

M. FRÖHLICHOVÁ*, R. FINDORÁK*, J. LEGEMZA*

STRUCTURAL ANALYSIS OF SINTER WITH TITANIUM ADDITION

ANALIZA STRUKTURALNA SPIEKU Z DODATKIEM TYTANU

Paper presents the results from the study of the effect of materials with titanium addition on the strength properties of the iron ore sinter.

The sinters with TiO₂ addition or without TiO₂ addition prepared in laboratory were applied in this research and were compared based on the structural and phase composition. Exploited was the method of the X-ray diffraction and method of elemental EDX analysis applying the electron raster microscope with the energo-dispersion analyser. Confirmed was the relationship between the sinter structure and its strength. Higher strength of the sinter without TiO₂ addition is the result of the different phase composition of the compared sinters. In the sinter production considered should be not only the chemical composition of the entry components of the charge and the chemical composition of the final product but also its structural and phase composition.

Keywords: Blast furnace, Titanium carbide, Titanium nitride, Phase composition, Microstructure, Life of refractory lining

W artykule tym przedstawiono wyniki badań wpływu materiałów z dodatkiem tytanu na właściwości wytrzymałościowe spieku z rudy żelaza. Spieki zawierające dodatek TiO₂, jak i bez dodatku TiO₂ przygotowane w laboratorium poddano porównaniu w oparciu o ich strukturę i skład fazowy. W badaniach zastosowano metodę dyfrakcji rentgenowskiej oraz metody analizy elementarnej EDX, badania te przeprowadzono na mikroskopie elektronowym przy zastosowaniu analizatora dyspersji energii. W wyniku pomiarów potwierdzono związek pomiędzy strukturą martwicy i jej wytrzymałością. Wyższa wytrzymałość spieku bez dodatku TiO₂ jest rezultatem różnicy składu fazowego porównywanych spieków. Podczas wytwarzania spieku powinno brać się pod uwagę nie tylko skład chemiczny składników wejściowych i skład chemiczny produktu końcowego, lecz także jego strukturalne i skład fazowy.

1. Introduction

Blast furnace is the mostly applied facility for the pig iron production. Based on the comparison of the blast furnace technology with other alternative production methods, it follows out that the blast furnace will for certain remain for other tens of years the main producer of the pig iron. The effort to reduce the production costs and the increase of the requirements related to the quality and quantity of pig iron, is accomplished with the intensification of the iron production based on the blast furnace. One way how to intensify the process and reduce the production costs is the prolongation of the blast furnace campaign, which significantly reduces the price of the pig iron. The period of the blast furnace operation is limited by the life of the furnace hearth life.

The refractory materials applied in the furnace hearth are the most critical part of the blast furnace and its life is affected mainly by the condition of the hearth. The most critical region is the transition region between the furnace wall and bottom of hearth. The main role in the wearing plays the productivity, frequency of the furnace shut down – mainly those longer than 48 hours, water leakage from the cooling system, coke and metal bearing charge quality.

The thermocouples may assist in the hearth wearing diagnostics; these are embedded in the hearth lining and monitor the temperature anomalies indicating the local erosion of the hearth. If the critical value is exceeded, this fact inevitably calls for the countermeasure application.

The common practice under the condition of the industrial operation is to implement the partial replacement of the furnace lining up to such extend as it is necessary from the point of retaining the furnace integrity in course of its life. Such method can be applied in the region of the blast furnace shaft and bosh. This procedure implementation in the region of furnace hearth and bottom is highly physically demanding. In many cases implemented must be the complete replacement of the lining due to the localised preliminary failure of the furnace hearth or bottom. It represents the highest capital investments. Therefore the solution of the hearth issue is of high importance. One possibility is the addition of the titanium - bearing materials to the blast furnace with the aim to create the protection layer on the hearth walls. The process is based on the presumption that due to the intensive reduction process within the blast furnace TiO₂ is reduced. Research on this process has shown that the reduced out titanium reacts with carbon and nitrogen and forms TiC, TiN a TiCN [1-6].

