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COMPOSITION AND PROPERTIES OF TiO_2 POWDER GOT HYDROMETALLURGICALLY

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Properties of TiO_2 powder got hydrometallurgically from the slag that was, together with pig iron, a product of reductional red mud electromelting were investigated using physico-chemical methods of analyzing. The samples of TiO_2 powder contain high quantity of titanium compared with the used raw material - granulated slag. Investigating the mophology of the powder samples, it has been found out that aggregation of particles and forming of bigger aggregates take place. They differ in form and size. A granulometric analysis of the powder determined a weight portion of the biggest aggregates in it, as well as its specific surface.

Key words: *red mud, separation TiO_2, morphology, specific surface*

Sastav i svojstva hidrometalurški dobivenog praha TiO_2. Fizikalno-kemijskim metodama analize ispitana su svojstva hidrometalurški dobivenog TiO_2 praha iz troske koja je uz sirovo željezo produkt redukcijskog elektrotaljenja crvenog mulja. Uzorci praha TiO_2 sadrže visoku količinu titana u usporedbi s korištenom sirovinom - granuliranom troskom. Istraživanjem morfologije uzoraka praha ustanovljeno je da dolazi do agregacije partikula i nastajanja većih agregata, koji se međusobno razlikuju po obliku i veličini. Granulometrijskom analizom praha utvrđen je težinski udio najkrupnijih agregata u njemu, kao i njegova specifična površina.

Ključne riječi: *crveni mulj, separacija TiO_2, morfologija, specifična površina*

INTRODUCTION

A description of a complex red mud and high silica bauxites processing procedure [1-3], including solvent extraction processing of the sulphuric acid solutions of the treated granulated slag, got during their reducing electromelting was given several times. After leaching of the slag (4.31% Ti) by sulphuric acid, a solution contained, mol·dm^{-3}: Al_2O_3 0.059-0.078, Fe_2O_3 0.019-0.031, TiO_2 0.006-0.012 (pH = 0.6). Solvent extraction was carried out by 5% di-(2-ethylheyl) phosphoric acid solution in kerosene with addition of 2% of 2-ethylhexanol as phase modifier (O:W = 1:1.6) in a four-stage mixer-settler cascade capacity (hold-up) of 50 dm^3 each. During solvent extraction together with titanium (D = 160, E = 99.5%) zirconium and rare earth elements passed into the organic phase. Reextraction was carried out by 10% Na_2CO_3 solution in two stages, the phase ratio being 2 to 1, in order to obtain the useful constituents mentioned above. After that the organic phase was used again in the process of solvent extraction, practically without losses. From the Na_2CO_3 solution the hydrolized $Ti(OH)_4$ precipitate was separated using a vacuum filter, washed and purified bacause during the stripping a part of coextracted iron (III) also precipitated. The washed $Ti(OH)_4$ was then calcined into TiO_2. A study of properties of TiO_2 powder got in the described hydrometallurgical procedure is the subject of this investigations.

EXPERIMENTAL

There was no need for additional fragmentation of TiO_2 powder samples so they were directly further investigated. The chemical composition of the TiO_2 sample was determined by a classical analytical method and a method of atomic absorption spectrometry (micro-components). The phase composition of the TiO_2 powder is identified on the base of the X-rayed difractional spectrum applying CuKα X-ray tubes, and its microstructure on scanning electronic microscope and microanalyzer. The morphology of the sample and the presence and distribution of Ti, Mg, Si, Al, Fe, Mn, Ca, K and Na were carried out. The investigations were carried out by a qualitative scanning microanalysis. A granulometric analysis of the TiO_2 powder sample was carried out on a MALVERN 3600 type of apparatus.

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RESULTS AND DISCUSSION

A quantitative chemical composition of the TiO_2 powder sample got by chemical analysis shows that it is the sample containing a relatively high concentration of titanium, though other elements should not be forgotten. The results of the chemical analysis of the TiO_2 powder sample given in Table 1 enable certain comparisons.

