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Investigation on in-flight melting behavior of granulated alkali-free glass raw material under different conditions with 12-phase AC arc

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ABSTRACT

An innovative in-flight melting technology with 12-phase alternating current (AC) arc has been developed to investigate the melting behavior of granulated alkali-free glass raw material. Results show that the melted particles have spherical shape with smooth surface and compact structure. Lower vitrification and decomposition degrees of raw material as well as lower volatilization of B_2O_3 are attributed to less heat transferred per particle under larger flow rate of carrier gas and higher feed rate. The high vitrification and decomposition degrees indicate that the new in-flight glass melting with 12-phase AC arc will be a promising technology for glass production.

1. Introduction

The glass industry is a large global industry that annually produces more than 100 million tons of glass products such as sheet glass, container glass, fiber glass, optical glass, etc. [1]. The current glass melting technology is mainly the result of an evolutionary process that began with the development of the Siemens furnace during 1860s. The Siemens furnace incorporates continuous glass production with waste-heat recuperators and liquid or gas fuel [2]. In the air-fuel fired furnace the heat transfer from above burner flame to glass melt is so low that the conventional melting technology is energy-intensive and time-consuming, especially, in the melting and refining process. Huge emissions of greenhouse gases such as CO_2 and NO_x bring more environmental responsibility due to the firing of fossil fuel during glass production. In the past decades, the glass industry advanced the glass melting process in many and varied areas, including changing raw material mixtures, increasing heat transfer, replacing air with oxygen, improving combustion efficiency, renewing furnace configuration, and accelerating the refining. Since the fundamental technology has not been changed, most of these improvements yield small energy saving, sometimes only 1–2% [3]. Slow energy exchange, low thermal efficiency, and severe foam layer on glass melt are still the fatal problems for the conventional technology. With the rapid growth of glass usage and the increased energy and environment issues, it is crucial to develop a new glass melting technology. A favored glass melting technology should take into account the capital, energy and environmental factors by developing batching, melting and refining processes.

Due to some unique advantages such as high enthalpy, high chemical reactivity, alterable oxidation or reduction atmosphere, easy and rapid generation of high temperature as well as the rapid quenching rate [4], thermal plasmas have been developed in many fields ranging from materials processing to the destruction of toxic wastes [5–7]. Among various kinds of thermal plasma reactors, multi-phase arc is more effective than radio-frequency (RF) plasma due to the following advantages: cheap equipment investment, feasible mass production, and high energy efficiency [8]. It has been applied in the welding and cutting of metals, steelmaking, synthesis of nanoparticles and spheriodization of particles [9]. Under the financial support of New Energy and Industrial Technology Development Organization (NEDO) project, a new in-flight glass melting technology with 12-phase AC arc was developed. The granulated glass raw material was injected into arc plasma and melted by surrounding high temperature in the process of in-flight heating. Compared with above-mentioned conventional technology, the in-flight glass melting technology mainly utilizes conduction heating. This fully changes the traditional radiation heating and improves the thermal efficiency. The granulated raw material increases the velocity of homogenization of molten glass. The high temperature (5000–10 000 °C) generated by arc plasma enables it easy to melt the glass raw material quickly to shorten production cycle and save energy. The decomposition of raw material during flight decreases

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the forming of bubbles in molten glass to reduce the refining time. The usage of electric power lights the burden of environmental responsibility. In addition, the equipment using the new technology is smaller and cheaper. Hence, the innovative in-flight glass melting technology with 12-phase AC arc can be used to produce some special glass products or accelerate the production cycle of ordinary glass as a subsidiary heat source.

In the research, an innovative glass melting technology with 12-phase AC arc was developed to melt the granulated alkali-free glass raw material with energy savings and environmental benefits. The powders were synthesized under different conditions and characterized by various analysis methods. The effects of flow rate of carrier gas and feed rate on the heat transfer and in-flight particle behavior were investigated to provide a valuable guideline for glass industry.

