In-flight melting method with an oxygen-excess gas burner for glass making

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This study investigated the in-flight melting method using an oxygen-excess gas burner with which glass powder with specific elemental components can be easily produced in one quick energy-saving-process (<1 s). First, granulated raw powder was formed from soda-lime-glass batch components by using a spray-drying machine and dropped directly into an oxygen-excess gas burner with a vertical downward converging flame. Partially or fully melted materials with powder-like shapes were formed in the flame and collected along the flight path through the flame. Granulated raw powder and powder-like sample materials collected at different positions in the flight path were observed by X-ray diffraction (XRD), optical microscopy, and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). The granulated raw powder included only crystals. The XRD peaks of these crystals disappeared and the halo identifying them as glass materials became more pronounced in the powder-like materials collected in going from the upstream to downstream positions in the flight path. We calculated the vitrification ratios by using the main peak intensities of SiO₂ in the XRD data; the vitrification ratio for a ~600-mm-long path was ~85 %. We observed changes in the morphology and elemental distribution on the surfaces of the samples by using optical microscopy and SEM-EDS and in cross sections of the samples by SEM-EDS. Although the sodium and oxygen, the silicon and oxygen, and the calcium partial distributions differed from each other on the surfaces and in the cross sections of the granulated raw powder and sodium parts were often observed around the silicon part on the surfaces and in the cross sections of the granulated raw powder and samples collected at upstream positions, the elemental distributions of the collected materials became more homogenous as vitrification proceeded from up-to-downstream, and the materials eventually became glass.

Key-words : Glass, XRD, SEM-EDS, In-flight melting, Oxygen gas burner

1. Introduction

Energy-efficient processes for producing materials, such as glass, must have good reproducibility and quality control for industrial applications such as insulator powder, optronics, and optics. Nowadays, glass powder (granulated glass powder) for industry is produced in two steps that consume a large amount of energy; first, a large amount of solid glass with the desired components is formed from molten glass; second, the solid glass is crushed into powder with uniform particle sizes and selected by size. Here, if we could instead produce the desired glass at once with one simple energy-saving method, substantial cost and manufacturing-time savings would be had.

One of the present authors (Keizo Sato) has developed a large (about 1-m long) high-efficiency oxygen-excess gas burner. The flares produced by this gas burner diverge very little. We have been developing a smaller oxygen-excess gas burner (about 30-cm long) since 2012 and, moreover, have made two of these compact gas burners for use in experiments. We expect that the use of the in-flight melting method with our oxygen-excess gas burner has potential as an energy-saving process for producing glass powders. The in-flight melting method is rather different from the conventional melting method. The conven-
tional method using a Pt crucible maintains a glass-liquid material temperature of 1470 °C for about four hours and the material is cool downed slowly to room temperature within about eight hours to produce soda-lime glass. The conventional industrial glass-making method employed in Japan uses an average of about 2100 kcal/kg of glass (this basic unit is not scientific and is used only within the industry; the value is calculated from the total volume of glass produced and energy used). Combined with our oxygen-excess gas burner, the in-flight melting method can produce materials that are free of contaminants because it does not employ a container. We also consider that it has the potential to produce new materials quickly and easily without special craftsmanship techniques at below 1500 kcal/kg of glass.

To produce a material with the in-flight melting method and the oxygen-excess gas burner, we start by forming granulated raw powders from raw particles of the base batch components. Next, we drop these granulated raw powder into the burner where they melt in a vertical downward converging flame, as shown in Fig. 1. The granulated raw powder is considered to be melted by thermal convection in the flame (the temperature of the outer flame was estimated to be about 1900 °C). We collect partially or fully melted materials as they are falling through the flame. The distance from the base of the burner to the sample pick-up position is nearly equal to the vertical distance along the flight path in the flame. We use an iron ladle so that the collection position can be changed and so that the materials can be cooled down rapidly. We suppose that the materials collected at different positions in the flame receive different total energies for vitrification.

Our aim is to use the in-flight melting method with an oxygen-excess gas burner to produce various glasses quickly and easily at low cost, within one second and using ~1500 kcal/kg of glass, which is much smaller than the 2100 kcal/kg of glass mentioned in the previous paragraph. However, little is yet known about the processes that occur in the flight path or the nature of the in-flight melting materials. To apply this method to industrial applications efficiently, we must establish a means of reproducible production and clarify the features of the materials as they are melting in-flight. Accordingly, we conducted this study to investigate the properties of granulated raw powders and samples collected at three positions along the flight path, from near the base of the gas burner to downstream near the bottom of the furnace (see Fig. 1).

