

Formation of zirconia films by aerosol gas deposition method using zirconia powder produced by break-down method

Eiji FUCHITA,^{*,**†} Eiji TOKIZAKI,^{*,**} Eiichi OZAWA^{*,**} and Yoshio SAKKA^{**}

^{*}Fuchita Nanotechnology, Ltd., 2-25-57 Tamatsukuri, Narita, Chiba 286-0011

^{**}National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047

The purpose of this study is to form a film of dry-milled zirconia powders by aerosol gas deposition (AGD). Recently, we reported that we could form a high-density zirconia film using wet-type zirconia powders prepared wet-chemically. From the stand point of industrial use, the dry-milled zirconia powder seems to be much more advantageous than the wet type. In this study, we examined the possibility to fabricate zirconia film using commercially available dry-milled zirconia powders with a mean diameter range that is nearly the same as those of wet-type ones, for example, 0.73 to 10.2 μm in mean diameter. As a result, we were able to make a zirconia film from all powders, although the film formation conditions for the wet-type powder was very much limited in the diameter and the specific surface area. In conclusion, dry-milled zirconia powders are considered to have high potential for industrial use.

©2010 The Ceramic Society of Japan. All rights reserved.

Key-words : Dry-milled zirconia powder, Break-down method, Aerosol gas deposition, Film formation, Mean particle size

[Received June 9, 2010; Accepted August 19, 2010]

1. Introduction

The aerosol gas deposition method is a completely dry and low-temperature process and needs no special heat sources or gas precursors.^{1),2)} Furthermore, the method allows ceramic powder to be deposited in a very local area to form a thin film. Hence, many applications have been proposed for films produced by this method. Thermal barrier coatings for high-temperature systems, such as a turbine engine, and some special electric devices, such as sensors and solid oxide fuel cells, are examples.³⁾⁻⁸⁾ Aluminum oxide, titanium oxide, and lead titanate zirconate (PZT) films have been reported to be easily fabricated by this method.⁹⁾⁻¹⁴⁾ However, there were very few reports on zirconia film formation.^{15),16)} There are two types of zirconia powders: a wet-type one chemically prepared and a dry-milled one. The wet-type powder mainly consists of agglomerated fine particles with low powder density, but the dry-type one comprises dense particles. We have attempted to clarify the film formation conditions using wet-type zirconia powders and have clarified the formation conditions of the film.¹⁷⁾ Judging from the production cost of zirconia powder, the dry-milled powder is much cheaper than the wet-type powder. No one has attempted to deposit zirconia film using dry-milled powder until now. For this reason, we are interested in dry-milled zirconia powder as a starting material for zirconia film formation.

2. Experimental procedure

2.1 Materials used

Commercially available zirconia powders (Daiichi Kigenso Kagaku Kogyo Co., Ltd.) were used as starting powders. Five different sizes of powder produced by the break-down method were utilized to examine the effects of particle size on film formation. **Table 1** shows the characteristics of these powders.

[†] Corresponding author: E. Fuchita; E-mail: fuchita@nanotechjip.com

Table 1. Characteristics of zirconia powders

No.	Mean particle size D_{50} μm	Specific surface area m^2/g	$\text{ZrO}_2+\text{HfO}_2$ SiO_2 Fe_2O_3 TiO_2				Product
			%	%	%	%	
1	0.73	6.1	Main elements	0.14	0.12	0.17	TMZ-T
2	1.12	4.7	Main elements	0.07	0.08	0.15	TMZ
3	2.9	2.7	Main elements	0.18	0.16	0.17	BR-3QZ
4	7.4	1.6	Main elements	0.12	0.05	0.18	BR-QZ
5	10.2	1.5	Main elements	0.19	0.04	0.21	BR-12QZ

Their mean particle size and specific surface area were as follows: TMZ-T (mean particle size 0.73 μm and specific surface area 6.1 m^2/g), TMZ (mean particle size 1.12 μm ; specific surface area 4.7 m^2/g), BR-3QZ (mean particle size 2.9 μm ; specific surface area 2.7 m^2/g), BR-QZ (mean particle size 7.4 μm ; specific surface area 1.6 m^2/g) and BR-12QZ (mean particle size 10.2 μm ; specific surface area 1.5 m^2/g). The five powders had a particle size in the range of 0.73 to 10.2 μm and specific surface areas ranging from 1.5 to 6.1 m^2/g .

