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CHEMICAL AND PHASE CHARACTERISTICS OF TITANIUM COMPOUNDS PRODUCED IN IRON BLAST FURNACE DRIPPING ZONE

CHARAKTERYSTYKA CHEMICZNA I FAZOWA ZWIĄZKÓW TYTANU WYTWORZONYCH W STREFIE ŚCIEKANIA W WIELKIM PIECU

Completed research covered potential for formation of high-melting titanium compounds in the metal-slag system, for any slag with chemical constitution corresponding to initial slag and end slag in iron blast furnace. Research temperatures matched dripping zone temperatures. The TiO_2 reduction from slag phase was carried out using solid carbon (crucible walls) and carbon dissolved in iron. Then, the researchers made a qualitative analysis of microstructure in selected spots at metal-slag, metal-crucible, slag-crucible division boundaries, and phase identification from selected reaction system areas.

Przeprowadzono badania nad możliwością tworzenia się trudnotopliwych związków tytanu w układzie metal-żużel, dla żużli o składach chemicznych odpowiadających żużłom: pierwotnym i końcowym w wielkim piecu. Temperatury badań odpowiadały temperaturom strefy ściekania. Redukcję TiO_2 z fazy żużlowej prowadzono z wykorzystaniem węgla stałego (ściany tygla) jak i węgla rozpuszczonego żelazie. Następnie wykonano jakościową analizę mikrostruktury w wybranych punktach na granicy podziału metal-żużel, metal-tygiel, żużel-tygiel oraz przeprowadzono identyfikację fazową z wybranych obszarów układu reakcyjnego.

1. Introduction

Striving to reduce pig iron production costs leads to developing new and improving already existing iron production technologies. Extended iron blast furnace campaign radically reduces indirect cost of its product, that is pig iron. One of the actions undertaken to achieve this is to deliver titanium compounds into the iron blast furnace. The factor that limits iron blast furnace campaigns is its refractory lining, first of all in the zone of the process liquid products (pig iron, slag), that is in the hearth zone. Present work discusses the beneficial action of titanium compounds deposits on furnace walls.

2. Potential for titanium compounds formation in iron blast furnace

The main sources of titanium in the blast-furnace process are: ilmenite, titanium magnetite and special additives, e.g. SorelFlux mix or titanium sinter. The two first are natural materials, generally added to enrich the

product. On the other hand, SorelFlux or titanium sinter, which are often directly and intentionally brought into the iron blast furnace with ilmenite and titanium magnetite as a mix that facilitates presintering and slag formation [1]. It is known that if TiO_2 is delivered with blast-furnace charge, then titanium compounds including TiC , TiN , Ti(C,N) will be formed in the blast-furnace process conditions and the (“titanium bear”) lining will be deposited on the furnace walls and will form microscopic protective layer. They ensure longer service life of refractory lining in blast furnace hearth [2].

Mechanisms, which allow to achieve this include reduction, dissolving and forming of complex Ti(C,N) compounds, characterised by very high melting point. Generally, the amount of titanium delivered into the furnace with the charge may decide of refractory lining strength and lifetime. Typical values may range within $4\text{-}7\text{kg/Mg}_{\text{pigiron}}$, but adding more than $20\text{kg/Mg}_{\text{pigiron}}$ causes dangerous phenomena in pig iron melting process. Delivered titanium is distributed between slag and liquid iron solution.

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Considering complicated nature of titanium distribution between individual phases, which additionally highly depends on thermodynamic conditions prevailing in the blast furnace working space, it is very difficult to match the TiO_2 additive to the charge so as to guarantee formation of protective layer within specific time. Regardless of the method used to deliver TiO_2 with the charge, we may state that the Ti compounds are subject to reduction in conditions of strong reducing environment within range of suitable temperatures.

