STRUCTURAL ANALYSIS OF TITANIUM COMPOUNDS IN BLAST FURNACE HEARTH

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ŠTRUKTÚRNA ANALÝZA ZLÚČENÍN TITÁNU V NISTEJI VYSOKEJ PECE

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Abstrakt

Príspevok je venovaný sledovaniu karbonitridov titánu tvoriacich sa v nísteji vysokej pece za účelom jej ochrany pred predčasným opotrebením. Pridávanie titánu do vsádzky vysokej pece je vysoko efektívny spôsob predĺženia životnosti vysokej pece používaný celosvetovo v hutníckych podnikoch. Deje sa to usadzovaním nitridov, karbidov a karbonitridov titánu na stenách výmurovky nisteje. Po vsadení titanonosných materiálov s klesajúcou vsádzkou a zvyšujúcou sa teplotou dochádza k priebehu zložitých chemicko-fyzikálnych dejov. Zlúčeniny titánu sa redukujú až na kovový titán, ktorý prechádza do surového železa a reaguje s uhlíkom a dusíkom za vzniku karbonitridov titánu, ktoré zabezpečujú ochranu nisteje vytvorením garnisáže.

Vsádzanie titanonosných materiálov je dôležitou súčasťou kontroly vysokopecného procesu a je potrebné jeho sledovanie z ekonomického hľadiska. Optimálnym bodom je pridávania presného množstva dostatočného na vznik ochrannej vrstvy čo je sledované termočlánkami umiestnenými v žiaruvzdornej výmurovke nisteje.

Sledovanie štruktúry ochrannej vrstvy počas kampane vysokej pece je možné iba na laboratórne pripravených vzorkách. Preto je sledovanie odobranej vzorky počas generálnej opravy jedinečnou príležitosťou na sledovanie zlúčenín titánu ako aj ostatných prítomných fáz vzniknutých v reálnych podmienkach vysokej pece.

Abstract

This article presents investigation of titanium carbonitrides which are generated in blast furnace hearth in purpose of its protection against prematurely erosion. Adding titanium into blast furnace burden is highly effective way of prolongation of blast furnace campaign and is used in steel mills worldwide. It is done by deposition of titanium nitrides, carbides and carbonitrides on blast furnace hearth walls. Once titanium materials are charged into declining burden and increasing temperature then starts composite chemical and physical processes. Titanium oxides are reduced into metal titanium which precipitate into pig iron and react with carbon and nitrogen and titanium carbonitrides are formed which ensure protection of hearth by forming protective layer on it.

Charging of titanium bearing materials is important part of blast furnace control process and is necessery to be monitored. The optimal way is adding exact sufficient amount of titanium to create protective layer. This is monitored by thermocouples placed in hearth refractory.

Structure analysis of protective layer during campaign of furnace is possible only by laboratory prepared samples. Therefore examination of sample taken directly from blast furnace hearth during general repairing is unique to analyse structures of titanium compounds and other present phases created in blast furnace conditions.

Keywords: Blast furnace, titanium nitrides, titanium carbonitrides, hearth protective layer

1. Introdution

Highly effective way of extending lifetime at high blast furnace hearth wear is introduction of titanium bearing materials. It is used in steel mills worldwide. Phenomena of titanium layer forming was initially detected as problem in blast furnaces which used ores rich on titanium. In this cases was problem with viscosity associated with presence of titanium oxides. There was possible to control creation and dissolution of these oxides by adjusting of charged titanium and temperature and amount of pig iron in hearth after that. The viscosity of slags were determined and there was concluded that controlled titanium use have no effect on on blast furnace operation [1]. Subsequently was introduced controlled charging of titanium into furnace in many countries in purpose of protective layer forming for hearth protection effect. It is ensure by deposition of titanium nitrides, carbides and carbonitrides on hearth refractory walls. From "post mortem" study of blast furnaces was confirmed that deposits rich on titanium on hearth bottom represents additional protective layer on lining [2]. Results of many characteristics of carbon linings subjected to laboratory simulations assist to explain mechanism which cause creation of titanium protection layer on refractory. Deposits (or titanium salamanders) grow into thickness of 2-30 mm covering refractory. Understanding of this mechanism emphasising importance of preventive outages of blast furnace. During these outages is ideal conditions for formation of protective layer [3,4].

