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Effect of process gas on deposition efficiency of zirconia film in granule spray in vacuum

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Monoclinic zirconia films were deposited by spraying monoclinic zirconia granules on glass substrates in a low vacuum environment. In order to spray the granules through a nozzle, air and He were used to carry and accelerate the granules. Flow rates of air and He were varied in order to study their effect on granule velocity and deposition efficiency. For both air and He, granule velocity increased with their flow rate. For the same gas flow rate, granule velocity was much higher when He was used than when air was used. Variation of deposition efficiency according to the gas and gas flow rate was similar to that of granule velocity. Highest deposition efficiency was 1.87% which may be the highest deposition efficiency of ceramic films by room temperature spray of ceramic particles or granules to date. The results support that granule velocity is closely related to deposition efficiency. The deposited films were quite dense and retained the crystalline phase of the granules.

Keywords: Granule spray in vacuum (GSV), Zirconia film, Deposition efficiency, Granule velocity, Process gas.

Introduction

Aerosol deposition method (ADM) has been attracting a lot of attention mainly due to its unique advantages for making ceramic films [1-7]. It can deposit dense nano-structured ceramic films simply by spraying the individual fine ceramic particles (with a particle size range of 0.08-2 μm) mixed in a carrier gas through a nozzle in a vacuum chamber at room temperature [1]. The deposited films have almost the same chemical composition as that of the starting ceramic powder. ADM can also deposit films fast especially when the film area is small. Although ADM has such attractive merits for making ceramic films, it still needs improvement for a better performance [8]. For example, Mihara et al. pointed out a problem with the aerosol chamber which was mechanically vibrated for generating the aerosol [8]. The mechanical vibration gradually changed the state of powders from floppy to densely packed inside the aerosol chamber. As the powders were densely packed, the amount of particles floating up in the aerosol chamber and mixed in a carrier gas decreased. That means the amount of particles delivered to the nozzle by a carrier gas decreased as the deposition proceeded.

Granule Spray in Vacuum (GSV) was developed in order to attain long-term-feed stability of of ADM. Since flowable granules are used, GSV does not require mechanical vibration for feeding the raw materials to a nozzle and thereby long-term-feed stability can be accomplished. Details of GSV were introduced in the previous reports [9, 10]. GSV is similar to ADM in many aspects. For example, it deposits dense ceramic films at room temperature as ADM does [9]. There are some differences between ADM and GSV, too. One of the biggest differences can be found in what collides with the substrate. While individual particles well dispersed in a carrier gas impinge upon the substrate in ADM, spherical agglomerates of particles (granules) collide with it in GSV.

An important issue about both ADM and GSV may be the deposition efficiency (DE) that is defined as mass of the deposited film divided by mass of powder consumed. DE is considered important especially when the film thickness and area are large. A high DE can decrease both the deposition time and the raw material consumption at the same time. Naoe et al. reported that DE of ADM for Al_2O_3 was as low as 0.088% [11]. Johnson et al. reported average DE of 0.082% for barium hexaferrite films deposited by ADM [12]. They found DE of ADM barium hexaferrite film weakly increased with deposition time. Fuchita et al. reported on aerosol gas deposition (AGD) of zirconia powder [4]. Details of AGD seem very similar to ADM and

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may be categorized as the same method as ADM. Although Fuchita et al. did not provide DE specifically in the report, we can estimate DE of the zirconia film formation using data in the article and the theoretical density of monoclinic zirconia (5.84 g/cm^3) [13]. The maximum estimated DE was 0.65%. It is apparent that the DE of ADM is quite low and significant improvement is needed. Both Johnson et al. and Akedo reported that very fine particles were forced to flow away without collision with the substrate by the carrier gas because their mass was too small [12, 14]. In GSV, those very fine particles as well as larger particles are agglomerated into a granule that is massive enough to reach and impact with the substrate. Therefore, GSV may be a possible technique for improving DE compared to ADM.

We investigated DE of monoclinic zirconia film formation by GSV. Since the only energy involved in the deposition is the kinetic energy of the granules, we examined the effects of different types of carrier gases and flow rates on the particle velocity and DE.

