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<td>Author(s)</td>
<td>Iwamoto, Nobuya; Umesaki, Norimasa</td>
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Crystallization Behavior of Synthetic Blast Furnace Slag by TiO₂

Nobuya IWAMOTO* and Norimasa UMESAKI**

Abstract

To reutilize blast furnace slag, crystallization behavior of synthetic one with the addition of TiO₂ which plays effectively for nuclei formation was studied with the use of many analyzing means such as differential thermal analysis (DTA), X-ray diffraction, infrared absorption (IR), optical and scanning electron microscopes.

KEY WORDS: (Slag) (Steelmaking) (Ironmaking) (Glass) (Crystallization) (Rutile)

1. Introduction

In iron- and steel-making, slag plays an important role for the refinement. However a large quantity of slag, amounts to 40 per cent of pig iron, can be produced. Since sixteenth century blast furnace slag has been utilized on a small scale. At present it is widely used for civil engineering such as pavement and aggregate for concrete. In such utilization it is necessary to give a suitable strength and hardness to slag. The technique of partial crystallization was applied in order to get such properties¹,².

Usually TiO₂ and ZrO₂, which are effective nucleating catalysts¹⁻⁸, are contained in blast furnace slag. Therefore it became necessary to separate the combined effects to know precisely each action for controlling the crystallization behavior of slag.

In this paper, crystallization behavior of synthetic blast furnace slag containing varying amounts of TiO₂ was studied with the use of various analyzing means such as differential thermal analysis (DTA), X-ray diffraction, infrared absorption (IR), optical and scanning electron microscopes.

2. Experimental Procedures

The composition of parent synthetic blast furnace slag is given in Table 1. The parent slag and TiO₂ weighed were thoroughly mixed and melted in platinum crucible at 1500°C for one hour in air, and then quenched into ice-cooled water. To cause crystallization, these specimens were then heattreated for one hour at 950°C or 1000°C, and then quenched into ice-cooled water. In order to know the degree of crystallization in these specimens, DTA, X-ray diffraction and IR measurements were carried out. Further, the observations under optical microscope and SEM were performed. These experimental conditions are as follows:

[DTA]
- Heating rate: 5°C/min.
- Specimen: powder
- Standard material: corundum

[X-ray diffraction]
- Target: CuKα, with Ni filter
- Current and Voltage: 35 KV × 15 mA

[IR]
- Range: 2000 - 400 cm⁻¹
- Specimen: KBr disk

[Optical microscopy]
- Etchant: 5% nital (30 min)

[SEM]
- Etchant: 5% nital (30 min)
- Accelerating voltage: 20 KV
- Surface treatment: Au evaporation

In Table 2, measuring instrument used and the remark of each specimens are summarized.

Table 1 Chemical composition of parent slag (Wt%)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>CaO/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.00</td>
<td>42.88</td>
<td>15.98</td>
<td>5.46</td>
<td>0.35</td>
<td>1.225</td>
</tr>
</tbody>
</table>

† Received on September 17, 1979
* Professor
** Research Associate

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Table 2 Analysis performed and changes detected in the slag after each heat-treatment cycle.

<table>
<thead>
<tr>
<th>Specimen TiO₂ (Wt%)</th>
<th>Heat-treatment (°C x time)</th>
<th>Analysis performed</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>As-quenched glass</td>
<td>DTA, Xrd, IR, Optm, SEM</td>
<td>Dark brown colour</td>
</tr>
<tr>
<td></td>
<td>950 x 1 hr</td>
<td>Xrd, IR, Optm, SEM</td>
<td>Opalescence</td>
</tr>
<tr>
<td></td>
<td>1000 x 1 hr</td>
<td>Xrd, IR</td>
<td>Ceramics</td>
</tr>
<tr>
<td>2</td>
<td>As-quenched glass</td>
<td>DTA, Xrd, IR, Optm, SEM</td>
<td>Dark brown colour</td>
</tr>
<tr>
<td>5</td>
<td>As-quenched glass</td>
<td>DTA, Xrd, IR, Optm, SEM</td>
<td>Dark brown colour</td>
</tr>
<tr>
<td></td>
<td>950 x 1 hr</td>
<td>Xrd, IR, Optm, SEM</td>
<td>Opalescence</td>
</tr>
<tr>
<td></td>
<td>1000 x 1 hr</td>
<td>Xrd, IR</td>
<td>Ceramics</td>
</tr>
<tr>
<td>10</td>
<td>As-quenched glass</td>
<td>DTA, Xrd, IR, Optm, SEM</td>
<td>Dark brown colour</td>
</tr>
<tr>
<td></td>
<td>950 x 1 hr</td>
<td>Xrd, IR, Optm, SEM</td>
<td>Opalescence</td>
</tr>
<tr>
<td></td>
<td>1000 x 1 hr</td>
<td>Xrd, IR</td>
<td>Ceramics</td>
</tr>
</tbody>
</table>

