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TITANIUM IN THE PROCESS OF SMELTING PIG IRON WITH AN INCREASED SILICON CONTENT

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In connection with future utilization of magnetite - titanium ores deposited in Poland in the region of Suwałki - the test were performed to get information regarding the influence of titan and vanadium admixtures on the quality of pig iron and the run of blast furnace process. As a blast furnace charge, there were used magnetite - titanium concentrates similar to the ores deposited in the Suwałki region. The test consisted of iron ores sinter production and its usage in the process of preparation of foundry pig iron. The amount of TiO_2 charge into the blast furnace was equal to 10 kg/Mg of pig iron. It was ascertained that the quality of sinter remained the same, but the output of sinter was lower by proxy. 4 %, compared to the production without TiO_2 addition. These tests have proved the possibilities of utilization of titanium - bearing magnetite - concentrates in the portion up to 10 kg/Mg of pig iron, which gives possibilities to take advantages of entire deposit of titanium - bearing magnetite ores in Poland, using the blast furnace technology.

Key words: *titanium, sintering, high basicity sinter, blast furnace*

Titan u procesu talenja sirovog željeza s povećanom količinom silicija. Vezano za iskorištavanje magnetita - nalazišta titanske rudače u Poljskoj u području Suwalki - provedena su ispitivanja radi dobivanja informacija glede utjecaja smjese titana i vanadija na kvalitetu sirovog željeza i odvijanje procesa u visokoj peći. Kao šarže visoke peći koristile su se koncentracije magnetit - titan slične nalazištima rude u regionu Suwalke. Ispitivanje se vršilo na sinteru željezne rude i njenoj uporabi na procesu pripreme ljevačkog sirovog željeza. Količina šarže TiO_2 u visokoj peći iznosila je do 10 kg/Mg sirovog željeza. Utvrđeno je, da je kvaliteta sintera ostala ista, ali je potrošnja sintera bila niža za približno 4 % u usporedbi s proizvodnjom bez dodavanja TiO_2. Ova ispitivanja su dokazala mogućnost iskorištavanja koncentracije titana koji sadrži magnetit u odnosu od 10 kg/Mg sirovog željeza, što daje mogućnost da se u Poljskoj iskoristi cijelo nalazište magnetitne rude koja sadrži titan za potrebe tehnologije visoke peći.

Ključne riječi: *titan, sinter, visokobazični sinter, visoke peći*

INTRODUCTION

The problem of the reduction of titanium in the blast furnace has become an up-to-date issue for the Polish iron metallurgy in connection with the prospective utilization of the documented complex ore deposit in the region of Suwałki.

One of the proposed variants of the processing of those ores is to obtain two concentrates from them, namely:

a) a titanium-magnetite concentrate for the needs of iron metallurgy,
b) an ilmenite concentrate intended for the production of titanium white and metallic titanium.

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Calculations indicate that the titanium-magnetite concentrate obtained from these ores will contain: up to 65 % of iron, up to 0.7 % of vanadium, 2.0 - 9.0 % of titanium dioxide and 0.4 - 2.0 % of silica [1].

Vanadium, which does not form separate minerals in the useful mineral and its atoms are included in the crystallographic lattice of magnetite, remains almost in whole in the titanium-magnetite concentrate.

Besides the weakly magnetic ilmenite, FeO, TiO_2 titanium is also contained in the useful mineral associated with magnetite, mainly in the form of titanium-magnetite $(Fe, Ti)_3O_4$ and ulvite $2FeO \times TiO_2$ [1, 2].

Vanadium contained in the complex ore in the region under consideration forms a very valuable constituent of the ore, which may be decisive to the economical aspects

of the future utilization of the deposit. In the Polish conditions, it can be obtained from the titanium-magnetite concentrate essentially by the two following methods:
- by smelting concentrates (after they have been lumped) in the blast furnace, with the subsequent recovery of vanadium from the pig iron and titanium from the slag;
- by means of the pyro-hydrometallurgical processing of the titanium-magnetite concentrate, as a result of which vanadium is obtained by precipitating its compounds from the water solution, whereas the component resulted from vanadium removal may constitute a charge for the production of sinter and pig iron.

The both processes have an inherent possibility of applying the blast-furnace technology to the smelting of the preliminarily lumped titanium-magnetite concentrate or titanium-hematite.

The content of titanium in a possible obtained titanium-magnetite concentrate is not an obstacle to the direct use of the concentrate as a blast-furnace charge.

On the other hand, titanium introduced to the blast furnace in excessive amounts is likely to cause a difficulty in conducting the process, mainly because of thickening of the slag by TiO_2. Having this in mind, the hitherto existing blast-furnace practice has tried not to use too large amounts of titanium-bearing materials in the charge.