Materials and Method

Granule preparation

Commercially available monoclinic zirconia powder (Grade MIZ, Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka, Japan) was used as the starting material. Average particle size of the powder (d_{50}) measured by a particle size analyzer (LS 13320, Beckman Coulter, Inc., Fullerton, CA, USA) was 1.1 μm. The crystalline phase of the powder was analyzed by an X-ray diffractometer (XRD) (D/Max-2500VL/PC, Rigaku, Tokyo, Japan), and the obtained XRD pattern matched well to the monoclinic zirconia (JCPDS card number 13-307). The zirconia powder was granulated by spray drying at Dongjin Technology Institute, Ansan, Korea. Granules were heated to 973 K for two hours in air to remove the organics added for spray drying. There was about 2 wt% decrease after the heat treatment that corresponded well to the organic additive content information from Dongjin Technology Institute. After the heat treatment, granules were passed through a sieve with a 425 μm mesh. Granules were observed by scanning electron microscopy (SEM) (JSM 5800, Jeol, Tokyo, Japan). About 1,834 granules from images of five different areas under the same magnification were used for the size measurements, which was performed using an image analysis software (Avizo Fire 7, Thermo Fisher Scientific Inc., Waltham, MA, USA).

Particle velocity measurement (Slit cell method)

The particle velocity was measured by slit cell method (SCM) according to the previous report [14]. Fig. 1(a) shows SCM apparatus schematically. Two 1 mm thick stainless steel plates, bottom and top plate were attached to a rotor. The top plate was the impact surface for the sprayed granules and was positioned above the bottom plate at a distance, L of 10 mm from the bottom plate. The bottom plate had slit dimensions of 35 mm × 0.8 mm and was positioned above the spray nozzle which had a throat with dimensions of 35 mm × 0.8 mm. The nozzle throat was aligned to the slit of the bottom plate so that granules ejected from the nozzle passed through the slit of the bottom plate and impacted with the top plate. Due to the high rotation speed (u) of the plates, collision with the top plate occurred off the projection line of the slit of bottom plate. By rotating the plate-assembly clockwise and counter clockwise, two lines were formed on the top plate as shown in Fig. 1(b). Experiments were performed as follows. Rotor assembly with the two plates were clamped to a high speed motor and placed 2 mm off the nozzle. Rotor assembly, high speed motor and nozzle were contained in a vacuum chamber called as deposition chamber. The nozzle was connected to the outlet of a Y-shape tube with outside diameter of 9.525 mm as shown in Fig. 1(a). Granules from the feeder were carried by either air or He and were introduced to one inlet of the Y tube. The other inlet of Y tube was for supplemental gas which was also either air or He. After the granules were poured into the feeder, the deposition chamber was evacuated by vacuum pump system consisting of a filter, a rotary pump and a booster pump. When vacuum level reached 6.5 Pa, the high speed motor was powered on to rotate the plates at 9,000 rotation per minute (rpm). Then, both carrier gas and accelerating gas were supplied. The carrier gas flow rate/supplemental gas flow rate values are in liters per minute (LPM) were either 5/10 or 5/30. Each gas flow rate was controlled by a mass flow controller (EL-Flow F-202AV, Bronkhorst, AK Ruurlo, Netherlands). Since the MFC was calibrated for air, a conversion factor of 1.454 was applied for flowing He [15]. After the gas flow rates became stable, the feeder was powered on to allow zirconia granules to flow into the carrier gas. Granules were sprayed for about 15 min for each rotational direction. After spraying in both directions, the vacuum was broken and the plates were removed from the rotor assembly. The distance between the two lines (d) formed on the top plate and distance from center of rotation (r) were measured as shown in Fig. 1(b). From these values the granule velocity was calculated according to the equation based on assumption that traveling time of the granule from the bottom plate to the top plate is the same as half that taken for the plates to move d by rotation. Therefore, granule velocity in m/s = $\pi ruL/(15{,}000d)$ where r, u and L are 52.5 mm, 9,000 rpm and 10 mm, respectively.

Zirconia film deposition and characterization

Fig. 2 shows a schematic diagram of the experimental apparatus. In order to measure the granule consumption directly, the granule feeder was placed on top of an electronic balance (HJ-33K, Shinko Denshi Co., Ltd.,