2. Material preparation

2.1 Forming granulated raw powders

The base batch components of soda-lime glass are shown in Table 1. First, we weighed the raw particles; fine silica sand quartz (SiO₂), α-alumina (α-Al₂O₃), calcium carbonate (CaCO₃), sodium carbonate (Na₂CO₃), hematite (α-Fe₂O₃), and sodium sulfate (Na₂SO₄) powders of industrial-grade purity (the sizes of the raw particles of base batch components as shown in Table 1 were about 1–10 μm), according to the weight percent (wt %) ratios of SiO₂, Al₂O₃, CaO, Na₂O, Fe₂O₃, and SO₃. We stirred and mixed these raw fine particle components well. Second, we stirred the mixture with an adequate amount of water (about half the mass-weight of raw particles) at an adequate temperature (~30–~50 °C) for solubility to make a slurry by ball milling it with balls and a pod with an inner surface made of SiO₂. The amount of water mainly influenced the size and yield of the granulated raw powder. Third, we used a spray-drying machine to turn the slurry

Table 1. The base batch components in weight percent (wt %). The values with these significant digits were taken from the final report of “Energy Innovation Program/Development for Innovative Glass-Melting Process Technology” (FY2008-FY2012) of the NEDO project (project code P08019; https://www.nedo.go.jp/activities/FK_00105.html, in Japanese). See Table III-2-Ⅰ-1-32 on page III-36 of the pdf file of the final report (https://www.nedo.go.jp/content/100564243.pdf)

| (wt %) | SiO₂ | Al₂O₃ | CaO | Na₂O | Fe₂O₃ | SO₃ |
|--------|------|-------|-----|------|-------|-----|
| SL-08  | 72.1 | 2.0   | 10.0 | 15.6 | 0.02  | 0.28|

*: Because the total value 100.0 % is necessary, the value 72.0 (SiO₂ value) in the final report is shifted to 72.1.
into granulated raw powder. The average size of the granulated raw powder from the base batch components in Table 1 was about 115 µm (D50 = 115 µm). Raw particles of 1–10 µm, such as SiO2, α-Al2O3, CaCO3, Na2CO3, α-Fe2O3, and Na2SO4 were mixed and gathered randomly and changed to granulated raw powder of about 100 µm by spray-drying process (see the top flow figure in Fig. 1).

2.2 System setup

We used the second gas burner described in the report of the NEDO project.1) The gas was standard-calorie city gas (type 13A, Tokyo Gas Co., Ltd.), which included 89.6 % methane, 5.62 % ethane, 3.43 % propane, and 1.35 % butane, at 10.8 Mcal/m³ at 101.325 kPa pressure conversion at 0°C.11) The main combustion process was as follows: CH4 + 2O2 → CO2 + 2H2O. We used 13A gas and oxygen gas at flow rates of 7.9 m³/hour and ~18 m³/hour, respectively. These gases were supplied from high-pressure gas cylinders and flowed from the top to the bottom of the gas burner tube (Fig. 1). Because the gases were mixed and burned outside of the tube (bottom front), the granulated raw powders were not melted inside it. A simulation (using the calculation code of CHEMKIN12)) of oxy–fuel combustion with methane was carried out by W. Fujisaki et al. (Tokyo Gas Co., Ltd.),13) and it predicted an adiabatic flame temperature of about 2700°C with 100 % oxygen.13) The presence of ~20 % radical groups such as OH, O, and H was also observed in the flame.13) As shown in Fig. 1, the temperature of the outer flame in the furnace was estimated to be about 1900°C,11) which is higher than the temperature 1470°C9) for producing soda-lime glass with a Pt crucible.

The furnace chamber was made from heat-resistant bricks, and the volume of the in-flight melting region was about 1 m³, as shown in Fig. 1. The length of the flame from the bottom of the chamber to the base of the gas burner was 643 mm. This furnace can produce partially or fully melted the material collected at position 3 completely and cooled the materials collected at positions 1–3, we embedded them in resin (Aron Alpha GEL-10, Toagosei Co., Ltd.) and polished their surfaces by hand with wrapping sheets made of Al2O3 (3M Japan Ltd.). To make cross sections of the granulated raw powder and the sample collected at position 1, we also used a cross-section polisher (CP) device (IB-19520CCP, JEOL Ltd.) with a 4.0 kV accelerator voltage and 70–80 µA ion-beam current. As preparation for CP, we sanded the samples with two carbon tapes including an aluminum sheet and two copper plates 50 µm in thickness (the copper plates were outermost). We did not use resins for CP. We set them with a 100 µm edge distance on the CP device and milled them for about eight hours. We kept the samples at about −10°C to prevent radiation damage.

