Influence of TiO$_2$ on the Alkali Resistance and Structure of Invert Glass

ZHAO Qing-lin  WU Zheng-ming  BU Heng-zhi

Wuhan University of Technology

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Abstract: Through measuring the alkali resistance of the invert glass and the quantity of SiO$_2$ and TiO$_2$ migrating from the glass into the solution, the influence of TiO$_2$ on the alkali resistance of the glass is discussed and its structure is also analyzed by infrared spectroscopy. It is concluded that TiO$_2$ has double functions for the alkali resistance of the invert glass. On one hand, both TiO$_2$ polarizing the secondary ions in glass and TiO$_2$ isomorphism replacement of SiO$_2$ make the alkali resistance of the glass decrease. On the other hand, TiO$_2$ patching network and anti-erosion covering help to increase the alkali resistance.

Key words: invert glass; doped oxide; alkali resistance

1 Introduction

The invert glass is a kind of glass whose number of bridge oxygen $y$ is not bigger than 3. When there is only one glass former SiO$_2$, its molar content is no more than 66.7%. On this occasion, the glass structure may change from three-dimensional consecutive network to laminar network ($y = 3$), chain structure ($y = 2$), and island structure ($y = 0$). The influence of TiO$_2$ on the alkali resistance and structure in the invert glass has not been reported. This paper will discuss it in detail.

2 Experimental

The materials used were chemical pure SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$CO$_3$, MgCO$_3$ and CaCO$_3$. The required materials were mixed in a mortar according to the calculated proportion and ground, then were put into a quartz crucible to be molten in a stove at 1360°C for 1 h. The molten was poured on a iron flat and cool in the open air. Finally the glass for the experiment is obtained.

We used the powder weight loss method to measure the alkali resistance. The solution after being filtrated was used to analyze the changing quantity of SiO$_2$ and TiO$_2$ from the glass to the solution. The amount was measured by the spectrophotometric analysis.

3 Results and Discussion

The basic structure of invert glass is 52SiO$_2$·10Al$_2$O$_3$·5FeO$_2$·15MgO·13CaO·5Na$_2$O. The TiO$_2$ isomorphism replacement of SiO$_2$ is performed. The experimental results are shown in Table 1 and Fig. 1. Fig. 1(a) is the glass powder weight loss proportion (wt%) vs TiO$_2$ content. Fig. 1(b) is the SiO$_2$ relative weight loss proportion ($\Delta$SiO$_2$/2SiO$_2$%) , i.e., the ratio of the content of SiO$_2$ migrating into solution to the content of SiO$_2$ introduced in the glass, vs the content of TiO$_2$. Fig. 1(c) is the TiO$_2$ relative weight loss proportion ($\Delta$TiO$_2$/2TiO$_2$%) vs the content of TiO$_2$.

From Table 1 and Fig. 1, it can be seen that after TiO$_2$ replaced SiO$_2$, the alkali resistance of the system hardly changes, in other words, the whole weight loss hardly changes. As for the influence on the alkali resistance of the system, TiO$_2$ and SiO$_2$ are almost equivalent. But when more and more TiO$_2$ replace SiO$_2$, the migrating quantity of TiO$_2$ into the solution becomes smaller and smaller (Fig. 1(b)), the migrating quantity of SiO$_2$ becomes bigger and bigger (Fig. 1(a)). The results may be caused by several factors as follows.

Firstly, we consider the structure changes in a series of glass. In the invert glass, the initial glass formation is SiO$_2$, the intermediates are TiO$_2$ and Al$_2$O$_3$. When we only consider SiO$_2$, SiO$_2$ appears as [SiO$_4$], [Si$_2$O$_7$] and so on. Al$_2$O$_3$ enters into the silicon-oxygen network in the form of [AlO$_4$] before [TiO$_4$] tetrahedron, and links these dispersing[SiO$_4$], [Si$_2$O$_7$] together to form a strong short chain. This is the process of network patching, which can be shown as follows:\[1\] .