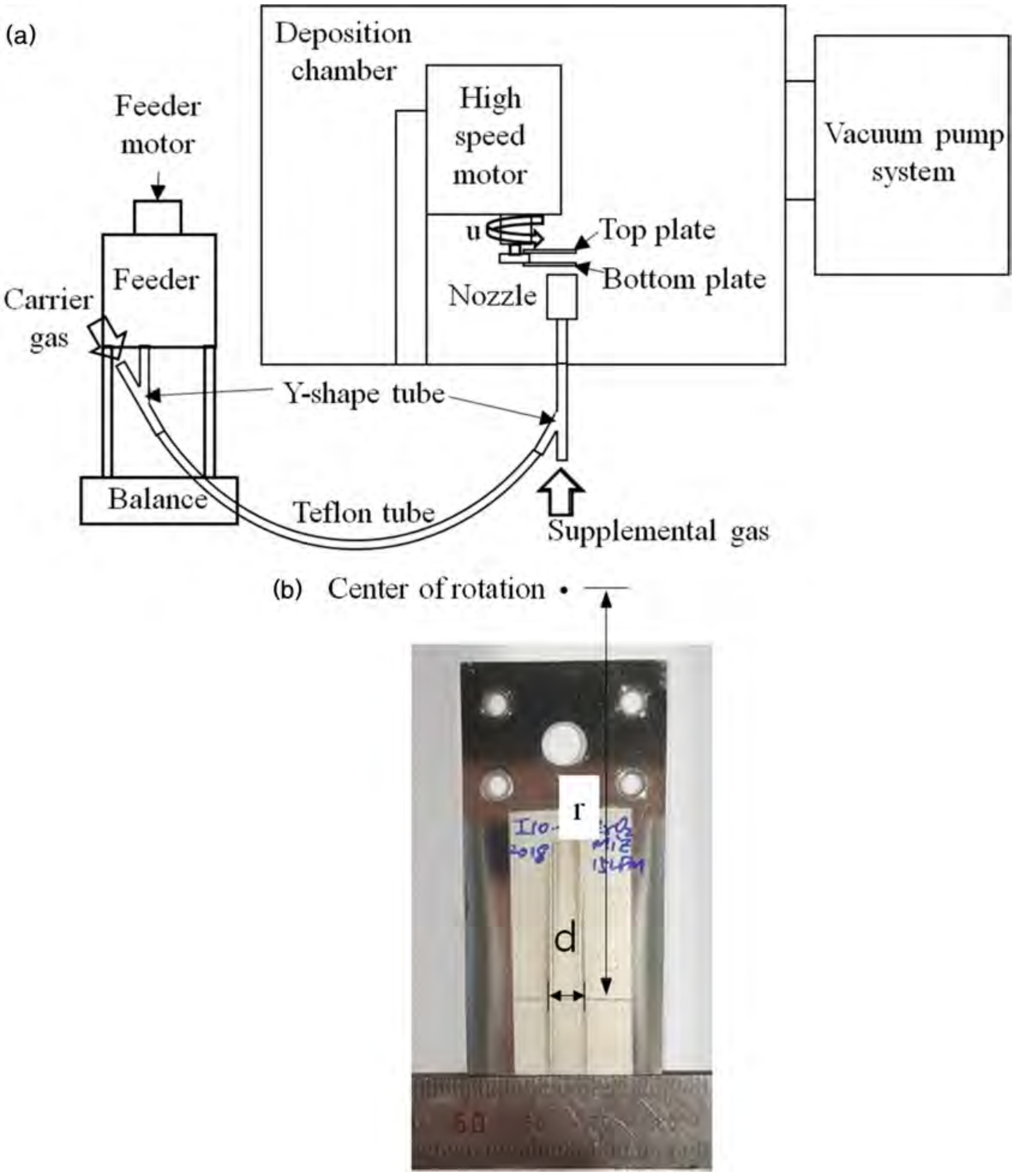

Fig. 1. Schematic diagram of apparatus for granule velocity measurements (a) and the top plate after the experiment (b).

Tokyo, Japan) which can measure up to 33 kg with accuracy of 0.1 g. About 50 g of monoclinic zirconia granules were poured in the feeder. The mass of the feeder with granules, Teflon tube between feeder and nozzle, and nozzle were measured. A soda lime glass plate with dimensions of 60 × 90 × 2 (thickness) mm^3 was used as a substrate. The mass of the glass substrate was measured with a precision electronic balance (AG135, Mettler Toledo, Greifensee, Switzerland) which can read 0.1 mg up to 101 g. The substrate surface was cleaned with ethanol and affixed to a stage shown in Fig. 2 by using a scotch tape. Tape was placed to avoid any interference with deposition. The stand-off distance from nozzle was 10 mm.