3. Experiments

3.1 XRD measurements

We put the crushed granulated raw powders, samples collected at positions 1–3, and the reference material with MgO on a Si non-reflecting plate. We observed the XRD signals by using a multipurpose XRD system with a one-dimensional semiconductor detector [SmartLab9kW with a copper (Cu) target with a nickel filter, Rigaku Co., Ltd.] with a 45 kV accelerator voltage and 200 mA current. The scanning step was 0.01 degree, and the observed 2-theta range was from 5 to 80 degrees.

3.2 Optical microscope measurements

We determined the morphology of the granulated raw powders, the samples collected at positions 1–3, and the reference material by using pan-zoom and normal enlargement modes from 30 to 1000 magnitude of an optical microscope (reflection microscope VHX 6000, Keyence Co., Ltd.).

3.3 SEM-EDS measurements

We observed the morphology and elemental distribution of the surfaces of the granulated raw powders, samples collected at positions 1–3, and the reference material in areas from about 120 × 150 µm square to 4 × 5 mm square by changing the magnification of the SEM-EDS devices (TM3030Plus Miniscope, Hitachi Co., Ltd. and SwiftED3000, Oxford Instruments) with a 15 kV accelerator voltage. The SEM-EDS measurements showed
information down to a few µm in depth and were influenced by surface irregularities, the detector position, and the elements (escape depth for each element). Surface morphology affects the intensity of the emitted X-rays, and various elements with different shapes on the surface show the matrix effect. To exclude matrix effects and compare the homogeneities in the elemental distribution by EDS mapping, we also observed cross sections of the granulated raw powders and samples by using SEM-EDS at a 15 kV accelerator voltage in areas of about 25 × 30 µm.

3.4 Thermogravimetry measurements

We performed thermogravimetry measurements with Pt crucible on the reference material and granulated raw powders. In particular, we performed differential scanning calorimetry (DSC) on the reference material and granulated raw powders (Thermo plus Evo DSC8270, Rigaku Co., Ltd.) in air with 10 °C/min heating rate. The thermogravimetry–differential thermal analysis (TG–DTA) measurements on granulated raw powders (STA7200, Hitachi Co., Ltd.) in N₂ gas with 20 °C/min heating rate, which indicated that the gas released from the granulated raw powders was mainly CO₂.

4. Results and analysis

The results of the XRD measurements are shown in Fig. 2, and those of the optical microscope observation are shown in Fig. 3, while the SEM-EDS observations are shown in Figs. 4–7 and the TG-DSC/DTA observations are shown in Fig. 8. We did no additional processing of the samples for the SEM-EDS measurements in Figs. 4 and 5. The samples collected by iron ladle at positions 1–3 might have had cracks and surface irregularities/unevenness because they were cooled rapidly. We performed additional cross-section polishing on the samples for the SEM-EDS measurements in Figs. 6 and 7.

4.1 XRD measurements

If the XRD signal shows peaks, the material includes crystal components, while if it shows a halo, the material includes amorphous (glass) components. If the crystal peaks disappear and all signals show only halos, we can judge the material to be amorphous on the macro scale.

Figures 2(a)–2(e) show the XRD results for the granulated raw powders, the samples collected at positions 1, 2, and 3, and the reference material with the background subtracted. Figure 2(f) shows the background and the raw data of reference material. The background signals in Fig. 2(f) have no peaks. Figure 2(a) shows crystalline peak signals of MgO (periclase, reference), SiO₂ (quartz), CaCO₃ (calcite), CaNa₂(CO₃)₂·2H₂O, Na₂CO₃ (natrite), NaH(CO₃)₂·2H₂O and ghost peaks from the Cu Kₐ line of the target material in the XRD machine (from SiO₂ 26.6 or 20.9 keV crystal peak). Moreover, the signals have no halo. Figures 2(b)–2(d) show crystalline peaks whose origins are the granulated raw powders. On the other hand, Figs. 2(b)–2(d) show halos at 2θ = 20–30°. The halo increased from position 1 [Fig. 2(b)] to position 3 [Fig. 2(d)], while...
the intensities of the SiO$_2$ quartz peaks decreased. Therefore, we concluded that the vitrification process proceeded from positions 1 to 3. We also concluded that the vitrification was not complete at position 3 because all the samples had SiO$_2$ quartz peaks. For the reference materials, only halo and peaks of MgO were observed, as shown in Fig. 2(e). Moreover, we measured the DSC of the reference material and granulated raw powders, and found that these samples showed melting points (glass transition points determined by TG-DSC) and the temperatures were ~553 and 586°C, respectively (see section 4.4). Accordingly, we concluded that the reference material was amorphous (glass).