As a result of intense TiO_2 reduction process in iron blast furnace, it gets reduced to the products including: Ti_2O_3 , TiO , TiC , and often TiN (when N_2 from blast is available) and causes rapid increase of viscosity. Final products of the TiO_2 reduction, that is TiC and TiN (among other ones) are the main reason for slag densification. It is difficult to explain why viscosity of slag containing only small amount (a few percent) of TiC increases so rapidly [3]. Most of TiO_2 added to blast-furnace charge passes into the slag, and the major part leaves blast furnace in it. Some titanium oxides are reduced to Ti soluble in liquid metal, while the rest of them form TiC and TiN , and then remain in the blast furnace as a deposit on its lining, or gets dispersed in liquid phases. Excessive amount of TiO_2 added not only increases the cost of blast-furnace process operations, but also deteriorates slag and metal liquidity. Surplus TiC or TiN on refractory lining reduces available furnace capacity. Thus, it is necessary to know conditions governing formation of the Ti(C,N) compounds in this system. Titanium distribution between slag and metal in the iron blast furnace should be adequate. However, these conditions are not fully known, and the mechanism of Ti(C,N) formation is not fully explained [3].

The authors [2] carried out a research on the Ti(C,N) separation from liquid $\text{Fe-C}_{\text{sat}}\text{-Ti-N}$ solution which, as they maintain, may describe the mechanism of the Ti(C,N) release in iron blast furnace hearth. The experiment consisted in cooling down the iron solution in a crucible to the temperature, at which first crystals appeared at high cooling rate. The deposited crystals on crucible walls for various temperatures are shown in Fig. 1. The largest cluster of the Ti(C,N) crystals is visible at the crucible “cold end”, whereas only a few small crystals have been found at its “hot end”.

Temperature separation of Ti(C,N) decreases with dropping titanium amount in liquid metal. In other words, the Ti(C,N) concentration for hot metal with Ti added will be higher at lower temperatures. This is the reason for location of large Ti(C,N) amounts on the blast furnace refractory lining, where temperature drops due to local erosions. The Ti(C,N) deposit improves the isolating properties and its release proceeds until the lo-

cal temperature reaches the average value. The number and volume of the Ti(C,N) crystals precipitates decreases with growing temperature [2].

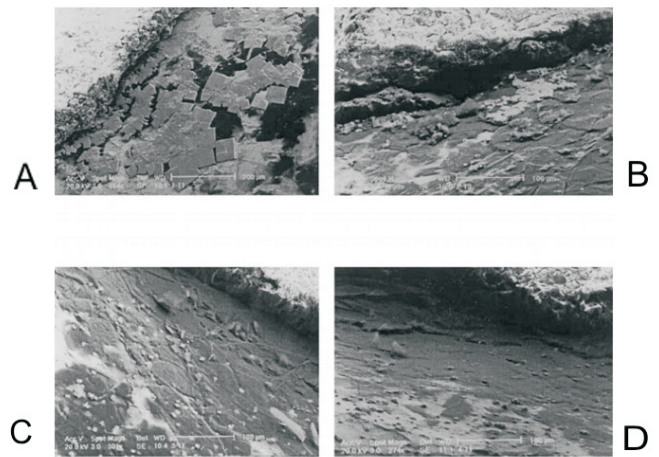


Fig. 1. Microscopic images of the Ti(C,N) crystals precipitated in different temperature zones on the crucible walls: (A) 1509K; (B) 1596K; (C) 1629K; (D) 1665K [2]

On the basis of new thermodynamic data and typical parameters of blast-furnace process, the authors [2] have determined that at the temperature of 1773K, the minimum amount of Ti needed to obtain Ti(C,N) crystals is ≈ 0.18 mass%. Proper TiO_2 concentration in slag was 1.8~2.6 mass%, the value of the $[\text{Ti}]\text{mass}\% / (\text{TiO}_2)\text{mass}\%$ ratio was: 0.07~0.1; proper titanium addition for slag amount of 200kg/ $\text{Mg}_{\text{pigiron}}$: 3.6~5.2 kg $\text{TiO}_2/\text{Mg}_{\text{pigiron}}$. Calculations proved [2] that 3.5kg $\text{TiO}_2/\text{Mg}_{\text{pigiron}}$, should be used when the refractory lining corrosion proceeds.

