Reaction between α , β - Al_2O_3 Ceramics and Ba, Sr-Alkali Silicate Glass

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 α , β - Al_2O_3 セラミックスと Ba-Sr-アルカリ-シリケートガラスの反応

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Reaction between α , β - Al_2O_3 ceramics (produced by fusion cast method) and Ba-Sr-alkali-silicate glass was studied on samples from glass melting tank. This tank had been used for about 6.5 years. Dendritic leucite (KAlSi_2O_6) crystals were observed at the interface between ceramics and glass. These crystals were about $120\text{ }\mu\text{m}$ long at the position of the glass meniscus line. Leucite was crystallized in Al_2O_3 -rich liquid due to the corrosion of α , β - Al_2O_3 ceramics. β - Al_2O_3 crystals in the ceramics showed no morphological change but chemical substitution of K, Ba and Sr for Na occurred. Leucite and β - Al_2O_3 -like crystals are occasionally found as a defect in glass production. It is clear that these crystals are formed at the interface between α , β - Al_2O_3 ceramics and molten glass.

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Key-words : α , β - Al_2O_3 ceramics, Reaction, Molten glass, Glass defect, Leucite

1. Introduction

α , β - Al_2O_3 ceramics produced by fusion cast method are popular materials in glass industry. These materials are normally used as molten glass contact materials, especially under 1200°C . α , β - Al_2O_3 ceramics give less contamination in glass products. These refractory materials are widely used in working end of glass melting tank.

These ceramics are tough materials against molten glass. No alteration is observed with naked eye observation after using. Therefore, it is normally used for a long period at least 5 years. However, if microscopic observation is done, small scale alteration is observed. And it is very important to study α , β - Al_2O_3 alteration when concerning defects in glass.

In this report, α , β - Al_2O_3 ceramics alteration was studied and discussed in relation to defects in glass.

2. Experimental

2.1 Materials

α , β - Al_2O_3 ceramics were originally made by fusion cast method and were a mixture of α - Al_2O_3 (corundum) and β - Al_2O_3 .^{1),2)} Figure 1 shows the back scattered electron image (BSE) of the texture of this material. Relatively white phase is β - Al_2O_3 and grey one is α - Al_2O_3 .

Ba,Sr-alkali silicate glass for cathode ray tube was melted in the fusion cast Al_2O_3 - ZrO_2 - SiO_2 material around at 1500°C and then glass was cooled down to 1100°C in the α , β - Al_2O_3 ceramics in order to obtain the good forming temperature. This glass melting tank was used about 6.5 years. The chemical composition of the glass is shown in Table 1. This glass contains heavy metal ions such as Sr^{2+} , Ba^{2+} , Zr^{4+} for prevention of X-rays, and also contains Sb^{3+} for decreasing blisters in glass.

After stopping glass production, the melting tank was gradually cooled down to room temperature. Figure 2 shows the schematic representation showing how and where the samples were obtained. Small pieces of α , β - Al_2O_3 ceramics with glass were obtained from the position of forehearth. About $100\text{ mm} \times 10\text{ mm} \times 10\text{ mm}$ samples were cut from the block and then divided into 5 pieces. As shown in this figure, samples were obtained around the glass meniscus line.

2.2 Characterization

After buried in resin, the samples were polished by diamond media. Finally, the samples were coated with carbon by vacuum evaporation. Microscopic observation was done by an electron probe microanalyzer (Shimadzu, EPMA 1600). And the chemical composition was also determined by EPMA. Measuring conditions are as follows.

Accelerating voltage : 15 kV

Beam size : $20\text{ }\mu\text{m}\phi$ and $10\text{ }\mu\text{m}\phi$

Sample current : 15 nA

Measuring time : 10 s in each element

Powder X-ray diffraction measurements were performed using a Rigaku RAD-IIA assisted by MXP software system of MAC Science Co., Ltd.

