[Article ID] 1003 - 6326(2000)04 - 0520 - 04

Separating titania from treated slag by gravity separation or flotation①

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[Abstract] In the blast furnace slag, titanium disseminates in various mineral phases. Titanium could be concentrated mainly in perovskite, which could be selectively precipitated and grown by optimizing the operation factors like slag composition, temperature of heat treatment and additives. The titanium slag mineralography and the distribution in the as-received slag and the treated slag, as well as the methods of perovskite separation were studied. After treatment, the grain size is increased from 5 μm to 200 μm, the content of TiO_2 in perovskite increases from 48 % to 81 %, the morphology changes from snow-shaped grain to coarse dendrites or equiaxed crystals. A concentrate is produced by gravity separation analyzing 35.25 % TiO_2 with a recovery of 68.28 % and a tailing analyzing 9.53 % TiO_2. A concentrate analyzing 40.08 % TiO_2 and a tailing analyzing 9.28 % TiO_2 can be obtained by flotation.

[Key words] gravity; flotation; slags
[CLC number] TF534.2; X757 **[Document code]** A

1 INTRODUCTION

China is a titanium rich country, whose 92.4 % of titanium resource is vanadium-titanium bearing magnetite. About 53 % titanium were in iron concentrate after mineral processing, by which the blast furnace slag containing about 25 % TiO_2 were produced[1]. The content of TiO_2 in such slag is too low to separate titanium dioxide, and it is also too high to produce slag cement[2]. In Paizhihua iron mine, P. R.China, it has been accumulated 50 million tons so far, and it is still increasing at a rate of 3 million tons per year, resulting in a waste of titanium resources and pollution of environment.

Due to the dispersed distribution of titanium component in various mineral phases, very fine grains (< 10 μm) and complex interfacial combination, it is very difficult to recover titanium component from the slag by traditional separating technique.

In this paper, a novel technique to recover titanium from the waste slags is proposed[3,4], on which three continuous processes are involved: selective concentrating, selective growing and selective separating. The perovskite is designed as a titanium-rich phase, in which the most titanium is concentrated promptly, then perovskite could be selectively grown and coarsened by optimizing the heat treatment and the appropriate additives[5,6]. The grain size of perovskite phase was larger than 80μm, and the crystals appeared as coarsening dendrites or equiaxial grains like lump.

The mineralogical characteristics of the as-received and the treated slag were also examined with particular emphasis on the distribution of titanium and the increase in grain size for liberation. Attempts were made to separate the slag by gravity concentration and to explore the possibility of flotation.

2 EXPERIMENTAL

A received blast furnace slag taken from Panzhihua Iron and Steel Company was dried and mixed evenly(as-received slag). The slag powder or powder mixed with appropriate additives, were placed in a crucible in a nitrogen-purged corundum tube, the chemical composition was adjusted and the heat treatment was optimized. The experiments were carried out in vertical $MoSi_2$ furnace. For each experiment, about 100 g slag was placed in a crucible, which was lowered into the hot zone of the furnace. It increased to the required temperature and held for 30 min, then decreased at a rate of 1 K/ min. The slag obtained after these treatments was called treated slag, in which perovskite could be selectively precipitated and grown.

The chemical compositions and mineralogical phases of the slag were examined by chemical analysis, optic microscope and XRD. The microstructures and the chemical composition of the main minerals were examined under SEM(JSM-610F).

The treated slag samples were ground to grains (< 150 μm) in a porcelain grinder, screened into four class: 150 ~ 100 μm, 100 ~ 75 μm, 75 ~ 38 μm, < 38 μm, and then separated on an XYZ-1100 × 500 shaking table. The equipment employed in flotation tests included XFG-76 flotation unit cell, PHS-25 acidi-

① **[Foundation item]** Project (59574021) supported by the National Natural Science Foundation of China and project supported by the State Key Lab for RSA **[Received date]** 1999 - 08 - 27; **[Accepted date]** 1999 - 11 - 10

tymeter and IR-435 infrared spectrophotometer. To investigate flotation characteristics of perovskite and titanaugite, the 38 ~ 74 μm grains were selected, separated on shaking table repeatedly until perovskite with a purity of 95 % was obtained, then the pure mineral was washed with distilled water for several times and dried in air at room temperature.