Table 1. **Chemical composition of a TiO_2 powder sample**
Tablica 1. **Kemijski sastav uzorka praha TiO_2**

Element	Ti	Mg	Si	Al	Fe
%	54.296	0.049	0.836	0.232	3.365
Element	Mn	Ca	K	Na	
%	0.013	0.077	+	0.036	
+ Under the limit of sensibility of the method					

Compared to a starting material - granulated slag with 4.31% of Ti, a portion of Ti is 12.6 times larger in the powder. The elements in the powder have the largest mass portion of Fe, Si and Al whereas the portions of Ca, Mg, Na and Mn are much smaller. These results are considered very important to evaluate the economy of the hydrometallurgical getting of TiO_2 from the slag resulting after a pyrometallurgical red mud processing.

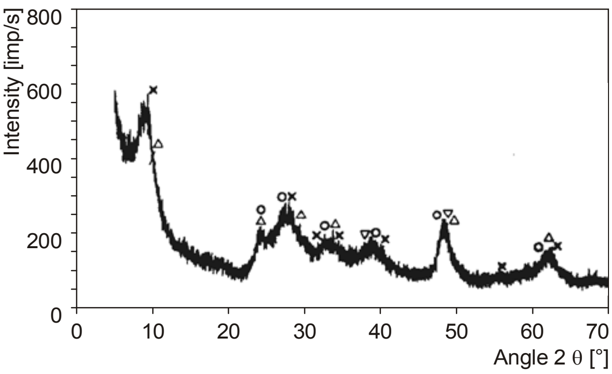

Figure 1. **X-ray diffraction pattern of a TiO_2 powder sample: ○-$NaFeTi_3O_8$, ×-$NaAl_2(Si, Al)_4O_{10}(OH)_2$, Δ-$Na_{0,7}(Ti_{1,75}Mg_{0,35})O_4$, ∇-$FeSi_2$**
Slika 1. **Difraktogram uzorka praha TiO_2: ○-$NaFeTi_3O_8$, ×-$NaAl_2(Si, Al)_4O_{10}(OH)_2$, Δ-$Na_{0,7}(Ti_{1,75}Mg_{0,35})O_4$, ∇-$FeSi_2$**

X-ray difractional analysis of the TiO_2 powder sample has shown that it is amorphous with a small portion of crystalline mass of some admixtures. The following phases have been identified from the difractional spectrum (Figure 1): $NaFeTi_3O_8$, $NaAl_2(Si,Al)_4O_{10}(OH)_2$, $Na_{0.7}(Ti_{1.75}Mg_{0.35})O_4$ and $FeSi_2$. The portion of the remaining admixtures in the powder sample is small and they are not identified as crystalline mass.

The TiO_2 powder was first characterized by the particular phenomena among its particles, then by granulometric composition and by the largeness of its specific surface. The solution of the powder morphology enables to conclude about the compactness and arrangement of the particles. The powder morphology was taken down on a chosen position in the picture of secondary electrones magnified 100x and 10000x, Figure 2. The aggregation of the particles and formation of larger aggregates differing in form and size, can be noted. The slab-like aggregates appeare as single formations, whereas the spheroidal aggregates appeare in a form of unsymmetrical grains spread freely in the space (Figure 2a). The spheroidal aggregates are smaller than slab-like aggregates and they are not compact in structure as the slab-like ones. Each larger grain consists of a large number of small grains (Figure 2b). Formation of large grains depends of the quality of small grains surface which is influenced by chemical and minerological composition. The number of small grains contacts increases with the decreasing of their size. This is why such larger grains, where a great number of contacts have happened (i.e. made of smaller grains), are less porous (more compact).