After the deposition chamber was evacuated to 6.5 Pa, the stage with substrate traversed a distance of 65 mm back and forth at 200 mm/min. Both carrier gas and supplemental gas were on. Gases used and their flow rates were the same as those used for granule velocity measurements. When the gas flow rate was stabilized, the pressure in the chamber was recorded. Then, the feeder was activated and the granules were delivered to the nozzle. Granules were further accelerated by the supplemental gas. Deposition was performed for about 400 s. The sample surface was cleaned with laboratory tissue and compressed air. Then, the mass of the sample was measured with a precision electronic balance for obtaining the film mass. The mass of the feeder, tube and nozzle after the experiment was also measured by the electronic balance for obtaining granule

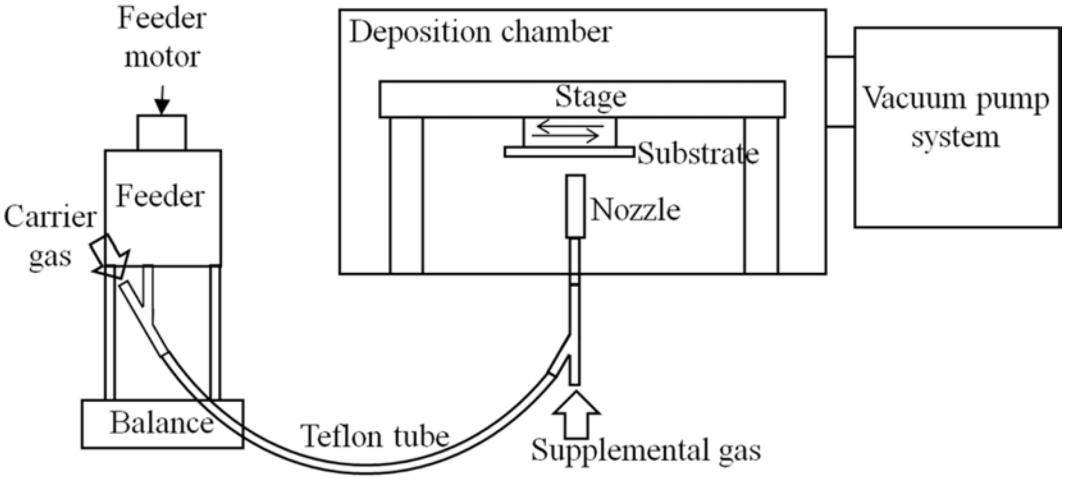

Fig. 2. Schematic diagram of GSV system.

consumption. DE was calculated as the film mass divided by amount of granules consumed. Each experiment was repeated 4 times and the average value and standard deviation were calculated. Ultrasonic cleaning was performed on some of the samples by immersing them in ethanol for 30 min in order to test film stability and adhesion. Both top surface and fracture surface of the sample was observed with SEM. XRD was carried out for phase analysis of the sample.

A three pass experiment was carried out by using a double-side carbon tape as substrate that travelled only once in order to examine smashed granules on the substrate. Carrier gas flow rate and supplemental gas flow rate were 5 LPM and 10 LPM, respectively. All the other experimental conditions and procedures were the same as described above.

Results and Discussion

Fig. 3(a) and (b) show an SEM image of monoclinic zirconia granule feedstocks used for this study and their size distribution, respectively. They were in a flowable spherical shape and their average size was 38.2 μm. Fig. 4(a) and (b) are SEM micrographs of double-side carbon tape after the three-pass experiment. From Fig. 4(a) it is evident that the granule remained intact during transport through the nozzle and was squashed up impingement with the substrate as indicated by the dashed circle. Fig. 4(b) shows that particles much finer than the average particle size (1.1 μm) as well as bigger ones that collided with a substrate. Akedo reported that very small particles evaded the substrate by following the flow of the carrier gas due to their small mass. However, even those very small particles can reach the substrate by being agglomerated in a granule. In other words, more particles including very small ones possibly impinged upon the substrate in GSV than in ADM, possibly giving rise to higher DE.