* DEPARTMENT OF FERROUS AND FOUNDRY METALLURGY, TECHNICAL UNIVERSITY OF KOŠICE, PARK KOMENSKÉHO 14, 042 00 KOŠICE, SLOVAC REPUBLIC

The above mentioned components of titanium feature with the high melting temperature and act as the protective layer and prevents from the hearth further erosion.

The method of the titanium-bearing materials addition to blast furnace depends on the nature of the hearth. The most frequently added material is ilmenite, which occurs mainly in form of the titanium-magnetite ores – titanomagnetites (Fe,Ti)₃O₄. These may be defined as the mechanical mixture of ilmenite with Fe minerals (magnetite Fe₃O₄ and partially hematite Fe₂O₃). Another possibility is also the Ti addition into the sinter charged into blast furnace.

The implemented technology of Ti materials addition into the blast furnace is from the upper section – through the blast furnace top or in the lower section – through the blast furnace tuyers [7-9]. The present paper focuses on the material which may be charged through the blast furnace top together with the blast furnace charge. Ti- materials may be in form of the lumpy ore and used may be various agglomerated raw materials in form of agglomerate, pellets or briquettes. However met should be the principal requirement, i.e. charged materials are to feature the good strong-holding properties, not to disintegrate in course of the process, which fact could cause the worsening of the furnace charge permeability. With regard to the fact that the principal metal-bearing raw material is sinter, research has focused on this component of the blast furnace charge.

2. Work methodology and materials

The production of high quality sinter is possible only after acquiring the deep knowledge on the relationships among the parameters affecting the sintering process. In course of the sinter formation undergoing are certain chemical and physical processes and the generally valid principles, which could have made it possible to predict the composition of the final product, have not been derived so far. However the requested sinter can be produced when observed are the certain known relationships and dependability. The final properties of the sinter are subject not only to its chemical composition, but they are substantially affected by its mineralogical composition i.e. by the present phases. Mineralogical phases may have various structural forms depending on the conditions of the sinter formation. Principally, these are the crystalline phases and glass. Relatively large portion of the mass is in the form of the solid solutions of the unsettled composition, which fact complicates the quantitative and qualitative evaluation of the share of the contribution of the individual phases to the strength of the sinter. With regard to this fact, proclaimed can be the general deductions only.

The above mentioned facts provide the conclusion that in the sinter production considered should be not only the chemical composition of the charge entry components, but also the physical and mechanical properties and technology parameters of the process. Generally holds that all technology parameters affect the phase composition and structure of the sinter and these on the other hand affect the mechanical properties of the sinter.

The effect of the titanium application with the aim to prolong the blast furnace campaign can be considered as the

preventive one and as one serving to upgrade the condition of the blast furnace hearth. Present paper deals with the sinter preparation for the preventive purpose of the blast furnace hearth protection. It means that titanium should be added in small amounts into the furnace in course of the entire year. Amount of Ti and TiO₂ shall be continually checked based on the balance of the chemical composition of iron and slag. Ti content in the pig iron should not exceed 0,2% and in slag 1,2 through 3,0% [9].

With this objective the preparation of the titanium containing sinter was realised in the laboratory in the sintering pan at the Department of Iron Metallurgy and Foundry, HF TU in Košice. The sintering mixture consisted of materials, which are used under the operation conditions in USS Košice. All sintering procedures were conducted in the laboratory under the same conditions and with the same raw materials in the charge; the chemical composition of which is given in Table 1.