3. Results

3.1 Back scattered electron images

As shown in Fig. 2, samples were obtained from upper to lower part of the meniscus line. Figure 3 shows the back scattered electron (BSE) images of the samples at the inter-

Fig. 1. Texture of α , β - Al_2O_3 ceramics produced by fusion cast method. White phase : β - Al_2O_3 . Grey phase : α - Al_2O_3 .

Table 1. Chemical Composition of the Ba,Sr-Alkali Silicate Glass for Cathode Ray Tube

	mass %
SiO ₂	61.0
Al ₂ O ₃	2.0
Na ₂ O	7.5
K ₂ O	7.5
ZrO ₂	2.3
SrO	8.5
BaO	8.5
Sb ₂ O ₃	0.3
Others	2.3

Table 2. Size of the Dendritic Crystals Observed in Figs. 3(b)–3(e)

position	size (μm)
No.2	120
No.3	30
No.4	15
No.5	15

Table 3. Chemical Compositions of the Dendritic Crystals Observed in Fig. 3(b)

	mass %		
	No.2	No.2	Theoretical
	crystal	crystal	leucite
SiO ₂	52.20	53.50	55.0
Al ₂ O ₃	21.70	23.10	23.4
Na ₂ O	0.39	0.82	
K ₂ O	19.40	19.90	21.8
SrO	0.00	0.02	
BaO	0.24	0.25	

Table 4. Chemical Compositions of the Glasses in the Reaction Zone Observed in Figs. 3(a)–Fig. 3(e)

	mass %				
position	No.1	No.2	No.3	No.4	No.5
	glass	glass	glass	glass	glass
SiO ₂	56.00	55.90	60.30	64.20	60.70
Al ₂ O ₃	21.50	18.60	13.20	14.20	13.60
CaO	0.00	0.64	0.40	0.42	0.48
Na ₂ O	0.59	2.94	2.84	5.85	6.21
K ₂ O	19.40	11.10	11.20	8.51	8.54
ZrO ₂	1.47	1.88	1.07	1.77	1.75
SrO	0.03	0.18	1.94	1.93	2.84
BaO	0.03	0.19	1.22	1.46	3.37

Fig. 2. Observed zones of reaction between α, β -Al₂O₃ ceramics and Ba, Sr-alkali silicate glass.

face between the α, β -Al₂O₃ ceramics and glass obtained at various positions. We can easily find that these are different from each other. Small crystals (white small granule) are found in No. 1 (Fig. 3(a)). These crystals are baddeleyite (ZrO₂) recrystallized in glass. Large dendritic crystals are observed in No. 2 (Fig. 3(b)). These crystals are leucite (KAlSi₂O₆). Dendritic crystals are also found in Nos. 3, 4 and 5 (Figs. 3(c)–(e)). The size of the dendritic crystals are shown in Table 2. The crystal size gradually decreases from No. 2 to No. 5. The dendritic crystals in No. 2 are about 120 μm long, which is much larger than those observed at the other positions. It is supposed that this size variation resulted from difference in the glass compositions, which are caused by the corrosion of the ceramics. On the other hand, the crystals in the α, β -Al₂O₃ ceramics showed no change in morphologies.

3.2 Alteration of glass reaction zone

As described in the previous section, some crystals are observed precipitated in the reaction zone. It is supposed that the crystallization is caused by the change of the glass composition due to the ceramics corrosion. The analyzed

compositions of the dendritic crystals and glasses are shown in Tables 3 and 4, respectively.

The compositions of the dendritic crystals are almost equal to the theoretical value of leucite (KAlSi₂O₆). The composition of the glass at position No. 1 is also close to leucite. Dendritic crystals, however, were not detected at position No. 1. So, all crystals of position No. 1 are leucite. The Al₂O₃ and K₂O contents of No. 2 glass is higher than those at the other lower positions. This may be the reason for the growth of the larger dendritic crystals in No. 2. As shown in Fig. 2, position No. 2 is at the meniscus line. Basically, materials at meniscus position are more corrosive than those at the other positions, which can explain the higher Al₂O₃ content in glass No. 2. On the other hand, positions No. 3 to No. 5 are lower than the meniscus. The corrosion may occur more slowly than No. 2, which leads to lower Al₂O₃ content.