Titanium rich ores charged into furnace are reduced because TiO_2 is very stable oxide and in conditions of blast furnace only direct reduction can be run over:

$$TiO_2 + 2C_{koks} = Ti + 2\,CO\ ;\ \ H° = 710332\ kJ.mol^{-1} \tag{1}$$

The final product of reduction is TiC which melting point is 3250°C and is soluble in pig iron.

Formation of carbonitrides is controlled by diffusion process therefore need more time to run. Once titanium material is charged with declining burden and increasing temperature then composite chemical and physical processes starts. Titanium oxides are reduced into metal titanium which precipitate into pig iron and react with carbon and nitrogen and titanium carbonitrides are formed which ensure protection of hearth by forming protective layer on it. Carbides and nitrides starts form in bosh area. We can predict following:

$$TiO_2 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiC_xO_y \rightarrow TiC \tag{2}$$

$$TiO_2 \rightarrow [Ti] \rightarrow TiC \text{ alebo } TiN \text{ alebo } Ti(CN) \tag{3}$$

Maximum concentration TiC and TiN is on tuyer level and with declining of burden from tuyers into hearth concentration of TiC and TiN is dropping in result of Ti(CN) oxidation [5].

2. Materials and experimental equipment

Sample acquired from quenched blast furnace was subjected. Technically was sample taken in form of lump during removing of salamander and rest of hearth refractory and then was piece cut on x and y axis and two smaller samples suitable for metallographic examination was chosen. Samples were observed by scanning electron microscope Jeol JSM-7000F and analyzed by EDX analyzer INCA Energy OXFORD Instruments.

3. Results and discussion

During observing of macrostructure was possible to determine more compounds consist of metal phase and residual carbon refractory (Figure 1). Distribution of residual carbon refractory in metal matrix was confirmed by further analysis.

Fig.1 Sample macrostructure of metal phase and residual carbon refractory (no magnification)

Single analysis was performed from lower magnification by 80x when area analysis was performed to determine all present elements in sample. On figure 2 is structure magnified by 80x and marked area (Spectrum 1) of element analysis and analyzed spectrum. We can observe presence of C, Fe, O, Na, Al, Si, Cl, K, Ti, Mn elements. High content of carbon results from sample character and it is carbon refractory of blast furnace hearth. Next elements are commonly present in blast furnace process as alkali metals such as Na and K (in form of oxides Na_2O and K_2O) which are cumulated and circulated in furnace.