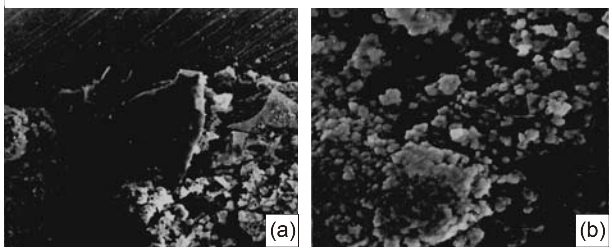

Figure 2. **SEM micrographs of a TiO_2 powder sample (magn.: (a) 100x, (b) 10000x)**
Slika 2. **Scanning mikrografije dobivene pretražnom elektronskom mikroskopijom uzorka praha TiO_2 (povećanje: (a) 100x, (b) 10000x)**

The electronic microanalysis of spheroidal and a slab-like aggregates that are in the first plan of the Figure 2a has been done [4]. Distribution of the elements present in a spheroidal and a slab-like aggregate can be seen in Figure 3 and 4 by analyzing characteristic X-radiation emited by the elements present in the sample (Ti, Si, Al, Fe, Mn, Ca, K and Na). There can be seen that in formation of the spheroidal aggregates mostly Ti and Fe and less Si and Al take part (Figure 3) and in the slab-like aggregate there are mostly Si and Al and up to some limit Ti and Mg (Figure 4). The rest of the elements, except Ca, take almost equal part in formation of the both aggregates.

The granulometric analysis of the TiO_2 powder is given in Table 2. There can be seen that the differences in size of aggregates are large. The size of the biggest aggregates does not go over 118.4 μm, and the one of the smallest is not under 1.5 μm. The largest weight share (30.3%) in the powder have those of 54.9-118.4 μm size. The weight portion of the fractions under 54.9 μm in the powder is

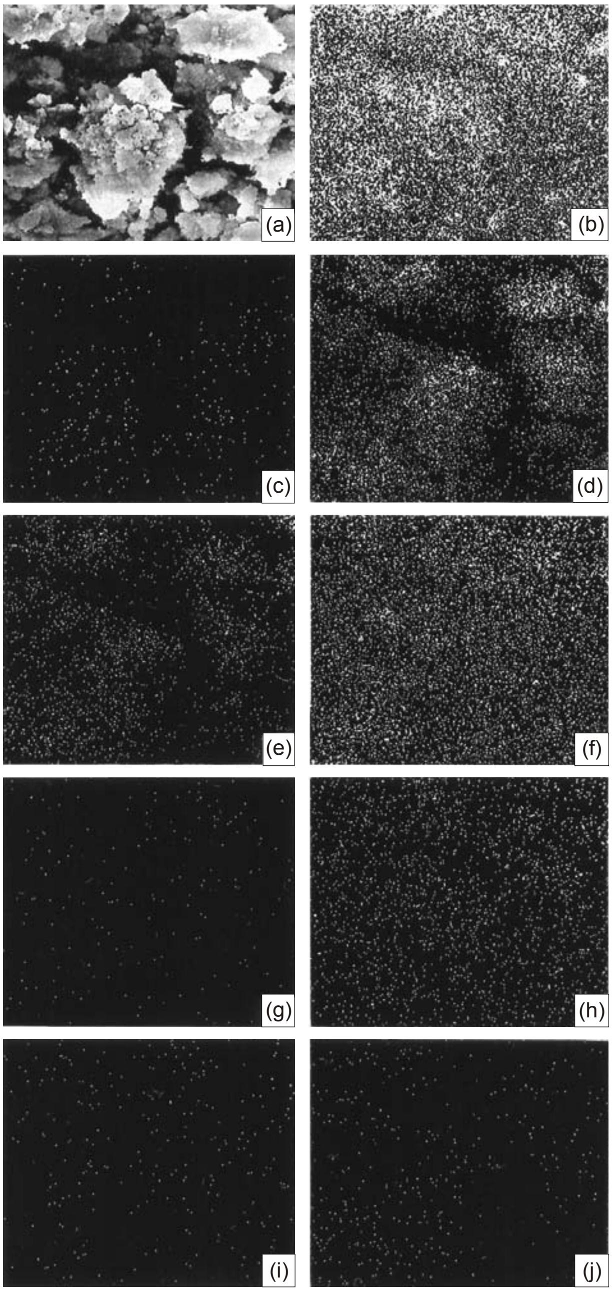

Figure 3. **SEM micrograph and X-ray microanalysis pictures of a spheroidal aggregate in a TiO_2 powder sample (magn.: 800 x)**
(a) SEI micrograph, (b) Ti, (c) Mg, (d) Si, (e) Al, (f) Fe, (g) Mn, (h) Ca, (i) K, (j) Na