It should also be noted that using the blast-furnace containing increased admixtures of titanium has not been fully investigated. Any results of investigations undertaken on this subject are only a small part of the problem of smelting pig irons from the charge of increased titanium content.

In the future, the use of domestic titanium-magnetite concentrate should be expected to be used for pig iron production in Poland. Therefore, an industrial trial of using a similar concentrate containing titanium for the production of sinter, and then using thus obtained sinter for the production of pig iron was undertaken.

PURPOSE AND SCOPE OF STUDY

The primary goal of the study was to investigate the behavior of titanium in the blast-furnace process, while considering:
- effect of silicon content of pig iron on its titanium content;
- effect of slag basicity on the ratio of titanium distribution to the slag and the pig iron and on the yield of titanium to the pig iron.

The scope encompassed:
- producing a trial batch of sinter with a titanium content of up to 10 kg Ti per 1 ton of sinter, with taking samples to determine the strength [3];
- using the produced sinter as a charge to the blast-furnace process;
- taking pig iron samples on each pig iron tapping in order to determine the chemical composition;
- determining the yields of titanium and vanadium;
- using mathematical statistics and based on the approximation method, establishing a relationship of the yield and slag-to-metal titanium distribution ratio on the basicity and silicon content of the pig iron;
- discussion of the obtaining results and drawing conclusions.

INDUSTRIAL TRIAL OF SINTER PRODUCTION AND PIG IRON PRODUCTION FROM THE TITANIUM-CONTAINING CHARGE

Taking into account practical data related to the smelting of pig irons from the titanium-containing charge, the consumption of such an amount of the titanium-magnetite concentrate was assumed for sinter production, which would assure the introduction of about 10 kg TiO_2 per 1 ton to the blast furnace. The shares of sintering mixture constituents are shown in Table 1.

Table 1. **Shares of titanium sinter constituents**
Tablica 1. **Udio titana medu konstituentima sintera**

Material	Amount [kg]	Yield [kg]	Fe [kg]	SiO_2 [kg]	CaO [kg]	MgO [kg]	TiO_2 [kg]	V [kg]
Mixture of ores	163.3	160.2	93.2	13.2	9.5	3.6	-	-
Katchkanarsk concentrate	200.0	200.0	121.6	9.8	3.6	5.8	4.98	0.60
Hematite ore	456.0	420.0	234.0	86.2	3.6	0.9	-	-
Milling scale	80.5	80.5	56.8	1.3	-	-	-	-
Limestone	182.8	104.4	0.9	5.5	93.2	0.5	-	-
Dolomite	48.2	27.0	1.7	0.8	15.2	8.3	-	-
Quick coke	52.0	7.7	0.6	3.3	0.5	0.3	-	-

The share of 200 kg titanium-magnetite concentrate in the sintering mixture allowed a sinter of the contents of 0.48 % TiO_2 and 0.059 % V to be obtained. The introduction of titanium-magnetite concentrate to the production of sinter caused a reduction of sintering belt output by about 4 % with an increase in quick coke consumption by about 5 %. The increased consumption of quick coke allowed the proper strength properties of the sinter to be maintained.

During the operation of the sintering plant, a sinter sample was taken for the determination of sinter strength by the ISO drum method [4, 5] and for the determination of the chemical composition.

Data related to the chemical composition and strength of the sinter are given in Table 2. The behavior of titanium in the blast-furnace process was investigated when smelt-

Table 2. **Chemical composition and strength indices of sinter samples**
Tablica 2. **Kemijski sastav i indeksi čvrstoće uzoraka sintera**

Sinter sample no.	Fe [%]	FeO [%]	SiO_2 [%]	CaO [%]	MnO [%]	TiO_2 [%]	V [%]	Strength. ISO test W [%]	S [%]
1	51.6	10.06	10.4	11.4	1.44	0.48	0.050	58.0	5.6
2	51.6	8.00	10.9	11.8	1.44	0.46	0.059	56.6	5.7
3	50.4	11.87	12.9	12.6	1.87	0.50	0.059	58.4	5.2
4	50.4	11.61	12.8	11.8	1.58	0.48	0.057	57.7	5.2
5	51.2	8.51	11.4	11.4	1.73	0.47	0.057	57.6	5.4
6	50.3	10.06	11.9	12.4	1.58	0.49	0.058	58.2	5.3
7	51.2	12.38	10.8	12.0	1.58	0.48	0.058	58.4	5.6

ing foundry pig iron. The furnace loading, R/K, during the tests was 2.6.