2.2 Experimental procedure

The AGD facility used was the same one introduced in the previous paper.¹⁷⁾ **Figure 1** shows a schematic diagram of the AGD apparatus, which is composed of an aerosol container, a deposition chamber, and a transfer pipe. First, the chamber is evacuated, then nitrogen gas is introduced into the chamber from the bottom of the aerosol container, and the gas is transported to the deposition chamber through the transfer pipe. The zirconia powder, which is encased in the aerosol container, is entrained by the supply gas and ejected out of the nozzle in the deposition

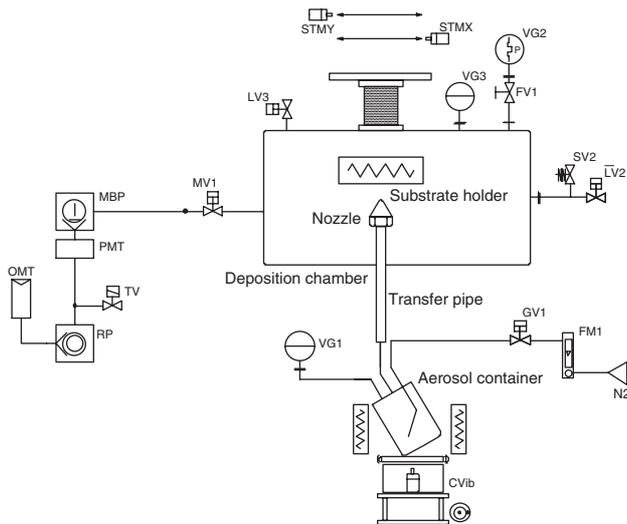


Fig. 1. Schematic diagram of the AGD apparatus.

chamber, where it is deposited on a substrate to form a film. The experimental conditions in this paper were as follows. Each purchased powder was heat-treated at 773 K for 1 h before its use as a starting powder. The nozzle had a width of 30 mm and a slit of 0.3 mm width. Micro slide glasses (S9224) made by Matsunami Glass Ind., Ltd. were used as substrates for deposition. The size of substrates was about 70 mm (length) \times 50 mm (width) \times 1 mm (thickness). The pressure of the aerosol container was varied from 22 to 42 kPa (differential pressure). The amount of source powder consumed for each batch was 80 g, and the nitrogen gas flow was varied from 4 to 16 L/min in the film formation procedure. Scanning was performed from 50 to 1000 times along the X direction to obtain the final film. The entire deposition process was carried out at room temperature.

2.3 Characterization

A heating furnace (Isuzu Seisakusyo Co., Ltd., DSTR-11K) was used to standardize the humidity of the starting powders. A laser diffraction particle size analyzer (Shimadzu Corporation, SALD2100) and Micromeritics FlowSorb II 2300 surface area analyzer were used to measure the mean particle size and the 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 SEM and a micrometer (Mitutoyo, MDE-25PJ) was used to measure the thickness of the films.

3. Results

3.1 Zirconia film formation

Table 2 shows the performance of the film, such as the film quality, the film thickness and the film formation rate. All powders could be used to fabricate transparent and high-density films with 6 to 30 μm thickness.

Figure 2(a) shows the SEM micrograph of the BR-QZ powder with particles of 7.4 μm diameter. The particle has many angles introduced in the process of crushing a massive zirconia solidified from melt. **Figures 2(b) and 2(c)** show cross sections of the film obtained. The film density was rather high and the thickness of the film was about 25 μm . We could not observe any peeling out of the film from the substrate. The surface of the film was rather flat. **Figure 2(c)** shows the SEM image of the central part of the film at a high magnification. We can observe many small particles with 100 to 200 nm diameter, which are one-fiftieth the size of source particles. These experimental results indicate that source powders were crushed and deposited on the substrate glass.

