47	21.6	Main elements	0.012	0.002	0.001	—	UEP
2	0.58	82.7	Main elements	0.010	0.002	0.002	—	UEP
3	2.2	5.1	Main elements	0.002	0.002	0.001	0.004	EP-5
4	2.1	7.1	Main elements	0.003	0.002	0.001	0.004	EP-7
5	2.1	13.0	Main elements	0.004	0.002	0.001	0.004	EP-13
6	2.2	22.0	Main elements	0.004	0.001	0.001	0.004	EP-22
7	2.1	26.1	Main elements	0.002	0.002	<0.001	0.003	EP-P
8	2.7	6.5	Main elements	0.026	0.002	0.110	0.012	SPZ
9	3.5	6.1	Main elements	0.005	0.001	0.003	0.006	SPZ
10	3.4	4.4	Main elements	0.004	0.002	0.001	—	SPZ
11	7.3	9.3	Main elements	0.005	0.002	0.001	0.001	WG-8S

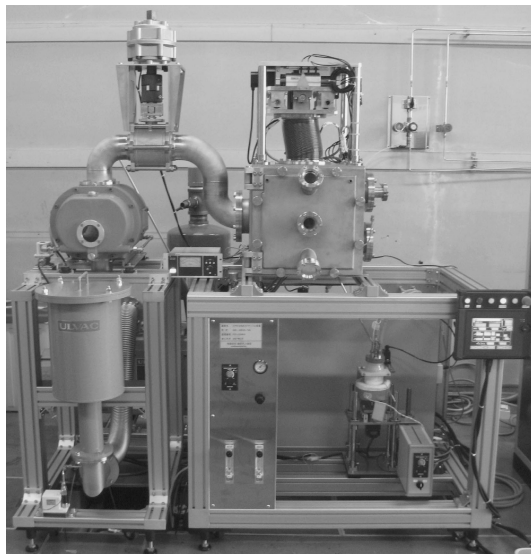


Fig. 1. Photograph of the GD-AE04/SS AGD facility with dimensions of  $W2000 \times D1500 \times H2000$  mm.

The experimental conditions were as follows. Prior to use, each purchased powder was heat-treated at 773 K for 1 h. The pressure of the aerosol container was varied from 23 to 59 kPa (differential pressure). The amount of source powder consumed in each batch was varied from 40 to 80 g, and the nitrogen gas flow was varied from 3 to 12 L/min during film formation. The entire deposition process was carried out at room temperature.

### 2.3 Characterization

The humidity of the starting powders was standardized by drying them in a heating furnace (Isuzu Seisakusyo Co., Ltd., DSTR-11K). A laser diffraction particle size analyzer (Shimadzu Corporation, SALD2100) and a Micromeritics FlowSorb 2300 apparatus were used to measure the mean particle size and specific surface area of the source powders, respectively. The particle size of the starting powders and the cross section of the deposited films were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM),

