Formation Mechanism of Titanium Carbide in Titanium-bearing Blast Furnace Slag

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Abstract: The formation of titanium carbide (TiC) may result in slag thickening, slag foaming and difficulty in separation between hot metal and slag etc during the blast furnace smelting process with Vanadic Titanomagnetite. Therefore, it is very important to understand and manage the formation of titanium carbide. The formation mechanism of titanium carbide during the reduction process of blast furnace slag-bearing titanium was studied with theoretical calculations and experiments. In the experiment, blast furnace slag-bearing titanium was subjected to 6 hours’ isothermal treatment at temperature range of 1300℃-1550℃ in graphite crucible with Ar flow rate of 2L/min (1 atm). The reduced slag was characterized by mineralogical microscope and SEM-EDS detection methods. As a result, the formation of titanium carbide started at a temperature higher than 1400℃.

1. Introduction
During the blast furnace smelting process with Vanadic Titanomagnetite, it is inevitable to form titanium carbide (TiC), which has high melting point (3140℃) and quite small particle size (several micrometers), either disperses in the slag or wraps around the surface of iron droplet, thus causing slag thickening, slag foaming and difficulty in separation between hot metal and slag etc[1-4]. Many studies aimed at the problems. Thermodynamic calculation showed that the reduction of slag bearing-titanium to form titanium carbide was related to the chemical composition of slag, temperature and atmosphere[5-8]. Experimental studies mainly focus on viscosity evolution of slag bearing-titanium under reduction condition. Researches about the formation of titanium carbide during the reduction process of slag bearing-titanium were rare, and they concentrated on either the influence of blast furnace slag bearing-titanium raw materials on protecting the blast furnace hearth or the preparation of ceramic materials[9-15]. The paper investigated the formation condition of titanium carbide during the reduction process of blast furnace slag bearing-titanium, which would help to understand the evolution of slag properties such as viscosity during the reduction process of slag bearing-titanium, and more importantly to control the formation of titanium carbide.

2. Thermodynamic Calculation
The slag compositions were based on that of the in situ slag from Panzhihua Iron and Steel Corporation, as showed in Table 1. In the calculation, 100g of slag was assumed to involve in the reduction and then about 10g of carbon was assumed. The ratio of slag to carbon was 1:3 stoichiometrically according to...
Formula(1). The reduction was assumed under an atmospheric pressure of Argon in the temperature range from 1300℃ to 1550℃ with temperature interval of 1℃.

\[ TiO_2 + 3C = TiC + 2CO \] (1)

| Composition | CaO | SiO₂ | TiO₂ | Al₂O₃ | MgO | Total | CaO/SiO₂ |
|-------------|-----|------|------|-------|-----|-------|----------|
| Mass Fraction(%) | 28.81 | 26.19 | 23.00 | 14.00 | 8.00 | 100 | 1.10    |

3. Experimental
Slag sample of 100 g were prepared for reduction experiments. CaO, SiO₂, MgO, Al₂O₃, and TiO₂ were mixed with analytical grade according to Table 1, which contained in a corundum crucible and melt in the molybdenum disilicate furnace at 1450℃ under an argon atmosphere (flow rate was 2L/min) for 2 hours. The sample was then taken out of the furnace immediately and then rapidly quenched in air. Afterwards, the sample was crushed in a ball mill to obtained homogenized slag powders, which was used for reduction experiment later[16].

About 2.6 grams of the milled slag powders obtained above were contained in a graphite crucible (with inner size as Ø10×25mm, thickness as 5mm), which acted as container as well as reductant. Then the graphite crucible was placed at the low-temperature end in the tube furnace. A flowing Ar atmosphere (2L/min) was adopted from the very beginning and throughout the heating, reduction and cooling process. The furnace chamber was heated at a rate of 3℃/min up to the destination temperature, at which the starting materials (including the slag powders and the graphite crucible) were placed in the uniform temperature zone by upping the elevator of the furnace into the heating chamber. Then the starting materials were subjected to isothermal treatment time of 6 hours in the temperature range of 1300℃ to 1550℃ with an interval of 50℃. Subsequently, the treated samples were quenched rapidly by lowering the elevator of the furnace into the cooling chamber.

The symmetrically vertically section, grinding and polishing process were employed for the quenched samples. The phases in the polished samples, especially titanium carbide, were identified by observing the section using mineralogical microscope (ZEISS Axioskop 40 microscope and Panasonic wv-GP240 image sensor) and SEM-EDS (TESCAN VEGA II and oxford INCA Energy 350) method.

4. Results and Discussions
4.1. Morphological study
The existence and variation of gas holes in the samples treated at different temperatures could be confirmed to be related to the gas sources and melting behaviors of slag. Actually, for all the samples, the slag powders inevitably caused air entrainment. The slag partially melted to form certain amount of viscous eutectic solution, which would agglomerate the surrounding slag powders and prevent the escape of initially entrained air. So the air holes were caused in the slag at 1300℃ and 1350℃. When the temperature increased to 1400℃ and 1450℃, on the one hand, the slag totally melted and the initially entrained air almost escaped; simultaneously the reaction between the blast furnace slag-bearing titanium and the graphite commenced along with the formation of new gas (CO) on the other hand. Consequently, only small amount of residual gas existed in the slag ultimately. For the samples above 1500℃, the fierce reduction of blast furnace slag-bearing titanium with graphite, which was characterized by the formation of titanium carbide mentioned later, contributed to the formation of big bubble in the slag.

4.2. Mineralogical Morphology Analysis
As showed in Fig. 1, the longitudinal section of the sample isothermally treated at 1450℃ is selected to observe the mineralogical morphology in various parts, where gas holes are not obviously visible to
naked eyes and slag are not floated up to separate from graphite. A strip of white points aggregation, which supposed to be TiC, appeared both on the border between the slag and the gap of slag and graphite crucible (down in picture A) and on the bonding layer between the slag and the graphite crucible (left in picture B), while the white points did not dispersed in the inside body of slag (all in picture C) [17]. Other white cross-lines far from the border between the slag and the gap of slag and graphite crucible may be perovskite.

![Fig. 1 Mineralogical morphology of sample isothermally treated at 1450°C](image)

4.3. **SEM-EDS Analysis**

The polished section of sample isothermally treated at 1550°C was identified by SEM-EDS method to indentify the phases observed in the mineralogical investigation. Results of area scanning and line scanning were showed in **Fig. 2**.

**Fig. 2** were the results of line scanning by SEM-EDS method. Comparison of these elements mapping suggest that the white small area enrich in Ti and C, which confirmed the formation of titanium carbide presented as white points that were located on the border between the slag and the graphite. Thus, from **Fig. 3**, it can be seen that the particle size of titanium carbide was less than 5 micrometers, which may be responsible for slag thickening.
5. Conclusions

Both the thermodynamic calculation by FactSage and the experiment about the reduction of blast furnace slag-bearing titanium at temperature range from 1300°C to 1550°C under Ar atmosphere were conducted, and the conclusions can be summarized as follows:

The TiC initially formed at about 1400°C. With the increase of temperature, the reduction proceeded more actively, the amount of TiC increased and the amount of generated gas (CO) increased so much that the slag floated up. However, the amount of TiC found in experiment was at least low 68.61% than that calculated by FactSage due to limitation of kinetic condition. TiC mainly formed on the border between the slag and the graphite, except for that in the case of 1500°C TiC particles dispersed in the slag body due to that the slag totally floated up to separate from the bottom of graphite crucible. Furthermore, TiC particles had quite small size of minus 5 micrometers, which could be responsible for slag thickening.

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