Description:
DTA, differential thermal analysis
Xrd, X-ray diffraction
IR, infrared absorption
Optm, optical microscopy
SEM, scanning electron microscopy

3. Experimental Results

3.1 Differential thermal analysis

Figure 1 shows result of DTA. In Table 3, transition point of glass (T₆) and crystallization with exothermic peak

![Figure 1](image)

Table 3 Transformations during DTA.

<table>
<thead>
<tr>
<th>Specimen TiO₂ (Wt%)</th>
<th>Transition point of glass T₆ (°C)</th>
<th>Crystalline temp. T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>766</td>
<td>936, 963</td>
</tr>
<tr>
<td>2</td>
<td>757</td>
<td>955</td>
</tr>
<tr>
<td>5</td>
<td>753</td>
<td>940</td>
</tr>
<tr>
<td>10</td>
<td>738</td>
<td>929</td>
</tr>
</tbody>
</table>

(T_c) obtained from Fig. 1 are summarized. Endothermic peak ranging before and after nearly 900°C is originated from softening and nucleation. The peak changed to lower temperature with increasing TiO₂ content. T_c means that the degree of crystal growth becomes maximum at this temperature. The parent slag without TiO₂ showed two peaks at 936°C and 963°C. It seems probable that crystallized specimen at 936°C commences phase transition at 963°C.

When TiO₂ was added, separation of T_c did not occur and T_c decreased.

3.2 X-ray diffraction

X-ray diffraction patterns obtained are shown in

![Image](image)
Figure 2. When parent slag without TiO$_2$ and slag containing 5% TiO$_2$ were heat-treated at 950°C for 1 hr, few peaks showing formation of crystal were observed except broad pattern.

Fig. 2 X-ray diffraction patterns of slag, parent and containing TiO$_2$, heat treated at various temperatures.

However slag containing 10% TiO$_2$ exhibited many peaks after that heat treatment and their intensities became stronger with the heat treatment at higher temperature.

Crystal precipitated from each specimens is melilitite which is solid solution from gehlenite (Ca$_2$Al$_2$Si$_2$O$_7$) and akermanite (Ca$_2$MgSi$_2$O$_7$). In fig. 2, sites and intensities of diffraction patterns of gehlenite and akermanite were shown. At present diffraction peak appeared in the specimens, parent slag heat treated at 950°C and 1000°C and slag containing 5% TiO$_2$ heat treated at 950°C, remain unresolved.

3.3 Infrared absorption

Infrared absorption spectra are shown in Figure 3. Broad absorption from 1100 to 800 cm$^{-1}$ originates to Si-O $\nu_3$ stretching. Although every specimens heat treated at 1000°C exhibited many absorption peaks, it remains unknown to where the peaks must be assigned.

3.4 Optical and scanning microscopy, and electron probe analysis

Photo. 1 show textures of parent slag without TiO$_2$ heat treated at 950°C and 1000°C for 1 hr. Precipitates were observed at surface and interior of specimen heat treated at 950°C. As the temperature increased to 1000°C, probably smallest crystals were formed wholly and found traces of larger spherical crystal.

Photo. 2 show that spherical precipitate appeared by heat treatment at 950°C contains much magnesium than matrix. Probably it means that at first akermanite precipitated in the crystallization process.

In Table 4, energy of characteristic X-ray is given.

