

Investigation of Titanium Compound Formation in the Blast Furnace Hearth

JUAN-YIH WU and CHUNG-KEN HO

*Steel and Aluminum Research & Development Department
China Steel Corporation*

In order to find a proper operational procedure, it is necessary to clarify the influence of adding TiO_2 -containing materials into a blast furnace. A series of experiments concerning the reduction of TiO_2 , precipitation of titanium compounds and erosion of carbon block by flowing hot metal were carried out. The $\text{Ti}(\text{C},\text{N})$ nucleation is predominantly located on a rough surface, but not limited to superficial carbon material only. The growth rate of titanium compounds is controlled by Ti diffusion. Both a lower temperature and higher titanium content of hot metal are beneficial to the precipitation of $\text{Ti}(\text{C},\text{N})$. The minimum titanium concentration in hot metal necessary to form titanium carbonitride deposits at 1,400 and 1,500 were estimated to be 0.067% and 0.118%, respectively. In practice, the best way to form a protective layer on the hot face is to increase the titanium concentration in hot metal by adding a significant amount of titanium raw material and controlling the furnace heat to a little higher level before shutdown with intensifying hearth cooling.

1. INTRODUCTION

The main wear mechanisms for the lining of the hearth are abrasion caused by flowing hot metal/slag and corrosion caused by dissolution or chemical reaction. Once eroded, refractory are not repaired easily. Therefore, the campaign life of a blast furnace is essentially limited by the wear condition of the hearth refractory. Prolonging the campaign life of a blast furnace can be achieved by improving the design of the refractory/cooling system and furnace operation, collectively. There are many methods to decrease hearth refractory wear such as lowering productivity, temporarily throttling tuyeres, intensifying wall cooling, and adding TiO_2 -containing materials into the blast furnace. Because of its advantage of maintaining high productivity, adding TiO_2 -containing materials has been widely used. This countermeasure has two approaches: feeding with burden materials; and through tuyeres. This practice augments titanium content in hot metal to promote the formation of a protective layer on the hot face. This layer acts as an excellent insulator for refractory from erosion, thereby extending the refractory's campaign life.

TiO_2 dissolved in the slag phase will react with carbon to procure low valence titanium compounds and metallic titanium (TiO_2 , Ti_3O_5 , Ti_2O_3 , TiO , Ti).⁽¹⁻²⁾ Part of the titanium is dissolvable in hot metal, and the remainder stays in the slag phase with

low valence titanium compounds. The metallic titanium will react with carbon and nitrogen to form TiC and TiN and result in changing the properties of hot metal and slag⁽³⁾. Basically, the mechanisms of forming a protective layer on the hot face of the hearth can be divided into the following two categories⁽⁴⁻⁵⁾:

(1) Precipitation

The reactions of titanium with carbon and nitrogen in the metal phase form TiC and TiN . If the nucleation occurs on the surface of the carbon block, the nucleus can grow and form titanium carbonitride which is an ideal solid solution consisting of TiC and TiN . The content ratio of TiC/TiN in $\text{Ti}(\text{C},\text{N})$ depends on temperature and partial pressure of nitrogen. At higher temperature and lower nitrogen partial pressure, the TiC constituent becomes rich in the solid solution. The melting point of TiN and the TiC are 2,930 and 3,140, respectively. Once the titanium compounds form, they do not dissolve easily into the hot metal again. Therefore, titanium compounds are effective in extending the campaign life of the hearth refractory.

(2) Solidification

The other mechanism is the formation of a solidified layer on the surface of refractory. The hearth refractory is prone to wear due to the severe thermal, chemical and mechanical conditions existing inside the hearth. On the other hand, if the hot face of

the refractory is close to the eutectic temperature of the iron and carbon mixture, a solidified layer will be formed and the refractory wear will cease. Therefore, the erosion rate of the hearth refractory gradually decreases until a thermal equilibrium is reached. In case of the addition of TiO_2 -containing materials, the fluidity of hot metal lessens effectively as its viscosity increases, therefore a solidified protective layer forms. Although it is built up in a short time, the solidified layer will dissolve again if the thermal equilibrium is disturbed.