It was determined that every third charge would contain 100 kg phosphorus during loading, in order to supply the appropriate amount of P.

Table 3. **Chemical composition of pig iron in successive casts**
Tablica 3. **Kemijski sastav željezne rude u nizu livova**

Cast no.	Chemical composition of pig iron				
	Si [%]	Mn [%]	Ti [%]	V [%]	S [%]
1	2.32	0.68	0.14	0.042	0.014
2	2.29	0.71	0.15	0.065	0.012
3	2.27	0.64	0.19	0.067	0.013
4	2.74	0.55	0.23	0.105	0.027
5	3.11	0.60	0.28	0.078	0.024
6	2.80	0.57	0.28	0.072	0.027
7	2.43	0.57	0.22	0.102	0.035
8	2.57	0.56	0.19	0.104	0.046
9	2.35	0.55	0.16	0.077	0.049
10	2.25	0.49	0.16	0.063	0.032
11	2.04	0.42	0.17	0.093	0.017
12	2.35	0.64	0.19	0.080	0.017
13	2.38	0.72	0.19	0.081	0.020
14	2.74	0.86	0.28	0.106	0.012
15	2.35	0.73	0.16	0.074	0.014
16	2.21	0.60	0.15	0.041	0.020

Coke used in the tests was characterized by good strength indices. The drum test showed the following index values: M30 - 61 to 81.9 % and M10 - 5.0 to 5.2 %, the amount of ash ranged from 0.7 to 10.3% and the amount of volatile matter was from 0.9 to 1.1 %.

Directly after the blast furnace had been loaded with the test charge and its operation stabilized, samples of pig iron and slag were taken during each tapping in order to determine the chemical composition.

The chemical compositions of obtained pig iron and slag during the investigated blast furnace operation period are reported in Tables 3. and 4.

Table 4. **Chemical composition of slag in successive casts**
Tablica 4. **Kemijski sastav šljake u nizu livova**

Cast no.	Chemical composition of slag						
	CaO [%]	SiO_2 [%]	MgO [%]	Al_2O_3 [%]	Ti [%]	V [%]	$\frac{CaO}{SiO_2}$
1	46.0	38.0	5.41	8.80	0.23	< 0.02	1.21
2	45.6	37.5	5.40	8.67	0.30	< 0.02	1.22
3	45.9	38.3	5.36	9.01	0.36	< 0.02	1.20
4	45.5	38.6	5.25	9.12	0.45	< 0.02	1.18
5	44.6	37.2	5.25	8.54	0.46	< 0.02	1.20
6	44.2	36.5	5.60	8.41	0.51	< 0.02	1.21
7	41.2	39.0	5.59	8.32	0.55	< 0.02	1.06
8	43.8	40.0	5.80	8.29	0.64	< 0.02	1.09
9	43.2	41.2	5.80	8.03	0.65	< 0.02	1.05
10	41.2	40.4	6.50	7.40	0.74	< 0.02	1.02
11	41.2	41.0	5.35	7.27	0.73	< 0.02	1.00
12	42.0	41.4	5.11	7.78	0.82	< 0.02	1.01
13	41.2	41.2	6.76	7.84	0.84	< 0.02	1.00
14	43.5	38.5	6.49	7.71	0.63	< 0.02	1.13
15	41.4	38.2	6.21	7.27	0.47	< 0.02	1.08
16	42.3	38.1	5.66	7.27	0.15	< 0.02	1.11

DISCUSSION OF INVESTIGATION RESULTS

Sinter samples were taken during sintering of mixtures containing titanium-magnetite concentrate in order to asses the quality of the product obtained. It is seen from Table 2. that sinters (tested by the ISO drum method) were characterized by a good strength of 56.6 to 58.4 % and did not deviate from the presently produced sinter.

Also, abrasion resistance did not differ from that of the presently produced sinter, being from 5.2 to 5.7 %. It was found that the output of the sintering belt on which the sinter was produced had decreased by about 4% in relation to the results obtained from the mixtures without titanium-magnetite concentrate. In this case, the reduction of output was caused by two parameters, namely: a 5 % increase of coke content in the charge and, probably, a worsening of mixture permeability to air due to the use of an non-conditioned concentrate.

Recording of the masses of pig iron and slag charge materials and the results of the chemical analyses of blast-furnace materials and products during the investigated period of blast furnace operation have enabled the calculation of the pig iron-to-slag titanium distribution ratio and the determination of the ratio of titanium yield in the pig iron.

The results of these calculations are given in Table 5.

