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Author(s)	Iwamoto, Nobuya; Umesaki, Norimasa
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Crystallization Behavior of Synthetic Blast Furnace Slag by TiO_2 †

Nobuya IWAMOTO* and Norimasa UMESAKI**

Abstract

To reutilize blast furnace slag, crystallization behavior of synthetic one with the addition of TiO_2 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 untilized 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 properties[1),2)].

Usually TiO_2 and ZrO_2, which are effective nucleating catalysts[1) -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 TiO_2 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 TiO_2 weighed were throughly 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° 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:

Table 1 Chemical compostion of parent slag (Wt%)

SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	CaO/SiO_2
35.00	42.88	15.98	5.46	0.35	1.225

[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 summerized.

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* Professor
** Research Associate

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

Specimen TiO_2 (Wt%)	Heat-treatment (°C x time)	Analysis performed	Remarks
0	As-quenched glass	DTA, Xrd, IR, Optm, SEM	Dark brown colour
	950 x 1 hr	Xrd, IR, Optm, SEM	Opalescence
	1000 x 1 hr	Xrd, IR	Ceramics
2	As-quenched glass	DTA, Xrd, IR, Optm, SEM	Dark brown colour
5	As-quenched glass	DTA, Xrd, IR, Optm, SEM	Dark brown colour
	950 x 1 hr	Xrd, IR, Optm, SEM	Opalescence
	1000 x 1 hr	Xrd, IR, Optm, SEM	Ceramics
10	As-quenched glass	DTA, Xrd, IR	Dark brown colour
	950 x 1 hr	Xrd, IR, Optm, SEM	Opalescence
	1000 x 1 hr	Xrd, IR, Optm, SEM	Ceramics

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 (T_g) and crystallization with exthermic peak

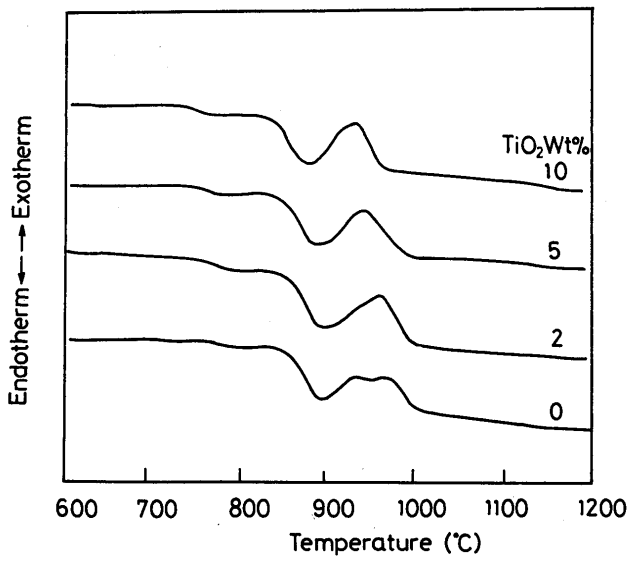

Fig. 1 Thermograms of slag, parent and containing TiO_2.

Table 3 Transformations during DTA.

Specimen TiO_2 (Wt%)	Transition point of glass T_g (°C)	Crystalline temp. T_c (°C)
0	766	936, 963
2	757	955
5	753	940
10	738	929

(T_c) obtained from Fig. 1 are summerized. Endothermic peak ranging before and after nearly 900°C is originated from softing and nucleation. The peak changed to lower temperature with increasing TiO_2 content. T_c means that the degree of crystal growth becomes maximum at this temperature. The parent slag without TiO_2 showed two peaks at 936° and 963°C. It seems probable that crystallized specimen at 936°C commences phase transition at 963°C.

When TiO_2 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

Figure 2. When parent slag without TiO_2 and slag containing 5% TiO_2 were heattreated at 950°C for 1 hr, few peaks showing formation of crystal were observed except broad pattern.