The signals from MgO in these five materials all had the same intensity within the margins of error, as shown in Figs. 2(a)–2(e). Since the measured widths of the main SiO$_2$ peaks in Figs. 2(a)–2(d) were nearly the same within the margins of error, moreover, we calculated the vitrification ratio as the peak intensity ratio. We estimated the approximate vitrification ratio from the intensity ratio between the peak and the halo at the typical main peaks of SiO$_2$ (quartz) in the XRD data. The results showed the vitrification ratios at positions 1, 2, and 3 to be respectively 50, 75, and 84%. For 20.9 degrees (Table 2). The average vitrification ratios were 48–50, 75–76, and 84–85% at positions 1, 2, and 3, respectively.

4.2 Optical microscope measurements
The low- and high-magnification optical images are shown in Figs. 3(a)–3(e). The scale bars are 1000 µm (100 µm) in the left (right) images.

The samples collected at positions 1–3 were powder-like and partially or fully melted. The granulated raw powder and the samples collected at positions 1–2 had ball-like or broken shapes. The shape of our target granulated raw powder was ball-like with a diameter of about 100 µm (see the introduction), as shown in Figs. 3(a) (right) and 5(a) (see also the SEM-EDS measurements). On the other hand, the sizes of the round objects and broken objects in the samples were about 100–300 and 5–100 µm, respectively.

The granulated raw powder and the sample collected at position 1 were nearly white [optical images of Figs. 3(a) and 3(b)]. However, the states in the surfaces varied (heterogeneity), as shown in the right panels in optical images of Figs. 3(a) and 3(b) and in the SEM images in Figs. 5(a) and 5(b) (see also the following paragraph). On the other hand, the samples collected at positions 2 [optical images of Fig. 3(c)] and 3 [optical images of Fig. 3(d)] had both slightly transparent and partially opaque parts. The reference material was transparent [optical images of Fig. 3(e)]. The samples had different surface states and morphologies, as shown in the right panels of Figs. 3(b)–3(d) and in the SEM images in Figs. 5(b)–5(d) (see also the following paragraph). The surface morphologies were considered to depend approximately on the distance along the flight path.

4.3 SEM-EDS measurements
It was difficult to conduct an average quantitative element analysis by SEM-EDS at multiple points on the surfaces of the granulated raw powders and samples collected at positions 1–3 because the samples had many surface irregularities. Moreover, the particle distributions in the SEM and EDS images could not be analyzed, because they showed many crushed small parts together with the larger

### Table 2. Vitrification ratios calculated from the main peak intensities of SiO$_2$ (quartz) in the X-ray diffraction data in Figure 2

| Vitrification rate (%) | Calculated | Average |
|------------------------|------------|---------|
|                        | At SiO$_2$ 20.9 deg | At SiO$_2$ 26.6 deg | At SiO$_2$ 26.6 deg |
| Granulated raw powder  | 100         | 100     | 100     |
| Sample from Position 1 | 49.8        | 48.7    | 48–50   |
| Sample from Position 2 | 75.7        | 75.1    | 75–76   |
| Sample from Position 3 | 84.5        | 85.2    | 84–85   |
| Reference material$^{(i)}$ | 0          | 0       | 0       |

$^{(i)}$: Melted and cooled material produced from the sample collected at position 3.
samples. We therefore compared the elemental distributions on the surface of each sample.

Low- and high-magnification SEM-EDS images of the surfaces are shown in Figs. 4(a)–4(e) and 5(a)–5(e). These measurements were made using backscattered electron compositional SEM which can reveal differences in the average atomic number (compositional differences) in a specimen, in this case for fluorescence X-rays from oxygen (O), sodium (Na), silicon (Si), and calcium (Ca) that were excited by electron beams. The increments of the scale bars in Figs. 4(a)–4(e) and 5(a)–5(e) are 1000 and 100 µm, respectively. We found it necessary to compare the EDS and SEM images in Figs. 4 and 5 because the EDS images’ distribution in Figs. 4 and 5 included fluorescent X-rays from each element and effects of surface irregularities (heterogeneity).