TABLE 1
Chemical composition of the raw materials (wt.%)

	Ore S.B.	Conc. MICH.	Limestone	Dolomite	Coke	Ti ore
Fe	60.05	64.79	-	-	-	34.64
TiO ₂	0.031	0.007	-	-	-	30.44
FeO	0.21	23.93	-	-	-	24.33
Fe ₂ O ₃	85.46	65.64	-	-	-	22.56
SiO ₂	11.65	8.91	0.42	1.38	-	11.68
CaO	0.06	0.19	55.8	29.72	-	1.95
MgO	0.06	0.22	0.2	20.76	-	3.58
Al ₂ O ₃	0.71	0.13	0.3	0.62	-	5.08
Mn	0.03	0.02	-	-	-	0.18
P	0.042	0.015	-	-	0.032	0.058
S	0.01	.011	-	-	0.53	1.1
Ash					14.8	

Calculation of the charge composition related to the requested composition of sinter was carried out using the mathematical model. Chemical composition of the sinter is given in Table 2.

TABLE 2
Chemical composition of the sinter (wt.%)

	Sample 4	Sample 7		Sample 4	Sample 7
Fe	50,49	46,08	MnO	0,039	0,077
FeO	7,9	7,54	TiO ₂	0,10	3,67
Fe ₂ O ₃	63,44	57,53	Na ₂ O	0,099	0,218
SiO ₂	10,12	11,15	K ₂ O	0,076	0,076
CaO	12,26	12,05	S	0,027	0,063
MgO	3,76	4,01	Zn	0,001	0,004
Al ₂ O ₃	0,73	1,24	Pb	0,001	0,001
P ₂ O ₅	0,064	0,048	As	0,0008	

Technological conditions of the sintering process as well as the methodology of the processing and evaluation of the obtained results are provided in literature [10-12]. The above mentioned literatures provide the evaluation of the common sinter and titanium containing sinter from point of the chemical composition, acquired physical properties and of course of the economical and ecological aspects. Based on the obtained results it could be stated that the titanium containing sinter features with the lower strength holding characteristics, which fact plays an important role in the process of the blast furnace production of pig iron. The above conclusions gave rise to the requirement to evaluate the sinters from the point of microstructure and phase composition and seek for the relationships between the sinter strength and its structure.

The chemical composition of the starting raw materials for the sinter production and the chemical composition of the sinter provided in Table 1 and Table 2. is the input information basis for the sinters description from point of their structure.

To estimate the phase composition of sinter adopted was the method of X-ray diffraction. To scan the samples adopted was the diffractometer fy. SEIFERT XRD 3003/PTS. Parameters of the measurement are given in Table 3.

TABLE 3

Conditions of measurement	
Generator	35 kV, 40 mA
X-ray radiation	Co -line focus
Filter	Fe
Scan step	0.02 theta
Range of measuring	10-130°2theta
Input slits	3 mm, 2 mm
PSD Detector	Meteor1D

Diffraction record was analysed applying the software ZDS-Search Match with the database PDF2 and program TOPAS. Mineralogical analysis of the sinter was performed on metallographic specimens, which were observed adopting the method of elemental EDX analysis using the electron raster microscope HITACHI S450 with energy-dispersion analyser KEVEX.

To analyse the effect of Ti addition on the strength of the sinter selected was the sinter No.4 representing the sinter without Ti and sinter No.7 representing Ti containing sinter.

3. Results and discussion

The sintering process is realised in the heterogeneous gas– liquid – solid phase system, where the gaseous phase assumes the course of the decisive phenomena (fuels combustion, heat transfer, reduction and oxidising processes). Melting the fine grains of ore and other particles, enabling the crystallisation of magnetite, hematite, calcium ferrite and partially also the silicates forms the liquid phase. Following their solidification it assumes the conjunction of these phases into the porous sintered mass – the sinter. Due to the chemical non-homogeneity in the micro-volumes of the originated melt and a high rate of its solidification, rather extended variabil-

ity of the base-like sinters and the variety of micro-textures is formed. It results in the different crystal limitation of the existing minerals.