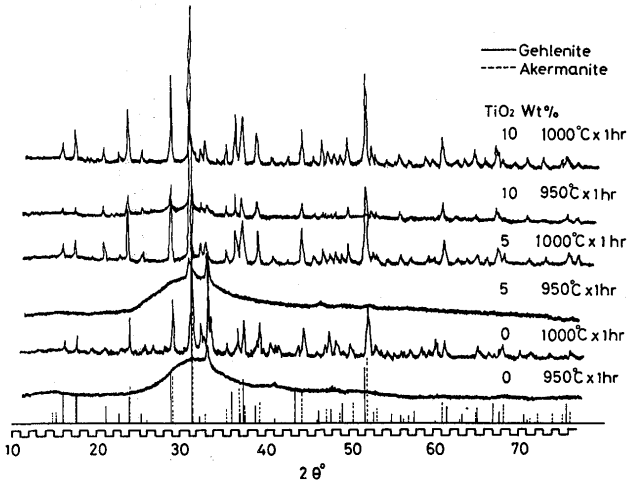

Fig. 2 X-ray diffraction patterns of slag, parent and containing TiO_2, heattreated at various temperatures.

However slag containing 10% TiO_2 exhibited many peaks after that heattreatment and their intensities became stronger with the heattreatment at higher temperature.

Crystal presipitated from each specimens is melilite which is solid solution from gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$). 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 heattreated at 950° and 1000°C and slag containing 5% TiO_2 heattreated 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 ν_3 stretching. Although every specimens heattreated at 1000°C exhibited many absorption peaks, it remains unknown to where the peaks must be assigned.

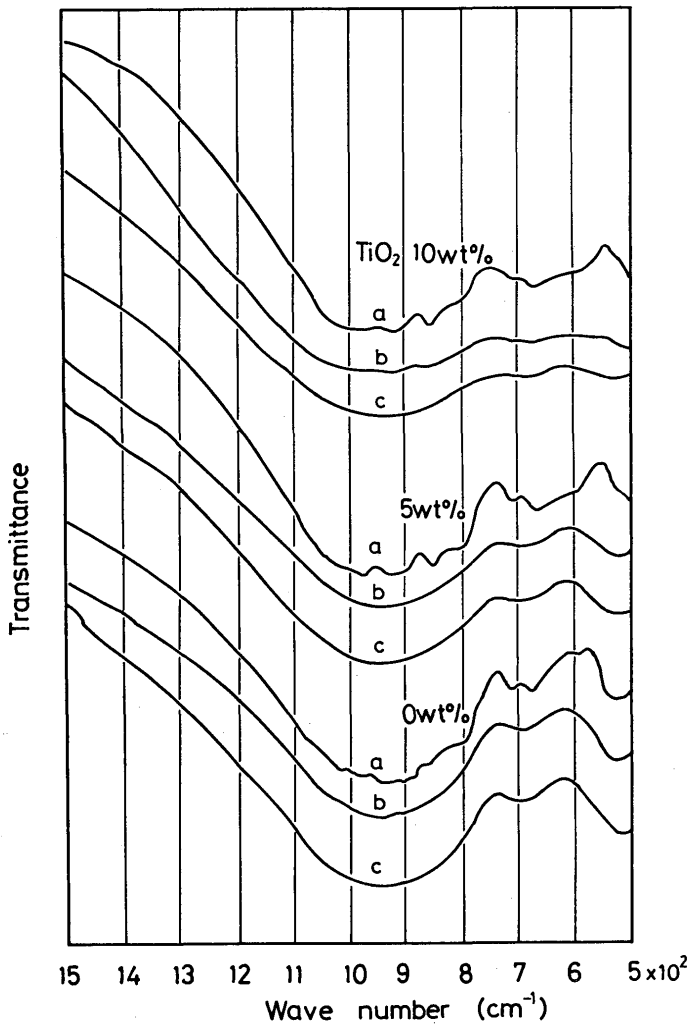

Fig. 3 Infrared absorption result of slag, parent and containing TiO_2, heattreated at various temperatures.
(a): heattreated at 1000°C for 1 hr
(b): heattreated at 950°C for 1 hr
(c): original glassy specimen

3.4 Optical and scanning microscopy, and electron probe analysis

Photo. 1 show textures of parent slag without TiO_2 heattreated at 950° and 1000°C for 1 hr. Precipitates were observed at surface and interior of specimen heattreated 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 heattreatment 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