3.2 Relationship between film thickness and amount of supplied gas and scanning times

Figure 3(a) shows the relationship between the film thickness and amount of supplied gas for zirconia powder (BR-QZ) with 7.4 μm diameter under 50 scans. The thickness of the film increases with the increment of the amount of supplied gas. Three micrometer thickness was obtained with a gas flow rate of 6 L/min and 25 μm thickness with a 14 L/min gas flow rate. **Figure 3(b)** shows the relationship between the film thickness and the number of scans from 50 to 1000 times with a 4 L/min gas flow rate. The thickness increases linearly with the number of scans.

Figure 4 is a summary of the relationship between the film thickness and amount of supplied gas for 5 types of starting powder. Film thickness increases with the increment of the amount of supplied gas for all powders. However, it is indicated the small-grained powder (TMZ-T) and large-grained powder (BR-12QZ) have a high efficiency of deposition rate for film formation compared with medium-size powders (BR-3QZ and TMZ).

4. Discussion

All powders could be used to fabricate transparent and high-density films with 6 to 30 μm thickness. The mean diameter of particles composing the powders ranges from 0.73 to 10.2 μm . That is, the film formation was conducted in a wide range of particle size. This experimental result was different from the one obtained with wet-type zirconia powder because the formation condition of the wet-type powder was greatly constrained by the particle size and specific surface. However, the primary particle

Table 2. Formation conditions and results of film fabrication

No.	Characteristics of powders		Formation condition		Result of film fabrication		
	Mean particle size D_{50} (μm)	Specific surface area (m^2/g)	Amount of supplied N_2 gas (L/min)	Differential pressure (kPa)	Quality of film	Film thickness (μm)	Deposition rate ($\mu\text{m}/\text{scans}$)
1/1	0.73	6.1	16	42	Good	28	0.56
2/1	1.12	4.7	12	36	Good	6	0.12
3/1	2.9	2.7	14	38	Good	8	0.16
4/1	7.4	1.6	10	32	Good	14	0.28
5/1	10.2	1.5	8	28	Good	30	0.6
5/2	10.2	1.5	4	22	Good	7	0.14

*Scanning speed: 1 mm/s. *Substrate: slide glass.