The structure of sinter No.4 is given in Figure 1, which, as it is obvious from the macrostructure, is rather non-homogeneous. With regard to this structural non-homogeneity, on the sinter plane marked were the areas of different micro-volumes, which were subjected to the thorough analysis.

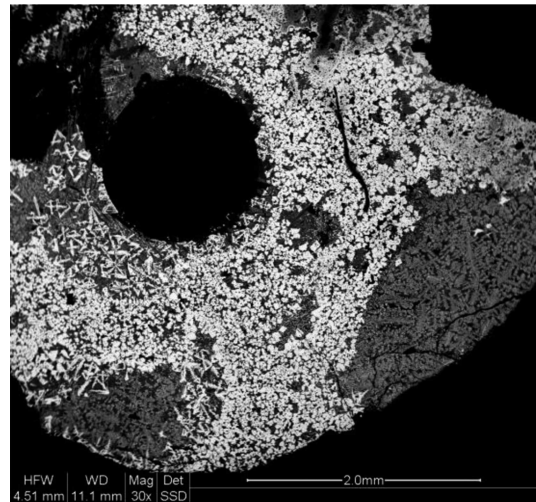


Fig. 1. Macrostructure of the sample No. 4 - sinter without Ti

Based on the X-ray phase analysis, the following mineral components were identified in the evaluated iron ore sinter without Ti: magnetite, wustite, hematite, calcium ferrites, iron and calcium olivine, pyroxene, dicalciumsilicate and residual quartz. Identified phases are given in Table 4.

TABLE 4

Phase composition of samples

Identified phase composition		Sample 4	Sample 7
Chemical formula	Mineralogical name	Content [wt.%]	Content [wt.%]
FeO	Wustite	2.1	–
Fe ₃ O ₄	Magnetite	37.4	29.6
Fe ₂ O ₃	Hematite	30.7	38.3
FeTiO ₃	Ilmenite	–	2.9
SiO ₂	Quartz	3.9	4.6
Ca ₂ SiO ₄	Larnite	10.1	8.9
(Ca, Na)FeSi ₂ O ₆	Hedenbergite	5.4	15.8
CaAl ₄ O ₇	Grossite	3.0	–
Ca ₂ Fe ₂₂ O ₃₃	–	3.0	–
Ca ₂ Fe ₂ O ₅	Srebrodolskite	1.5	–
CaFe ₃ O ₅	-	1.5	–
Ca ₃ Si ₃ Al _{1.3} Fe _{0.7} O ₁₂	Grossular	1.3	–

Microstructure of the evaluated sinter is given in Fig. 2, 4. EDX spectrum of the analysed surfaces and corresponding elemental analysis is provided in Fig. 3, 5, Table 5.

