Effect of suppression of devitrification by chlorine-containing silica glass

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Characteristics of the devitrification of silica glass containing 1000 mass ppm of Cl were investigated. The magnitude of the devitrification was evaluated by the depth at the center of the crystallization area grown by putting a grain of NaCl crystal on a flat polished surface of silica glass plate. The devitrification characteristics were compared with those of various types of silica glasses containing no Cl and various amounts of OH. The slope of devitrification depth in the Arrhenius plot changes abruptly at $T_C\approx1000°C$; The slope at a temperature higher than $T_C$ of the Cl-containing silica is considerably smaller than those of other silica glasses. This fact indicates that the Cl-containing silica glass is durable to devitrification, especially at temperatures higher than $T_C$. ©2019 The Ceramic Society of Japan. All rights reserved.

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Devitrification, the crystallization of glass from the surface upon heating, of silica glass degrades the lifetime of the silica glass products used at high temperatures such as metal-halide lamp bulbs and containers of furnaces used for manufacturing semiconductor devices. The devitrification characteristics depend strongly on the temperature, the holding time, silica glass impurities, and contaminants from ambient materials.1,2

Wagstaff et al. reported the dynamics of devitrification of silica glasses.3–7 They measured the crystallization rate of stoichiometric and oxygen-deficient silica glasses. Under a humidified atmosphere, the activation energy of the crystallization becomes approximately half of that in a dry atmosphere. In general, vitreous silica crystallizes at temperatures higher than approximately 1100°C without contaminants.8 Therefore, reports in the literature are limited to examinations conducted at temperatures higher than approximately 1200°C. Devitrification of vitreous silica is promoted when it contacts alkali metal compounds. Amorphous silica is devitrified at temperatures as low as 1000°C when in contact with alkali metal compounds.9–12 Basset13 and Higuchi14 reported crystallization of silica glasses with diffused alkali metal compounds of various types. These studies specifically examined the phase transitions of the silica crystal, and did not address the crystallization dynamics. These studies are useful to ascertain the effects of devitrification on silica glass products, such as lamp bulbs, which degrades the lifetime of those products. In these studies, silica glass powder was used to study devitrification.12,13 To elucidate devitrification characteristics, however, plate-type samples must be used as in the case of the study conducted by Wagstaff and colleagues.3–6

In a previous study,15 we examined the devitrification conditions of various types of silica glass contacted with a NaCl grain. To accelerate the silica glass crystallization at temperatures as low as 800–1150°C, we placed a precisely measured NaCl crystal grain on a silica glass plate. We compared the crystal growth in silica glasses of various types using different production methods containing various amounts of OH. Results show that the devitrification depth at the center of the devitrified region of a sample was proportional to the square root of the heating time. The slope in the Arrhenius plot of the devitrification depth is linear and is bent sharply at ca. 1000°C. We inferred that the devitrification of silica glass contacted with a NaCl grain has similar crystallization processes to those of multi-component glasses such as soda glass. The sodium ions that diffused from the surface of the sample exert effects resembling those of the sodium in the soda glass. Characteristics of the crystallization among the different kinds of silica glasses containing different amounts of OH, 10–1000 mass ppm, are mutually similar, which indicates that the SiOH structure affects the dynamics of the crystallization only slightly when silica glass contacts with alkali metal compounds.

Metal-halide lamp bulbs are made of silica glass. The bulb temperature becomes greater than 1000°C. When alkali metal compounds are sealed into the lamp, devit-
Devitrification is promoted even at temperatures lower than \( \approx 1000^\circ \text{C} \). Studies of devitrification in contact with alkali metals and/or alkali metal compound are important to ascertain the devitrification characteristics, which can provide useful insights to improve the lifetime of silica glass products such as bulbs of metal-halide lamps.

In a previous study,\(^\text{15)}\) we did not examine devitrification of Cl-containing silica glass. This time, we specifically investigated the characteristics of the crystal growth of a Cl-containing silica glass, and compared them with those of other types of silica glasses that were described in that earlier report.