In general, based on the ability of providing hydrogen ion, the slag component can be divided into two categories, i.e. acid compounds and basic compounds. From this viewpoint, TiO_2 is an amphoteric compound. In theory, the viscosity of slag slightly decreases with increasing TiO_2 content. However, according to blast furnace operating experience, the viscosity of slag increases remarkably with the addition of TiO_2 . The reason is that part of TiO_2 particles are reduced to produce Ti(C,N) particles which disperse into the slag and promote the process of heterogeneous nucleation. As some anions accumulating on the surface of Ti(C,N) particles form a charge layer, the viscosity of slag increases resulting in lower fluidity. The smaller the Ti(C,N) particle size, the larger the surface area, the higher the slag viscosity.

Titanium disperses in hot metal as Ti(C,N) when its content exceeds the solubility. With the formation of Ti(C,N) , the viscosity of hot metal increases. When the titanium content is greater than 0.2%, the viscosity of the hot metal becomes remarkably sensitive to temperature⁽⁶⁾. A transition point exists on the relationship curve between the viscosity and temperature of hot metal. As long as temperature is lower than the transition point, the viscosity of the hot metal increases drastically resulting in more difficult tapping.

Therefore, overfeeding TiO_2 -containing materials may bring some operational troubles such as difficult tapping, poor permeability in the deadman and a negative influence on the product quality. It is necessary to clarify the influence of adding TiO_2 -containing materials into a blast furnace in order to find a proper operational procedure.

2. EXPERIMENTAL METHOD

To investigate the behavior of titanium in the hearth, a series of experiments, concerning the reduction of TiO_2 , the precipitation of titanium compounds and the erosion of the carbon block by flowing hot metal, were carried out. The static experiments were performed in a graphite electric furnace. The reactants were put into a graphite crucible and reduced at various temperatures under a nitrogen atmosphere. Two graphite crucibles

were used in the experiments with diameters of 22 mm and 29 mm, respectively.

The dynamic experiments were conducted in a high-frequency induction furnace. After adjusting the titanium concentration of the hot metal, carbon block samples were immersed in the slag/metal mangle and rotated circularly for one hour under a nitrogen atmosphere. To study the effect of the velocity of the hot metal on forming a protective layer, stirring rates were adjusted to simulate various flow velocities of hot metal under blast furnace conditions.

X-ray diffraction analysis was used to analyze the components of the metal sample. Metallographic analysis was done by scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1 Effect of Precipitation

To study the precipitation behavior of Ti(C,N) , the iron samples with various titanium content were held at 1,400 and 1,500 for 3hr, respectively. The relationships between the final and initial titanium content of iron are shown in Figure 1. The final titanium content of iron at 1,500 was higher than that at 1,400. Fig. 2 shows the SEM images and the element mappings of the sample reacted at 1,500 and 1,400 under 0.358% Ti content. A lot of titanium compounds were observed at the boundary between the metal phase and the wall of the graphite crucible. At the lower temperature, more titanium compounds were obtained than at the higher temperature.

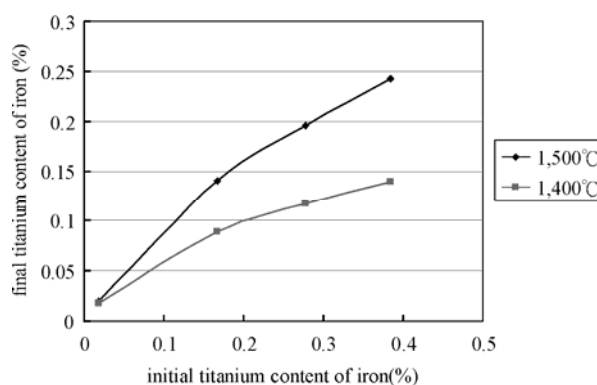


Fig. 1. Effect of initial titanium content on final titanium content in metal at various temperatures.