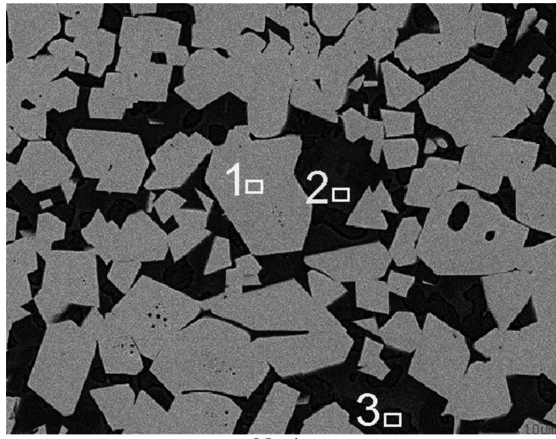


Fig. 2. Microstructure of the sinter



Fig. 4. Microstructure of the sinter

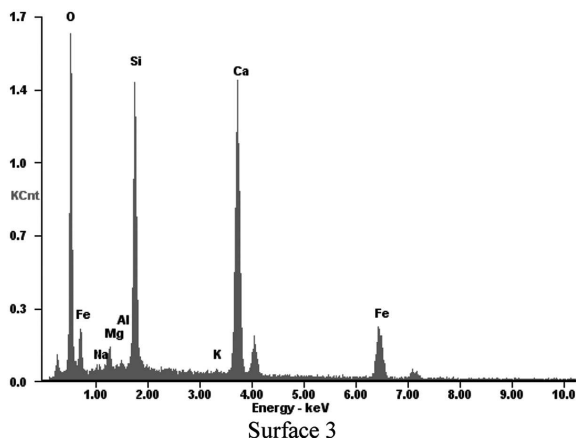
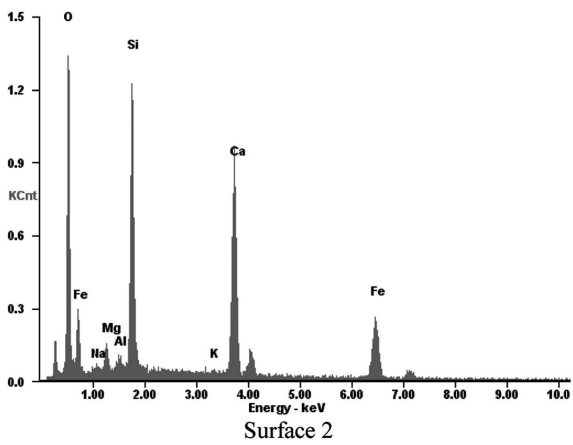
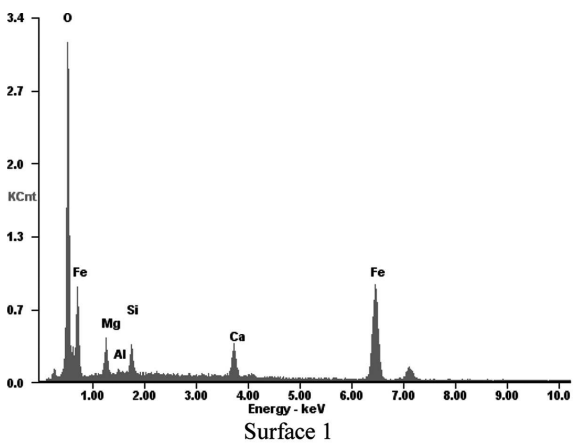


Fig. 3. EDX spectrum of surface 1, 2, 3

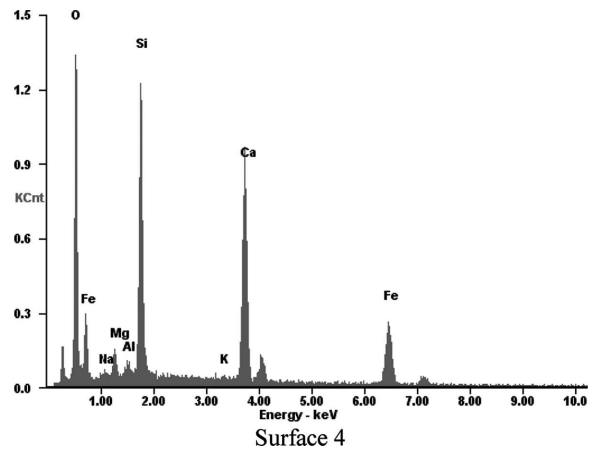


Fig. 5. EDX spectrum of surface 4

TABLE 5
Elemental analysis of spectrum 1, 2, 3, 4 (wt.%)

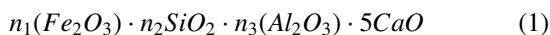
Element	Spectrum			
	1	2	3	4
O	30.01	35.26	36.39	33.44
Na	00.00	00.69	00.30	00.45
Mg	03.63	01.46	01.07	01.40
Al	00.43	01.03	00.39	00.59
Si	02.64	14.82	13.83	14.97
K	00.00	00.51	00.27	00.35
Ca	04.73	20.61	27.89	22.54
Fe	58.56	25.61	19.85	26.25

As it follows out from the above figures, the matrix of the sinter is formed of primary magnetite in the form of automorphous grains of the quadratic and triangular shape. The dendritic shapes of the secondary magnetite of the skeleton construction and these are included into the structure of the olivine-bounding phase. There is well visible formation of the calcium like silicates. At the grains edges observed can be also

the grains of the calcium like ferrite. There are also visible oval grains of the globular magnetite and wüstite FeO.