| Table 1: The Results of the Alkali Resistance of the Invert Glass |
|------------|------------|------------|------------|------------|
| Glass composition/mol% | Results of the alkali resistance |
| SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO$_2$ | MgO | CaO | Na$_2$O | wt% | $\Delta$SiO$_2$/2SiO$_2$% | $\Delta$TiO$_2$/2TiO$_2$% |
| 52 | 0 | 10 | 5 | 15 | 13 | 5 | 5.76 | 6.68 |
| 50.5 | 1.5 | 10 | 5 | 15 | 13 | 5 | 5.22 | 5.78 | 0.080 |
| 49 | 3 | 10 | 5 | 15 | 13 | 5 | 5.70 | 7.52 | 0.110 |
| 46 | 6 | 10 | 5 | 15 | 13 | 5 | 5.63 | 8.33 | 0.053 |
| 43 | 9 | 10 | 5 | 15 | 13 | 5 | 5.60 | 8.64 | 0.034 |
| 40 | 12 | 10 | 5 | 15 | 13 | 5 | 5.30 | 9.46 | 0.026 |

ZHAO Qing-lin: Born in 1972; Lecturer; Ph.D Center of Silicate Engineering, Wuhan University of Technology, Wuhan 430070, China

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As we all know, according to the evaluation principle of captions ability to form glass, titanium, belonging to the intermediate, cannot transform to glass, no matter it is oxide or not. By the crystal chemistry theory, in the process of glass formation, the introducing of titanium compounds modifier will lead to the destruction of edge bond in the crystal and change the linking character of titanium polyhedron from hard linking at the same prism to flexible linking at the peak, and also decrease the coordination number of titanium and oxygen. As a result, the function of TiO₂ in glass is complex.

In the present glass, Al₂O₃ content is 10%, and TiO₂ content is not bigger than 12%, so the free oxygen provided by Na₂O, MgO and CaO is 13.2%, which can help completely form [AlO₄], make 3.2% of Ti⁺ exist in the form of [TiO₆] octahedron out of the glass network, functioning as filling.

The influence of [TiO₄] on the alkali resistance of the glass is exerted in two aspects. On the one hand, [TiO₄] replacement of [SiO₄] makes [SiO₄] be out of the glass framework, a part of which is easy to be eroded by alkali and migrate into the lye. So relative weight loss of SiO₂ becomes bigger. On the occasion that alkaline oxide is adequate, the more TiO₂ is introduced, the more the [TiO₄], the more the [SiO₄] being replaced out of the framework, the bigger the relative weight loss of SiO₂. On the other hand, the graft effect is the same as the process of Al₂O₃ network patching, which makes [TiO₄₋₂] and [SiO₄₋₂] form a mixed framework of silicate titanate, and can enhance the alkali resistance.

When TiO₂ content comes to a certain degree, the proportion of Ti⁴⁺ may increase, the [SiO₄] quantity stops increasing, and the quantity of [TiO₄] begins to increase. The influence of [TiO₄] on the alkali resistance of the glass is also exerted in two aspects. In one aspect, [TiO₄] causes secondary ions polarization and decreases the alkali resistance. Ti⁴⁺ field strength is strong such as 1.25 in [TiO₄] which leads to Si—O bond anti-polarization and even makes [SiO₄] break. To a certain degree, the bigger the content of TiO₂, the more intense the anti-polarization, the more the broken [SiO₄], and the bigger the relative weight loss of SiO₂. This is secondary ions polarization (anti-polarization) of TiO₂. This not only makes the alkali resistance decrease, but also easily leads to its phase change (phase separation or crystallization). As a result, the glass is opaque instead of transparent. The other aspect is [TiO₄] power anti-erosion covering, which can increase the alkali resistance. The alkali erosion process of silicate glass may be considered as dissolution. TiO₂ erosion can be described as follows:

\[
\text{Ti}(IV) + 4\text{OH}^- + (n - 2)\text{H}_2\text{O} = \text{TiO}_2 \cdot n\text{H}_2\text{O} (\text{existing in the form of } [\text{TiO}_4]^{-})
\]

\[
\text{TiO}_2 \cdot n\text{H}_2\text{O} + 2\text{NaOH} = \text{Na}_2\text{TiO}_3 + (n + 1)\text{H}_2\text{O}
\]

4 IR Spectroscopy Analysis

In order to explain the interdict structure of glass, IR spectroscopy was used. Transparent thin sheet glasses numbered as 1, 4 and 6 were made by KBr tablet pressing method after drying them by an infrared lamp and put on