Table 5. Ratios of pig iron-to-slag titanium distribution
Tablica 5. Omjer odnosa rasporeda sirovog željeza - šljake - titana

Sample no.	Mass of Ti_S [t]	Mass of Ti_Z [t]	$\frac{Ti_Z}{Ti_S}$	$\frac{CaO}{SiO_2}$	$\frac{Ti_Z}{Ti_S+Ti_Z}$	$\frac{Ti_S}{Ti_Z+Ti_S}$
	4 ⇒ 2 x 3	7 x 5 x 6	8 ⇒7 : 4	9	10 ⇒4:(4+7)	11 ⇒4(4+7)
1	0.176	0.184	1.04	1.21	0.511	0.489
2	0.205	0.270	1.32	1.22	0.568	0.430
3	0.162	0.198	1.22	1.20	0.550	0.450
4	0.267	0.337	1.26	1.18	0.557	0.443
5	0.280	0.299	1.07	1.20	0.516	0.484
6	0.459	0.510	1.11	1.21	0.526	0.474
7	0.158	0.275	1.74	1.06	0.635	0.365
8	0.276	0.608	2.20	1.10	0.686	0.313
9	0.146	0.390	2.67	1.05	0.727	0.273
10	0.166	0.518	3.12	1.02	0.757	0.243
11	0.182	0.511	2.80	1.00	0.606	0.394
12	0.331	0.343	2.85	1.01	0.740	0.260
13	0.205	0.588	2.87	1.00	0.741	0.250
14	0.588	0.382	1.50	1.13	0.600	0.400
15	0.205	0.376	1.83	1.08	0.647	0.353
16	0.193	0.135	0.70	1.11	0.411	0.589

The data shown in Table 5. have made it possible to establish the following relationships: titanium content of pig iron on its silicon content (Figure 1.); the metal-to-slag titanium distribution ratio on slag basicity (Figure 2.); and the yield of titanium on slag basicity (Figure 3.). When determining the latter, an assumption was made that the titanium contents of pig iron and slag were equal to their contents in the charge.

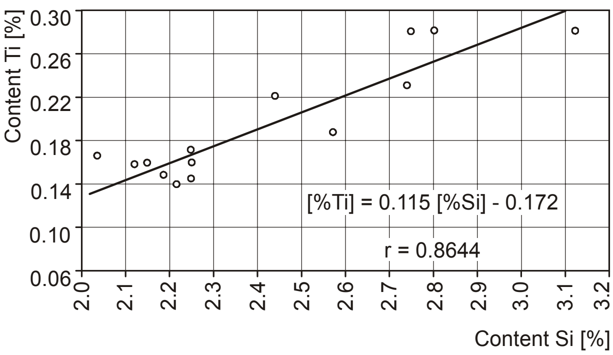

Figure 1. **Relationships of titanium content of pig iron on its silicon content**
Slika 1. **Odnos sadržaja titana u sirovom željezu na sadržaj silicija u njemu**

Figure 1. indicates that the increase in the silicon content of foundry pig iron is accompanied by an increase in its titanium content, according to the regression line equation:

$$[Ti] = 0.1505[Si] - 0.1719$$

where

[Ti] and [Si] - percentage contents of the elements in the pig iron.

This equation is valid in the interval of definition of [Si] ∈ <2 %; 3.2 %>.

It should be expected that for pig irons of a smaller silicon content the ratio of titanium distribution to the pig iron will be smaller.

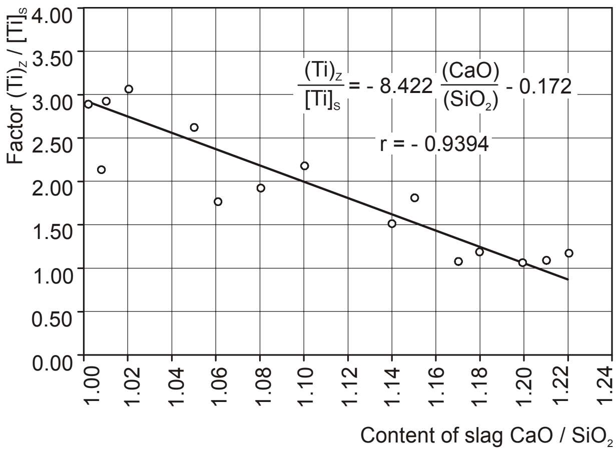

Figure 2. **Relationship of the metal-to-slag titanium distribution ratio**
Slika 2. **Odnos rasporeda: metal-šljaka- titan**

The test has shown (Figure 2.) that the slag-to-metal titanium distribution ratio decreases with increasing slag basicity, according to the equation:

$$\frac{(Ti)_Z}{[Ti]_S} = -8.422\frac{(CaO)}{(SiO_2)} + 11.266$$

in the range of

$$\frac{(CaO)}{(SiO_2)} \in \langle 1.0; 1.22 \rangle$$

where

$[Ti]_S$ - content of Ti in the pig iron, kg;
$(Ti)_Z$, (CaO), (SiO_2) - contents of the constituents in the slag, kg, %.