Hematite Fe_2O_3 forms the romboedric and table like crystals. It is present in three basic morphological types indicated as hematite H1, H2 and H3 (from the hematite genetically relatively oldest to the relative youngest one). Hematite H1 forms the major part of the relict of non reacted chips of the hematite ores, where it forms the typical grainy, less porous up to compact aggregates. Hematite H2 form the individual grains or clusters of grains, mostly of skeleton like, sometimes even automorphous boundary. Its crystals grow at the account of basic silicate mass and crystals of magnetite. Hematite H3 forms the thin bars inside the individual grains of the magnetite and it originated after the solidification of the basic silicate mass of the secondary oxidation of the earlier crystallised magnetite.

Calcium ferrites are mostly of the complex composition. The principal component is hemicalciumferrite $CaO \cdot 2Fe_2O_3$, in which isomorphously admixed are SiO_2 and Al_2O_3 . It is labelled as ferrite SFCA in literature and has general formula:



where the sum $n_1 + n_2 + n_3$ equals approximately to 12. Differentiate are its three morphology types : balls, needles and bars. Close to the insufficiently reacted basic additives, dicalciumferrite $2CaO \cdot Fe_2O_3$ and monocalciumferrite $CaO \cdot Fe_2O_3$ can be found [13]. Silicate compounds in the sinter form iron and calcium containing olivines, pyroxenes, calcium-silicates and glassy solidified silicates.

Iron and calcium containing olivines $(Ca_xFe_{1-x})_2 \cdot SiO_4$ form various solid solutions between fayalite $2FeO \cdot SiO_2$ and dicalciumsilicate $2CaO \cdot SiO_2$. They exist in form of the prolonged columnar crystals. Pyroxenes, belonging in the group of diopsid. $CaO \cdot MgO \cdot 2SiO_2$, can be found as hedenbergite $(Ca, Na) \cdot FeSi_2O_6$.

Dicalciumsilicate $2CaO \cdot SiO_2$ can exists in three modifications: as bredigite $\alpha' - 2CaO \cdot SiO_2$, larnite $\beta - 2CaO \cdot SiO_2$ and shannonite $\gamma - 2CaO \cdot SiO_2$. Modification $\alpha' - 2CaO \cdot SiO_2$ (stabilised by the rapid cooling and bivalent iron addition) exists in form of the prolonged needles with high relief on the glass background. Stabilised larnite $\beta - 2CaO \cdot SiO_2$ found in the structure occurs in irregularly limited and rounded grains. As long as it is not stabilised, it is transformed in modification of shannonite $\gamma - 2CaO \cdot SiO_2$ with the volume increased by 12%, what causes the disintegration of the sinter [14].

Silicate glass is distributed in the structure of the sinter non-uniformly. In some places it form the major part of the sinter matrix, but in other places only thin surfaces among the crystallised silicate and oxide phases.

The structure of the iron ore basic sinter with Ti addition is given in Fig. 6. Based on the X-ray phase analysis the following mineral components were identified in the evaluated iron ore sinter: hematite, magnetite, iron-calcium olivines, pyroxenes, dicalciumsilicate, residual silica (Table 6).