3 RESULTS AND DISCUSSION

3.1 Mineral components and crystal characteristic

The microstructures of the as-received slag samples and the treated slag samples are shown in Fig.1. The four phases in the as-received slag are identified in the treated slag. They are perovskite, rich-titanium diopside, titanaugite and spinel[7]. While the grain sizes, appearance and quantity vary, the grain sizes of perovskite in the as-received slag are extremely fine, about 5 ~ 20 μm, and the crystals mostly appear as fine dendrites or snow-shaped grains. Perovskite is locked with spinel and titanium rich diopside, even wrapped by them. The grain sizes of titanium rich diopside, titanaugite and spinel are highly variable, ranging from extremely fine to relatively coarse in as-received slag, as shown in Figs.1(a) and (b). Perovskite grains grow larger and more uniform after heat treatment. The precipitating quantity approaches 30 %, and the grain size is larger than 80 μm, as well as the crystals appear as coarsening dendrites or equiaxed crystals like lump, as shown in Figs.1(c) and (d). The crystals of titanaugite appear as granular aggregate in as-received slag, and as thin fiber or feathered crystals in the treated slag.

The chemical compositions of treated slag are listed in Table 1. Table 2 lists the EDS analysis results of major mineral phases in treated slag. Much of the titanium is found in the perovskite phase which analyzed 56.49 % TiO_2, while titanium rich diopside, titanaugite and spinel were analyzed 14.26 %, 6.87 % and 6.09 % TiO_2, respectively.

Table 1 Chemical compositions of treated slag (%)

Component	Content	Component	Content
CaO	38.84	V_2O_5	0.52
SiO_2	15.40	FeO	3.36
MgO	6.23	MnO	1.67
Al_2O_3	10.37	S	0.18
TiO_2	22.54	K_2O	0.89

The content of mineral phases was determined and the distribution of TiO_2 in mineral phases was calculated, as listed in Table 3. The distribution of TiO_2 in perovskite occupied the total TiO_2 of the slag was increased from 48 % in as-received slag to 81 % in treated slag.

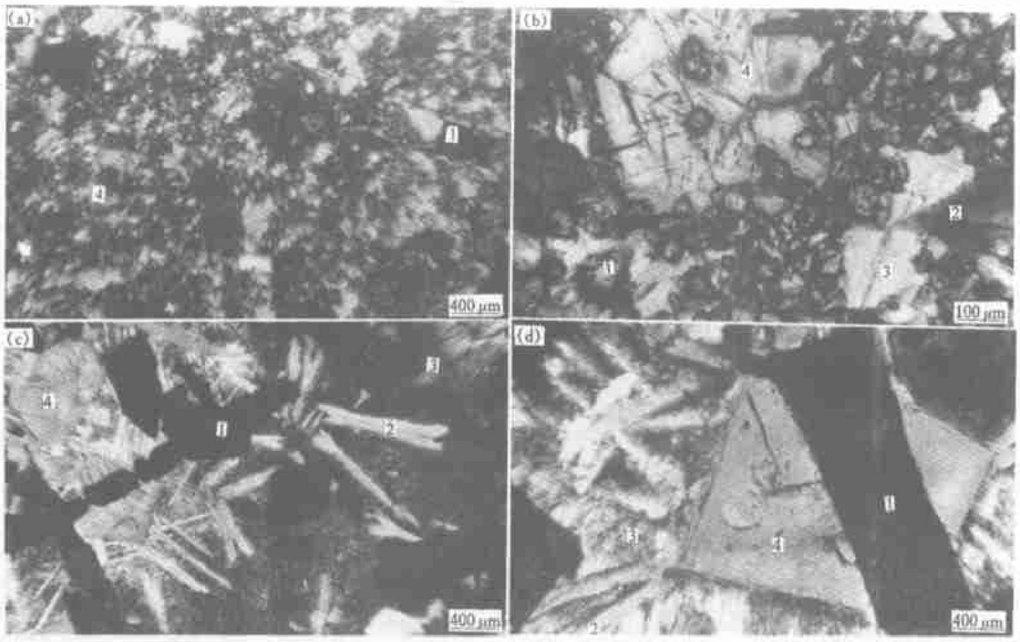

Fig.1 Microstructures of as-received and treated slag
(a),(b) —As-received slag; (c),(d) —Treated slag; 1 —Perovskite; 2 —Ti-rich diopside; 3 —Titanaugite; 4 —Spinel

Table 2 Chemical compositions of major minerals (%)