Slika 3. **Scanning mikrografija dobivena pretražnom elektronskom mikroskopijom i snimke mikroanalize sferoidnih agregata u zorku praha TiO_2 (povećanje: 800 x)**
(a) SEI mikrografija, (b) Ti, (c) Mg, (d) Si, (e) Al, (f) Fe, (g) Mn, (h) Ca, (i) K, (j) Na

69.7% (Figure 5). The specific surface of the powder determined by BET method was 49.19 m^2/g, while bulk density was not possible to determine because the available method was not reliable.

At the end, it is necessary to remind the degree of utilization of TiO_2 contant in the slag is 85-90%, and the average of 12-15 kg of TiO_2 powder is obtained per ton of pig iron produced by reductional electromelting of red mud [5]. Tech-

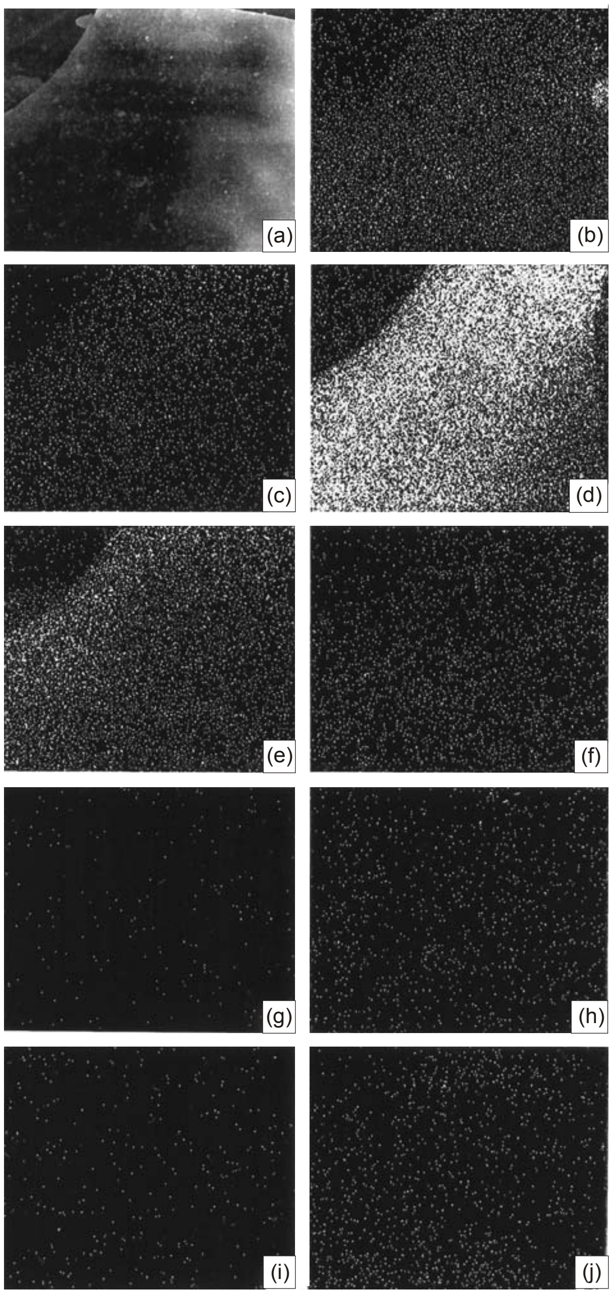

Figure 4. **SEM micrograph and X-ray microanalysis pictures of a slab-like aggregate in a TiO_2 powder sample (magn.: 800x)**
(a) SEI micrograph, (b) Ti, (c) Mg, (d) Si, (e) Al, (f) Fe, (g) Mn, (h) Ca, (i) K, (j) Na

