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2. Evaluation of Upward Drilling Corrosion in Glass Furnace

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The upward drilling corrosion is commonly observed in glass furnace. The evaluation of upward drilling, however, has not been established. The new experimental method was developed by use of L-shaped test pieces. The corroded L-shaped test pieces were cut and polished to measure the residual size. In order to evaluate the corrosion resistance against the non-alkaline borosilicate glass, the following samples were selected; FZ-A (prepared from near the skin of fused ZrO_2 ingot), FZ-B (from the interior), Zircon and Tin-oxide refractory. FZ-A was only slightly corroded although noticeable upward drilling was observed in FZ-B and Tin-oxide refractory. It is considered that the differences are dependent on their microstructure, especially the grain size and homogeneity of the components. The refractory with homogeneous microstructure composed of fine grains shows higher corrosion resistance.

1. Introduction

The upward drilling corrosion is commonly observed in glass furnace, especially in the refractory that is located above molten glass, for example, facer block of the throat and hole of the cross wall. Although the life of glass tank furnace is sometimes influenced by this type of corrosion, the evaluation of upward drilling has not been established.

The difficulties to evaluate the upward drilling in adequate manner are as follows; 1)how to generate bubbles in the same density, and 2)how to measure the depth of drilling holes. In order to solve these problems, the new experimental method, in which re-melted glass cullet and L-shaped test piece are used, was developed.

To evaluate the corrosion resistance against the non-alkaline borosilicate glass, the following samples were selected; FZ-A (prepared from near the skin of fused ZrO_2 ingot), FZ-B (from the interior), Zircon and Tin-oxide refractory.

2. Experimental Methods

2.1 Preparation of re-melted glass

In order to achieve the experimental condition that the bubbles are generated with the same size and density, the glass for corrosion testing was prepared by re-melting the cullet with the controlled size of 1-2mm. Re-melting was carried out by heating the cullet at 1200°C for 6h. Heating/Cooling rate was 300°C/h. By this method, the glass involving the bubbles with the size of 0.5-1mm could be obtained with high reproducibility.

2.2 L-shaped test piece

The size and shape of L-shaped test piece is shown in **Fig. 1**. The reasons why the L-shape is chosen are mainly as follows; 1)easy to capture the bubbles, 2)relatively light, and 3)easy to determine the area of the corroded region. The schematic image of the experiment is also shown in **Fig.1**.

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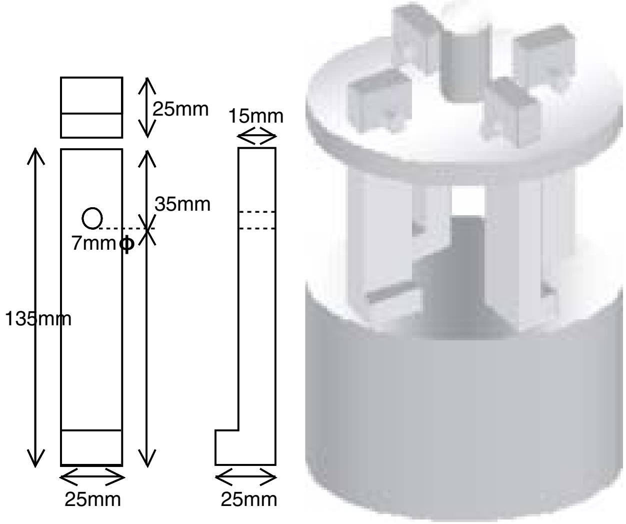

Fig. 1 L-shaped test piece and the schematic image of the corrosion test.

2.3 Procedure

The experimental procedure is as follows; 1) preparation of re-melted glass, 2) setting test pieces, 3)plunging the test pieces into molten glass after heating them together to 1600°C, 4) maintaining the conditions for 336h, 5)pulling the test pieces out and cooling, 6) cutting the test pieces into two parts and polishing the cross section, and 7)measuring the residual shape of the bottom portion of test pieces at intervals of 0.5mm.

3. Experimental Results

3.1 FZ-A

The test piece is prepared from near the skin of fused ZrO_2 ingot and is characterized by the more homogeneous microstructure in comparison with that of the interior. The bottom plane after the test was very smooth and any noticeable drilling hole was not observed. The lowest point of vertical plane, i.e., the edge of horizontal plane, was not

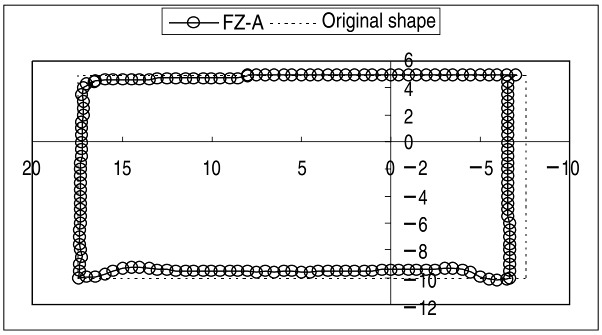

Fig. 2B Measured residual shape of the lower part of L-shaped test piece of FZ-A (mm).

so corroded. It is considered that the bubbles were not captured and drifted under the bottom plane because they could not escape due to the downward flow of high ZrO_2 containing glass which were formed at the vertical boundary between FZ-A and glass (**Figs. 2A** and **2B**).