The above relationship shows that in order to decrease the fraction of titanium passing to the pig iron, the process should be conducted with possibly acidic slags. This is in agreement with the data relating to the technology of smelting ferrotitanium in electric furnaces, according to which increased CaO content in the slag favours the reduction of titanium, as well as with the results of laboratory tests.

It is characteristic that with the change of basicity from 1.0 to 1.22 the $(Ti)_Z/[Ti]_S$ ratio decreased by almost three times (from the value of 3.0 to 1.0).

A confirmation of this is the converse dependence of pig-iron titanium yield on slag basicity (Figure 3.), expressed by the equation:

$$\frac{[Ti]_S}{[Ti]_S + (Ti)_Z} = 0.885 \frac{(CaO)}{(SiO_2)} - 0.608$$

with this yield increasing as slag basicity increased. High correlation coefficients (above 0.8) for these relationships

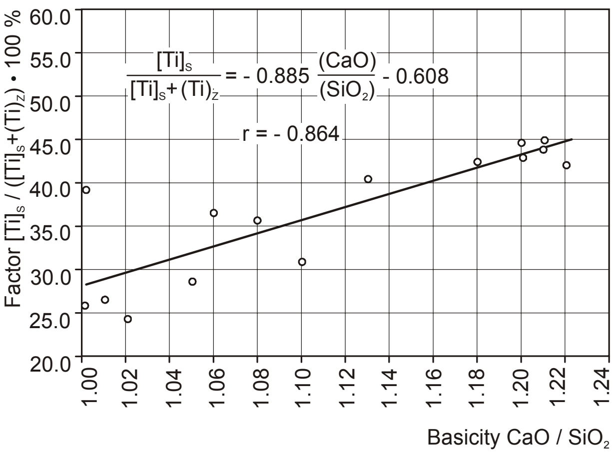

Figure 3. **Relationship of the yield of titanium on slag basicity**
Slika 3. **Odnos prinosa titana i bazičnosti šljake**

indicate that from the obtained regression equations the behaviour of titanium in the foundry pig iron smelting process can be predicted with a high probability.

The brief material balance (Table 4.) shows that in the conditions of the trial period of blast furnace operation in the smelting of foundry pig iron of a silicon content of 2.0 - 3.2 % and with a slag basicity of 1.0 - 1.22, the pig-iron titanium yield was 35 %, on average.

Vanadium introduced to the blast furnace in these conditions passed to the pig iron in 80 - 90 %. On the average, less than 13 % of this element passed to the slag.

FINDINGS AND CONCLUSIONS

From the investigations carried out, the following findings have been obtained and conclusions drawn:

- introduction of 200 kg titanium-magnetite concentrate to the sintering mixture per one ton of sinter caused a reduction of output by 4% for the conditions investigated.
- in the smelting of foundry pig irons of a silicon content from 2.0 to 3.2 % and with slag basicities of 1.0 - 1.22, averagely 36 % of titanium pass to the pig iron.
- the passage of titanium to the pig iron is favored by an increased silicon content of pig iron and a higher slag basicity.
- the pig-iron vanadium yield in the conditions of trial blast furnace operation was 87 %, on average.
- introducing approx. 10 kg TiO_2/ton pig iron did not caused any side effects in the process of foundry pig iron smelting.

REFERENCES

1. R. Budzik: Metallurgical properties of sinter of 0.1 - 4.0 basicity obtained with different quantities of titanium - magnetite concentrates, Izwiestia Wyzszych Ucziebnych zawiedienij, Black Metallurgy, 9 (1987) (orig. in Russian)
2. W Sabela, R. Budzik, J. Mróz: Investigation of possibilities of production high basicity sinter in model and technical conditions, 1994 Technical University of Czestochowa, unpublished
3. J. Mróz, R. Budzik: Metallurgical properties of aglomeratem depending on the fraction of titanium - magnetite concentrate in the mixture, Mala Lucivna 2001, Slovakia
4. International Standard ISO 3271, Iron ore, drum test, 322 (1975), transl. Institute of Iron Metallurgy
5. M. Kowalewski, B. Mitka: Review of the main methods of estimation the quality of sinter, Hutnik, vol. 4 (1976), 16-21 (orig. in Polish)