2. Experimental

Alkali-free glass has received many attentions owing to its excellent dielectric property, good rigidity, high intensity as well as good thermal and chemical stability. It has been widely applied to many fields, such as liquid crystal display (LCD) and electroluminescence (EL) display, thin film transistor (TFT), charge coupled device (CCD), contact image sensor (CIS), solar cell, glass fiber and so on. Its main physical properties are as follows [10], transition temperature (T_g): 635 °C, strain point (T_{st}): 593 °C, softening point (T_s): 844 °C, liquid temperature (T_l): 920 °C, density (d): 2.77 g cm^{-3}. The ingredients of SiO_2, H_3BO_3, Al_2O_3, $BaCO_3$ and Sb_2O_3 in appropriate mass ratios were mixed into slurry, and then granulated into spherical powders by spray drying method. The mean diameter and porosity of powders were 80 μm and 72%, respectively. The $49SiO_2–15B_2O_3–10Al_2O_3–25BaO–1Sb_2O_3$ (mass%) is the target composition of alkali-free glass.

A new type of arc plasma reactor with 12-phase AC discharge has been developed to get stable and continuous arc by the transformers for converting from 3-phase AC to 12-phase AC. The single-phase AC arc welding transformers (B-250, DAIHEN, Japan) were used to realize the power supply for the generation of 12-phase arc. The input of the three-phase power supply was connected to 200 V (50 Hz) commercial power lines. The primary coils of transformers were divided into two parts: one was the Δ connection and the other was the Y connection. The turn's ratio of the windings between the primary and secondary coils of the transformer was set to $1/\sqrt{3}$. The output lines from transformers were connected directly to the corresponding electrodes of the reactor. Matsuura et al. [11] reported the detailed vector diagrams for converting from 3-phase to 12-phase.

Fig. 1 presents the schematic diagram of experimental setup which consisted of AC power supply, 12 electrodes, reaction chamber, powder feeder, and gas supply control systems. The configuration of 12 electrodes was symmetrically arranged by the angle of 30°. The 12 electrodes were divided into two layers to increase the plasma volume, upper six inclined electrodes and lower six horizontal electrodes, and the angle between upper and lower electrodes was 30°. The electrode material was tungsten (purity 99.9%) with 3.2 mm in diameter and the diameter of nozzle was 4 mm. The host of electrodes and the nozzle of powder feeder were cooled by water; argon gas (purity 99.99%) was injected around the electrodes to prevent them from oxidation at the flow rate of 36 l/min. Fig. 2 shows the electrode configuration in furnace and the generated plasma with 12-electrode discharge. In the experiments, the total power is 46 kW; total current 290 A, total voltage 185 V. The discharge voltage and current of each electrode were 35–50 V and 80–100 A, respectively. The distance from powder feeding nozzle to arc was 150 mm and the diameter of arc formed by 12 electrodes was about 100 mm during electrode discharging stably. The granulated raw material was injected into the plasma at the feed rate of 30–70 g/min with appropriate flow rate of air carrier gas by the powder feeder. The powders treated by 12-phase AC arc were quenched on the stainless steel pan at a distance of 1050 mm below the nozzle.

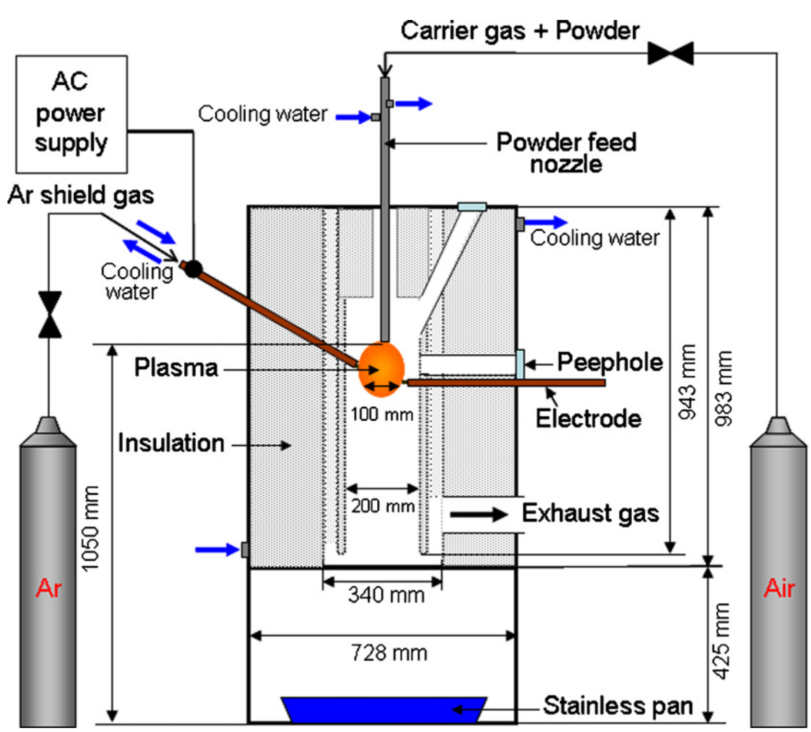

Fig. 1. Schematic diagram of 12-phase AC arc experimental setup.