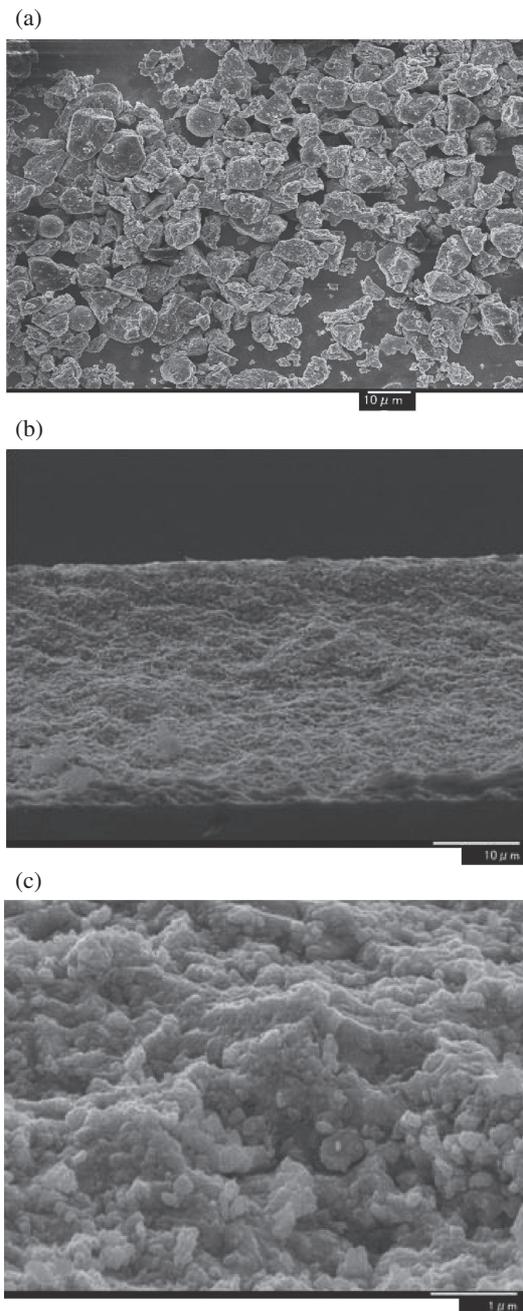
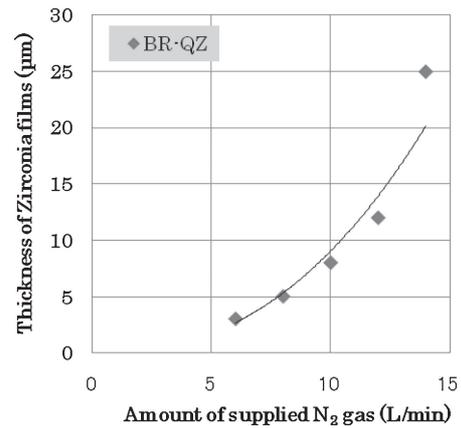
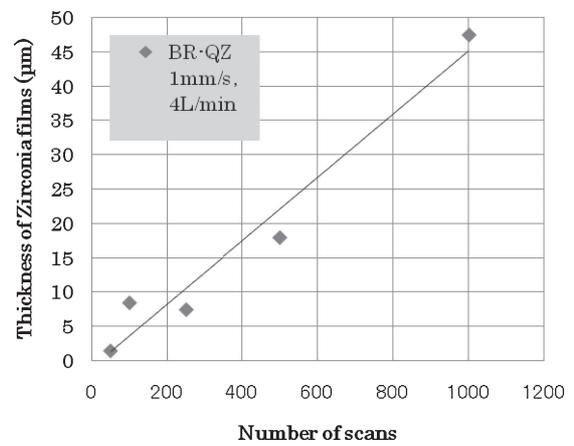


Fig. 2. (a) SEM micrograph of the BR-QZ (7.4 μm) powder. (b) SEM image of cross section of deposited film obtained from BR-QZ (7.4 μm) powder. (c) High-magnification image.

size of the films obtained was 100 to 200 nm according to SEM images, which was less than one-fiftieth that of BR-QZ. This result was nearly the same as the results for wet-type zirconia. These experimental results indicated that the source particles injected from the outlet of the nozzle collided with the surface of the substrate and were crushed to finer sizes and that the particles deposited to make a film comprising rearranged fine particles. The key point of the effective deposition of the powder in this procedure will be the kinetic energy of the source particles and the state of the powder. When particles collide with the substrate, the kinetic energy should be concentrated at the collision site of the particle on the substrate so as to crush the particles, leaving sediment layers. It is also important how easily the particles are



(a)



(b)

Fig. 3. (a) Relationship between the film thickness and amount of supplied gas. (b) Relationship between the film thickness and the number of scans.

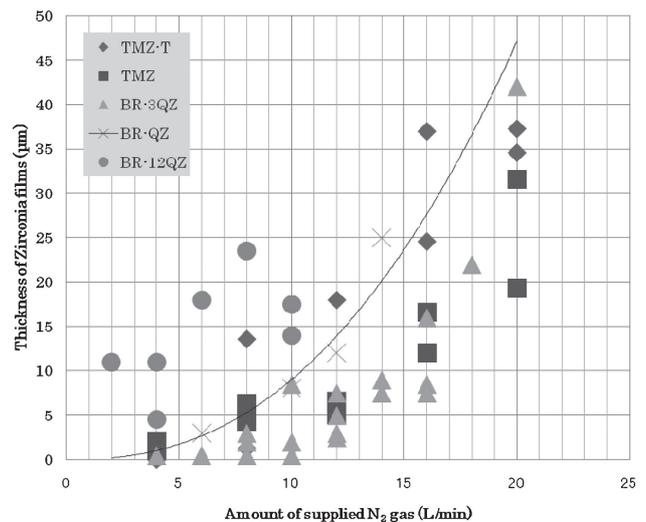


Fig. 4. Summary of the relationship between the film thickness and amount of supplied gas.

atomized at the site. Judging from the different performances of film formation between dry-milled and wet-type zirconia, the dry-milled type seems to have a more massive body and fragile characteristics than the wet-type. On the other hand, the wet-type

zirconia was not treated by the crushing process so that each particle composed of powder might not contain small cracks in the body, which reduced the fragility of the wet-type powder compared with dry-milled powder. In any case, the kinetic energy can be effectively consumed in crushing some of the source particles in the case of dry-milled zirconia.