Photo. 3 and 4 show textures under optical and scanning electron microscopes, and the result of microanalysis.
Photo 1  Texture under optical microscope (parent slag).
(a): heat treated at 950°C for 1 hr, surface
(b): heat treated at 950°C for 1 hr, interior
(c): heat treated at 1000°C for 1 hr, surface
(d): heat treated at 1000°C for 1 hr, interior

Photo 2  Micro analysis of parent slag heat treated at 950°C and 1000°C for 1 hr.
(a): analysis of spherical precipitate, 950°C × 1 hr
(b): analysis of matrix, 950°C × 1 hr
(c): micro structure, 1000°C × 1 hr
(d): analysis of specimen, 1000°C × 1 hr
Photo 3  Texture under optical microscope (slag containing 5% TiO_2).
(a): surface, 950°C X 1 hr  (c): surface, 1000°C X 1 hr
(b): interior, 950°C X 1 hr  (d): interior, 1000°C X 1 hr

Photo 4  Micro analysis of slag containing 5% TiO_2 heat treated at
950°C and 1000°C for 1 hr.
(a): analysis of rosette-like precipitate, 950°C X 1 hr
(b): analysis of spherical precipitate except rosette-like one, 950°C X 1 hr
(c): analysis of glassy matrix, 950°C X 1 hr
(d): micro structure, 1000°C X 1 hr
**Photo. 5** Texture under optical microscope (slag containing 10% TiO$_2$).

(a): surface, 950°C X 1 hr  
(b): interior, 950°C X 1 hr  
(c): surface, 1000°C X 1 hr  
(d): interior, 1000°C X 1 hr

**Photo. 6** Micro analysis of slag containing 10% TiO$_2$.

(a): analysis of surface layer precipitated, 950°C X 1 hr  
(b): analysis of matrix, 950°C X 1 hr  
(c): micro structure, 1000°C X 1 hr
of slag containing 5% TiO₂ which was heat-treated at 950°
and 1000°C. Similarly precipitation occurs at surface and
interior of specimen. When compared with parent slag, 
precipitating layer at surface becomes thicker. Further
another rosette-like precipitate was appeared in the
spherical one. According to the result by microanalysis,
rosette-like region contained much magnesium, but other
region contained much titan. It can consider that titan
works crystallization effectively. When heat-treatment
increased to 1000°C, rosette-like precipitate remained in a
small part.

Photos 5 and 6 show textures under optical and scanning
electron microscopes, and the result of micro-analysis
of slag containing 10% TiO₂ which was heat-treated at
950° and 1000°C. Likewise precipitation occurred from
surface and interior of specimen. When compared one from
specimen containing 5% TiO₂, the thickness of surface
layer and the size of spherical precipitate increased and
gross crystal boundary in whole crystals precipitated.
When the heat-treatment increased to 1000°C, texture
became homogeneous with the smallest crystals except
surface precipitate.

### Table 4

<table>
<thead>
<tr>
<th>Element</th>
<th>Kα₁</th>
<th>Kα₂</th>
<th>Kβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.25</td>
<td>1.25</td>
<td>1.30</td>
</tr>
<tr>
<td>Al</td>
<td>1.49</td>
<td>1.49</td>
<td>1.55</td>
</tr>
<tr>
<td>Si</td>
<td>1.74</td>
<td>1.74</td>
<td>1.83</td>
</tr>
<tr>
<td>Ca</td>
<td>3.69</td>
<td>3.69</td>
<td>4.01</td>
</tr>
<tr>
<td>Ti</td>
<td>4.51</td>
<td>4.52</td>
<td>4.93</td>
</tr>
<tr>
<td>Fe</td>
<td>7.10</td>
<td>6.41</td>
<td>7.06</td>
</tr>
</tbody>
</table>

### 4. Summary

When parent slag and slag containing 5 and 10% TiO₂
was heat-treated, precipitation layer at surface and spherical
precipitate in interior of specimen was found. With
the addition of TiO₂, temperature commencing nuclea-
tion and growth decreased. Accordingly crystallization
can be promoted in the case of slag containing TiO₂ with
same heat-treatment above crystallization temperature
when compared with slag without TiO₂. Especially with
the addition of 10% TiO₂ crystallization proceeded
rapidly.

Micro structure of spherical precipitate changed remark-
ably with or without TiO₂. In the specimen contain-
ing 5% TiO₂ heat-treated at 950°C for 1 hr segregation of
titan occurred in spherical precipitate. From this it can
recognize that titan works effectively changing the
concentration on crystallization⁹. Precipitate was mellilite
which is solid solution from gehlenite and akermanite.

### References

1) M.W. Davies, B. Kerrison, W.E. Cross, M.J. Robson and
39 (1956), p.188.