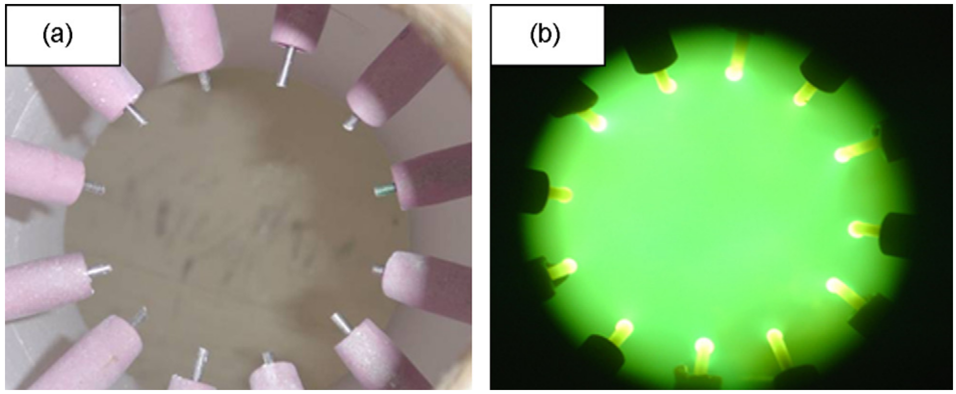

Fig. 2. Photos of (a) electrode configuration and (b) 12-phase AC discharging.

The morphology of the particles was performed with scanning electron microscope (SEM) apparatus (JSM5310, JEOL, Japan), and the average diameter was evaluated by the image analysis on SEM photos. The structures of powders were determined by X-ray diffractometry (XRD) which was carried out with Cu Kα radiation at 30 kV and 15 mA (Miniflex, RIGAKU, Japan). The data were collected in the 2θ range of 3–90° with a step size of 0.02° and a scan speed of 4°/min. The thermo-gravimetry (TG) was used to carry out the thermal analysis (Thermo plus TG8120, RIGAKU, Japan), the range of measured temperature was 20–1300 °C with the rate of 10 °C/min. The composition of prepared powders was analyzed by inductively coupled plasma (ICP) spectroscopy (PRODIGY, LEEMAN, USA).

In this paper, the vitrification degree is defined as the ratio of reacted SiO_2 in prepared powders to total crystal SiO_2 in raw material. The internal standard method was used to analyze the vitrification degree of raw material quantitatively, ZnO as the standard material [12]. First, the mixtures of pure SiO_2 and ZnO with various weights were used to obtain the calibration curve according to the peak intensities analyzed by XRD. Second, the mixture of the prepared powders and ZnO was analyzed to get respective peak intensities. Finally, the reacted SiO_2 (vitrification degree) can be accounted, combining the ratio of SiO_2/ZnO peak intensity and the SiO_2 content in prepared powders. The definition of decomposition degree is the percentage of reduction of raw material during in-flight heating to total reduction of raw material. The volatilization degree is defined as the percentage of the volatilization amount of B_2O_3 to total content of B_2O_3 in raw material. The decomposition degree and the volatilization degree were analyzed by TG and ICP spectroscopy, respectively.