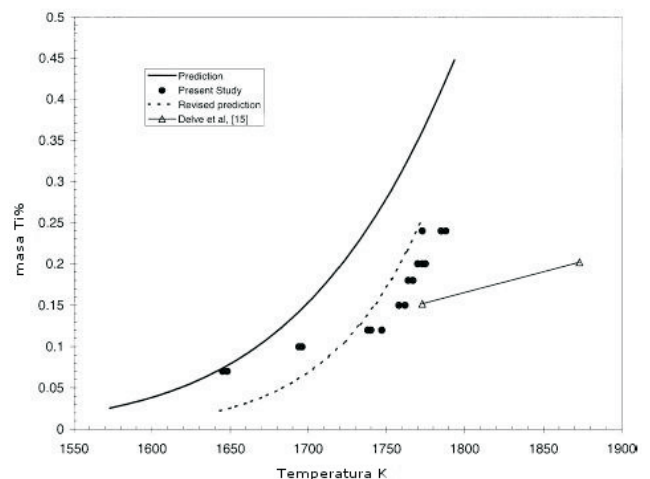


Fig. 2. Minimum titanium amount needed to form compounds of Ti(C,N) in $\text{Fe-C}_{\text{sat}}\text{-Ti}$, under the pressure of $\text{PN}_2=1.0$ atm. [2]

Titanium solubility in carbon-saturated iron in the absence of nitrogen drops with decreasing temperature. Minimum temperature necessary to precipitate Ti in

carbon-saturated iron, so as to form Ti(C,N) under pressure $p_{N_2}=1.0\text{atm.}$, should range from 1645 to 1785K, which is shown in Fig 2.

3. Own research

Taking into account relations specified before, the authors performed theoretical thermochemical calculations on transformations of titanium compounds in liquid phases (pig iron, slag) in variable conditions, which occur in the case of titanium compounds moving with blast-furnace charge from the softening zone to the blast furnace hearth.

Theoretical calculations were performed for given equilibrium conditions, chemical constitution of charge materials at the level of iron blast furnace dripping zone

(for the temperature exceeding 1250°C). The calculations were carried out using computer application FactSage – module Equilib. The authors determined possible content of titanium compounds (TiC, TiN), being formed in the state of equilibrium under the reducing atmosphere at a given, assumed gas pressure [4]. Moreover, thermodynamic analysis of titanium carbonitride formation reaction in iron blast furnace conditions was performed using the FactSage Reaction module. The standard thermodynamic potentials changes and inversion temperatures for 22 reactions of TiO_2 reduction and formation of titanium carbides in the assumed conditions, which correspond to the conditions of iron blast furnace sub-cohesion zone. Theoretical calculations provided grounds to choose reduction reactions, which may occur in the blast furnace. These reactions are specified in Table 1.

TABLE 1

Selected reduction reactions for titanium oxides

L.p.	Reactions of reduction:	ΔG_T°	$T_{\text{inversion}}$
1	$3\text{TiO}_2+\text{C}=\text{Ti}_3\text{O}_5+\text{CO}$	-219935	1061
2	$\text{TiO}_2+2\text{C}=\text{Ti}+2\text{CO}$	-107883	1874
3	$\text{TiO}+2\text{C}=\text{TiC}+\text{CO}$	-144572	1266
4	$\text{TiO}_2+3\text{C}=\text{TiC}+2\text{CO}$	-263864	1376
5	$\text{Ti}_3\text{O}_5+0,5\text{C}=1,5\text{Ti}_2\text{O}_3+0,5\text{CO}$	-53501	1486
6	$\text{Ti}_2\text{O}_3+\text{C}=2\text{TiO}+\text{CO}$	-78422	1710
7	$\text{Ti}_2\text{O}_3+3\text{C}=2\text{Ti}+3\text{CO}$	-52557	2092
8	$\text{Ti}_3\text{O}_5+5\text{C}=3\text{Ti}+5\text{CO}$	-175078	1989
9	$\text{Ti}_2\text{O}_3+5\text{C}=2\text{TiC}+3\text{CO}$	-364652	1419
10	$\text{Ti}_3\text{O}_5+8\text{C}=3\text{TiC}+5\text{CO}$	-643044	1391