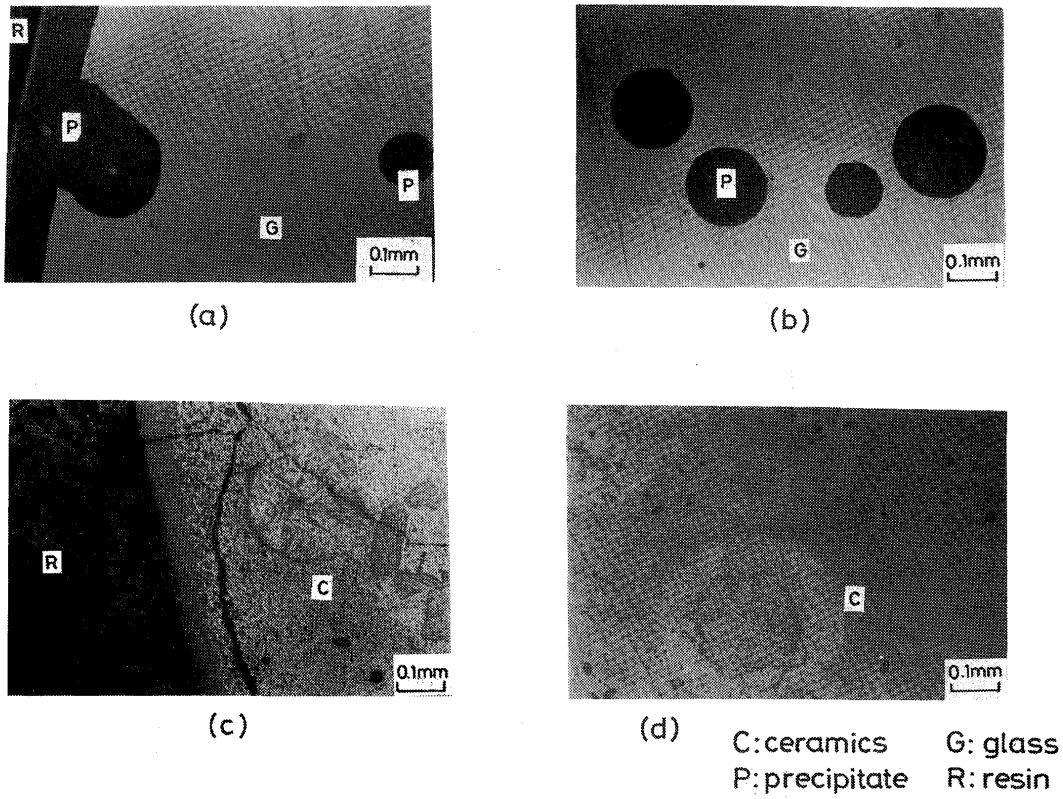

Photo. 1 Texture under optical microscope (parent slag).
(a): heattreated at 950°C for 1 hr, surface (c): heattreated at 1000°C for 1 hr, surface
(b): heattreated at 950°C for 1 hr, interior (d): heattreated at 1000°C for 1 hr, interior