3. Results and discussion

3.1. Effect of carrier gas flow rate

The raw material was injected into plasma at the feed rate of 30 g/min with 10–30 l/min carrier gas. The collecting ratios are respectively 10.5%, 16.2% and 59.7%, corresponding to the flow rates

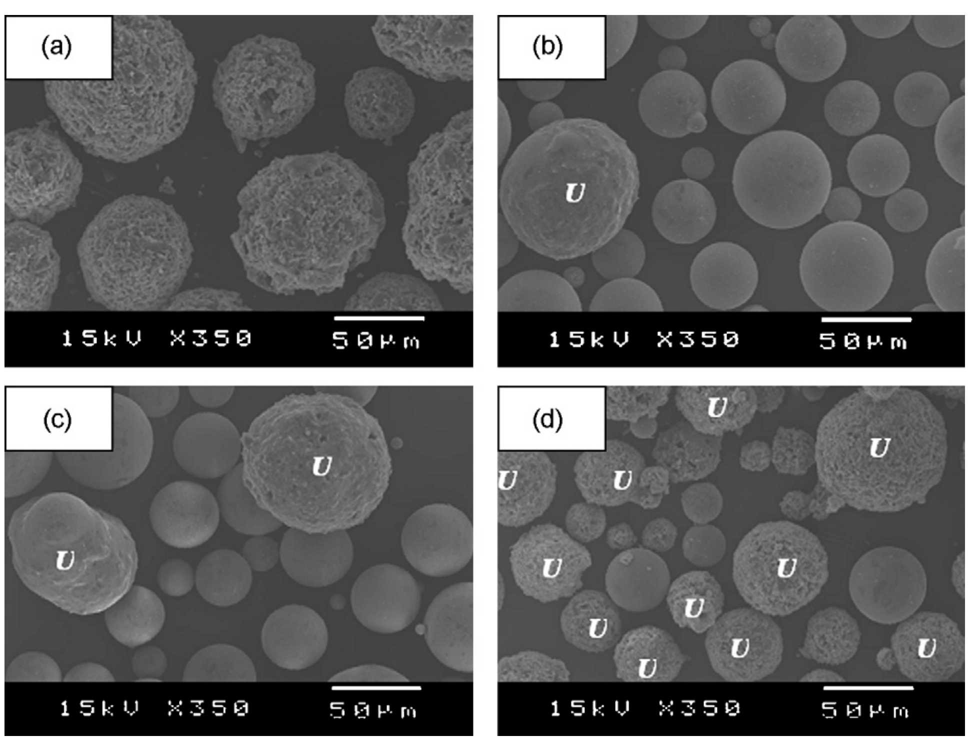

Fig. 3. SEM images of raw material and prepared powders at different flow rates of carrier gas: (a) raw material; (b) 10 l/min; (c) 20 l/min; (d) 30 l/min.