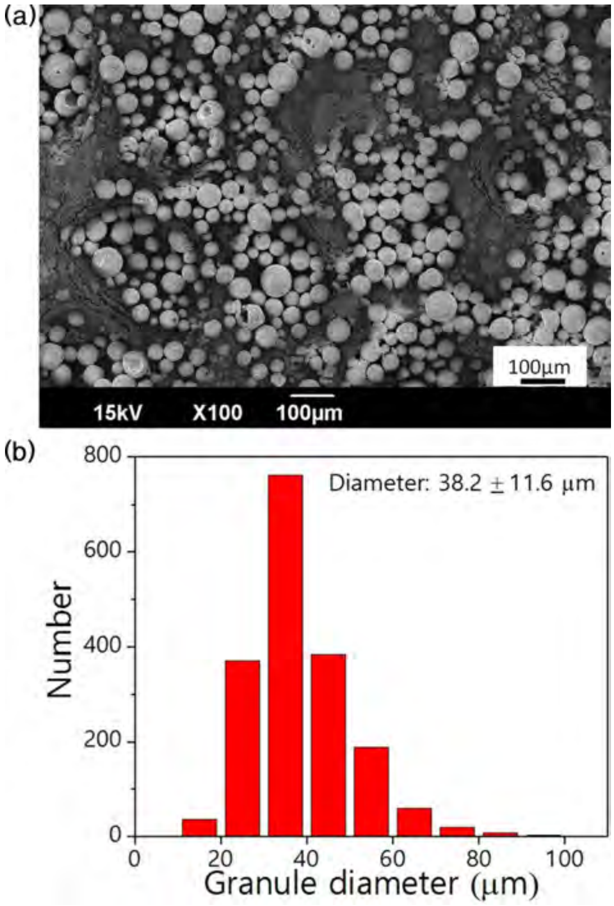

Fig. 3. SEM micrograph of monoclinic zirconia granules (a) and their size distribution (b).

Fig. 5 shows granule velocity according to the experimental conditions. Higher gas flow rate (5/30) resulted in higher granule velocity than lower gas flow rate (5/10) for both gases (i.e. air and He). Also, the granule velocity was higher when He was used than when air was used. The granule velocity results were consistent with Akedo's report on ADM [2]. We also

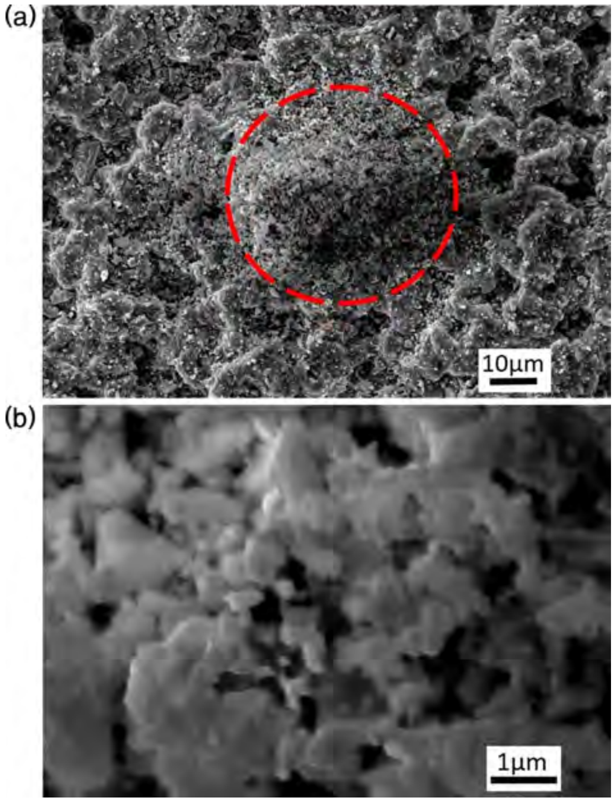

Fig. 4. SEM micrographs of double-side carbon tape after the single pass experiment; (a) low magnification and (b) high magnification.

measured chamber pressure during the experiments. When the two gas flow rates were 5/10 and 5/30, the pressures were 20 Pa and 46 Pa, respectively. They were the same for both air and He, suggesting the gas conversion factor (1.454 for He) was reasonable. According to Ning et al. and Ozdemir et al., He exhibited more than twice the gas velocity at the exit of their cold spray nozzles due to high specific heat ratio as well as the small molecular weight compared to nitrogen, which has similar physical property to air [16, 17]. They described that higher gas velocity resulted in higher particle velocity for He than for N_2. Even though the gas velocity at the nozzle exit was not measured in our study, the velocity of He was suspected to be higher than that of air as in the case of cold spray. The higher granule velocity in the He case shown in Fig. 5 may be mainly due to higher gas velocity of He than that of air. It is worth mentioning that the granule velocity increased only by 12% and 29% as air flow rate and He flow rate were increased more than twice, respectively. According to our previous report, the pressure difference between the feeder and deposition chamber (ΔP) increased as the gas flow rates were increased [10]. However, the increment was very small compared with that of the gas flow rates. ΔP was considered as a major driving force for acceleration of granules. Therefore, the small increase in granule