Whereas in the sinter without Ti addition, the matrix of sinter was formed of magnetite, in this case the metal bearing matrix is formed of hematite non-uniformly distributed in all three types. The primary hematite H1, which corresponds to the non-reacted chips of the hematite ores, is well visible in the microstructure, and hematite H2, which forms the individual

grains or clusters of grains, mostly of skeleton and sometimes even of auto-amorphous limitation. Its crystals grow on account of the basic silicate mass and magnetite crystals. Hematite H3, which was formed in course of the magnetite re-oxidation, is found in the structure in the smaller amount.

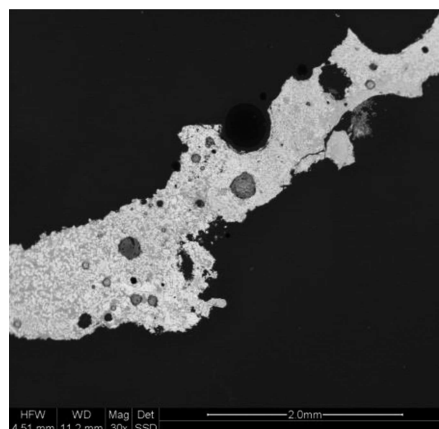


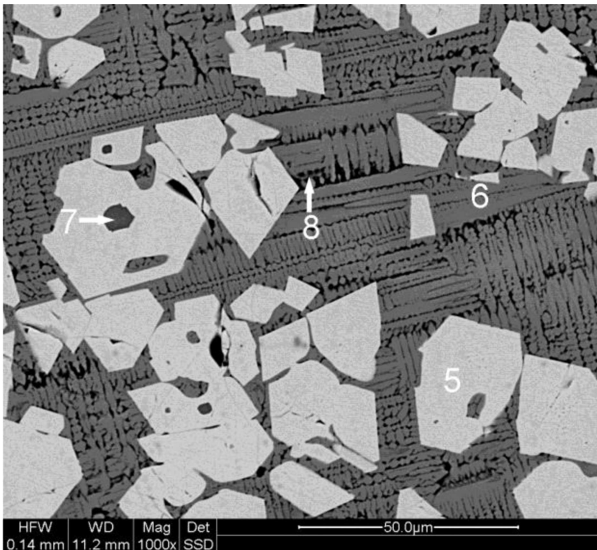
Fig. 6. Macrostructure of sinter – sample No.7 – sinter with Ti

TABLE 6
Elemental analysis of spectrum 5, 6, 7, 8 (wt.%)

Element	Spectrum			
	5	6	7	8
O	28.93	36.13	36.62	25.02
Na	00.00	00.62	01.06	01.16
Mg	02.08	00.58	00.52	00.50
Al	00.84	01.39	02.02	03.26
Si	01.42	12.62	13.76	15.78
Ca	02.14	19.83	21.33	22.61
Ti	01.59	07.18	09.61	06.83
Fe	63.00	21.65	15.10	24.84

Silicate components are formed of pyroxenes, calcium silicates and glassy solidified silicates. Pyroxenes, due to their mutable chemism form complicated group of silicates, are found in form of the grainy aggregates and columnar or bar-like crystals Fig.7. Pyroxenes identified by X-ray phase analysis are in the basic group Hedenbergite and form the main bounding matrix. The crystallised dicalcium silicate in the modification larnite $\beta - 2CaO \cdot SiO_2$ is well visible in the silicate- bounding phase. When comparing with the structure of sinter without Ti, FeO and calcite ferrites were not identified by X-ray analysis. Based on the results of X-ray analysis titanium occur in the oxide phase $FeTiO_3$.