Phase	CaO	SiO_2	MgO	Al_2O_3	TiO_2	V_2O_5	FeO	MnO	S	K_2O
Perovskite	40.18	0.10	0.63	0.59	56.49	0.87	0.34	0.30	0.14	0.42
Spinel	0.92	0.97	22.28	57.97	6.29	3.29	5.82	1.90	0.01	-
Ti-rich diopside	20.30	22.17	15.21	21.03	14.26	0.76	4.40	1.55	0.05	0.21
Titanaugite	38.21	25.99	6.96	14.52	6.87	0.29	3.34	2.08	0.43	1.27

Table 3 Contents of mineral phases and distribution of TiO_2

Mineral sort	w/ %	TiO_2 in minerals/ %	TiO_2 in total/ %	Distribution of TiO_2/ %
Perovskite	34.1	56.49	19.26	81.75
Spinel	4.5	6.29	0.28	1.19
Ti-rich diopside	10.5	14.26	1.50	6.37
Titanaugite	36.5	6.87	2.50	10.69
Iron bead	0.2			
Amorphous phases	14.2			
Total	100		23.54	100

3.2 Size characteristics and liberation of treated slag

Fig.2 shows the size characteristics of perovskite phase in treated slag. The distribution of perovskite whose grain is almost fine is uneven[8], the grain size is 20 ~ 80 μm, and the average grain size is 74 μm. So the circuit might need ground and separated many times.

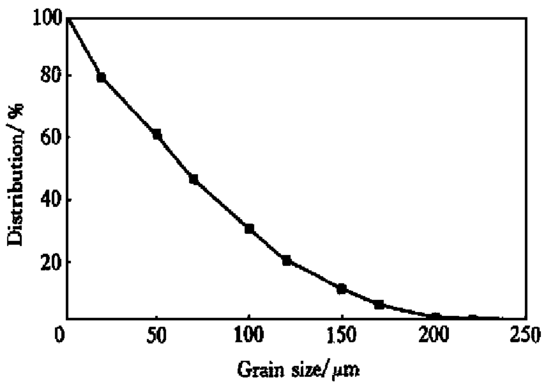

Fig.2 Size characteristic curve of treated slag

To avoid iron pollution, the treated slags were ground in porcelain grinding mill. Its particle distribution was analyzed, and titanium metal distribution was calculated according to the content of TiO_2, then the mineral monomer separation ratio was measured by stereomicroscope, the results are listed in Table 4.

It can be seen that TiO_2 wasn't concentrated in one or two class whose distribution is well-matched with the yield in each class, and the monomer separation ratio of perovskite isn't big. In the same class the monomer separation ratio of tailings is bigger than that of perovskite. Although the monomer separation ratio of perovskite is bigger in fine class(< 38 μm), it is difficult to recover for its fine grains.

3.3 Determination of principal circuit

The volume magnetic susceptibilities of perovskite and titanaugite are 24×10^{-6} cm^3/g and 16×10^{-6} cm^3/g, between magnetic and nonmagnetic, so the difference is too little to be separated by magnetic separation. While the density of perovskite is 4.1 g/cm^3, that of titanaugite is 3.4 g/cm^3; since separation coefficient $\eta > 1.29$, they can be separated by gravity[8]. According to the mineral composition and the physical and chemical properties of the samples, flotation can be adopted.

3.4 Gravity separation tests of treated slag

According to the granular characteristic of raw materials, shaking table was employed as the main equipment of gravity separation. The ground products was screened. Table 5 lists the result of the classification of gravity separation tests.

23.64 % slag analyzing 7.58 % TiO_2 whose grain size is 75 ~ 150 μm can be cast away as tailings previously, at the meantime rougher-concentrate could be obtained. Qualified concentrate assaying 42.78 % TiO_2 and tailing assaying 9.70 % TiO_2 could be achieved with grain size being 38 ~ 75 μm, because of fine size, easily to form sludge, so the tailings grade is higher, but qualified concentrate (grain size < 38 μm) could be obtained.

Back-scattered electron images for grains (75 ~ 150 μm) of the rougher concentrate and tailings were shown in Fig.3. In the rougher concentrate, a number of middling particles consisting of perovskite locked with titanic pyroxene and(or) spinel, as well as free and almost free perovskite particles, were observed. However, only a few middling particles and free gangue particles were found in tailings. Although perovskite particle selectively grew by heat treatment, it often locked with gangue minerals, even wrapped by them. Furthermore perovskite appeared