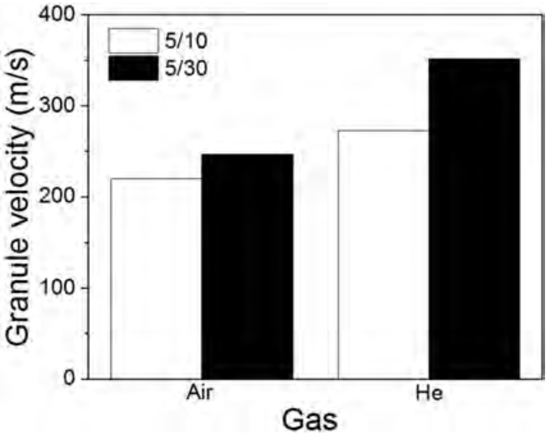

Fig. 5. Granule velocity obtained by slit cell method; 220 m/s, 247 m/s, 273 m/s and 352 m/s for 5/10 air, 5/30 air, 5/10 He and 5/30 He, respectively.

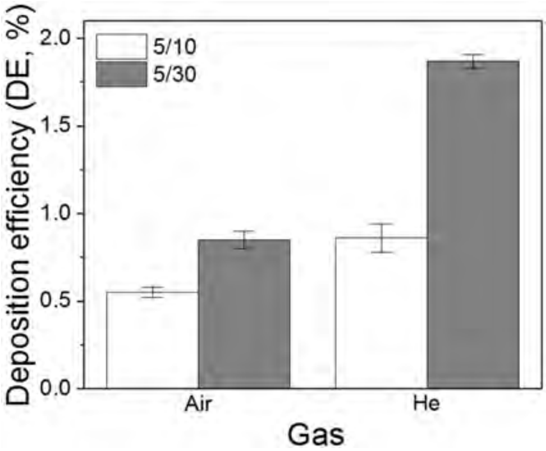

Fig. 6. DE according to the experimental conditions.

velocity due to the gas flow rate increase may be explained in part by the small ΔP. One way to increase the granule velocity may be the use of vacuum pumps with a large pumping capacity to decrease pressure in the deposition chamber and thereby increasing ΔP.

Fig. 6 shows DE of monoclinic zirconia granules according to the experimental conditions. Unlike most cases found in the literature, DE was obtained from direct measurement of granule consumption and the film weight. DE values obtained were 0.55±0.03%, 0.85±0.05%, 0.86±0.08% and 1.87±0.04% for 5/10 air, 5/30 air, 5/10 He and 5/30 He, respectively. It is worth noting here that higher gas flow rate resulted in higher DE and that He was more effective in improving DE than air. DE shows a similar trend with granule velocity shown in Fig. 5, only exaggerated in terms of the gas flow rate effect and gas species effect. It is suggested that the granule velocity played an important role in DE. Fuchita et al. used a similar zirconia powder to the one used for this study and nitrogen which has similar physical property to air [4]. DE value roughly estimated from their report (0.65%) was not much different from those shown for air (0.55% and 0.85%) in Fig. 6 although the details of deposition variables were different. We postulate that the DE might be improved by spraying granules because granules are able to include very small particles in the deposition process that would otherwise have been carried away by the gas flow. In other words, more particles are able to participate in film formation by minimizing the amount of particles evading the substrate due to their small size. However, the above two DE values (0.55% and 0.85%) were not high enough to mark an advantage from using granules compared with DE values of ADM calculated from the report of Fuchita et al. [4]. It also implies that only very small fraction of collisions of the particles with the substrate were successfully contributed to the film formation. Fig. 6 shows that He is an attractive gas for improving DE. Although not many DE values can be found in the literature, 1.87% was much higher than 0.65% estimated from Fuchita's report on deposition of the very similar monoclinic zirconia [4] and may be the highest DE of ceramic films by room temperature spray of ceramic particles or granules like ADM or GSV to the best of our knowledge.

Fig. 7 shows XRD patterns of the zirconia. Both the feed material (monoclinic zirconia granules) and deposited films exhibited monoclinic zirconia phase without any other detectable phase. Patterns of the films had broadened peaks with weaker intensity than those of the granules. Weak intensity of the film might be related to small thickness of the film. Peak broadening of the film implied that the film contained nano-scale crystallites with defects as reported previously [18]. Weight loss of the films after a 30-minute ultrasonic cleaning were 2.7%, 2.2%, 1.2% and 1.3% for the films deposited under 5/10 air, 5/30 air, 5/10 He and 5/30 He conditions, respectively. The weight loss was small enough to consider the films as being well-formed and the change in mass did not appreciably affect our calculation of DE. Fig. 8(a)-(d) show top