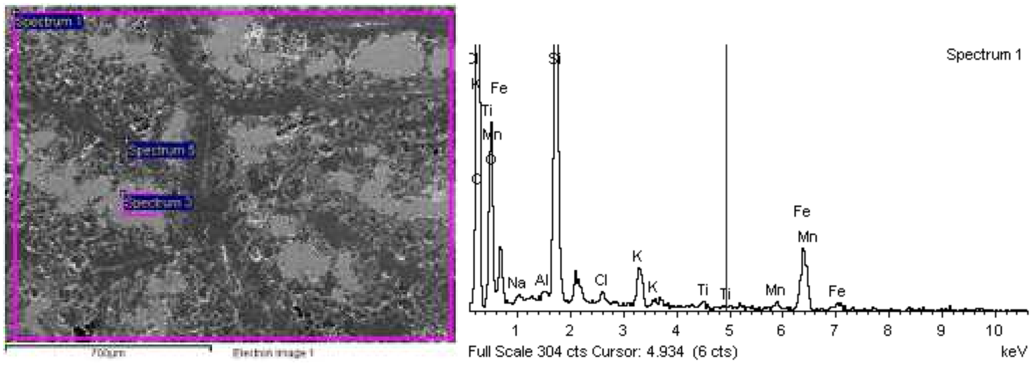

Fig.2 Structure at 80x magnification and analyzed spectrum 1

Table 1 Analysis of spectrum 3 and 5

Spectrum 3			Spectrum 5	
Element	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
C	8.47	27.48	97.31	97.97
O	4.43	10.80	2.69	2.03
Si	1.21	1.69	0	0
Ti	8.44	6.87	0	0
Fe	74.21	51.80	0	0
Nb	3.23	1.36	0	0
Totals	100.00		100.00	

Further analysis shown that in base material consisted mostly of carbon and iron more structural components are present. These can be good recognized by different contrast – figure 3.

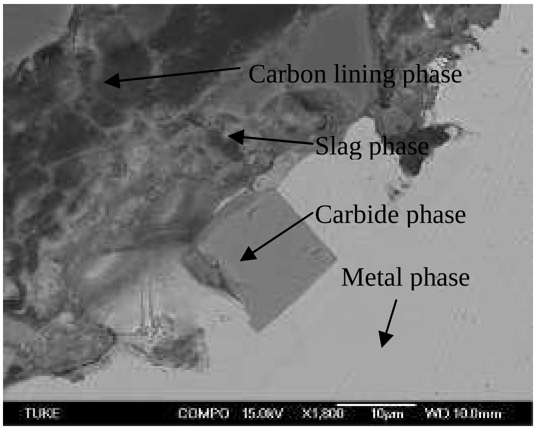

Fig.3 Individual structural phases

Table 2 Analysis of slag, metal and carbon lining phase from fig.3

Analysis	Slag phase	Carbon phase	Metal phase
Element	**Weight%**	**Weight%**	**Weight%**
C	0	93.24	2.80
O	43.87	2.95	0
Na	1.81	0	0
Mg	0.62	0	0
Si	34.21	0	0
Cl	0.72	0.58	0
K	10.06	0.60	0
Ca	2.22	0	0
Ti	1.35	0	0
Mn	5.14	0	0
Fe	0	2.63	97.20
Totals	100.00		

Summary results of carbon refractory, slag and metal phase are present in table 2. Slag is composed by alkali oxides of Na, K and Ca and also Si, Mg, Ti oxides are present. Also small amount of Cl is present. Silicon is localy present also in form of sheet crystals SiO_2 – figure 4. Rarely on interface of metal and carbon phase manganese sulphides are present in form of non-compact envelope of metal phase – figure 5.

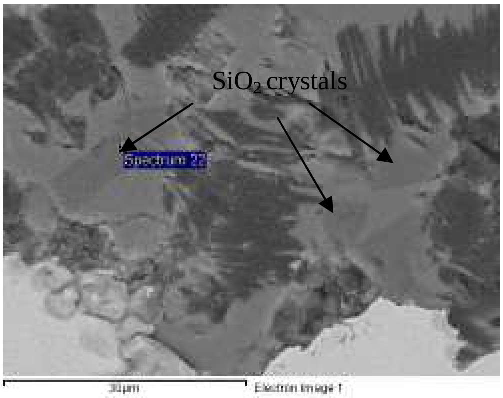

Fig.4 Shapes of SiO_2 crystals

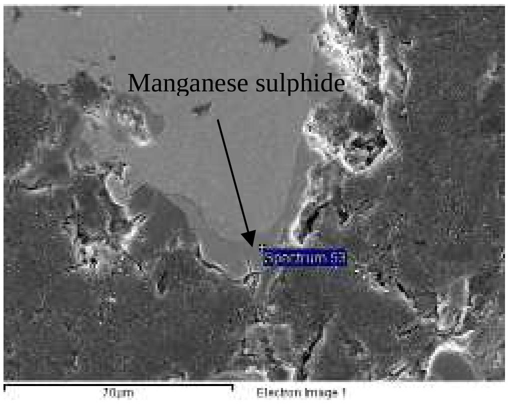

Fig.5 Manganese sulphide envelope

Table 3 Analysis of SiO_2 - spectrum 22 and manganese sulphide - spectrum 53 from fig. 4,5

