ISSN 0543-5846
METABK 44 (3) 179-182 (2005)
UDC - UDK 549.6:622.785:622.341.1–185=111

BEHAVIOR OF TITANIUM COMPOUNDS IN THE PROCESS OF SINTERING TITANIUM-MAGNETITE CONCENTRATES

Received - Primljeno: 2004-04-27
Accepted - Prihvaćeno: 2004-07-25
Preliminary Note - Prethodno priopćenje

The article presents the methods of identifying the behavior of titanium compounds in the process of sintering mixes containing titanium-magnetite concentrate of a basicity of 0,1 (without a limestone addition) and a basicity of 1,0 (with limestone added).

Key words: *sintering process, compound of titanium, mineralogical composition, titanium magnetite*

Ponašanje titanskih spojeva u procesu sinterovanja koncentrata titan-magnetit. Članak prikazuje metode identificiranja ponašanja titanskih spojeva u procesu sinterovanja mješavina koje sadrže koncentrat titan-magnetit bazičnosti 0,1 (bez dodavanja vapnenca) i bazičnosti 1,0 (s dodavanjem vapnenca).

Ključne riječi: *process sinterovanja, titanski spoj, mineraloški sastav, titan-magnetit*

INTRODUCTION

Presently, titanium-magnetite concentrates are only used to a negligible extend for the production of iron sinter in the world. Concentrates used are characterized by a very diverse chemical and mineralogical composition. In these concentrates, titanium most often occurs in different amounts in the form of titanium-magnetite $(Fe,Ti)_3O_4$, ilmenite $FeTiO_3$, ulvite (ulvo-spinel) Fe_2TiO_4 and rutile TiO_2.

In concentrates, titanium occurs frequently in the form of solid solutions in the FeO-Fe_2O_3-TiO_2CaO and FeO-Fe_2O_3-TiO_2-Al_2O_3 systems [1]. Many such types of titanium-containing systems have not been fully investigated yet. In the sintering process, titanium-containing compounds and phases enter into chemical reactions to form new compounds and phases. There are little data available in literature concerning the sintering of titanium-magnetite ores; also, there are no available data on the methods of obtaining mineralogical compositions of titanium-containing sinters. The behavior of titanium in the titanium-magnetite ore sintering process has not been fully explained so far. The data presented in this publication represent a part of the results obtained within an extensive research project concerning the sintering of Polish titanium-magnetite ores containing additional vanadium.

PURPOSE AND SCOPE OF INVESTIGATION

The main purpose of the investigation was to determine the behavior of titanium in the process of sintering mixes of basicities of 0,1 and 1,0, containing a titanium-magnetite concentrate. A further goal was to establish the mineralogical composition, while giving particular consideration to new phases and compounds forming, which contained titanium. The basic testing material was made up of sinters obtained from mixes with basicities, 0,1 and 1,0.

The scope of investigation covered:

- sintering of titanium-magnetite-containing mixes of basicities 0.1 and 1.0, and the preparation of testing samples for phase and mineralogical examinations; and
- determination of the mineralogical and phase composition of obtained sisters, with particular consideration being given to the behavior of titanium compounds in the sintering process.

Mixes containing 100 % of titanium-magnetite concentrate were used for the sintering process. Chemical and grain compositions of materials used for sintering and of obtained sinters are given in Table 1.

TITANIUM IN THE SINTERING PROCESS

Sintering is a process that occurs at an elevated temperature between the grains of palletized ore. The temperature causes the transition of some amount of the ore

---

R. Budzik, Faculty of Materials Processing Technology and Applied Physics Częstochowa University of Technology, Częstochowa, Poland

mix into a pasty-liquid state, and the presence of carbon and thermal conditions promote the development of oxidation-reduction processes.

The possibility of two opposite processes progressing during sintering should be explained by the micro-inhomogeneity of the mix layer. In addition to oxidation-reduction processes, processes between condensed phases also occur. Some of the compounds contained in the mix compounds can undergo either oxidation or reduction. Crude iron and titanium-bearing concentrates contain magnetite Fe_3O_4, titanium-magnetites $(FeTi)_3O_4$, ulvite (ulvo-spinel) Fe_2TiO_4, ilmenite $FeTiO_3$, rutile TiO_2 and gangue minerals (chiefly based on SiO_2 and CaO) [1]. Theoretically, the following reactions are likely to occur in oxidation conditions [2]:

$$2FeTiO_3 + ½O_2 = Fe_2TiO_5 + TiO_2$$

$$Fe_2TiO_4 + ½O_2 = Fe_2TiO_5$$

It has been found, that pseudo-brookite Fe_2TiO_5 [2] is a compound which is unstable in sintering conditions, so there is a possibility of the formation of TiO_2-based compounds chiefly with CaO and MgO compounds.

Unless free CaO lime is present, the compounds $CaO{\cdot}TiO_2$ and $CaO{\cdot}SiO_2TiO_2$ are likely to form.

