

炭素存在下에서 二酸化황에 의한 슐티탄 磁鐵鑛의 황화反應 (I)

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Sulfidization of Titaniferous Magnetite with Sulfur Dioxide in the Presence of Carbon (I)

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요 약

탄소 존재하에서 이산화황을 황화제로 한 함티탄자철광의 황화반응에 대하여 연구하였다. 본 연구에서는 반응온도, 반응시간, 함티탄자철광에 대해 첨가되는 탄소의 무게비, SO₂ 가스의 유량 그리고 함티탄 자철광의 입도 등의 변수가 황화반응에 미치는 영향을 검토하였다. 또 황화된 함티탄자철광으로부터 합성 rutile 을 제조하고자 하였다.

본 황화반응의 적당한 반응조건은 반응온도 : 800°C, 반응시간 : 1h, 함티탄자철광에 대해 첨가되는 탄소의 무게비 : 0.7, 함티탄자철광의 입도 : -150 mesh, SO₂ 유량(반응관크기 : 내경 = 2.8cm, 길이 = 100 cm) 100 cm³/min 였으며 황화된 반응물을 1M HCl 로 침출하여 제조된 합성 rutile 은 X-선 회절분석 결과 rutile 임이 확인되었으며 이의 함량은 82.15% TiO₂ 로 나타났다.

ABSTRACT

The sulfidization of titaniferous magnetite(Soyonpyongdo, Korea) with sulfur dioxide in the presence of carbon was studied.

The study of this reaction included reaction variables such as reaction temperature, time, weight ratio of added carbon to titaniferous magnetite, flow rate of sulfur dioxide, and particle size of titaniferous magnetite.

An attempt was made to produce synthetic rutile from titaniferous magnetite by the sulfidiza-

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tion.

The optimum conditions for the reaction were that reaction temperature was 800°C, reaction time, 1h, weight ratio of added carbon to titaniferous magnetite 0.7, particle size of titaniferous magnetite -15(mesh, and SO₂ flow rate (reactor size: ID = 2.8cm, length = 100 cm) 100 cm³/min. The synthetic rutile prepared by leaching the sulfidized product with 1M HCl was identified as rutile by the x-ray diffraction analysis and was found to contain 82.15% TiO₂.

1. Introduction

Metallic titanium, titanium oxide, titanium tetrachloride and other titanium compounds are industrially important products. Ilmenite (FeO·TiO₂) and rutile(TiO₂) are known as the main raw materials for the production of metallic titanium and its compounds. Especially when they are prepared by the chlorination process, rutile is more readily available than ilmenite.

Unfortunately, the world reserves of rutile are so scarce and unevenly distributed that the supply and demand are out of balance. Consequently, there is a general tendency around the world of preparing synthetic rutile from ilmenite or titaniferous magnetite((Fe₂O₃)_x·(FeO·TiO₂)_y) which is less costly and more abundant than rutile.

A number of reports and patents have been published for the preparation of titanium and its compounds by the sulfidization. Among earlier works on the treatment of titanium ore, there are numerous publications^{1~8)} in which the sulfidization is done by using sulfates or metallic sulfide as the sulfidizing agent. In addition to these works, there are publications^{9,10)} for upgrading of ilmenite by using hydrogen sulfide gas.

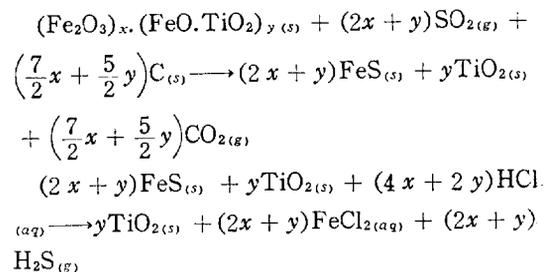
There were some cases in which sulfur dioxide gas was used as the sulfidizing agent.

Welch¹¹⁾ obtained rutile and pyrite by introducing the gas mixture which is produced by passing sulfur dioxide gas through a heated carbon layer at 1060°C to ilmenite ore at the same temperature.

Hiestler¹²⁾ also attempted the sulfidization of ilmenite ore by using SO₂-CO gas mixture but the results were not described in detail.

In this study, the products of the reaction between titaniferous magnetite and sulfur dioxide in the presence of carbon were examined by both chemical and x-ray analysis. The study of this reaction included such reaction variables as reaction temperature, time, weight ratio of added carbon to titaniferous magnetite, flow rate of sulfur dioxide and particle size of titaniferous magnetite.