Based on the results of the spectrum analysis (Fig. 8, Table 7) it can be assumed that there exists the migration of titanium from the grains of the ferrite oxides into the silicate phase, the integral part of which is the silicate glass. Silicate glass is non-uniformly distributed within the structure of the sinter; it can either be found in the crystallised silicate and oxide phases, or it forms in the certain micro volumes the matrix of the sinter. As titanium was not identified as the part of the bounding phase by the X-ray analysis in the sinter structure, it is possible to say that it is concentrated within



No.7a



No.7b

Fig. 7. Microstructure of sinter – samples

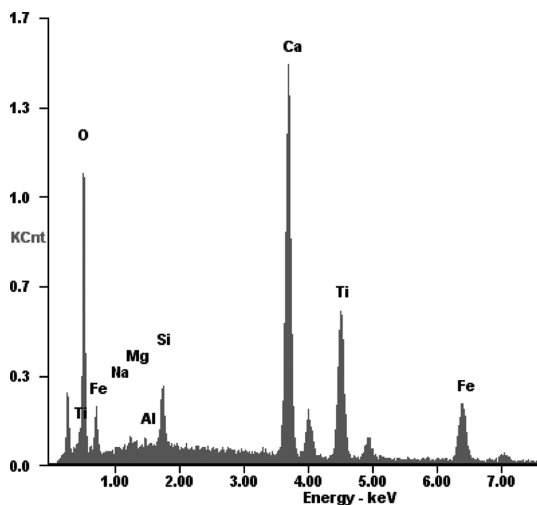


Fig. 8. EDX spectrum of surface No.7b

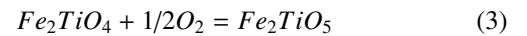
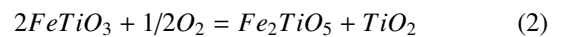
the glassy amorphous phase, which can not be determined applying this method. Titanium presence in the ferrite oxides is

significantly higher comparing to the silicate phase. Absence of calcium ferrite maybe explained by the reaction of TiO_2 with CaO .

TABLE 7
Elemental analysis of spectrum No.7b (wt.%)

Element	Wt %
O	33.09
Na	00.33
Mg	00.43
Al	00.35
Si	02.42
Ca	27.33
Ti	18.73
Fe	17.33

When considering the following oxidation reactions in course of the in the titanomagnetite ores sintering



than the formed Pseudobrookite Fe_2TiO_5 is under the sintering conditions non-stable phase and in the environment of the basic sinter it reacts preferably with CaO and formed is perovskite $CaTiO_3$ and titanite $CaO \cdot SiO_2 \cdot TiO_2$ [15].

The creation of the preferably oxidising conditions over reducing in practice calls for the smaller amounts of the coke powder and high air excess. Such conditions significantly affect the sintering process as well as the drop in the sinter strength.

4. Conclusions

Based on the results obtained from the study of phase and structural composition of the common sinter and sinter with titanium addition, it is possible to state as follows: The formation of the sinter structure is highly complex process accompanied by large number of factors related so to the process technology as to the chemical and physical phenomena occurring among the components of the sintering mixtures. Originated mineral phases may have different structural form depending on the conditions of the sinter production. Actual mass of the sinter is formed of the grains of the primary minerals, the crystals originated from the melt and the binding slag phase, which may be in form of crystals or glass. If the amount of melt phase is small, the strength of the sinter is defined by the strength of the primary phase or series of phases featuring with minimal strength. Number of the research works has been devoted to the definition of the strength of the individual phases, based on which it has been pointed out that the ferrous oxides (hematite, magnetite) feature by higher strength parameters comparing to the mineral phases forming the binding phase. Based on this knowledge, it can be stated that the main difference among the evaluated sinters was in the metal –bearing matrix of the sinter and the binding phase.

Matrix of the common sinter is formed of magnetite, which is characterised by the better strength properties in comparison to hematite. This formed the matrix of the sinter with titanium addition. The binding phase of the common sinter was formed of the ferro-calcium olivines, calcium ferrites and calcium silicates Ca_2SiO_4 in form of low temperature modifications β . In case of the sinter with titanium addition calcium ferrites were not identified, which in comparison to olivines were not identified feature with better strength properties. Based on the given difference, it is possible to conclude that the lower strength of the sinter with titanium addition can be found in the different phase composition of the compared sinters.

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