The Gibbs energy changes in above reactions regard pure reagents under standard pressure of 1 atmosphere. If either substrates (titanium oxides) or products (titanium oxides or metallic titanium) are present in solution phases, their activities or concentrations should be considered. However, the obtained results of calculations suggest that thermodynamic conditions are favourable for titanium oxides reduction and titanium carbide formation.

Experimental research on the reduction of titanium oxides in the slag-metal system was carried out in order to verify theoretical calculations. At the beginning, synthetic slag was produced, with characteristics corresponding to the blast furnace slag of initial and final type. The slag was produced through high-temperature synthesis of pure constituents. Pure Armco iron saturated with carbon up to 4% constituted metallic phase. The tests were carried out in alundum and graphite crucibles. Slag and metal weight was 30 and 60g, respectively. Chosen experiment conditions corresponded to real conditions

in iron blast furnace dripping zone. The experiments included temperature values obtained in the blast furnace both at the liquid initial slag level, and at the hearth zone level. The tests were performed at the following slag compositions:

	CaO	SiO ₂	Al ₂ O ₃	MgO	TiO ₂	FeO
I slag	13,0	40,0	10,0	2,0	10	25
II slag	37,0	35,0	8,0	7,0	10	3

The reduction was carried out at the temperatures of 1350°C or 1400°C , time of all tests – 2 hours. A – slag II sample in graphite crucible (temp. 1400°C), B – slag II sample in alundum crucible (temp. 1400°C), C – slag I sample in alundum crucible (temp. 1350°C).

After holding at chosen temperature for 2h, the samples were put to cooling with the furnace. Then, metal and slag originating from completed tests were subject to chemical, phase, morphological and structural analysis. As regards blast furnace practice, slag-metal,

metal-crucible wall, and slag-crucible wall division surfaces were particularly interesting. Crucible walls and bottom were simulated there by graphite lining of the blast furnace hearth. Figure 3 shows selected reaction system areas, from which samples were taken for analysis.

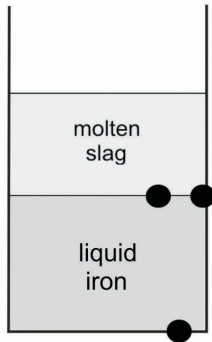


Fig. 3. The sample areas subject to chemical analysis

Analysis of titanium compounds was made at Institute for Ferrous Metallurgy (IMŻ) in Gliwice. The samples were put to tests with the Philips XL30 scanning microscope with the Edax DX4i analytical attachment. Qualitative analysis of microstructure was carried out in selected spots of areas at metal-slag, metal-crucible, slag-crucible division boundaries. All samples were subject to this analysis. Not all obtained results of analyses are shown here due to limitations of article volume. The authors present selected examples only.

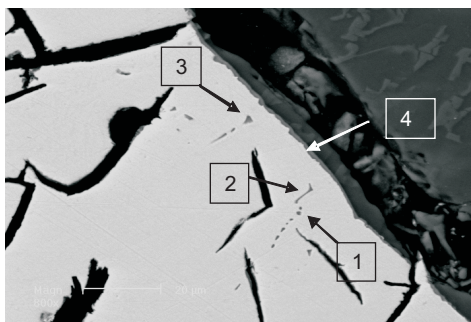


Fig. 4. The surface of sample A with the areas of local chemical analysis at metal-slag division boundary

Figure 4 presents surface microstructure in sample A at slag (right side) – metal (left side) boundary in the light of backscattered electrons, showing spots in which local analysis of chemical composition was made: 1 – globular precipitates (in metal), 2 – oblong precipitates

(in metal), 3 – triangular precipitates (in metal), 4 – layer at metal-slag boundary.