We observed many stick-like and rock-like shapes on the surfaces [see the pop-up very high-magnification SEM image in Fig. 5(a)] with sizes of less than 1 µm and a few tens of µm, respectively, on the surface of the granulated raw powders, as shown in the SEM images in Fig. 5(a). We also observed many holes in them. We considered that the larger rocky parts in the granulated raw powders derived from raw particles (see section 2.1). Although Na, Si, and O covered the surface of the granulated raw powder, areas where the distributions of Na and O and those of Si and O were different were observed, as shown in the O, Na, and Si images in Fig. 5. Ca partly covered the surface of the granulated raw powder (see the Ca image in Fig. 5).

We also observed the morphology and elemental distribution of cross sections of the samples, which were made by hand-polishing with resin (Fig. 6) and CP-machine polishing without resin (Fig. 7). High-magnification SEM-EDS images of cross sections (hand-polished with resin) from the granulated raw powder and samples collected at positions 1–3 are shown in Figs. 6(a)–6(d). High-magnification SEM-EDS images of cross sections (CP-machine polishing without resin) from the granulated raw powder and the sample collected at position 1 are shown in Figs. 7(a) and 7(b). Very high-magnification SEM images of granulated raw powder and the sample collected at position 1 are also shown in Figs. 6 and 7. There were also many holes and stick-like shapes in the cross-section in Figs. 6(a), 6(b), 7(a), and 7(b). The shapes of stick-like materials of the granulated raw powders [Figs. 6(a) and 7(a)] were different from those of the sample collected at position 1 [Figs. 6(b) and 7(b)]. We easily crushed the granulated raw powders into discrete parts of Na, Si, Ca, O, Na and O, Si and O, Ca and O, and Ca and Na by using an agate mortar and pestle. Because these discrete parts were not held together strongly and there were deep holes.

Fig. 4. Low-magnification SEM-EDS surface images [five images from left to right; a backscattered electron compositional SEM, oxygen (O)-image (blue), sodium (Na)-image (yellow), silicon (Si)-image (red), and calcium (Ca)-image (green)] of (a) granulated raw powder, (b) sample materials collected at position 1, (c) at position 2, (d) at position 3, and (e) reference material. The low-magnification images in Fig. 4 and high magnification images in Fig. 5 have the same field of view. The bars in Fig. 4 indicate 1000 µm.
Fig. 5. The same as in Fig. 4, but high-magnification SEM-EDS surface images and bars indicate 100 µm.

Fig. 6. High-magnification SEM-EDS cross-section images of hand-polished sample with resins (the same as in Fig. 5). The bars indicate 100 µm.
from the surface to the inner part of the granulated raw powders, it was easy to distort or split apart the raw powders. As a result, some amount of resin entered the holes and the granulated raw powder expanded a little but kept its original round shape [Fig. 6(a)]. By comparing Figs. 6(a) and 6(b), and Figs. 7(a) and 7(b), we concluded that the radiation damage from CP was not so large. Na, Si, Ca, O, Na and O, Si and O, Ca and O, and Ca and Na parts were observed on the surface [Fig. 5(a)] and in the cross section [Figs. 6(a) and 7(a)] of the granulated raw powder. The average elemental mixing ratio and distribution of each element part on the surface and in the cross section of the granulated raw powders were almost the same and homogeneous except Na. Each part in the granulated raw powder (small crystals; see the XRD results) were slightly melted, both on the surface and in the cross section of the sample collected at position 1 [Figs. 5(b), 6(b) and 7(b)]. These parts gradually merged from upstream [position 1; Figs. 5(b), 6(b) and 7(b)] to downstream [positions 2–3; Figs. 5(c) and 5(d), and 6(c) and 6(d)]. We observed many sodium parts around or near silicon parts on the surface and in the cross sections of the granulated raw powders and the samples collected at positions 1 and 2.