3.2 FZ-B

The test piece is prepared from the portion between the skin and the center of fused ZrO_2 ingot. This portion is characterized by the existence of heterogeneous microstructure, so-called WT (Worm Tracing), in which the amount of matrix glass is larger than that of baddeleyite crystals (ZrO_2).

Both horizontal and vertical planes after the test were very rough and several drilling holes were observed at the bottom (**Fig. 3A**). WT can easily capture bubbles at the bottom plane because the softened matrix glass is rich there and would be the origin of upward drilling corrosion (**Fig. 3C**).

Existence of WT also lowers the corrosion resistance generally. Corrosion along the vertical plane is often started from WT, although it is not deeper than upward drilling corrosion found at the bottom plane. The edge of horizontal plane was not so corroded as well as that of FZ-A (**Figs. 3A** and **3B**).

Fig. 2A Cross sections of FZ-A before (left) and after (right) the corrosion test.

Fig. 3A Cross sections of FZ-B before (left) and after (right) the corrosion test.

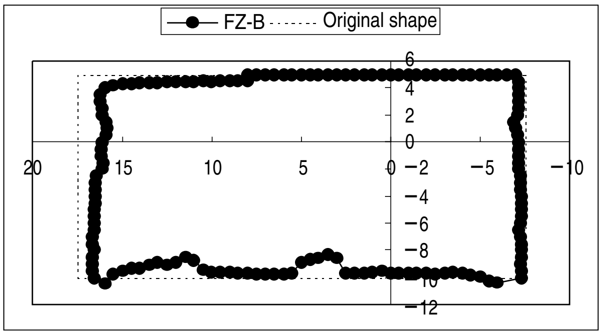

Fig. 3B Measured residual shape of the lower part of L-shaped test piece of FZ-B (mm).

Fig. 3C Upward drilling corrosion formed in WT at the bottom plane of FZ-B.

3.3 Zircon

The test piece showed slight expansion after the corrosion test (Z-O in **Fig. 4B**). The region near the skin changed in color from gray to white, and was constituted from pie-sheet-like aggregates of baddeleyite and SiO_2-rich glass (**Fig. 4A**). Those are considered to be formed as a result of reaction between zircon refractory and molten glass. The thickness of this reaction layer is about 2mm at the vertical plane and 1mm at the bottom plane.

The original structure inside the layer was protected from upward drilling corrosion because bubbles were blocked by heavy baddeleyite and highly viscous SiO_2-rich glass (Z-I in **Fig. 4B**). Although there were so many smaller bubbles in this SiO_2-rich glass, they could not migrate to coalesce probably because of the high viscosity of the glass, hence would not become the origin of the upward drilling corrosion (**Fig. 4C**).

Fig. 4A Cross sections of Zircon before (left) and after (right) the corrosion test.

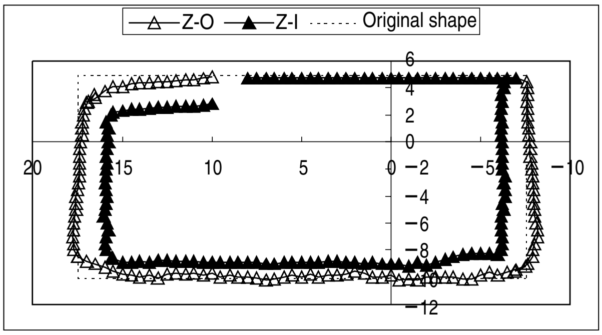

Fig. 4B Measured residual shape of the lower part of L-shaped test piece of Zircon (mm).

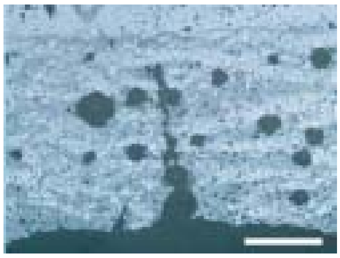

Fig. 4C Small bubbles found in the reaction layer of Zircon. Scale Bar: 1mm

3.4 Tin-oxide

Typical upward drilling phenomenon was observed in this refractory.

The corroded surface was smooth although many drilling holes were formed. The size of these holes is wide compared with that of FZ-B although the depth of them is almost the same (**Figs. 5A** and **5B**).

Fig. 5A Cross sections of Tin-oxide before (left) and after (right) the corrosion test.