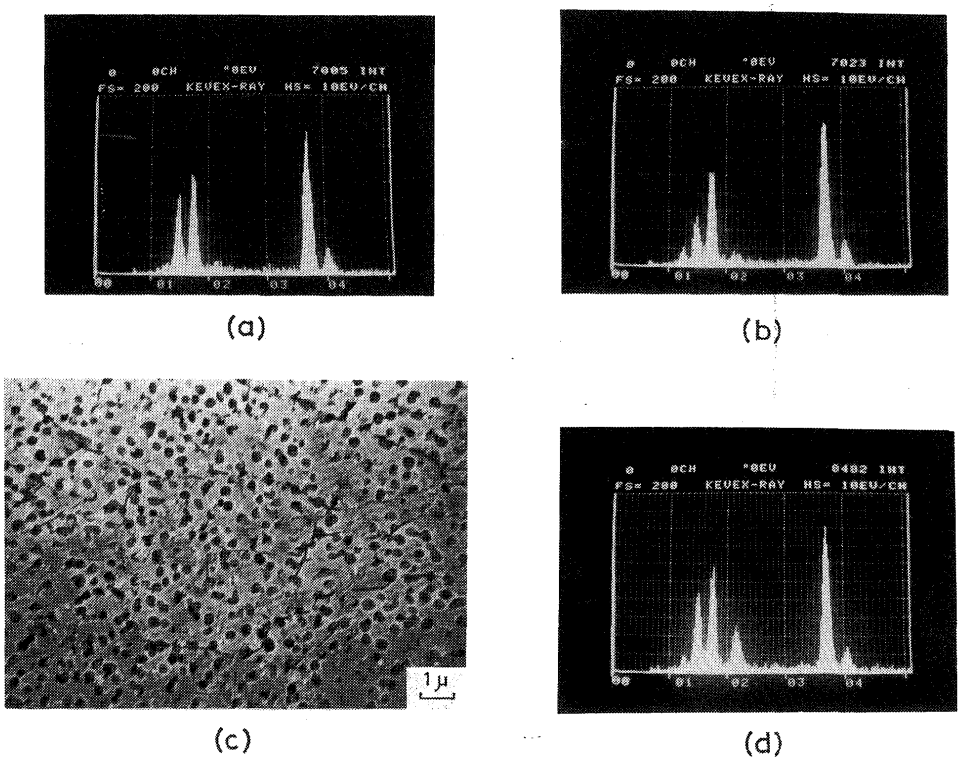

Photo. 2 Micro analysis of parent slag heattreated at 950° and 1000°C for 1 hr.
(a): analysis of spherical precipitate, 950°C × 1 hr (c): micro structure, 1000°C × 1 hr
(b): analysis of matrix, 950°C × 1 hr (d): analysis of specimen, 1000°C × 1 hr

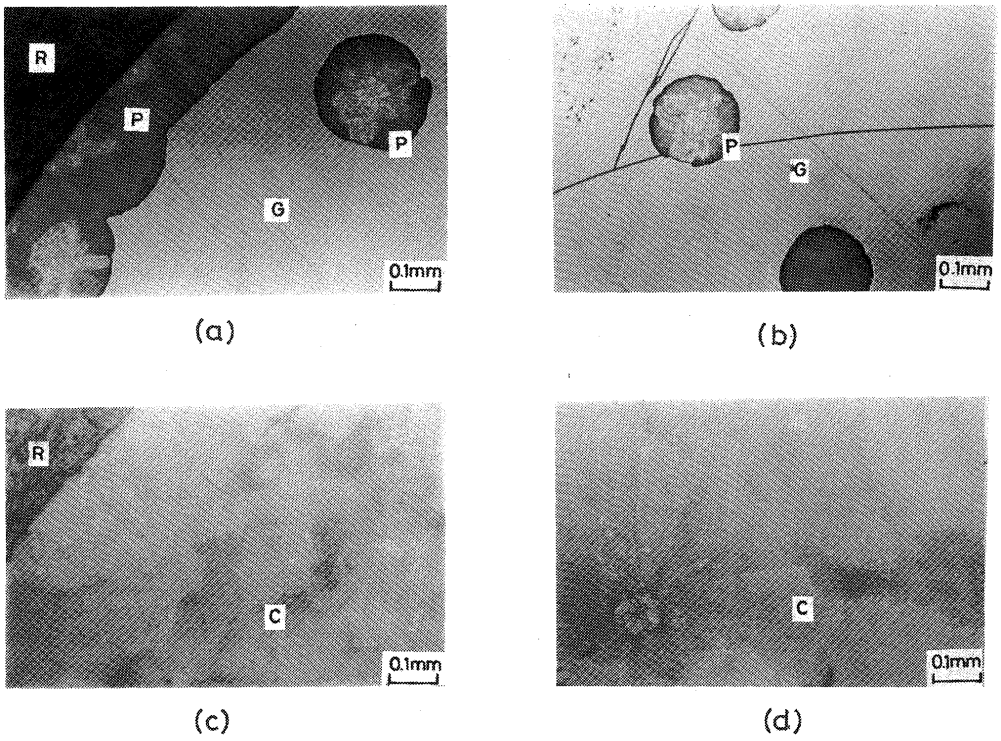

Photo. 3 Texture under optical microscope (slag containing 5%TiO_2).
(a): surface, 950°C × 1 hr (c): surface, 1000°C × 1 hr
(b): interior, 950°C × 1 hr (d): interior, 1000°C × 1 hr