Except for the precipitation reaction, no reaction took place in the process of experiment. The difference between the final and initial titanium content was regarded as the precipitated Ti amount. The relation between the precipitated Ti amount and the initial titanium content of iron is shown in Figure 3. A decrease of temperature boosted the precipitation of Ti(C,N) . On

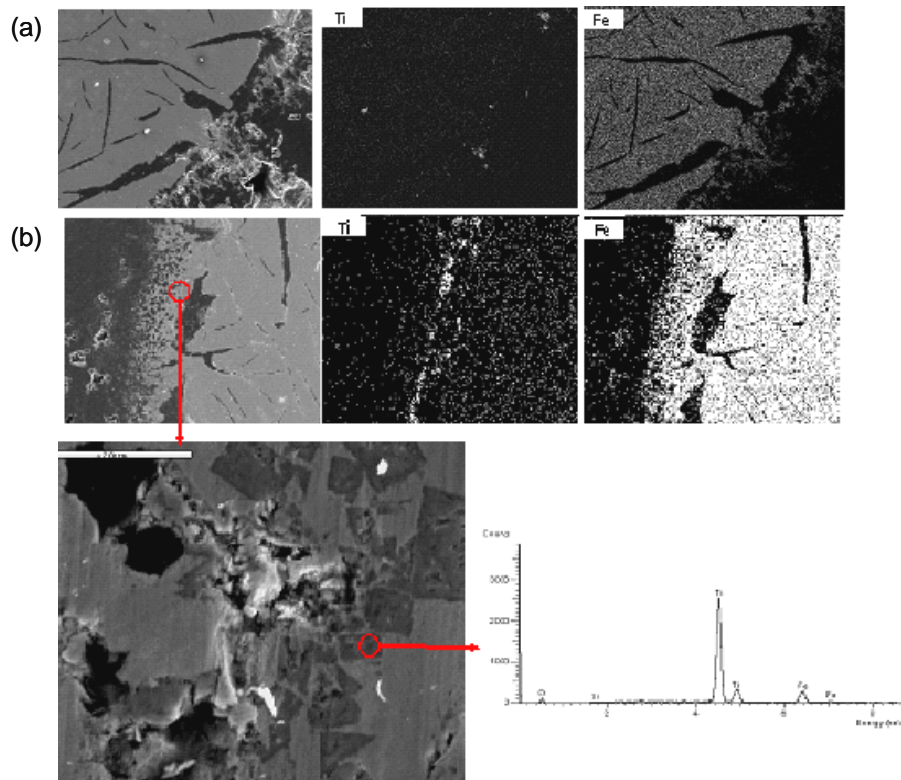


Fig. 2. The SEM images and element mappings of the 0.358% Ti content sample: (a) at 1500 °C; and (b) at 1400 °C.

the other hand, the higher the initial titanium in the metal, the greater the precipitation of Ti(C,N). As the temperature decreased, the solubility of titanium in hot metal lessened remarkably, and the supersaturated titanium in hot metal would precipitate as Ti(C,N). The lower the temperature, the larger the driving force of precipitation. The solid line was determined by a least-squares polynomial regression method and regarded as an approximately linear relationship between the precipitated Ti amount and the initial titanium content in the metal. The intersections of the regression line and horizontal-axis were ascertained by linear extrapolation as 0.067 and 0.118, respectively. Conclusively, the minimum titanium concentration in hot metal necessary to form titanium carbonitride deposits at 1,400 °C and 1,500 °C were estimated to be 0.067% and 0.118%, respectively.

To clarify the surface superiority of the carbon substrate for the nucleation of titanium compounds, a series of experiments were performed in the graphite crucible with an isolated layer coating the inner surface to prevent the hot metal from contacting the wall of the graphite crucible. Figure 4 shows the relationship between the precipitated Ti amount and the initial Ti content of iron at 1,400 °C for three hours. The mark plots the results of diameter of 22 mm without coating, and marks ▲ and ■ plot the results of diameter of 29 mm without and with coating, respectively. Firstly, accord-

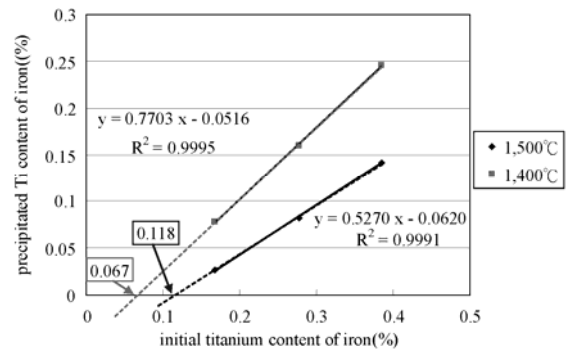


Fig. 3. Effect of initial titanium content on precipitated titanium content in metal at various temperature.