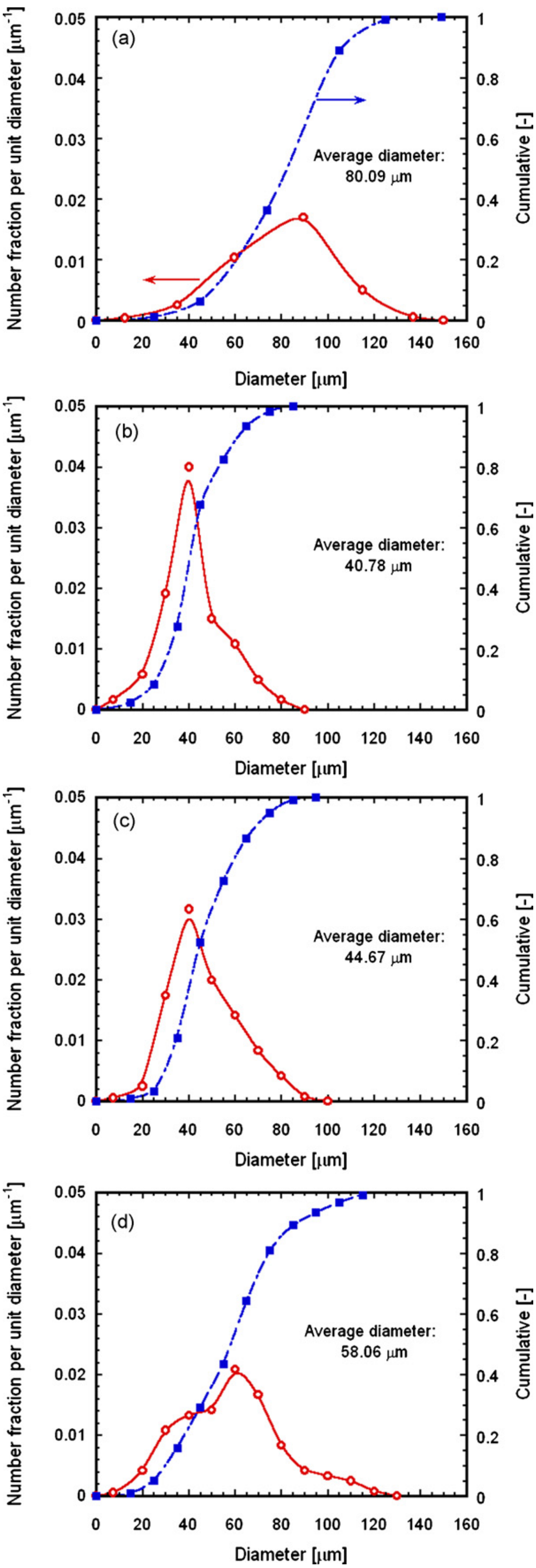

Fig. 4. Particle size distributions of raw material and prepared powders at different flow rates of carrier gas: (a) raw material; (b) 10 l/min; (c) 20 l/min and (d) 30 l/min.

of 10, 20 and 30 l/min. Compared with the theoretical output about 85%, the lower outputs are mainly attributed to the smaller hearth diameter which results in many products were deposited on the furnace wall. Fig. 3 shows the SEM images of raw material and prepared powders with different flow rates of carrier gas. The raw material powders granulated by spray drying have rough surface and porous structure. The melted particles in prepared powders in Fig. 3 have smooth surface and compact structure spherical shape. However, with increasing flow rate, some incompletely melted particles marked by "*U*" have a rough surface similar with that of raw material. And, the amount of these particles obviously increases. The increase of incompletely melted particles suggests the lower vitrification of powders prepared at larger flow rate of carrier gas.

The particle size distributions of raw material and prepared powders were performed by measuring 120 particles from SEM images, the results shown in Fig. 4. Before the plasma treatment the distribution range of raw material is widest and the number fraction is lowest. The particle size distribution of prepared powders becomes narrower and more uniform with decreasing flow rate of carrier gas. The average diameter of powders treated at the flow rate of 10 l/min, only 40.78 μm (50% of the starting diameter), is the smallest.

Fig. 5 shows the XRD patterns of raw material and powders treated by 12-phase AC arc. The powders prepared at flow rate of 10 and 20 l/min only appear the SiO_2 peaks, but the powders prepared at 30 l/min still contains some $BaCO_3$ peaks. It indicates that the $BaCO_3$ and H_3BO_3 in raw material almost decomposed completely at the smaller flow rate of carrier gas. The increase of the intensity of SiO_2 (1 0 1) main peak makes it clear that the crystal SiO_2 reacted with other compounds becomes diminished at larger flow rate.

The effect of carrier gas flow rate on vitrification degree is shown in Fig. 6. The analysis shows that the highest vitrification degree is 95.2% at the carrier gas flow rate of 10 l/min, but the vitrification decreases quickly at 30 l/min. The results are consistent with above SEM and XRD results. There are two main reasons to explain the low vitrification reaction under the larger carrier gas flow rate. Larger flow rate leads to lower plasma temperature due to more energy exchange between plasma and carrier gas, then lower plasma temperature brings less heat transferred to particle. Besides, larger flow rate results in shorter residence because of higher velocity of particle which caused by more momentum, then the less energy transferred to particles during the flight in plasma. Hossain et al. [13] presented that the increasing flow rate of carrier gas in induction thermal plasmas decreased the plasma temperature and increased the plasma velocity. On the assumption that the gas flow is under ideal condition, the velocity of carrier gas

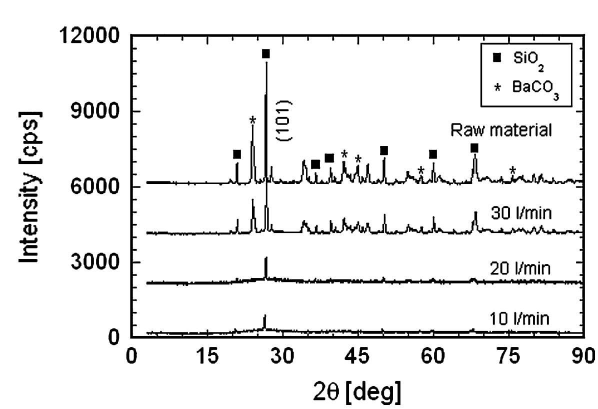

Fig. 5. XRD patterns of raw material and prepared powders at different flow rates of carrier gas.