Tables 2 and 3 present the results of local chemical analyses for selected sample areas.

TABLE 2

Local chemical analysis for area 3

Element/Emission line	Mass. %	At. %
CK	3.55	13.73
SiK	0.80	1.32
TiK	32.55	31.61
VK	9.53	8.70
FeK	53.58	44.63
Suma	100.00	100.00

TABLE 3

Local chemical analysis for area 4

Element/Emission line	Mass. %	At. %
CK	3.53	11.80
MgK	1.00	1.66
AlK	4.01	5.96
SiK	6.76	9.66
CaK	5.89	5.90
TiK	67.85	56.87
VK	3.75	2.96
FeK	7.22	5.19
Suma	100.00	100.00

Precipitates of titanium compounds in metallic layer and formation of layer with high titanium concentration are visible at iron-slag phase division boundary.

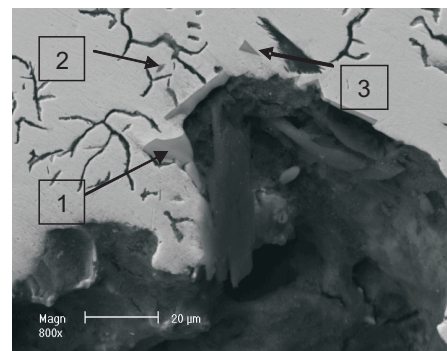


Fig. 5. The surface of sample A with the areas of local chemical analysis at metal-crucible division boundary

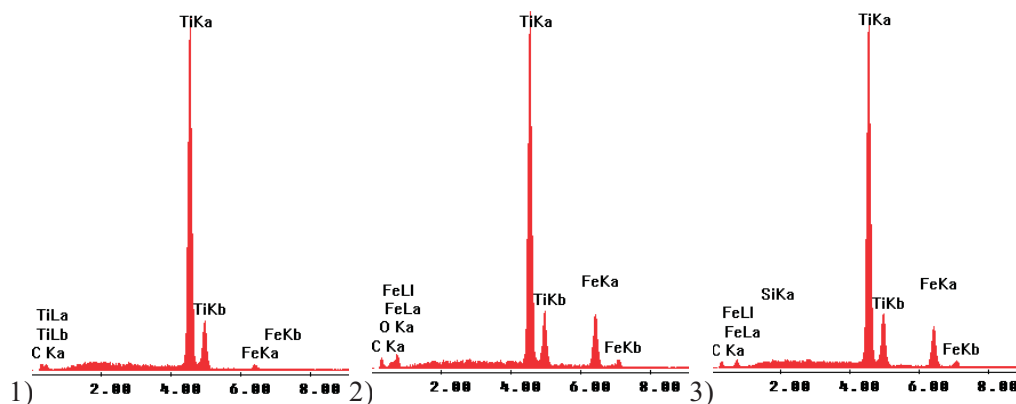


Fig. 6. Qualitative analysis in micro-areas

Figure 5 presents selected micro-areas of sample A, in which local chemical analysis was made, whereas Fig. 6 shows the results of qualitative analysis for areas 1, 2, 3 marked in the photo (Fig. 5) at metal-graphite phase division boundary.