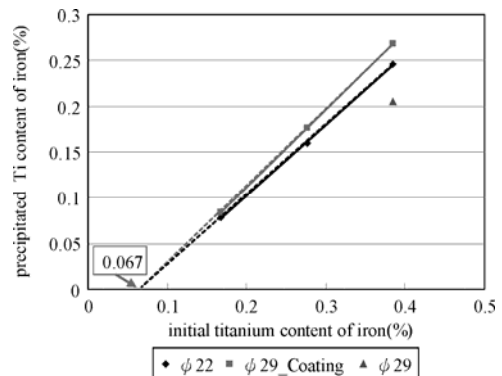


Fig. 4. Effect of initial titanium content on precipitated titanium content in metal at 1,400 °C for various diameter crucibles.

ing to the effects of coating under 0.358% Ti content, the precipitated Ti amount in the crucible with coating was higher than that without coating. This means that the nucleation also took place on the non-carbon substrate. The main difference was a rougher inner crucible surface after coating. The Ti(C,N) nucleation was predominantly located on rough surface to grow titanium compounds. Further, comparing the results of different diameters without coating under 0.358% Ti content, the precipitated amount in the small crucible was higher than in the large crucible. Due to the small crucible having a shorter diffusion path and smaller surface area, it is concluded that the precipitation of titanium compound was affected by the diffusion of titanium.

In addition, the precipitated Ti amounts of 29 mm-diameter with coating(■) were higher than those of 22 mm- diameter without coating(). It is evident that the nucleation of Ti(C,N) plays a decisive role in scaffolding. Despite having different Ti-precipitation rates, both regression lines have the same intersection with horizontal axis. This result confirms repeatedly that the

minimum titanium concentration in hot metal necessary to form titanium carbonitride at 1,400 is 0.067%. Furthermore, Ti(C,N) crystals were also found even if the hot metal contained as little as 0.018% Ti. A golden layer of Ti(C,N) crystals were found around the surface of iron contacting with crucible as shown in area A & B of Figure 5.

3.2 Effect of Velocity of Hot Metal

A comparison of the erosion of the carbon block samples stirred in molten hot metal/slag under various relative velocities is shown in Figure 6. The carbon block, BC-5, has been half eroded when the relative velocity was 0.5 m/sec. The erosion rate decreased with a decreasing relative speed. When the relative velocity was zero, the carbon block samples remained intact. For Carbural A/I, the carbon material on the surface of the block sample was slightly worn under a relative velocity 0.5 m/sec, and the frame structure remained integral. When the relative velocity was below 0.5 m/sec, erosion barely occurred in the block sample.

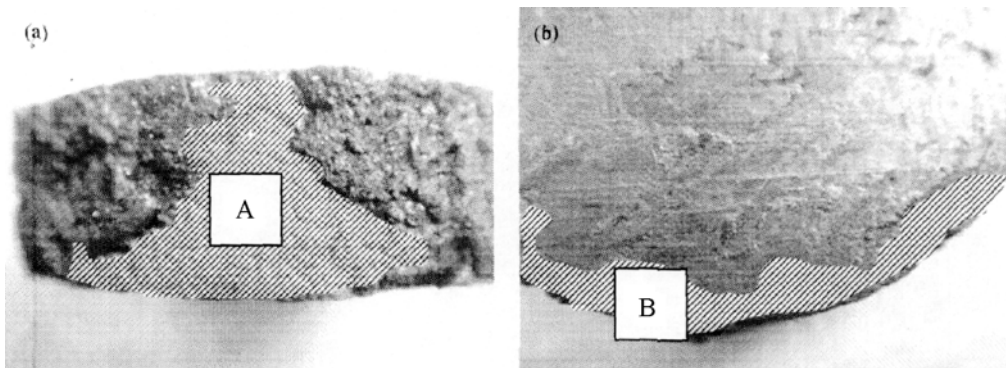


Fig. 5. Photographs of the sample reacted at 1,400 under 0.358% Ti content: (a) side wall; and (b) bottom.