In practice, creating the prevalence of oxidation processes over reduction processes requires the use of the smallest possible quick-coke addition to the sinter six and a large excess of air. On the other hand, the amount of quick coke added to the mix may not be too small in order that a well done sinter of good strength be obtained, which will meet the criterion for using it as a blast-furnace charge component.

The excess of air may not be to large [3], as it considerably lowers the temperature in the heat zone of the sintered layer and reduces the linear sintering rate, which, as a consequence, adversely affects the quality of the obtained sinter.

Taking account of the above theoretical analysis of the behavior of titanium compounds in the sintering process, the investigation took into consideration the findings concerning the addition of quick coke and the amount of lime added to the sinter mix. The quick-coke addition in the mixes was established experimentally at 70 kg/t of sinter. As investigation showed [1], this was a minimum amount, considering the general criterion of using sinter for the blast-furnace charge.

METHODS OF IDENTIFYING THE MINERALOGICAL COMPOSITION OF OBTAINED SINTERS

The mineralogical composition of tested sinter samples was identified on the basis of microscopic observations in reflected light carried out on a Poland, a microscope of German make, as well as a X-ray microanalysis. By the X-ray microanalysis, using an electron micro-probe, such sinter specimens were chosen, whose analysis, as conducted by this method, enabled the identification of forming phases, including chiefly the identification of titanium compounds and phases.

To carry out tests by the above-mentioned method, specimen microsections were spray-coated by an approximately 200 A-thick graphite coating (such a film provides electrical conductivity). The tests were performed by using a SEMQ X-ray micro-analyzer supplied by ARL of the USA. The tests covered a qualitative analysis of surface distribution of elements in selected micro-areas of the sinter microsection.

The electron images of a chosen microsection surface fragment and corresponding images of element distribution were produced by the surface scanning technique. The distribution of iron, titanium, aluminium, magnesium, calcium and silicon was analyzed.

LiF (iron analysis), ADP (calcium analysis) and RAP (aluminium, magnesium and silicon analysis) monochromators were used for analysis. The voltage accelerating electrons inducing X-radiation was 20 kV, while the electron beam current was approx. 150 μA. The images of element distributions within iron oxide grains and in the regions filling the space between those grains enable some hypotheses concerning the types of phases occurring during sintering to be advanced. The tests made it possible to track the process of formation of titanium compounds during sintering, vanadium-removed and vanadium-retained titanium-magnetite concentrates.

X-RAY PHASE ANALYSIS OF SINTERS

Sinters intended for phase composition examination, whose chemical composition is summarized in Table 1., were ground to a grain size of 75 μm. From thus obtained powders, flat test specimens were pressed out manually, which

Table 1. **Chemical composition of sinter mix components**
Tablica 1. **Kemijski sastav komponenti smjese sintera**

Material	Vanadium - retained Ti - magnetite concentrate	Limestone	Quick coke
Fe	63,92	0,57	1,02
TiO_2	6,06	-	-
CaO	0,85	55,01	2,57
SiO_2	0,45	0,86	4,89
MgO	1,18	0,68	0,44
P	n. d.	0,014	0,03
Grain size	up to 0,1	up to 0,3	up to 3,0

were subsequently taken for phase analysis tests using a diffractometer. Diffraction pattern records were made using a Philips PW 1140 diffractometer with a cobalt anode lamp and an iron filter, using an accelerating voltage of 35 kV and an anodic current of 10 mA. Diffraction patterns were identified in a standard manner based on the collection of data stored in the files of JCPRF (formerly ASTM) in 1979 [3] and additions included current literature reports. The diffraction patterns of medium specimens allow the detection of phases with a content of at least 3 %. In the case of sinter test samples designed for phase examination, there were many phases and compounds which did not exceed 3 % in content. For this reason, a trial of increasing the contents of dia- and paramagnetic phases by applying separation in a stationary magnetic field was made.

MINERALOGICAL COMPOSITION OF THE 0,1-BASICITY SINTER

Acid sinters of a basicity of 0,1 (without a limestone addition) are characterized by a finer crystalline structure compared with 1.0-basicity sinters, and a relatively uniform distribution of phases over the entire surface of microsections examined.

The silicate phase takes up 5 to 10 % in particular micro-areas. The composition of this phase included a slight amount of fayalite and traces of the SCAF (SiO_2-CaO-Al_2O_3-Fe_2O_3) ferrite phase. This phase was first identified by C. Dumortier [3]. The rest of the silicate phase is made up by magnetite and titanium-magnetite. In addition to magnetite, two more phases occur, which contain traces of titanium in $FeO \cdot TiO_2$ (ilmenite) and $2FeO \cdot Fe_3O_4 \cdot TiO_2$ (ulvo-spinel).

In topographic examination of element distribution in micro-areas, iron oxide grains contain uniformly distributed magnesium. The areas of coverage by magnesium and iron include magnetite $(FeMg)O \cdot Fe_2O_3$, the lattice of which contains atoms of magnesium. The observation of the electron image of iron oxide grains shows that their borders are lighter. This is hematite formed by the oxidation of the magnetite.