K₂O enrichment at the position Nos. 2 and 3 is curious. It is considered that this enrichment is owing to glass structure. SiO₂ and Al₂O₃ are network formers and the other oxides are network modifiers. As mentioned above, Al₂O₃ become higher than in the glass because of the ceramics corrosion. In general, the bonding distances of Al–O and Si–O in glass structure are 0.175 nm and 0.162 nm, respectively. It is thought that the vacancy become large in the case of Al₂O₃-rich glass. Feldspar (NaAlSi₃O₈, KAlSi₃O₈, etc.) glass structure is similar to that of silica glass.³⁾ Therefore, it is considered that the vacancy become large in relation to increasing Al₂O₃ in this glass. As a result, K⁺ ions are likely to be more stable in such Al₂O₃-rich compositions than the other alkali and alkali earth elements. This is an estimated reason for the K₂O enrichment in the Al₂O₃-rich glasses.

3.3 Alteration of α, β -Al₂O₃ ceramics

As shown in Fig. 3, no change was observed in the texture of the ceramics. The chemical composition of the α -Al₂O₃ crystals also showed no change. On the other hand, chemical composition of the β -Al₂O₃-like crystals had a small change at the interface. Table 5 shows the chemical composition of the β -Al₂O₃-like crystals in the ceramic bodies. All the crystals shown in Table 5 are not exactly β -Al₂O₃ because of the substitution of K, Ba and Sr for Na. It

$\alpha,\beta\text{-Al}_2\text{O}_3$ ceramics | glass

(a)

$\alpha,\beta\text{-Al}_2\text{O}_3$ ceramics | glass

(d)

$\alpha,\beta\text{-Al}_2\text{O}_3$ ceramics | glass

(b)

$\alpha,\beta\text{-Al}_2\text{O}_3$ ceramics | glass

(e)

$\alpha,\beta\text{-Al}_2\text{O}_3$ ceramics | glass

(c)

Fig. 3. BSE images of the samples obtained by EPMA.
(a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4 and (e) No. 5 positions.

Table 5. Chemical Compositions of β - Al_2O_3 -Like Crystals in the Reaction Zone Observed in Figs. 3(a)–Fig. 3(e)

	mass %				
	No.1	No.2	No.3	No.4	No.5
Al_2O_3	92.50	88.80	89.00	88.70	87.90
Na_2O	1.76	1.73	1.53	1.47	1.42
K_2O	3.62	4.24	3.73	3.64	3.58
SrO	0.36	1.27	1.12	1.02	1.20
BaO	0.25	2.38	3.86	4.43	5.27
SiO_2	1.50	1.55	0.80	0.77	0.61

Table 6. Atomic Plane Distances in the β - Al_2O_3 -Like Crystals before and after Used in the Glass Melting Tank

hkl	nm		
	β - Al_2O_3 Yamaguchi et al (1968)	This study β - Al_2O_3 before used	after used
002	1.131	1.127	1.138
004	0.566	0.563	0.569
102	0.446	0.445	0.446
107	0.269	0.268	0.269
114	0.251	0.250	0.251
Lattice constants			
a	0.5593	0.5607	0.5602
c	2.261	2.253	2.276

(a)

(b)

Fig. 4. BSE images of (a) dendritic leucite and glass knot defects, and (b) the α - and β - Al_2O_3 -like defects in the Ba,Sr-alkali silicate glass.