An attempt was made to produce synthetic rutile from titaniferous magnetite by a sulfidization in which iron oxides are converted selectively into pyrrhotite. Pyrrhotite is easily soluble in dilute acid.



2. Experimental

2-1. Materials

Titaniferous magnetite used in the present experiment was obtained from Soyonpyong-do (west island of Korea), containing 20.48% TiO_2 , 56.31% total Fe, 0.45% MnO, 0.17% SiO_2 , 1.52% MgO, 0.48% V_2O_5 , 0.55% CaO, and 0.024% Cr_2O_3 . The x-ray diffraction pattern of the sample showed the presence of ilmenite¹³⁾, magnetite¹⁴, and hematite¹⁵⁾ as ore forming minerals. Presence of rutile was not detected. Sieve analysis of the sample was as follows: 36.8% 150/170 mesh; 35.2% 170/200 mesh; 20.7% 200/270 mesh; 5.6% 270/325 mesh; 1.7% under 325 mesh.

The carbon used as the reducing agent in this experiment was prepared by the thermal decomposition of a guaranteed grade reagent glucose. This carbon was used in powder form of under 150 mesh.

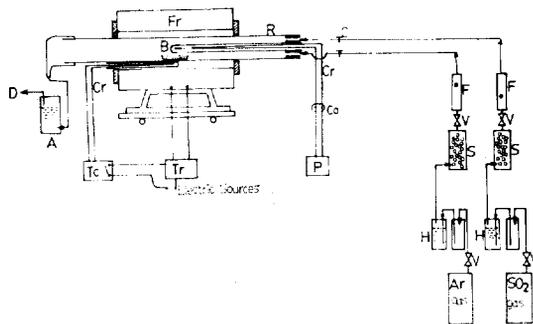
Gaseous sulfur dioxide and argon gas were dried by passing them first through concentrated sulfuric acid and then over P_2O_5 .

2-2. Procedures

Sulfidization of titaniferous magnetite was carried out in a quartz tube of 28mm ID and 1000 mm L as shown in Fig. 1. A mixture of titaniferous magnetite and carbon in a quartz boat (72mm L, 16 mm W, 9mm D) was placed in a transparent quartz reaction tube. Gaseous sulfur dioxide was then introduced into the reaction tube. The sample was positioned in the middle of the tubular electric furnace (heating length: 300mm) maintained at a specified temperature for a specified time period. The temperature of the sample part was maintained within $\pm 2^\circ C$. After heating, the sample was held at $100^\circ C$ for 1hr in an

argon stream in order to remove the absorbed sulfur dioxide on unreacted carbon.

The reaction between titaniferous magnetite and carbon in an argon stream, between sulfur dioxide and carbon, and between titaniferous magnetite and sulfur dioxide in the presence of carbon were separately examined in a similar manner.



- A : Absorption Bottle
- B : Quartz Boat
- C : Cock
- C_c : Cold Junction
- C_r : Thermocouple
- D : Draft
- F : Flow Meter
- Fr : Tubular Furnace
- H : Drying Bottle (H_2SO_4)
- R : Quartz Reactor
- S : Drying Bottle (P_2O_5)
- T_c : Temperature Controller
- T_r : Transformer
- P : Pyrometer
- V : Valve

Fig. 1. Schematic Flow Diagram

2-3. Analytical

The extent of reaction was determined by measuring its weight change after the reaction and also the amount of elemental sulfur formed in the reaction was determined by converting them into $BaSO_4$. Then the product was leached with dilute hydrochloric acid (1M), and the solution was subsequently analyzed to determine iron by the volumetric method with $KMnO_4$. The degree of conversion was then calculated as the ratio of the

amount of iron solubilized into the leach solution to the amount of iron originally present in the titaniferous magnetite. The x-ray analysis of the sample was performed with an x-ray powder diffractometer equipped with a proportional counter using Fe-radiation with an Mn-filter.

3. Results and Discussion

3-1. Reaction between titaniferous magnetite and carbon in argon stream

The products formed by heating a mixture of titaniferous magnetite (3.0g) and carbon (2.10 g) in argon stream (100 cm³/min) for 1hr were examined by the x-ray analysis. The results are shown in *Table 1*, together with the weight changes in the samples.