Calcium, silicon, magnesium and aluminium are not included in the iron- and titanium-rich phase located at the borders. It has been found that hematite does not occur in the form of single crystals, but it occurs at the magnetite borders, which is a result of oxidation taking place chiefly during cooling the sinter layer. Phase composition of obtained sinters is given in Table 2.

MINERALOGICAL COMPOSITION OF THE 1,0-BASICITY SINTER

In samples of the 1,0-basicity sinter, a predominant phase is magnetite, though a cementization of its crystals can be noticed. The hematite phase occurs in micro-areas in the amount of approx. 3 %. Also, calcium ferrite occurs, though in a very small number of up to 2,5 % of the surfaces examined. The electron image for a sinter obtained entirely from the titanium-magnetite concentrate and the distribution of iron indicates that the iron oxides occur in the form of polygonal grains and in the form of less numerous dendrites that have crystallized out of the liquid filling the spaces between the primary magnetite grains.

Table 2. **Phase composition of obtained sinters**
Tablica 2. **Sastav baze dobivenih sintera**

No.	Phase composition		
		$CaO/SiO_2 = 1,0$	$CaO/SiO_2 = 0,1$
1.	$(FeMg)O \cdot Fe_2O_3$	++++	++++
2.	Fe_2O_3	+++	++
3.	Fe_3O_4	+++	++++
4.	FeO	++	++
5.	$NaAlSiO_4$	++	++
6.	$FeSiO_4$	++	++++
7.	Ca_3SiO_5	++	+
8.	$CaO \cdot 2Fe_2O_3$	++	+
9.	faza SCAF	++	+++
10.	$2FeO \cdot Fe_3O_4 \cdot TiO_2$	+	+++
11.	$2FeO \cdot TiO_2$	+	++
12.	$CaO \cdot MgO \cdot SiO$	+	−
13.	$2CaO \cdot MgO \cdot 2SiO_2$	+	+
14.	SiO_2	−	++
15.	$CaO \cdot Fe_2O_3$	++	−
16.	$CaO \cdot TiO_2$	+	−
17.	$CaO\ SiO_2\ TiO_2$	+	−

++++ high, above 10 % ++ little, 3 - 5 %
+++ medium, 5 to 10 % + very little, below 3 %

Titanium occurs in magnetite grains; however, it exhibits a higher concentration at the grain borders than within the grains.

The phase filling the spaces between magnetite grains contains chiefly silicon and calcium, as well as iron and aluminium. The aluminium occurs in primary iron oxides, but is also included in the grains of oxides crystallized in the form of "snowflake" dendrites, whereas silicon and calcium do not migrate to the iron oxides.

The phase analysis shows that in the obtained sinters (Table 2.), the silicate phase includes traces of the SCAF ferrite phase, γ-$2CaO \cdot SiO_2$, $CaO \cdot SiO_2$, $CaO \cdot Al_2O_3$ and $CaO \cdot TiO_2 \cdot SiO_2$ [3]. Beyond the iron oxide region, there is a silicon- and calcium-rich phase, containing also iron, magnesium and aluminium. Phase analysis has confirmed that this is a complex ferrite phase of SCAF type; small amounts of α-SiO and $2CaO \cdot MgO \cdot 2SiO_2$ (ackermannite) have also been detected. Phase composition of obtained sinters is given in Table 2.

FINDINGS AND CONCLUSIONS

In the investigated titanium-vanadium magnetite concentrate, titanium occurs in titanium-magnetite $(FeTi)_3O_4$, as well as in ilmenite ($FeO \cdot TiO_2$) and, in a negligible amount, in ulvo-spinel ($2FeO \cdot TiO_2$).

A main oxide phase in 0,1-basicity sinter is the magnetite and titanium-magnetite phase. No titanium compounds containing calcium and magnesium were found in these sinters.

No migration of titanium to the silicate phase was found in any 1,0-basicity sinters tested, but it was found that titanium migrated from the magnetite lattice to hematite in the sintering process, this was taking place always toward the grain borders and in an oxidizing atmosphere.

The presence of titanium compounds, $CaTiO_2$ (perovskite) and $CaO \cdot SiO_2 \cdot TiO_2$ (calcium titanate), as well as iron titanates, $2FeO \cdot Fe_3O_4 \cdot TiO_2$ and $2FeO \cdot TiO_2$, were found in the silicate phase of the sinters tested. It can be presumed that the titanium compounds will have a great effect on the production of pig iron, so-called titanium pig iron.

REFERENCES

[1] R. Budzik, R. Stec, Własności metalurgiczne spieków o zasadowości do 8.0 przy różnym udziale koncentratów tytanomagnetytowych. Hutnik nos. 7-8, 1985.

[2] R. Budzik, Metallurgitcheske svoistva aglomeratov osnovnostiu 1.0–4.0 polutchenykh pri rozlitchnov rozkhode titanomagnetitovego aglomerata. Izv. Wyzhsch. Utch. Zav. Tchior. Met. (Russ.) no. 9, 1987.

[3] Dumotier, Metallurgy. Benelux, 16 (1976) 1, 35 - 40.