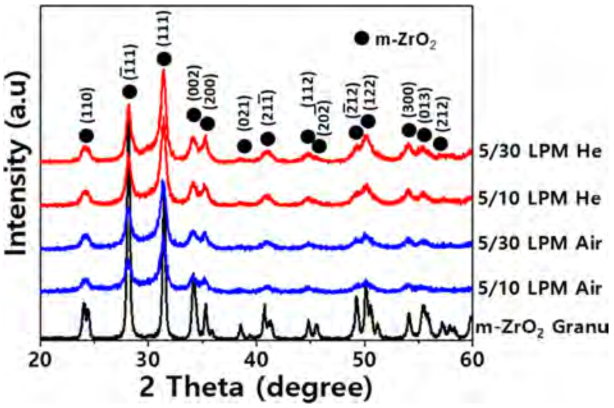

Fig. 7. XRD patterns of monoclinic zirconia granules and zirconia films deposited by GSV.

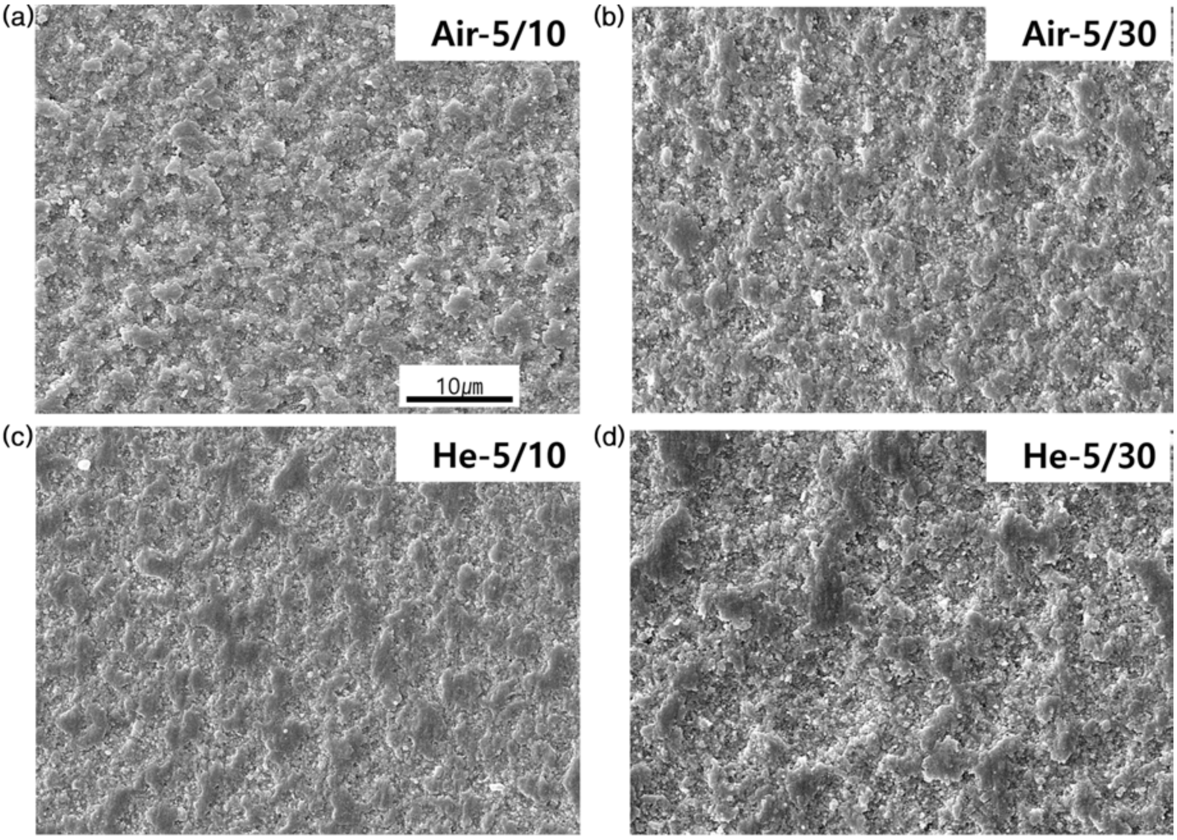

Fig. 8. SEM micrographs of top surface of samples; (a) 5/10 air, (b) 5/30 air, (c) 5/10 He and (d) 5/30 He.