The sample collected at position 1 and the granulated raw powders had many holes on the surface and in the cross-section, as shown in the SEM images in Figs. 5(b), 6(b) and 7(b), and 5(a), 6(a) and 7(a). On the other hand, the SEM images [Figs. 5(c) and 5(d)] revealed many bowl-shaped craters on the surfaces of the samples collected at positions 2 and 3. The surface and cross-section distributions of Na, and Ca of the sample collected at position 3, as shown in Figs. 5(d) and 6(d), were more homogeneous than those of the granulated raw powders, as shown in Figs. 5(a), 6(a), and 7(a). From Figs. 4–7, we concluded that the parts with different elements on the surface and in the cross section of the granulated raw powders partially or fully melted gradually according to the vitrification process as it advanced from positions 1 to 3, and eventually became glass. On the other hand, no characteristic morphological structures, elemental distribution, or holes/craters on the surface of the reference material (glass; see sections 4.1 and 4.4) were observed in Fig. 5(e).

4.4 Thermogravimetry measurements

We performed DSC on the reference material and granulated raw powders, and found that these samples had melting points (glass transition points determined by TG-DSC) and the temperatures were \( \sim 553 \) and 586 °C, respectively, as shown in Fig. 8(a). This indicated that the reference material was amorphous (glass). We also measured the TG–DTA of the granulated raw powders and found that the CO₂ gas release stopped at \( \sim 800 \) °C, as shown in Fig. 8(b). Two kinds of water were thought to be contained in the granulated raw powder, and the origin of endothermic peaks at 99 and 178 °C in Fig. 8(b) were thought to be absorbed water and crystalline water, respectively.

5. Discussion

The XRD observations revealed that the vitrification process proceeded from the upstream position (position 1) to the downstream position (position 3) in the flight path. The XRD measurements indicated that a certain portion of the samples collected at each position had vitrified, although we did not succeed in observing the diffraction pattern with the transmission electron microscope device because of sample damage caused by the strong electron beam. The reference material was revealed to be glass by the XRD and DSC measurements. We confirmed this with micro Raman spectroscopy measurements \(^{15}–^{18}\) by observing the boson peak. \(^{19}\) We also measured the X-ray fluorescence signals (ZSX100e, Rigaku Co., Ltd.) from the...
reference material and showed the elemental distribution with \( \sim 1\% \) analysis error for SiO\(_2\), Na\(_2\)O, and CaO: SiO\(_2\) 68.9, Al\(_2\)O\(_3\) 2.3, CaO 12.5, Na\(_2\)O 15.8, Fe\(_2\)O\(_3\) 0.2, SO\(_3\) 0.2 wt\%, which were nearly the same as the parameters in Table 1, within the margins of error. We calculated the vitrification ratios using the main peak intensities of SiO\(_2\) (quartz); the vitrification ratio after less than 1 s at position 3 was \( \sim 85\% \). In this case, the vitrification process was not completed at position 3 because the distance from the base of the burner to the bottom of the chamber (643 mm) was not long enough for full vitrification to occur. If the height of the furnace chamber, that is, the distance from the base of the burner to the bottom of the chamber, is lengthened to about 1000 mm or more, we expect that we can produce a completely glass powder within the flight path within one second.

The key characteristic of the vitrification process is considered to be melting of Na and Ca around Si. The SEM-EDS measurements showed that the distributions of Na and Ca on the surface and in the cross sections of the granulated raw powder and the samples collected at positions 1–3 were not the same. There were Na–Ca parts in the granulated raw powders and the samples collected at positions 1–2, while there were also a few Na–Ca parts around the Si parts. Many sodium parts, which had melted in the slurry during the spray-drying process, were observed around and near Si parts both at the surface and in the cross sections of the granulated raw powder and the samples collected at the upstream position in the flight path (i.e., position 1). We therefore thought that the many Na-rich parts around or near the Si parts of the granulated raw powders under oxy-fuel combustion were keys to rapid vitrification. We concluded that the O and Na contents are important to in-flight melting vitrification.

On the basis of the XRD and SEM-EDS measurements, the CaNa\(_2\)(CO\(_3\))\(_2\)–2H\(_2\)O and NaH(CO\(_3\))\(_2\)–2H\(_2\)O in the granulated raw powders were considered to be produced in the process of forming the granulated raw powder, and these materials and Na\(_2\)CO\(_3\) from the granulated raw powders were thought to be two other keys to rapid vitrification with the oxygen-excess gas burner. The melting speed of crystals including only Na was faster than those including Na and Ca, or only Ca. Thus, we consider that Na and O around Si on the surface and in the cross section contribute to fast SiO\(_2\) melting in the vitrification process.