Table 7. Chemical Compositions of Defects in Ba,Sr-Alkali Silicate Glass Observed in Fig. 4

	Fig.4(a)		Fig.4(b)	
	dendritic crystal	glass knot	β - Al_2O_3 -like crystal	α - Al_2O_3 -like crystal
SiO_2	55.10	61.60	0.87	0.54
Al_2O_3	23.20	10.80	87.00	98.00
Na_2O	0.29	6.77	1.46	0.31
K_2O	20.40	9.84	4.32	0.17
ZrO_2	0.00	2.62	0.26	0.08
SrO	0.03	3.46	0.65	0.12
BaO	0.67	4.25	4.29	0.17

is easily understood that SrO and BaO contents in the glasses at the reaction zone are lower than those in the mother glass because of this atomic substitution in β - Al_2O_3 crystals.

K, Ba and Sr substitution in the β - Al_2O_3 -like crystals is easily understood from the view point of the crystal structure of β - Al_2O_3 .⁴⁾ β - Al_2O_3 has layered structure perpendicular to the c -axis. It has tight Al-O bonding within a -plane, but has loose bonding between 001 planes. Table 6 shows atomic plane distances of the β - Al_2O_3 -like crystals before and after used in glass melting tank. After used in glass melting tank, 002 and 004 planes become slightly larger. Those of 102, 107 and 114 planes, on the other hand, are almost equal to each other. It was reported by Dyson and Johnson⁵⁾ and Groppi et al.⁶⁾ that Na in β - Al_2O_3 -like crystals was easily replaced by other elements such as K, Ba and Sr. Therefore, it is easily understood that K, Ba and/or Sr substitution for Na occurred at the interface between the ceramics and glass.

4. Relation between glass defects and reaction zone

There are many kinds of defects in face plate glasses for cathode ray tubes. Figure 4 shows the BSE images of two kinds of defects found in the present glass body. Figure 4(a) shows the image of the dendritic crystals and glass knot. The chemical compositions of the defects are shown in Table 7. It can easily be confirmed that the dendritic crystals are leucite (KAlSi_2O_6). The crystal size is about 250 μm . The order of the size is almost similar to that observed in position No. 2. (Fig. 3(b)) The glass composition around the leucite is also shown in Table 7. This result shows that glass around the leucite crystals is rich in Al_2O_3 and K_2O . The other elements are equal or less relative to those in the mother glass (Table 1). The Al_2O_3 enrichment is owing to corrosion of Al_2O_3 ceramics. Leucite is thought to have been crystallized in Al_2O_3 and K_2O rich liquid in a long period of time. This defect found in glass product (Fig. 4(a)) have almost the same compositions as those in the reaction zone mentioned above (Fig. 3 and Tables 3 and 4).

Figure 4(b) shows the BSE image of the another glass defects. The chemical compositions of these crystals are shown in Table 7. As seen in the Table 7, black color crystals are α - Al_2O_3 and grey color crystals are K, Ba and Sr-substituted β - Al_2O_3 -like crystals. In comparison with Table 5, the composition of the substituted β - Al_2O_3 crystals in Table 7 are close to those at position No. 4 (Table 5). Therefore, we can easily speculate that this defect was originate from the alteration zone of No. 4 of the α , β - Al_2O_3 ceramics.

5. Conclusion

Reaction between glass and α , β - Al_2O_3 ceramics used for about 6.5 years as glass melting tank was investigated. The results are as follows.

(1) Dendritic leucite (KAlSi_2O_6) precipitated at the interface between the ceramics and the glass.

(2) Dendritic leucite became larger in direction to the meniscus line. The largest size was about 120 μm .

(3) Altered glass formed at the interface was rich in Al_2O_3 and K_2O , which may have caused the leucite crystallization.

(4) α - and β - Al_2O_3 crystals in the ceramics showed no morphological change, but K, Ba and Sr atomic substitution for Na occurred in β - Al_2O_3 -like crystals.

(5) Glass defects containing leucite are thought to originate from the glass at the reaction zone, especially near the meniscus line.

(6) Glass defects containing K, Ba and Sr-substituted β - Al_2O_3 crystals are thought to originate from the ceramics

at the reaction zone.

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