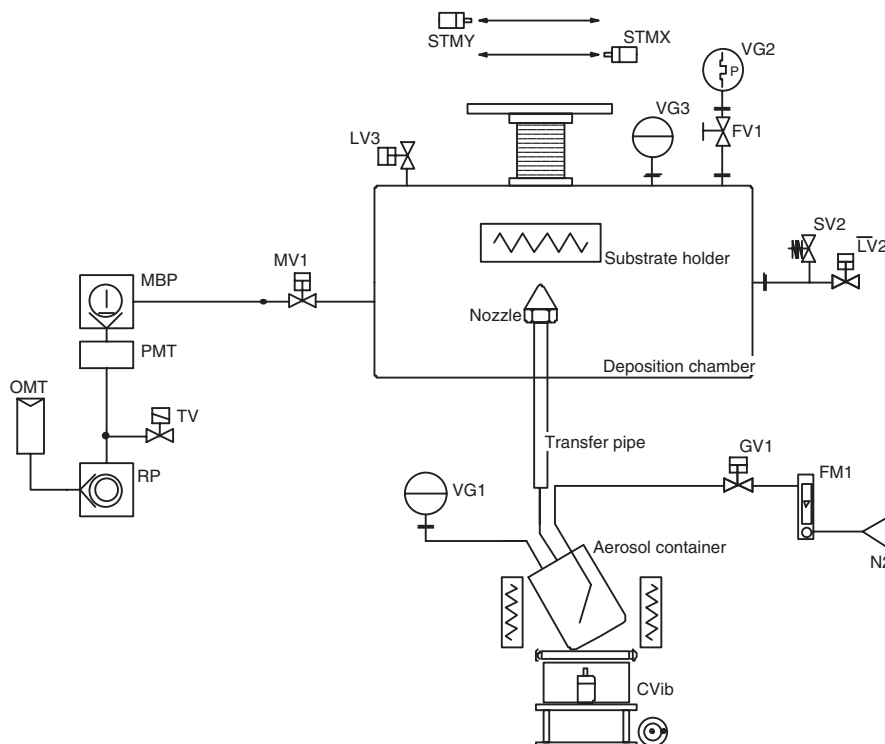


Fig. 2. Schematic diagram of the AGD apparatus.

Table 2. Formation conditions and results of film fabrication

No.	Characteristics of powders				Formation conditions					Results of film fabrication			
	Mean particle size $D_{50}$ ( $\mu\text{m}$ )	Specific surface area ( $\text{m}^2/\text{g}$ )	$\text{N}_2$ gas flow rate ( $\text{L}/\text{min}$ )	Differential pressure (kPa)	Nozzle width/slit width (mm)	Scanning speed (mm/s)	Number of scans	Charging powder (g)	Heat-treatment of raw powder	Substrate	Quality of film	Film thickness ( $\mu\text{m}$ )	Deposition rate ( $\mu\text{m}/\text{pass}$ )
1/1	0.47	21.6	5	47	$5 \times 0.3$	1	50	80	YES*	G	Green compact	—	—
2/1	0.58	82.7	5	47	$5 \times 0.3$	5	20	50	No treatment	G	Green compact	—	—
2/2	0.58	82.7	3	30	$5 \times 0.3$	1	5	80	YES	G	Green compact	—	—
3/1	2.2	5.1	8	27	$30 \times 0.3$	1	50	80	YES	G	Good	2	0.04 $\mu\text{m}$
3/2	2.2	5.1	12	34	$30 \times 0.3$	1	50	80	YES	G	Good	4	0.08 $\mu\text{m}$
4/1	2.1	7.1	8	28	$30 \times 0.3$	1	50	80	YES	G	Peeled off partially	—	—
4/2	2.1	7.1	12	35	$30 \times 0.3$	1	50	80	YES	G	Peeled off	—	—
5/1	2.1	13	8	27	$30 \times 0.3$	1	50	50	YES	G	Green compact	—	—
5/2	2.1	13	12	34	$30 \times 0.3$	1	50	50	YES	G	Green compact	—	—
6/1	2.2	22	6	23	$30 \times 0.3$	1	50	40	YES	G	Green compact	—	—
6/2	2.2	22	12	31	$30 \times 0.3$	1	50	40	YES	G	Green compact	—	—
7/1	2.1	26.1	7	59	$5 \times 0.3$	1	10	50	YES	G	Green compact	—	—
8/1	2.7	6.5	5	47	$5 \times 0.3$	1	30	50	YES	G	Good	24	0.8 $\mu\text{m}$
8/2	2.7	6.5	3	30	$5 \times 0.3$	1	10	50	YES	G	Good	6	0.6 $\mu\text{m}$
9/1	3.5	6.1	8	30	$30 \times 0.3$	1	150	70	YES	G	Good	20	0.13 $\mu\text{m}$
9/2	3.5	6.1	7	28	$30 \times 0.3$	1	50	70	YES	G	Good	5	0.1 $\mu\text{m}$
9/3	3.5	6.1	8	30	$30 \times 0.3$	1	120	50	YES	Nickel-base alloy	Good	20	0.17 $\mu\text{m}$
10/1	3.4	4.4	12	35	$30 \times 0.3$	1	50	80	YES	G	Good	10	0.2 $\mu\text{m}$
11/1	7.3	9.3	5	47	$5 \times 0.3$	1	50	50	YES	G	No film	—	—

\*773 K  $\times$  1 h

G; Slide glass

respectively, and the film thickness was measured by using a micrometer (Mitutoyo, MDE-25PJ). For comparison, a powder obtained using a planetary ball mill (Ito Seisakusyo Co., Ltd., LP-1) was also used for film deposition.