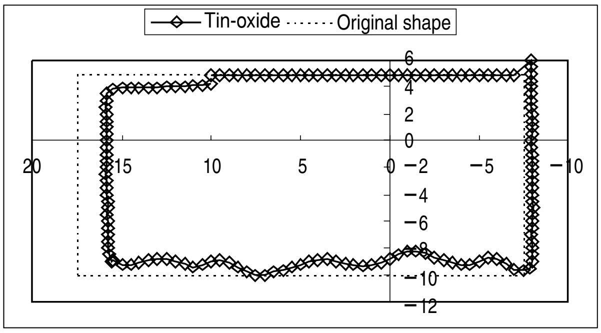

Fig. 5B Measured residual shape of the lower part of L-shaped test piece of Tin-oxide (mm).

4. Discussions

Corrosion was evaluated by determining the area of the corroded region at each portion, i.e., horizontal plane, vertical plane and corner in the lower part of the test piece. The method for calculation of the decrease in the area is shown in **Fig. 6** and the results are presented in **Table 1** and **Fig. 7**. The total decrease of the area was also calculated.

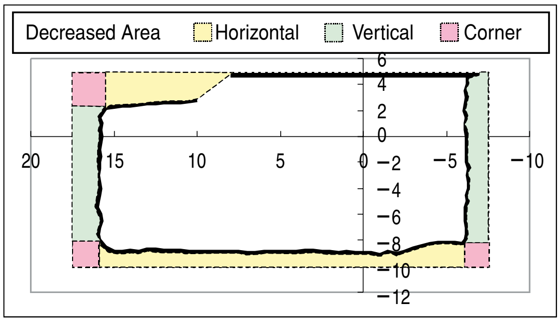

Fig. 6 The method for calculation of the decrease in the area at each portion.

The results of corrosion tests for FZ-A and FZ-B clearly show that the homogeneous microstructure in FZ-A, which is composed of small baddeleyite grains, is responsible for the high resistance against the upward drilling corrosion.

On the other hand, WT in FZ-B causes the upward drilling corrosion as shown in **Fig. 3C**. WT also causes the ordinary corrosion by molten glass, although the results indicate that WT is less resistible against the upward drilling corrosion than against the ordinary corrosion.

The important conclusion derived from these results is that Fused ZrO_2 refractory may become less durable with time against the corrosion, because the contact surface with molten glass must move inward from the skin (FZ-A) to the interior (FZ-B).

Table 1 Decreased Area on Cross Section (mm²).

Refractory Portion	Fused ZrO_2		Zircon		Tin-oxide
	FZ-A	FZ-B	Z-O	Z-I	
Horizontal	27.3	29.6	21.3	55.2	39.2
Vertical	16.9	20.9	-3.5	34.3	15.2
Corner	1.3	2.4	0.9	13.1	5.8
Total	45.5	53.0	18.7	102.6	60.3

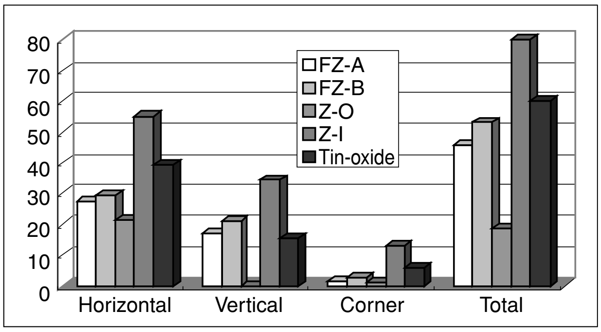

Fig. 7 Decreased area on cross section (mm²).

The result of the corrosion test for Zircon indicates that this type of refractory is more resistible, but reactive, against the static molten glass than Fused ZrO_2. In dynamic condition, however, kinetic corrosion becomes dominant and Zircon refractory may become less resistible than Fused ZrO_2. Therefore, these types of refractory should be used under the appropriate condition.

In the case of Tin-oxide refractory, the upward drilling corrosion is clearly observed as shown in **Fig. 5B**. The solubility of SnO_2 and ZrO_2 to non-alkaline borosilicate glass is not so different at 1600°C; that is 2-3wt%. Moreover, both Tin-oxide and FZ-A are composed of small grains with homogeneous microstructure. Significant difference is the array and morphology of the grains. Tin-oxide refractory is composed of the aggregates of SnO_2 grains with simple array, whereas FZ-A is composed of the aggregates of interfingering dendritic ZrO_2 crystals. It can be estimated that the less durability of Tin-oxide refractory is caused by the removal of SnO_2 grains from the aggregates.

5. Summary

The new experimental method was developed by use of L-shaped test pieces. Corrosion resistance against the non-alkaline borosilicate glass was evaluated by using the L-shaped test pieces for FZ-A (prepared from near the skin of Fused ZrO_2 ingot), FZ-B (from the interior), Zircon and Tin-oxide refractories.

FZ-A was slightly corroded although noticeable upward drilling was observed in FZ-B and Tin-oxide refractories. It was considered that the difference in the corrosion resistance was dependent on their microstructures. WT(Worm Tracing) in FZ-B was responsible for the upward drilling corrosion. On the other hand, FZ-A demonstrates higher corrosion resistance, being ascribed to the homogeneous microstructure composed of small, interfingering dendritic ZrO_2 grains.