The average elemental mixing ratio and distribution of each element part on the surface and in the cross section in the granulated raw powders were thought to be almost the same and homogeneous except Na. First, each crystal part of Na and O, Si and O, Ca and O, and Ca and Na in the granulated raw powders melted gradually both at the surface and in the cross section. Next, these parts blended together gradually. Eventually, all parts melted completely and became homogeneous glass. The SEM-EDS and XRD results indicate that CO\(_2\) gas is released during vitrification. There were many holes in the granulated raw powders and in the sample collected at sample 1, and the widths/size of the holes of the granulated raw powders were on average bigger than those of the sample collected at position 1. In general, CO\(_2\) gas is considered to be released at up to 900 °C during the vitrification of soda-lime glass in the conventional method. The vitrification reaction of these granulated raw powders formed by the spray-drying method started at \( \sim 800 \) °C, as shown in Fig. 8(b), which is \( \sim 100 \) °C lower than with a conventionally mixed raw materials.\(^{20}\)

6. Summary and conclusion

Granulated raw powders produced by the spray-drying method were dropped at a rate of 90 kg/hour for 1500 kcal/kg of glass on a vertical downward flight path in a downward-flame oxygen-excess combustion burner. Partially or fully melted materials formed in the flame and powder-like materials were collected along the flight path through the flame. The XRD measurements (macro measurements, not micro measurements or surface measurements) showed evidence of vitrification from the granulated raw powders and the powder-like materials collected...
in the flight path at positions 1–3. The granulated raw powders included only crystals of \( \text{SiO}_2, \text{CaCO}_3, \text{Na}_2\text{CO}_3, \) and \( \text{NaH(CO}_3)_2 \cdot 2\text{H}_2\text{O} \). The XRD peaks of these crystals disappeared and the halo increased in the materials collected from the upstream to downstream positions in the flight path.

Optical microscope and SEM observations revealed the morphological changes in the changes in the samples as they passed through the flame. The SEM-EDS measurements revealed morphological and elemental distributional changes on the surfaces and the cross sections (to a depth of a few \( \mu \text{m} \)). Na and O, Na and Ca, Ca and O or Si and O were observed on the surfaces and cross sections of the granulated raw powders, and their distributions were different. Na, O, Si, and Ca became more homogeneously mixed in going from position 1 to position 3. Sodium parts were often observed around or near silicon parts on the surfaces and in the cross sections of the granulated raw powders and the samples collected at upstream positions (positions 1–2). The element parts in the sample collected at position 1 had melted individually and were mixed as the vitrification process advanced, eventually becoming glass.

Our study of the vitrification process of the in-flight melting method with an oxygen-excess gas burner was to determine ways of producing powder-like glass materials with specific elemental components. We conclude that glass powder (granulated glass powder) can be produced by the in-flight melting method and oxygen-excess gas burner. We commented here that by scaling the manufacturing system, the in-flight melting method can easily produce glass powder directly at rates of from 10 g/min to 1000 ton/day.

Acknowledgements This work was funded by the Nippon Sheet Glass Foundation for Material Science and Engineering (12-005), the Murata Science Foundation (H24RS15), and the Sumitomo Foundation (143469). The gas burners were developed with financial support from the New Energy and Industrial Technology Development Organization in Japan (NEDO) from FY 2003 to FY2007 and from FY2008 to FY 2011 [1,2] (“Energy Innovation Program/Development for Innovative Glass-Melting Process Technology (FY2008-FY2012); project code P08019; https://www.nedo.go.jp/activities/FK_00105.html; Final report https://www.nedo.go.jp/content/100564243d.pdf”). Our samples were based on a project commissioned by the NEDO, and the experiment was the nineteenth one performed in 2012. We express our thanks to Dr. Shigeru Kimura, Dr. Tomoyuki Uruga, Dr. Yusuke Tamenori, Dr. Yuji Higo, Dr. Yoshinori Kotani, Dr. Shintaro Kobayashi, Mr. Sadao Honda (JASRI), Dr. Hajime Tanida (JAEE), Dr. Yoshitaka Matsushita (NIMS), Dr. Hirokazu Izumi (HI Tec), Dr. Yukihito Nagashima (Nippon Sheet Glass Co., Ltd.), Mr. Shingo Hara (Yamaka Clay Material Corporation), Mr. Toru Iseda, and Mr. Masakiyo Tonoike (New Glass Forum) for their discussions with us.

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