### 3. Results

#### 3.1 Zirconia film formation

Table 2 shows the powders from which thin films could be formed. Powder no. 1 and powder no. 2, which were fine powders with mean particle sizes of 0.47  $\mu\text{m}$  and 0.58  $\mu\text{m}$ , respectively, produced poor-quality, low-density films. These experimental results indicated that extremely fine powders were unsuitable for film formation. Five of the powders had particle sizes of 2.1  $\mu\text{m}$  or 2.2  $\mu\text{m}$  and specific surface areas ranging from 5.1 to 26.1  $\text{m}^2/\text{g}$ . Among these powders, only the powder with a specific surface area of 5.1  $\text{m}^2/\text{g}$  afforded high-density films that adhered strongly to the substrate. The strong adherence of the films to the substrate was confirmed from the difficulty in peeling off the films from the substrate by scratching with a needle. In Table 2, the state of the films is described in teams of "Good." High-density films with good adhesive strength were formed from zirconia powders containing large particles: powder no. 8 (SPZ/mean particle size, 2.7  $\mu\text{m}$ ; specific surface area, 6.5  $\text{m}^2/\text{g}$ ), powder no. 9 (SPZ/mean particle size, 3.5  $\mu\text{m}$ ; specific surface area, 6.1  $\text{m}^2/\text{g}$ ), and powder no. 10 (SPZ/mean particle size, 3.4  $\mu\text{m}$ ; specific surface area, 4.4  $\text{m}^2/\text{g}$ ). However, no film formation was observed when WG-8S, which had a very high mean particle size of 7.3  $\mu\text{m}$  and a specific surface area of 9.3  $\text{m}^2/\text{g}$ , was used as the starting material, and the particles ejected from the nozzle were scattered away from the substrate. Note that because of its fine particle size, powder no. 1, for which a patent was filed, did not afford any film.

#### 3.2 Observation of the source powder and the cross section of the obtained film

TEM images of the SPZ powder with a particle diameter of 2.7  $\mu\text{m}$  are shown in Figs. 3(a) and 3(b). Figure 3(a) shows a large number of aggregated particles with diameters of approximately 3  $\mu\text{m}$ ; this value is reasonably consistent with the data obtained by particle size measurements. It is confirmed that the primary particles observed in Fig. 3(b) range from 100 to 150 nm in size. These particles might be elementary particles generated during the particle formation process, and the aggregation of these primary particles might have led to the formation of larger particles during the manufacturing of the powder. The form and

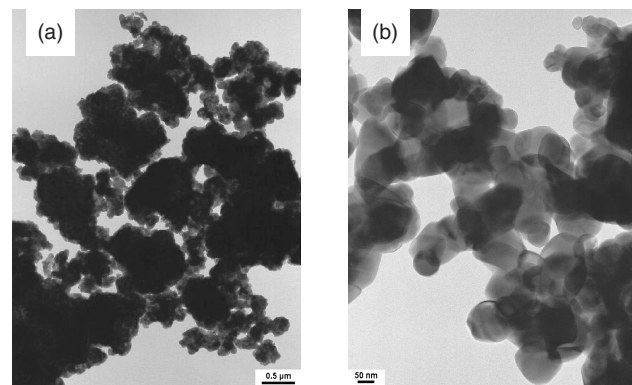


Fig. 3. (a) TEM photograph of the SPZ (2.7  $\mu\text{m}$ ) powder. (b) High-magnification photograph. (The source powder with mean diameter of 2.7  $\mu\text{m}$  is composed of primary particles with 100 nm diameter.)