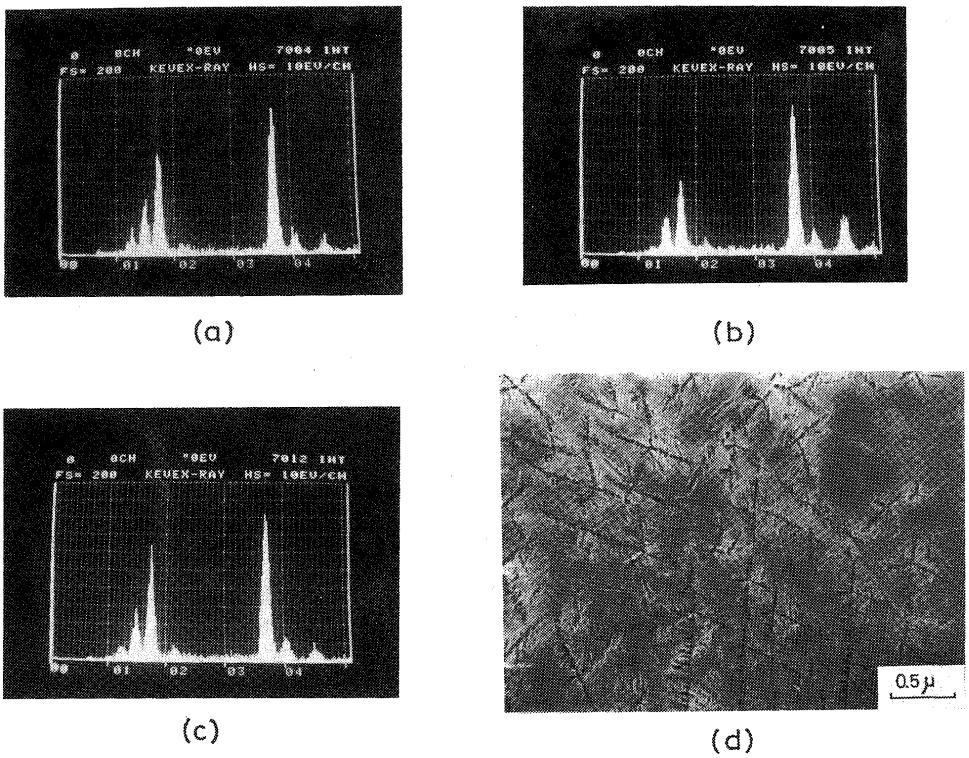

Photo. 4 Micro analysis of slag containing 5% TiO_2 heattreated at 950° and 1000°C for 1 hr.
(a): analysis of rosette-like precipitate, 950°C × 1 hr
(b): analysis of spherical precipitate except rosette-like one, 950°C × 1 hr
(c): analysis of glassy matrix, 950°C × 1 hr
(d): micro structure, 1000°C × 1 hr

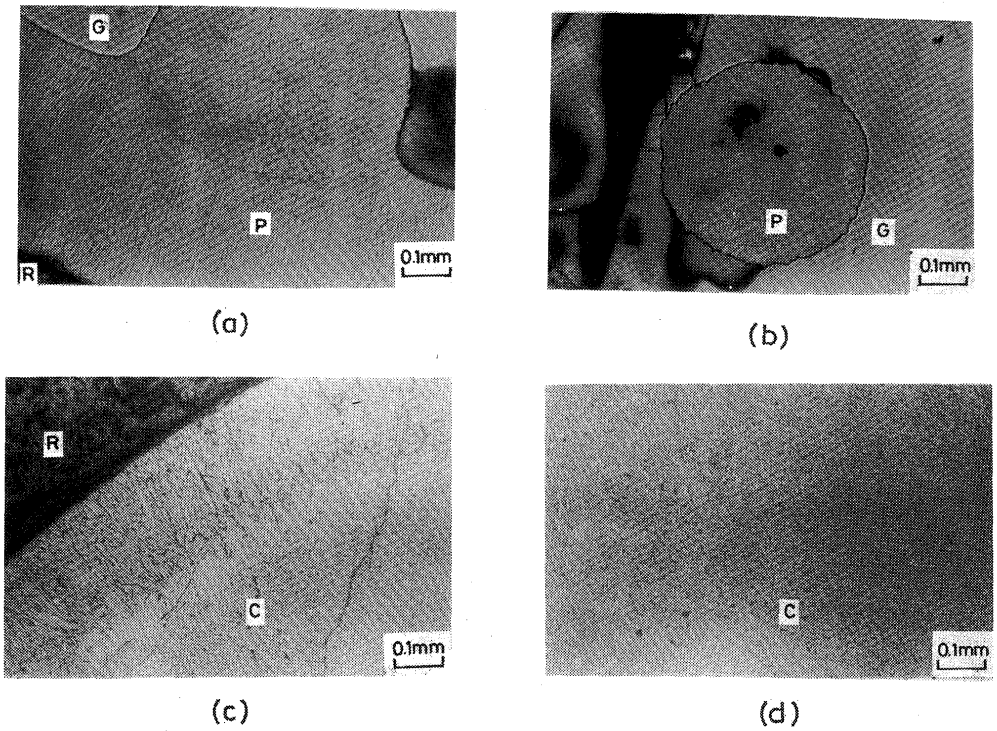

Photo. 5 Texture under optical microscope (slag containing 10% TiO_2).
(a): surface, 950°C × 1 hr
(b): interior, 950°C × 1 hr
(c): surface, 1000°C × 1 hr
(d): interior, 1000°C × 1 hr