Table 1. Experimental Results for the Interaction of Titaniferous Magnetite and Carbon in an Argon Stream

Reaction Temp. (°C)	Weight Loss (%)	Analysis of X-Ray Diffraction Pattern for the Solid Product in the Boat
600	0.2	Ilmenite, Magnetite, Hematite
650	0.2	Ilmenite, Magnetite, Hematite
700	0.3	Ilmenite, Magnetite, Hematite
750	0.4	Ilmenite, Magnetite, Hematite
800	0.8	Ilmenite = Magnetite
850	1.8	Ilmenite, Magnetite > Wuestite

The slight decrease in the weight of the sample was observed at 600°C. The amount of the sample was slowly decreased to ca. 800°C, and it was markedly decreased above ca. 850°C. The x-ray diffraction patterns of the products showed ilmenite, magnetite and hematite at 600°C, 650°C and 700°C respectively. In proportion to the increase of reaction temperature, amount of hematite was decreased. On the other hand, that of magnetite

was increased, and the diffraction-pattern of wuestite¹⁶⁾ appeared.

From the above results, one could conclude that Fe³⁺ in the titaniferous magnetite was converted to Fe²⁺ by the reduction.

3-2. Reaction between carbon and sulfur dioxide

By the sulfidization reaction in the system of iron oxide-carbon-sulfur dioxide, iron oxide is converted to pyrrhotite. It is very important to note that elemental sulfur is formed from sulfur dioxide in the presence of carbon. Therefore this reaction was examined in order to find the criterion of optimum reaction temperature for the reaction between titaniferous magnetite and sulfur dioxide in the presence of carbon. Carbon (2.10 g) was heated in a sulfur dioxide stream (100 cm³/min) for 1hr. A part of the elemental sulfur was deposited outside the heating zone, while the other part was absorbed by the unreacted carbon in the boat. The latter was determined by chemical analysis. The amount of sulfur formed is shown in *Fig. 2*, together with the weight change in the sample.

The slight increase in the sample weight at 500-650°C was due to the absorption of the elemental sulfur formed from the reaction onto the unreacted carbon. In proportion to the

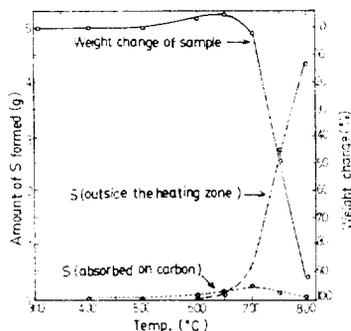


Fig. 2. Experimental Results for the Reaction between Carbon and Sulfur Dioxide

increase of the reaction temperature, the amount of elemental sulfur formed increased and the carbon weight decreased slowly. These phenomena were markedly apparent above ca. 750°C. As mentioned in Ryoo's report¹⁷⁾, the vapor pressure of sulfur in the reaction-atmosphere is an important factor for the sulfidization of metal oxides.

Consequently, from the above-mentioned experimental results, it is obvious that the sulfidization of titaniferous magnetite must be carried out at least above ca. 750°C.

3-3. Reaction between titaniferous magnetite and sulfur dioxide in the presence of carbon

3-3-1. Effect of the reaction temperature

Fig. 3 shows the conversion ratio of the products obtained by heating the mixture of titaniferous magnetite(3.0g) and carbon(2.10 g) (the weight ratio of added carbon to titaniferous magnetite = 0.7) at various temperatures in a sulfur dioxide stream(100 cm³/min).

With increase of the reaction temperature, the reaction rate and conversion ratio were

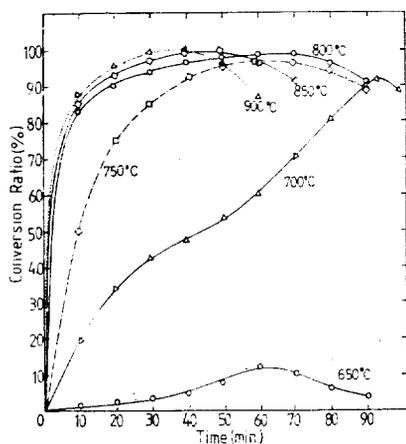


Fig. 3. Effect of Temperature on the Sulfidization Reaction of Titaniferous Magnetite

increased. Reaction rates were increased markedly above ca. 750°C, and in the range of 800°C to 900°C the temperature of the reaction did not appear to be significant. The phenomenon that the reaction rate and the conversion ratio rapidly increased above ca. 750°C was similar in tendency to the reduction of sulfur dioxide by carbon. From these results, it is obvious that the reduction stage of sulfur dioxide is an important factor in the entire sulfidization of titaniferous magnetite.