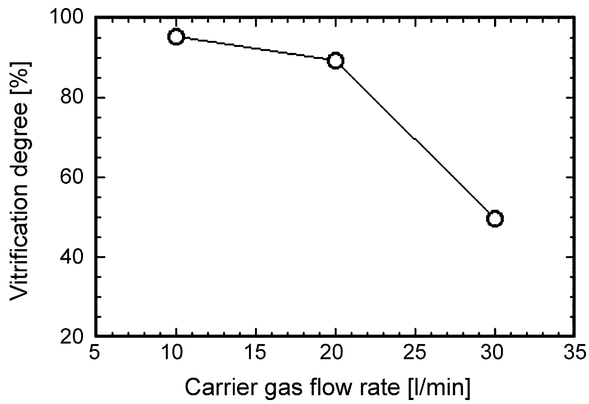

Fig. 6. Effect of flow rate of carrier gas on the vitrification degree of prepared powders.

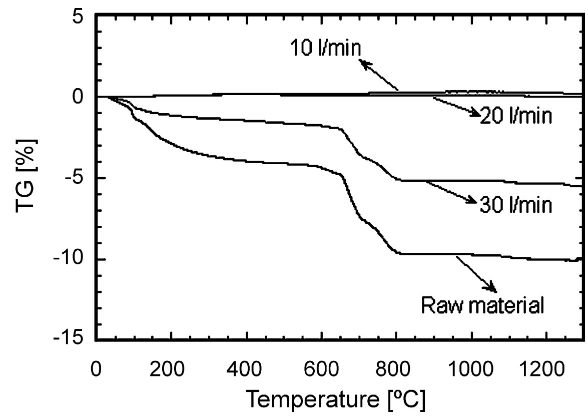

Fig. 7. TG curves of raw material and prepared powders at different flow rates of carrier gas.

at 10, 20 and 30 l/min is respectively 13, 26 and 40 m/s. Under the ideal state of particle flying, the residence time of particles along the centerline of nozzle is about 0.08 s from nozzle to substrate at the flow rate of 10 l/min. The high temperature and velocity of the plasma ensure that the new technology can reduce the melting time drastically.

A mass of bubbles formed by the decomposed and dissolved gas in molten glass will produce the foaming layer which decreases the heat transfer and glass quality, therefore, the refining is an important and indispensable process for glass industry. The glass refining is also an energy and time-consuming process for the conventional glass melting technology. Hence, the in-flight melting technology was developed to improve the process by releasing the decomposed gas while powder dropping. The TG curves of raw material and powders synthesized at different flow rates are shown in Fig. 7. The curve of raw material shows two main stages with total 10.1% mass loss in the process of heating. The first mass loss is attributed to the release of physically adsorbed H_2O and the decomposition of H_3BO_3 before 300 °C, and the second mass loss is due to the decomposition of $BaCO_3$ between 500 and 800 °C. The TG curves of powders treated at the flow rate of 10 and 20 l/min show no obvious mass loss which indicates that the H_3BO_3 and $BaCO_3$ almost decomposed completely during in-flight melting. However, the TG curve of powder treated at the flow rate of 30 l/min shows 5.03% mass loss. It suggests the incomplete decomposition of Ba_2CO_3 in powders which is in accord with the above XRD analysis. The decomposition degree of prepared powders is 100%, 99.4% and 50.2% at the flow rate of 10, 20 and 30 l/min, respectively. The high decomposition degree is helpful to decrease the forming of bubbles in molten glass and reduce the refining time.