Table 4 Results of particle distribution and monomer separation ratio

Grain size /μm	Productivity/ %		Content of TiO_2/ %	Distribution of TiO_2/ %		Monomer separation ratio of perovskite	Monomer separation ratio of tailings*
	Single	Accumulated		Single	Accumulated		
150 ~ 100	29.31	29.31	20.01	30.90	30.90	50.88	58.73
100 ~ 75	29.90	59.21	19.31	30.42	61.32	52.59	64.61
75 ~ 63	5.39	64.60	19.40	5.51	66.83	54.18	65.03
63 ~ 45	4.90	69.50	17.19	4.44	71.27	56.16	76.87
45 ~ 38	19.78	89.28	18.44	19.21	90.48	60.22	78.96
< 38	10.72	100.00	16.87	9.52	100.00	80.11	89.48

* Here tailings are all other minerals except for perovskite

Table 5 Results of gravity separation

Grain size/ μm	Products	Productivity/ %		Grade/ %	Recovery ratio/ %	
		Relatively	Absolutely		Relatively	Absolutely
150 ~ 100	Concentrate	28.28	8.28	35.08	49.59	15.32
	Middling	29.33	8.59	24.83	34.54	10.66
	Tailing	42.39	12.44	7.50	15.87	4.92
	Feed	100	29.31	20.01	100	30.90
100 ~ 75	Concentrate	26.61	7.96	40.20	55.39	16.85
	Middling	36.67	10.74	16.42	30.01	9.13
	Tailing	36.72	11.20	7.67	14.60	4.44
	Feed	100	29.90	19.31	100	30.42
75 ~ 38	Concentrate	21.11	6.35	42.78	49.05	14.31
	Middling	14.72	4.43	20.78	17.14	5.00
	Tailing	64.17	19.29	9.70	33.81	9.86
	Feed	100	30.07	18.41	100	29.86 29.17
< 38	Concentrate	8.68	0.93	41.67	21.41	2.04
	Middling	11.47	1.23	20.02	15.32	1.44
	Tailing	79.85	8.56	13.34	63.27	6.03
	Feed	100	10.72	16.87	100	9.51

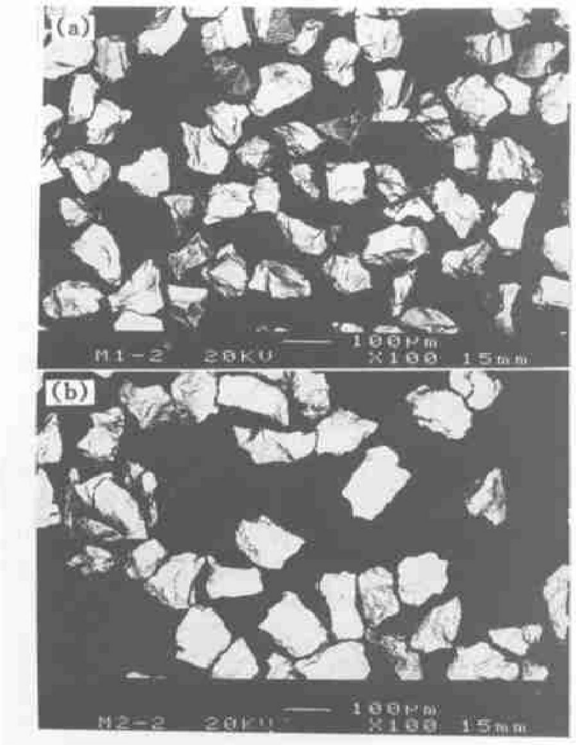

Fig.3 Back-scattered electron images of gravity products(75 ~ 150 μm)
(a) —Rougher concentrate ; (b) —Tailings

as long column, which is easily to be broken along column before liberated from the gangue mineral when grinding, so perovskite couldn't be liberated at coarse grain.

3.5 Flotation test of treated slag

The objective of this group of tests was to explore the possibilities of separating perovskite from the gangue minerals, or upgrading the rougher concentrate by removing locked perovskite by flotation. Pure perovskite and titanic pyroxene were obtained by repeated gravity separation and their flotation characteristics were tested respectively. The dosage of reagent, pH, amount of dispersant were systematically investigated and optimum flotation conditions were obtained. Perovskite could be selectively separated in weak acid pulp, combined with hydroxamate used as collector, and H_2SO_4 as regulator. The flotation condition established were tested on artificial mixtures, the ratio of perovskite and titanaugite being 1∶1, as a result the separation efficiency is 92 %. To the treated slag, a concentrate analyzing 40.08 % TiO_2 with a recovery of 67.08 % and a tailing analyzing 9.28 % TiO_2 with a recovery of 32.92 % could be obtained by 1 rougher and 4 cleaner refinements circuit.

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(Edited by HUANG Jin-song)