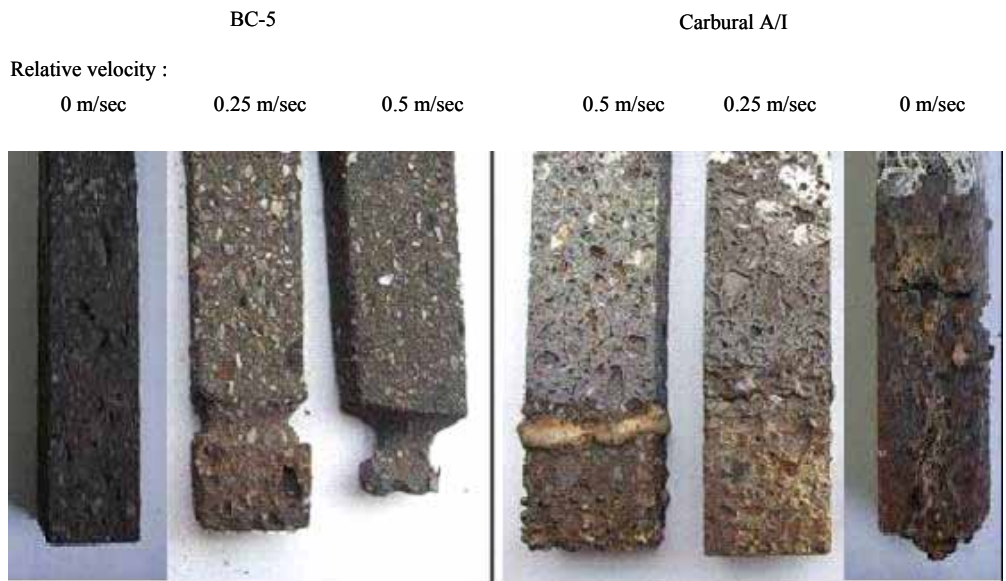


Fig. 6. The erosion of the carbon block samples stirred in molten hot metal/slag under various relative velocities.

Table 1 shows the properties of the carbon blocks of Carburized A/I and BC-5. A comparison of the oxidation effects on carbon block BC-5 and Carburized A/I is shown in Figure 7 (the left original and the right oxidized). The fixed-carbon composition of BC-5 reaches 90%, and small granules of non-carbon substance disperse in the carbon material. As the carbon material is eroded, the frame material will be exposed and peel off easily. Therefore, the frame material could not retard the erosion rate. In contrast to the BC-5, the Carburized A/I structure is built by inlaying carbon material into non-carbon substance to form a net frame structure. The frame material is made up of SiO₂, Al₂O₃ and SiC and is greatly resistant against erosion. Even when the carbon material is eroded, the frame material can retain its original net structure and protecting the carbon material from further erosion.

Due to high erosion rate and the smooth surface after erosion, it is difficult to precipitate the Ti(C,N) on a BC-5 surface. On the other hand, the surface of Carburized A/I became rugged as the carbon material was eroded, and a lot of Ti(C,N) crystals existed around the edge of the cavity. Accordingly, Carburized A/I has a su-

perior ability of anti-erosion to BC-5. Although greatly resistant to corrosion chemistry attack, carbon material is easily eroded by flowing hot metal or slag. If the flow rate of the hot metal is relatively small, formative Ti(C,N) crystals could remain and grow up to form a titanium bear.

Figure 8 shows the SEM images and the titanium mappings of the carbon block samples which reacted at 1,400 °C under 0.358% Ti content. The titanium compound is obviously precipitated on the interface of the iron and carbon block. More titanium compounds are observed on the boundary of Carburized A/I.