The B_2O_3 introduced from the reagent of H_3BO_3 is an indispensable material for alkali-free glass. The glass properties like the viscosity and softening point can be changed by controlling the B_2O_3 content. Since the B_2O_3 is a kind of volatile material, the exposure of this material to high temperature surroundings will increases the volatilization loss and the cost of glass production. Hence, the

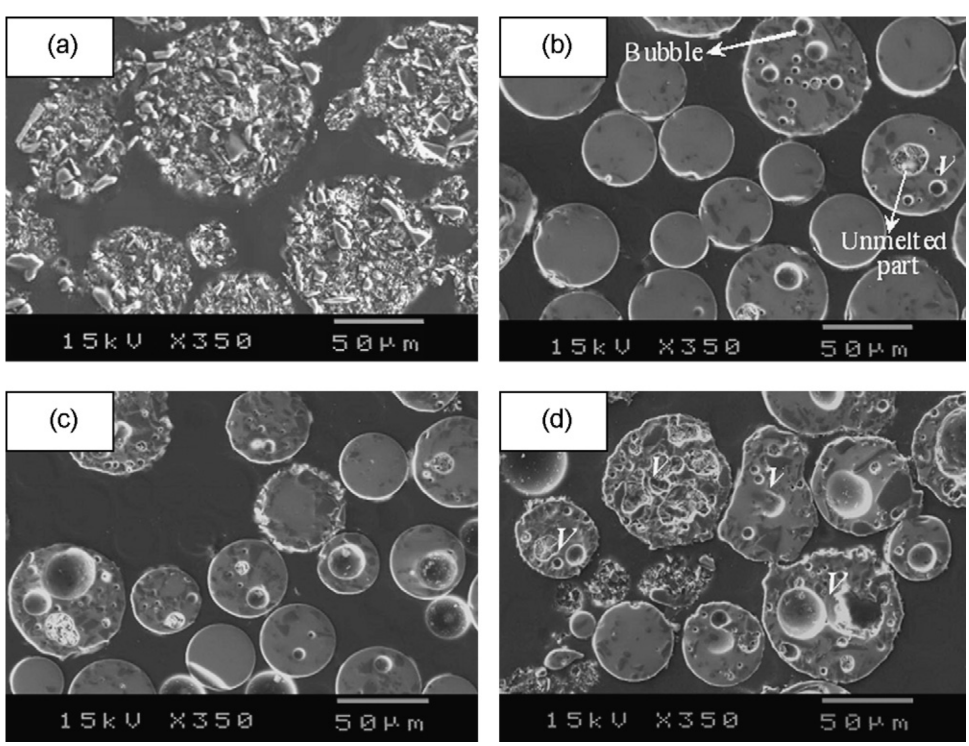

Fig. 8. Cross-section images of raw material and prepared powders at different feed rates: (a) raw material; (b) 30 g/min; (c) 50 g/min and (d) 70 g/min.

evaluation of volatilization degree of B_2O_3 is important to the alkali-free glass. The B_2O_3 content in powders treated by different flow rates was analyzed by ICP, and then calculated its volatilization degree. The volatilization degree of B_2O_3 in quenched powders is 41.7%, 30.2%, and 15.4% corresponding to the flow rate of 10, 20 and 30 l/min, respectively. Yao et al. [14] experimentally and numerically investigated the effect of carrier gas flow rate on the soda-lime glass powders in induction thermal plasmas. They found that smaller flow rate brings more energy transferred to particles which results in higher vitrification and volatilization of Na_2O in soda-lime glass powders. Their findings are similar with our experimental results. From the above vitrification and volatilization analysis results, it is notable that the high vitrification always accompanies with high volatilization of B_2O_3. High temperature of thermal plasmas leads to high vitrification, and short residence time within the high temperature region can suppress the volatilization of B_2O_3. A good balance between vitrification and volatilization can be obtained by controlling the appropriate conditions.

3.2. *Effect of feed rate*

The raw materials with different feed rates were injected into the plasma at the flow rate of 20 l/min carrier gas. The cross-section images of particles were performed with SEM to observe the image of particle inside, as shown in Fig. 8. The images show that the particle inside of raw material has incompact structure with many micropores which was caused by the evaporation of water in slurry droplets when the particles were dried. However, the particle inside of completely melted powders has a homogeneous and compact structure with spherical shape. The bubbles appeared on the particle inside were formed by the decomposed gas from raw material. Some incompletely melted particles marked by "*V*" present an inhomogeneous structure with irregular shape, and the amount of unmelted particles increases along with the feed rate increasing.