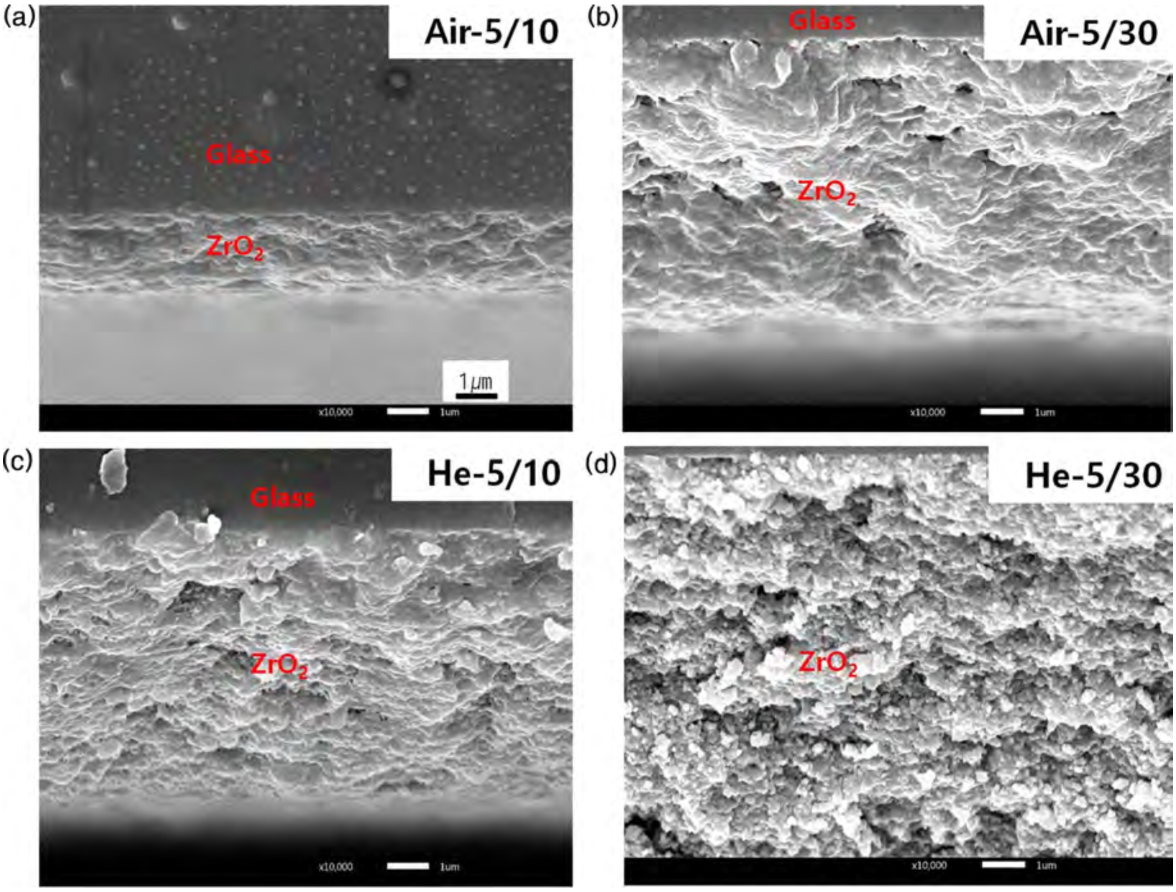

Fig. 9. SEM micrographs of fractured edge surface; a) 5/10 air, (b) 5/30 air, (c) 5/10 He and (d) 5/30 He.

surfaces of the zirconia films. They show typical features of ADM or GSV ceramic films; ridges and valleys. Fig. 9(a)-(d) are SEM micrographs of cross section obtained by cleaving the films. The film thicknesses were consistent with DE shown in Fig. 6 assuming the granule consumptions were similar for all the experiments. The films appear quite dense and inter-granular bonding looked strong even though there were some pores.

Conclusions

Deposition efficiency of monoclinic zirconia film prepared by granule spray in vacuum was obtained from direct measurements of granule consumption and the film weight. It increased as flow rate of process gas was increased possibly due to increased kinetic energy. He was more effective as the process gas for improving DE than air. The highest DE value achieved by using He was 1.87% which was more than double the value obtained by using air and may be higher than any other reported DE of ceramic films by room temperature spray of ceramic particles or granules like ADM or GSV to date. Since granule velocity varied in the same way as DE, we conclude that DE is closely related to the granule velocity. Zirconia films deposited by GSV retained the crystalline phase of the starting powder and peak broadening of their XRD patterns was observed as in the other ADM ceramic films. Morphology of the films observed from the top surface and the fracture surface revealed that well-adhered dense zirconia films were deposited.

Acknowledgments

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