Commercially available silica glasses of three kinds were used: HR, ED-B, and ED-C. They were provided by Tosoh Corp. HR is fused quartz produced by melting natural quartz powder containing ca. 1 mass ppm of OH. Samples ED-B and ED-C are the synthetic fused silica produced by soot remelting. ED-B contains no OH or Cl. ED-C contains no OH and approximately 1000 ppm of Cl. It was not used in the previous study. Each sample was cut to \( 20 \times 20 \times 1 \text{ mm} \) and was optically polished on two facing surfaces.

One NaCl crystal grain with mass of \( 0.13 \pm 0.01 \text{ mg} \) was placed on the center of the silica glass substrate. Then the substrate was heated in an electric furnace. A tubular furnace (ARF-50K; Asahi Rika Co. Ltd.) was used to heat the silica glass substrates. The soaking area length (\( \pm 5^\circ \text{C} \)) was 62 mm, with temperatures controlled within \( \pm 2^\circ \text{C} \). The silica glass substrate was placed on the silica glass stage at the center of the furnace. The heating temperatures were 800–1150°C. The heating time was counted after the temperature of the furnace reached the target temperature. The heat treatments were repeated after measuring the morphology and the profile of the devitrified region. The heat-treated sample was cooled to room temperature without temperature control.

The devitrification depth was determined from the distance from the backside of the substrate to the bottom of the devitrification region using a digital optical microscope (VH-7000; Keyence Co.). The depth \( z \) was determined as the product of the refractive index of the silica glass and distance estimated by the focal point of devitrified region at the bottom from back side surface of sample by the displacement of the microscope body.

The surface morphology of devitrified samples is presented in Fig. 1. The devitrified region is a double concentric circle. The inner circle of the devitrified area is whiter than that of the outer circle. The inner circle in Cl-containing silica glass ED-C is obscure compared to that of the other silica glasses, ED-B and HR. Figure 2 shows cross sectional profiles of ED-B and ED-C at various heat-treatment temperatures when heat-treated for 8 h. Both samples are OH-free silica glasses produced using the soot-remelting method. ED-C contains approximately 1000 mass ppm of Cl and ED-B contains no Cl. The profile of HR produced by electric melting of natural quartz powder was similar to that of ED-B. In a previous study,\(^\text{15)}\) we examined the devitrification of various types of silica glasses containing no Cl. No difference among samples was observed. Therefore, no significant difference among the samples was observed except for ED-C.
As Fig. 2 shows, the cross-sectional profile of the devitrification region consists of two regions: the outer plateau region corresponding to the outer concentric circle, and the inner deep region corresponding to the inner concentric circle. The cross-sectional profiles of chlorine-free silica glass ED-B is represented the same data in our previous paper15) for comparison. The devitrified region diameter was constant with changing temperature and heating time.15) The ED-C diameter was also constant with heating time. Therefore, we can compare with the amount of devitrification only by the depth at the center. Hereinafter, the center depth is designated simply as the devitrification depth.

Figure 3 shows Arrhenius plots of the devitrification depth at the heat-treatment time of 8 h. The data of NaCl grains was 0.13 ± 0.01 mg. The data of chlorine-free silica, HR and ED-B, are represented the same date in the previous paper15) for comparison. The depth of ED-C is less than a half of the ED-B at higher temperature than 1050°C. At temperatures lower than 1000°C, on the other hand, no significant difference of the depth between ED-C and ED-B was observed. These results indicate that the existence of Cl in silica glass suppresses silica glass devitrification at temperatures higher than ~1000°C. The slope of the devitrification depth in Fig. 3 is negative in the Arrhenius plot. The slope of the line of each sample bends sharply at a characteristic temperature \( T_c \approx 1000°C \), except for ED-C. The absolute value of the slope of the ED-C curve remains constant in the whole temperature range that was measured. It is less than that of the other samples at temperatures higher than \( T_c \). Figure 4 shows the heat-treatment time dependence of the depth. The depth is shown against the square root of time, \( t^{1/2} \). The growth rate of the devitrification depth of ED-C is lower than those of the other samples, which is attributable to the suppression effect for the devitrification in ED-C.

The temperature dependence presented in Fig. 2 and the heat-treatment time dependence of the depth portrayed in Fig. 4 indicate that the ED-C depth is less than a half of those in the other samples at temperatures higher than ~1000°C. ED-C and ED-B were produced using the soot-remelting method, and contain no OH. Only ED-C contains 1000 mass ppm of Cl. A previous paper15) reported no difference of the devitrification depth among different kinds of silica glasses containing various amounts of OH between <1 to 1000 mass ppm. Therefore, the hydroxyl structures in silica glass only slightly affect the devitrification of silica glass contacted with sodium chloride. The chlorine in silica glass suppresses devitrification.