Concerning the deposition rate for the 5 powders, both fine and large particles have faster deposition rates compared with medium-size powders. This might be a result of the low efficiency of crushing particles of medium-size powder. However, why the medium-size powder shows a slow deposition rate is not yet clear. We should examine the particle crushing process in greater detail. In particular, the properties of the particles composed of powder should be checked.

5. Conclusion

All powders of dry-milled zirconia could be used to fabricate transplant and high-density films with 6 to 30 μm thickness. The mean diameter of particles composing the powders ranges from 0.73 to 10.2 μm , which indicates that film formation was possible in a wide range of particle size.

Acknowledgements We would like to express our deepest gratitude to Mr. Akira Kohara (Daiichi Kigenso Kagaku Kogyo Co., Ltd.), whose comments and suggestions were of immense value in this work. We would also like to thank Mr. Haruki Kimura (Graduate Student at the University of Tsukuba), whose SEM observations were an enormous help to us. Finally, we gratefully appreciate the financial support of New Energy and Industrial Technology Development (NEDO), which made it possible to complete our research.

References

- 1) S. Kasyu, E. Fuchita, T. Manabe and C. Hayashi, *Jpn. J. Appl. Phys.*, **23**, L910–L912 (1984).
- 2) C. Hayashi, *Mater. Sci. Forum*, **246**, 153–180 (1997).
- 3) S. Somiya, N. Yamamoto and H. Yanagida ed., *Advances in Ceramics*, **24A** (1986).
- 4) I. O. Golosnoy, A. Cipitria and T. W. Clyne, *J. Therm. Spray Technol.*, **18**, 809–821 (2009).
- 5) M. Mori, H. Nishimura, H. Yahiro and Y. Sadaoka, *J. Ceram. Soc. Japan*, **116**, 777–780 (2008).
- 6) O. Vasyukiv, Y. Sakka, Y. Maeda and V. V. Skorokhod, *J. Am. Ceram. Soc.*, **88**, 639–644 (2005).
- 7) Y. Sakka and K. Hiraga, *Nippon Kagaku Kaishi*, 497–508 (1999).
- 8) G. Suárez, Y. Sakka, T. S. Suzuki, T. Uchikoshi, X. Zhu and E. F. Aglietti, *Sci. Technol. Adv. Mater.*, **10**, 025004 (2009).
- 9) S. Kasyu and Y. Mihara, *J. Jpn. Soc. Powder Powder Metall.*, **42**, 314–317 (1995) [in Japanese].
- 10) Japanese Patent 1660799, Japanese Patent 1513241 [in Japanese].
- 11) J. Akedo, *J. Am. Ceram. Soc.*, **89**, 1834–1839 (2006).
- 12) Y. Imanaka, N. Hayashi, M. Takenouchi and J. Akedo, *J. Eur. Ceram. Soc.*, **27**, 2789–2795 (2007).
- 13) R. Sakamaki, T. Hoshina, H. Kakemoto, K. Yasuda, H. Takeda, J. Akedo and T. Tsurumi, *J. Ceram. Soc. Japan*, **116**, 1299–1303 (2008).
- 14) T. Miyoshi, *J. Ceram. Soc. Japan*, **117**, 899–903 (2009).
- 15) Japanese Patent P2003-73855A [in Japanese].
- 16) Japanese Patent P2008-137860A [in Japanese].
- 17) E. Fuchita, E. Tokizaki and Y. Sakka, *J. Ceram. Soc. Japan*, **118**, 767–770 (2010).