The powders prepared at feed rate of 30 g/min only include the SiO_2 peaks, but the powders at 50 and 70 g/min still contain some weak peaks of $BaCO_3$ (Fig. 9). The appearance of $BaCO_3$ peaks indicates the incomplete decomposition of powders at higher feed rate. The increased intensity of SiO_2 (1 0 1) main peak suggests the decreased vitrification of raw material, which also can be demonstrated from above cross-section images. Fig. 10 shows the measured vitrification degree and average diameter of powders prepared at different feed rates. As the feed rate increases, the vitrification degree decreases and the average diameter of prepared powders increases.

Fig. 11 presents the decomposition degree of raw material and the volatilization degree of B_2O_3. Both decomposition and volatilization degrees are lower at higher feed rate. It indicates the less heat transfer from plasma to particle under higher feed rate. Although the total heat transferred to all particles increases with feed rate, the vast energy exchange between particles and plasma leads to lower plasma temperature which causes less energy transferred to per particle. The inference is well explained by the simulation of plasma–particle heat exchange by Hossain et al. [15].

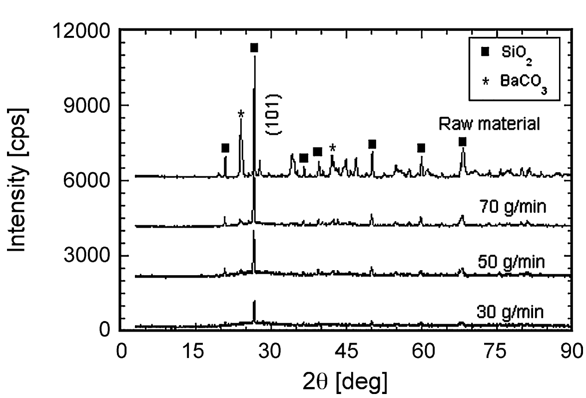

Fig. 9. XRD patterns of raw material and prepared powders at different feed rates.

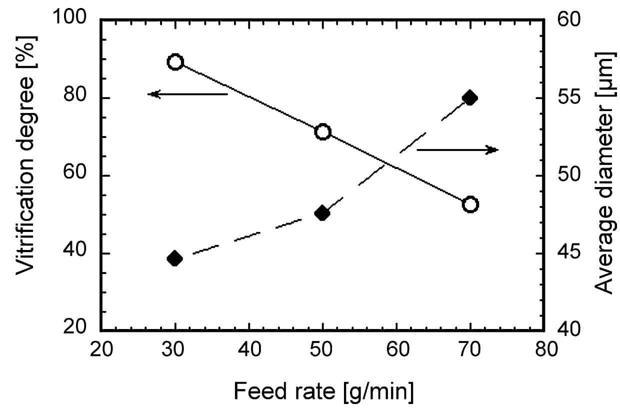

Fig. 10. Effect of feed rate on the vitrification degree and average diameter of prepared powders.

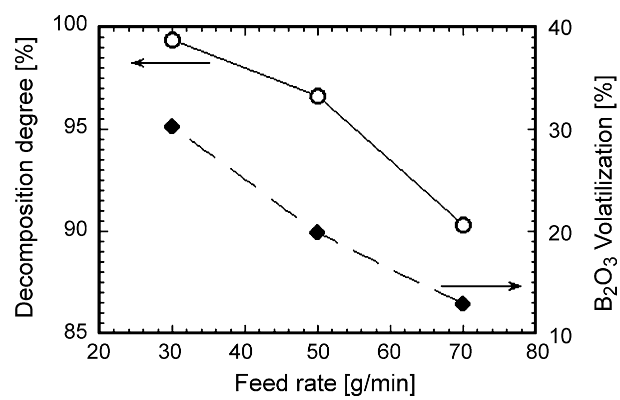

Fig. 11. Effect of feed rate on the decomposition degree and the volatilization of B_2O_3.

4. Conclusion

The stable 12-phase AC arc with 100 mm in diameter was obtained under the power of 46 kW. The in-flight glass melting technology with 12-phase AC arc was successfully developed to melt the granulated alkali-free glass raw material and the effects of carrier gas flow rate and feed rate on the in-flight particle behavior were investigated. Experimental results show that the high vitrification degree was almost finished within very short time at the flow rate of 10 l/min and feed rate of 30 g/min. The high decomposition of prepared powders is helpful to reduce the refining time after glass melting. The shrinkage of particle is strongly dependent on the vitrification degree. Larger carrier gas flow rate and higher feed rate result in lower heat transfer to particle.

Acknowledgement

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