The results of analyses for sample A indicate the presence of the layer highly enriched with titanium, which is visible at metal-slag boundary. The analysis of chemical composition in micro-areas has not shown titanium presence in the solution in metal, whereas titanium in slag is bounded in light grey phase. In dark grey phase titanium occurs in small amount only. Phase constituents, which differ in aluminium and magnesium content and contain no titanium, are also found in slag. Near metal-slag boundary in slag there are separated particles, which are different in size, and contain titanium and iron. In metal, one may also see precipitates, which are different in size and shape, and contain titanium and vanadium. In sample A near metal-graphite crucible, there are clusters of precipitates visible in the crucible material, which differ in size and consist of: titanium, iron and oxygen, and small amounts of calcium and sulphur, magnesium, silicon and sodium. At metal-crucible boundary there is a layer visible, which consists mainly of titanium, and near the boundary on metal side – there are single precipitates, which differ in shape and size, and also contain titanium. Titanium forms precipitates also at graphite-metal boundary region, at the distance of approximately 100 μm from metal-graphite boundary. Local chemical analysis proved presence of small titanium amounts in the graphite.

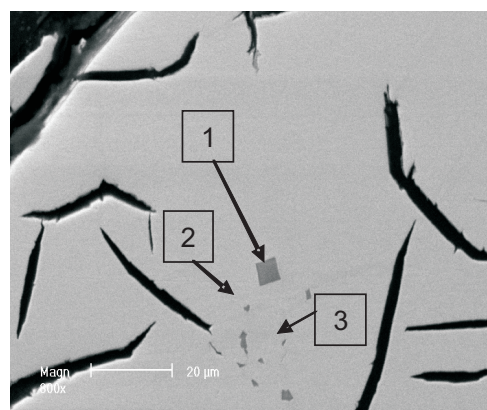


Fig. 7. Surface microstructure in sample B near metal-slag boundary (from metal side), in the light of backscattered electrons

The results of local analysis of chemical composition in spots 1-3 are shown in Fig 7 respectively. Area 1 – Fig. 8a – qualitative analysis of chemical composition for large, regularly shaped precipitate; Area 2 – Fig. 8b – qualitative analysis of chemical constitution for minor precipitate; Area 3 – Fig. 8c – qualitative analysis of chemical composition for minor, oblong precipitate.

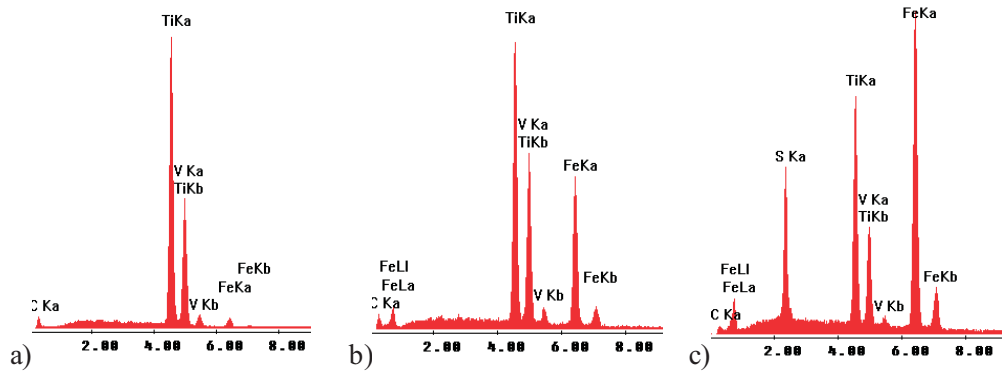


Fig. 8. Qualitative analysis in areas 1, 2, 3

In sample B, similarly to the sample A, a layer is visible at metal-slag boundary which, apart from iron and titanium, contains small amounts of vanadium, calcium, aluminium, silicon and sulphur. Chemical analysis of metal did not show the presence of any other elements than iron. Single precipitates or their small clusters are observed at the distance of up to several dozen microns from that boundary. Apart from titanium, precipitates also contain vanadium, iron, and sulphur. Layers and precipitates of iron oxides are visible at metal-crucible boundary. Precipitates in metal do not form clusters, one may observe only single precipitates, which differ in size and shape. Like near metal-slag boundary, qualitative analysis of chemical composition confirmed the presence of titanium, vanadium and iron.