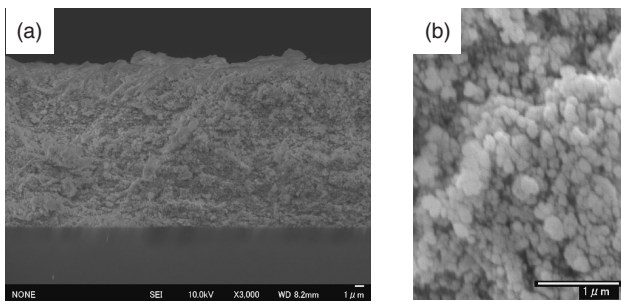


Fig. 4. (a) SEM image of cross section of deposited film obtained from SPZ (2.7  $\mu\text{m}$ ) powder. (b) High-magnification image.

specific surface area of the condensed powder can be varied by controlling the manufacturing process.

Figures 4(a) and 4(b) show the SEM photographs of the cross section of the deposited films obtained from the SPZ powder with a particle size of 2.7  $\mu\text{m}$ . The film has high density, and there are no cracks at the film–substrate interface. As is evident from the high-magnification image in Fig. 4(b), this film is composed of particles with sizes of approximately 100 nm, which is close to the diameter of the primary particles in the starting powder (as observed by TEM).

#### 4. Discussion

As shown in Table 1, powders no. 3, 4, 5, 6, and 7 have specific surface areas in the range 5.1–26.1  $\text{m}^2/\text{g}$ , and the particle size of these powders is adjusted to approximately 2  $\mu\text{m}$ . Among these, only the powder with a specific surface area of 5.1  $\text{m}^2/\text{g}$  affords the desired films. The particle size (2.7  $\mu\text{m}$ ; shown in Fig. 3) of the source powder in the aggregated state appears to be the deciding factor for the film-forming ability of the zirconia powder. That is, the mean particle size of the starting powder (secondary particle size) strongly affects the success of film fabrication by AGD. This is because the high density of the films obtained from powders with a mean particle size of 2.1 to 3.5  $\mu\text{m}$  is mainly attributed to the rearrangement of the primary particles induced by the jet flow. Moreover, it is suggested that a specific surface area of 6.5  $\text{m}^2/\text{g}$  or lesser is important for successful film deposition. Source powders with a large specific surface appear to be less strongly aggregated than the small-specific-surface-area powders used for film deposition. This implies that for successful film formation by AGD, the zirconia powders must comprise compactly arranged particles having a size of 2–3  $\mu\text{m}$ . On the other hand, a green compact is obtained from the SPZ (2.7  $\mu\text{m}$ ) powder treated by planetary ball mill processing (180 rpm for 2 h). Ball mill processing causes the particles in the aggregated powder to break, and hence, the particle size reduces from 2.7  $\mu\text{m}$  to the submicron level. For this reason, film deposition is not achieved when using the ball-milled powder. The abovementioned decrease in the particle size corresponds to an increase in the specific surface area.

In the case of small particles, rearrangement of the primary particles in the aggregated powders might be difficult under the

differential pressure (60 kPa) employed in this study. On the other hand, large particles adhere weakly to the substrate and thus flake off the substrate.

#### 5. Conclusions

(1) It has been demonstrated that particle size and specific surface area play an important role in the fabrication of films from zirconia powder by AGD. High-density films are formed when the mean particle size ranges from 2.1 to 3.5  $\mu\text{m}$  and the specific surface area ranges from 4.4 to 6.5  $\text{m}^2/\text{g}$ .

(2) High-density films are not formed when zirconia powders with a very small (approximately 0.5  $\mu\text{m}$ ) or very large particle size (7.3  $\mu\text{m}$ ) are used. In addition, zirconia powders with a specific surface area of 7.1  $\text{m}^2/\text{g}$  or more do not afford high-density films, even when their mean particle size is 2.1  $\mu\text{m}$ .

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