Sodium concentration at the center part of the devitrified region is higher than at the outer part, based on measurements obtained using electron probe microanalysis.15) The sodium dissolution into silica glass during lightening is a controlling factor determining the lifetime of the metal halide lamps containing sodium compounds such as NaI enclosed in the bulb. Suenaga et al. reported that diffusion of the sodium into the silica glass occurred more rapidly at temperatures higher than ~1100°C.16) Because the amount of sodium compounds in the present case is much higher than in their case, the effect of the sodium diffusion might be apparent even at temperatures lower than 1100°C. Upon the diffusion of sodium, the depth of the center part (in Fig. 2) increased. Therefore, the devitrification depth must depend on the amount of the contacting impurities such as sodium compounds. The fact that devitrification is suppressed in ED-C suggests chlorine in silica glass can interfere with the diffusion of Na into the silica glass.

In summary, characteristics of the devitrification of silica glass containing 1000 mass ppm of Cl were investigated. Amounts of devitrification were evaluated by the

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**Fig. 3.** Arrhenius plot of the devitrification depth of ED-B, HR and ED-C with heat treatment time of 8 h. The data for ED-B and HR are the same as in Ref. 15 for comparison.

**Fig. 4.** Heat-treatment time dependence of the devitrification depth of ED-B, HR, and ED-C at 1150°C. The data for ED-B and HR are the same as in Ref. 15 for comparison.
depth of the crystallization region grown by contacting a polished surface of silica glass and a NaCl crystal grain at various temperatures. The devitrification characteristics were compared with those of various types of silica glasses containing no Cl with various amounts of OH. The slope of the devitrification depth, the depth at the center of the devitrification region, changes abruptly at \( T_c \approx 1000^\circ C \) in the Arrhenius plot. The slope at \( > T_c \) of the Cl-containing silica is considerably smaller than that of the other silica glasses. Therefore, the Cl-containing silica glass is durable against devitrification, especially at temperatures higher than \( T_c \).

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References
1) R. Brükner, *J. Non-Cryst. Solids*, 5, 123–175 (1970).
2) A. Nukui, *Taikabutsu*, 44, 596–606 (1992).
3) F. E. Wagstaff, *J. Am. Ceram. Soc.*, 51, 449–453 (1968).
4) F. E. Wagstaff, *J. Am. Ceram. Soc.*, 52, 650–654 (1969).
5) F. E. Wagstaff and K. J. Richards, *J. Am. Ceram. Soc.*, 49, 118–121 (1966).
6) F. E. Wagstaff, *J. Am. Ceram. Soc.*, 52, 650–654 (1969).
7) P. P. Bihuniak, *J. Am. Ceram. Soc.*, 66, C188–C189 (1983).
8) H. Sudou, in “Hishousitsu Silica Zairyou Ouyou Hand- book (Handbook for Application of Amorphous Silica)”, Ed. by H. Kawazoe, K. Awazu, Y. Ohki, N. Kuzu, S. Todoroki, A. Hayashi and H. Fukuda, Realize, Tokyo (1999) p. 89.
9) W. L. Keyser and R. Cypres, *Silicates Ind.*, 26, 237–243 (1961).
10) O. W. Flörke, *Geologie*, 3, 71–73 (1954).
11) J. Papailhau, *Compt. Rend.*, 245, 1443–1445 (1957).
12) Y. Tsurita and K. Okada, *Bull. Chem. Soc. Jpn.*, 71, 503–511 (1998).
13) D. R. Bassett, E. A. Boucher and A. C. Zettlemoyer, *J. Mater. Sci.*, 7, 1379–1382 (1972).
14) M. Higuchi and Y. Azuma, *J. Ceram. Soc. Jpn.*, 105, 385–390 (1997).
15) N. Horii, M. Kamide, A. Inouye and N. Kuzu, *J. Ceram. Soc. Jpn.*, 118, 318–320 (2010).
16) M. Suenaga and M. Yamane, *J. Light Visual Environ.*, 2, 2–5 (1978).