The analysis of slag phases in the light of backscattered electrons allows to distinguish minimum three phases as regards difference in chemical composition. Phase constituents mainly differ in their magnesium and aluminium content, whereas titanium is bounded in all of them.

4. Test results for phase identification of samples

The phase identification was carried out on the basis of a set of diffraction lines, and thus a few or even several dozen diffraction lines correspond to one phase in the diffraction pattern.

Below you will find test results for sample A, compiled in Table 4-6. The phase constituents were identified for:

1. the isolate obtained through melting of the matrix at metal-slag and metal-graphite crucible boundary,
2. crucible material, taken from crucible-metal boundary surface,
3. slag material, taken from slag-crucible-metal boundary,
4. slag material, taken from slag-metal surface.

Table 4 lists identified phase constituents for the isolate.

TABLE 4

The isolate phase constituents

Graphite C
Cementite Fe ₃ C
Slag constituents (for slag present on metal surface):
– akermanite Ca ₂ MgSi ₂ O ₇
– gehlenite Ca ₂ Al ₂ SiO ₇
Magnetite Fe ₃ O ₄
Titanium carbide TiC
Titanium nitride with small carbon amount added (carbonitride)TiN (Ti(N,C))
Titanium-vanadium carbide (Ti,V)C – solid solutions with different vanadium contents

Phase constituents were identified on the basis of the diffractogram for sample taken from crucible surface contacting metal. Like in case of the isolate, standard recording indicates the presence of graphite, iron α -Fe, and weak lines of magnetite Fe_3O_4 . Another recording revealed diffraction lines of other phases present in the tested sample. The results are compiled in Table 5.

TABLE 5
Phase constituents of sample taken from crucible surface contacting metal

Graphite C, Iron α -Fe, Cementite Fe_3C , slag constituents: – akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$, Magnetite Fe_3O_4 , Hematite α – Fe_2O_3 , Titanium carbonitride $\text{Ti}(\text{C}_{0.3}\text{N}_{0.7})$
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Phase identification of slag material taken from slag-crucible-metal boundary and from slag-metal surface shows no substantial differences. The phase composition is alike (Table 6). In both samples titanium occurs only as titanium carbonitride $\text{Ti}(\text{C}_{0.3}\text{N}_{0.7})$. Moreover – concluding from the microanalysis results – it gets incorporated in the akermanite and gehlenite crystal lattice, and thus forms solid solutions and causes slight shifts in diffraction lines of both these phases, which are visible in the diffraction pattern.

TABLE 6
Phase constituents of slag samples taken from the slag-crucible-metal boundary and from the slag-metal surface

Graphite C Iron α -Fe Akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ Augite $\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$ Titanium carbonitride $\text{Ti}(\text{C}_{0.3}\text{N}_{0.7})$
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5. Observations and conclusions

Completed research and obtained results gave grounds to confirm theoretical calculations, among other

things concerning potential for TiO_2 reduction from liquid slag phase using solid carbon from crucible walls (in case of sample A). One may also observe the reaction involving titanium oxide reduction with carbon from iron solution (in case of sample B). In all cases, boundary layer that is richer in titanium compounds is observed in iron solution at metal-slag phase division boundary. The research confirmed potential for formation of titanium carbides through reduction at the temperature of 1400°C ; these compounds were found at metal-slag, metal-crucible wall division boundaries. Significant temperature impact on the TiO_2 reduction from slag phase was observed. Temperature values occurring within initial slag formation range (up to 1350°C) in iron blast furnace imply TiO_2 reduction, but they do not allow TiC and TiN to be formed in any of the analysed liquid phases. Due to the complexity of this phenomenon, there are still many unsolved issues, among other things regarding proportions between the mechanism of $\text{Ti}(\text{C},\text{N})$ compounds formation through reduction, and their separation from iron solution and deposition on the blast furnace hearth carbon lining. The reduction and precipitation processes proceed at diametrically different temperature conditions.

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