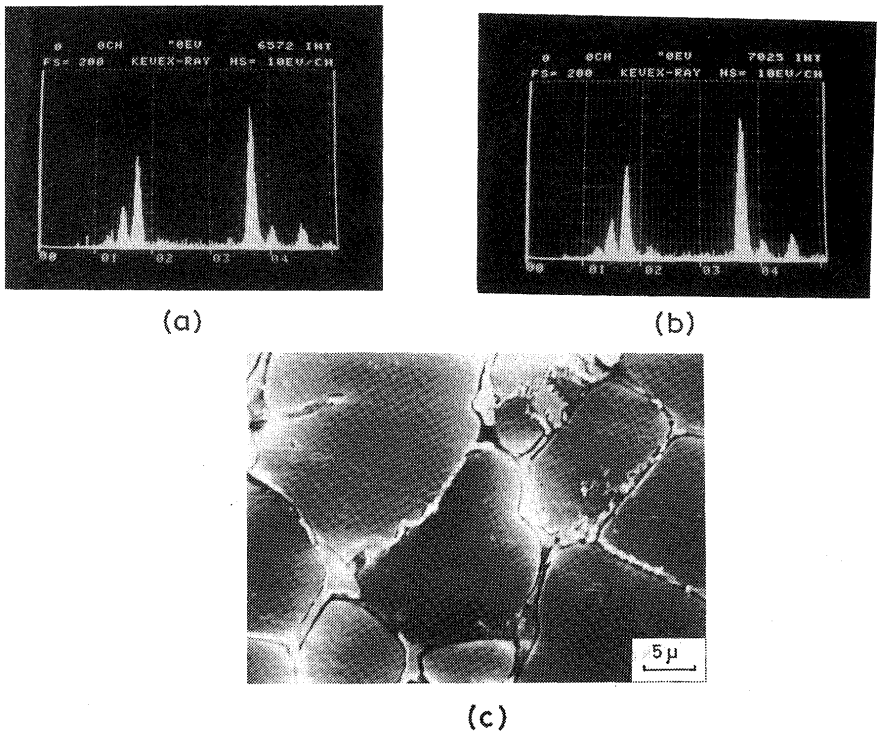

Photo. 6 Micro analysis of slag containing 10% TiO_2.
(a): analysis of surface layer precipitated, 950°C × 1 hr
(b): analysis of matrix, 950°C × 1 hr
(c): micro structure, 1000°C × 1 hr

Table 4 Energies of characteristic X-ray excited of elements composed of specimen.

Element	$K\alpha_1$	$K\alpha_2$	$K\beta$
Mg	1.25	1.25	1.30
Al	1.49	1.49	1.55
Si	1.74	1.74	1.83
Ca	3.69	3.69	4.01
Ti	4.51	4.52	4.93
Fe	7.10	6.41	7.06

of slag containing 5% TiO_2 which was heattreated 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 spheretical 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 heattreatment 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% TiO_2 which was heattreated at 950° and 1000°C. Likewise precipitation occurred from surface and interior of specimen. When compared one from specimen containing 5% TiO_2, the thickness of surface layer and the size of spherical precipitate increased and gross crystal boundary in whole crystals precipitated. When the heattreatment increased to 1000°C, texture became homogeneous with the smallest crystals except surface precipitate.

4. Summary

When parent slag and slag containing 5 and 10% TiO_2 was heattreated, precipitation layer at surface and spherical precipitate in interior of specimen was found. With the addition of TiO_2, temperature commencing nucleation and growth decreased. Accordingly crystallization can be promoted in the case of slag containing TiO_2 with same heattreatment above crystallization temperature when compared with slag without TiO_2. Especially with the addition of 10% TiO_2 crystallization proceeded rapidly.

Micro structure of spherical precipitate changed remarkably with or without TiO_2. In the specimen containing 5% TiO_2 heattreated at 950°C for 1 hr segregation of titan occurred inspherical precipitate. From this it can recogneize that titan works effectively with changing the concentration on crystallization[9]. Precipitate was melilite which is solid solution from gehlenite and akermanite.

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