Slika 4. **Scanning mikrografija dobivena pretražnom elektronskom mikroskopijom i snimke mikroanalize pločastih agregata u uzorku praha TiO_2 (povećanje: 800x)**
(a) SEI mikrografija, (b) Ti, (c) Mg, (d) Si, (e) Al, (f) Fe, (g) Mn, (h) Ca, (i) K, (j) Na

Table 2. **Results of the granulometrc analysis of a TiO_2 powder sample**

Tablica 2. **Rezultat granulometrijske analize uzorka praha TiO_2**

Size [μm]	Weight % under	Weight in band [μm]	Portion [%]	Light energy calculated	Light energy measured
118.4	100.0				
54.9	69.7	118.4 - 54.9	30.3	259	265
33.7	43.4	54.9 - 33.7	26.3	253	264
23.7	34.4	33.7 - 23.7	9.0	247	252
17.7	24.4	23.7 - 17.7	10.0	247	256
13.6	21.5	17.7 - 13.6	2.9	276	284
10.5	13.0	13.6 - 10.5	8.5	324	323
8.2	11.1	10.5 - 8.2	1.9	386	407
6.4	10.0	8.2 - 6.4	1.1	466	467
5.0	5.6	6.4 - 5.0	4.4	576	602
3.9	5.6	5.0 - 3.9	0.0	732	747
3.0	5.6	3.9 - 3.0	0.0	983	920
2.4	5.6	3.0 - 2.4	0.0	1231	1163
1.9	0.8	2.4 - 1.9	4.8	1556	1541
1.5	0.0	1.9 - 1.5	0.8	1906	2047
1.2	0.0	1.5 - 1.2	0.0	2047	1998

nological solutions for red mud processing have been the subject of our investigations for many years, but encouraging results are everything that has been achieved so far [6].

CONCLUSION

The chemical composition of TiO_2 powder got hydrometallurgicaly from the slag that was, together with pig iron, a product of reductional red mud electromelting have been determined. The mass portion of titanium in the powder (54.296 %) and in relation to the starting raw material is increased 12.6 times. Also, morphological and physical properties of the powder have been determined. It has been found that particles aggregate and larger aggregates that differ in form and size are formed. Within them elements are distributed uniformly and in mixed groups. The size of the largest aggregates in the powder does not exceed 118.4 μm, and with the smallest it is not under 1.5 μm. In this case the specific surface of the powder is 49.19 m^2/g.

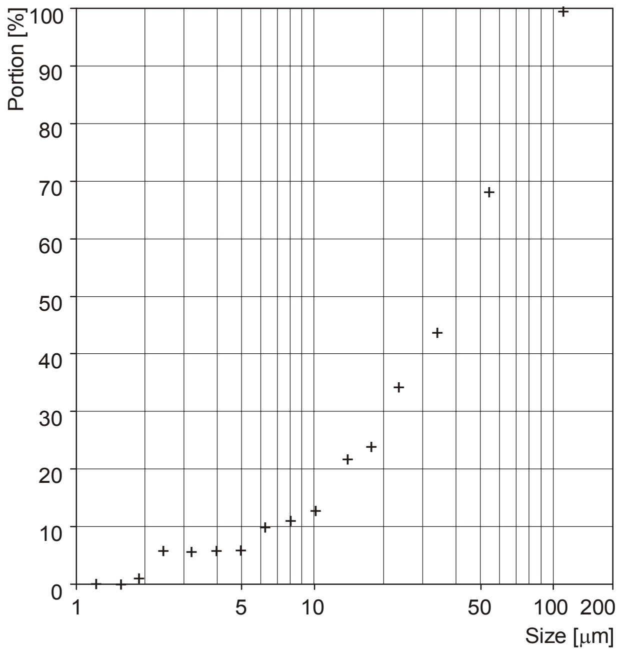

Figure 5. **The weight portion of the fractions in a TiO_2 powder sample**

Slika 5. **Težinski udio frakcija u uzorku praha TiO_2**

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