Analysis	Spectrum 22	Spectrum 53
Element	**Weight%**	**Weight%**
C	0	18.07
S	0	30.37
Mn	0	51.56
O	52.63	0
Si	47.37	0
Totals	100.00	

Most significant titanium phase in sample was just titanium carbonitrides. There are present mainly in metal phase in form of crystal developed units which in cross section are triangle or quadangle shape – figure 6. As figure shows they can be closed in metal phase or in contact vith carbon refractory or slag. Detail on titanium carbonitride and related EDX spectrums are shown on figure 7 and table 4.

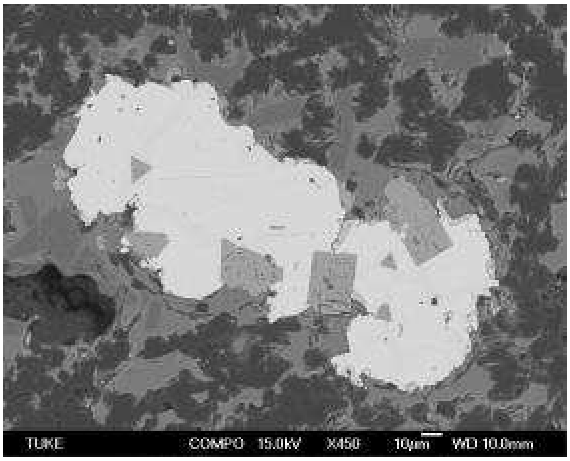

Fig.6 Shapes of carbonitride crystals

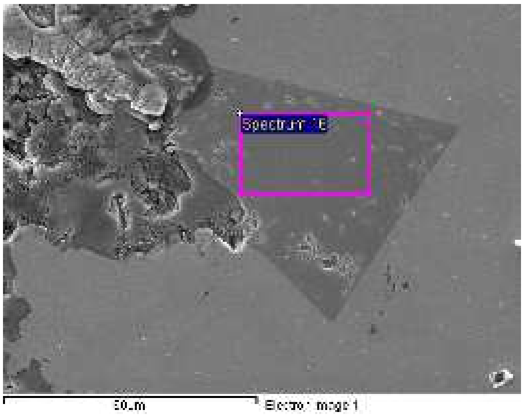

Fig.7 Detail on titanium carbonitride

Table 4 Titanium carbonitride spectrum

Element	**Weight%**	**Atomic%**
C	3.62	9.21
N	18.93	41.34
Ti	77.45	49.45
Totals	100.00	

Subjected sample taken from blast furnace hearth after shut-down is composed mainly by carbon refractory, metal phase and slag phase. Together with these components is also present minority of SiO_2 crystals sheets localized in slag and manganese sulphides segregated as metal phase envelope. Titanium carbonitride which are responsible for protection effect are in form of crystal developed units presented mainly in metal phase. Creation of titanium carbonitrides is complex process which runs in more phases. Titanium is introduced into blast furnace in burden in form of TiO_2. Process of TiO_2 reduction into metal titanium and sequence of carbonitride formation are described in introduction of this article.

4. Conclusion

In this article titanium compounds which are formed in blast furnace hearth during campaign was analyzed. In this relation detailed structure analysis of hearth was determined. From previous experiments we can conclude following:

1. Blast furnace hearth sample material is mainly composed from carbon refractory, metal and slag phase.
2. Beside of phases mentioned above sheet SiO_2 crystals located in slag phase and manganese sulphide in form of metal phase envelope are present.
3. Titanium carbonitride formation is complex process which consist from TiO_2 reduction into metal titanium and is described in the introduction of this article.

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