Table 1 Properties of carbon block BC-5 and Carburized A/I

	BC-5	Carburized A/I
Total Porosity (%)	20	2
Fixed carbon (%)	90	70
Ash (%)	8	-
SiC+SiO ₂ (%)	-	13
Al ₂ O ₃ (%)	-	9

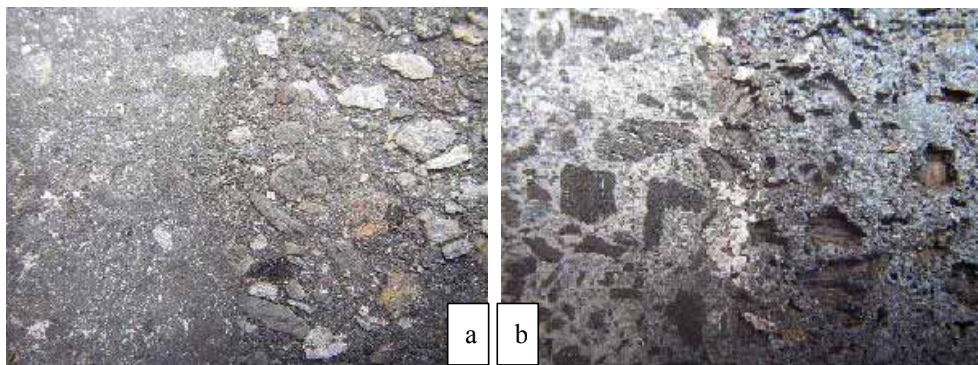


Fig. 7. Photographs comparing oxidation effects on carbon block: (a) BC-5; and (b) Carburized A/I.

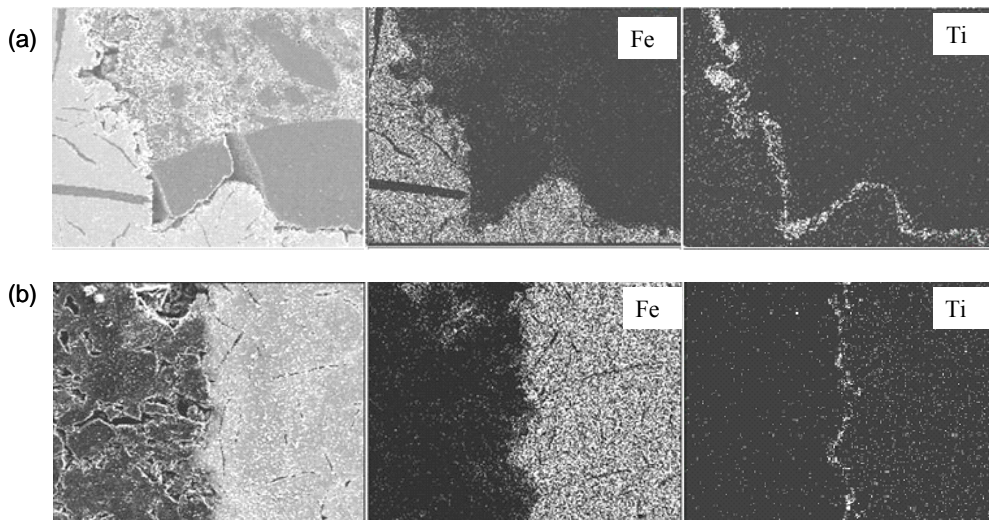


Fig. 8. The SEM images and element mappings of carbon block reacted at 1,400 °C under 0.358% Ti content: (a) Carburized A/I; and (b) BC-5.

4. SUMMARY AND CONCLUSIONS

The Ti(C,N) nucleation is predominantly located on the rough surface, but is not limited to superficial carbon material only. The growth rate of titanium compounds is controlled by Ti diffusion. Both lower temperature and higher titanium content of hot metal are beneficial for the precipitation of Ti(C,N). The minimum titanium concentration in hot metal necessary to form titanium carbonitride deposits at 1,400 and 1,500 were estimated to be 0.067% and 0.118%, respectively. In practice, the best way to form a protective layer on the hot face is to increase the titanium concentration in hot metal by adding a significant amount of titanium raw material and controlling the furnace at a slightly higher heat level before shutdown with intensifying hearth cooling.

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