In proportion to the increase of the reaction temperature, the conversion ratio increased in the range of 650°C to 800°C, and it arrived at the maximum conversion ratio at 800°C for 1hr. But, after reaching the maximum conversion ratio, a decrease in the conversion ratio appeared in all temperature ranges. This phenomenon is due to two-sided functions of sulfur dioxide, that is, as an oxidizing agent as well as a reducing agent.

With the exception of the case at 650°C, the reaction time for the maximum conversion ratio decreases in proportion to the increase of the reaction temperature. These tendencies

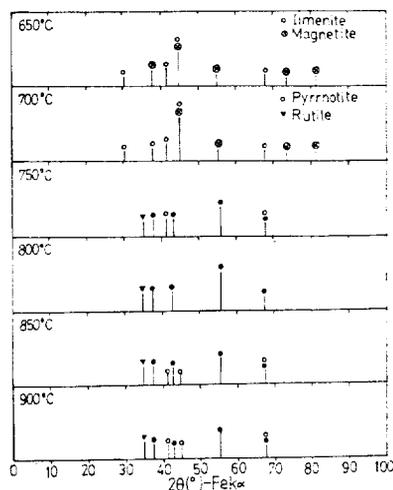


Fig. 4. X-Ray Diffraction Pattern at various Reaction Temperature

indicate that the effect of the reaction temperature in the sulfidization process is most significant.

Fig. 4 shows the diffraction patterns of the products obtained by heating the mixture of titaniferous magnetite (3.0g) and carbon (2.1g) at various temperature for 1hr in a stream of sulfur dioxide at a flow-rate of $100 \text{ cm}^3/\text{min}$.

The X-ray diffraction pattern showed the presence of rutile¹⁸⁾, ilmenite and pyrrhotite¹⁹⁾ at 750°C . At the 800°C , the diffraction pattern showed only rutile and pyrrhotite. But the diffraction pattern of ilmenite appeared again in the cases of 850°C and 900°C . These results are related to the tendency of the decreasing conversion ratio. The reason is the same as above.

From the above-mentioned experimental results, it is generally desirable that the reaction temperature be held at 800°C .

3-3-2. Effect of carbon on conversion ratio

Fig. 5 shows the conversion ratio of products obtained by heating the mixture of titaniferous magnetite(3.0g) and carbon which is in the range of 0.3 to 0.9 at 800°C for va-

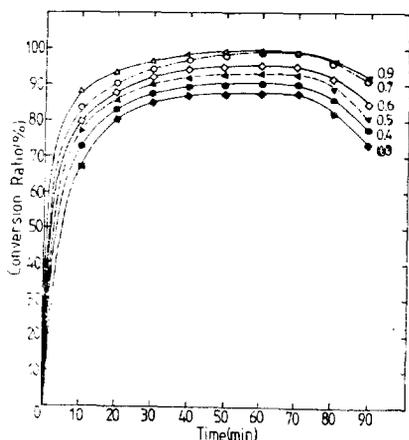


Fig. 5. Effect of Amount of Carbon on the Sulfidization Reaction of Titaniferous Magnetite

rious reaction time in a sulfur dioxide stream ($100 \text{ cm}^3/\text{min}$)-where the range, 0.3 or 0.9, is the weight ratio of added carbon to titaniferous magnetite.

In proportion to the increase of the carbon weight ratio the conversion ratio and reaction rate increased and these tendencies similarly appeared. With carbon weight ratio ranging from 0.3 to 0.7, the conversion ratio was proportionally increased, gradually as time passed, and it arrived at the maximum conversion ratio after 1hr. In the case of 0.9, although the higher rate of conversion was observed in the early stage of the reaction, the maximum conversion ratio was also obtained after 1hr. When the carbon weight ratio was higher than 0.7, this maximum conversion ratio appeared not to be sensitive to the carbon added.

Consequently an increase of carbon weight ratio over 0.7 cannot affect the increase of the conversion ratio. In addition to this, it was confirmed that the unreacted carbon (approximately 1%) was left in the boat. In every case, the maximum conversion ratio was obtained between the reaction times of 60 min

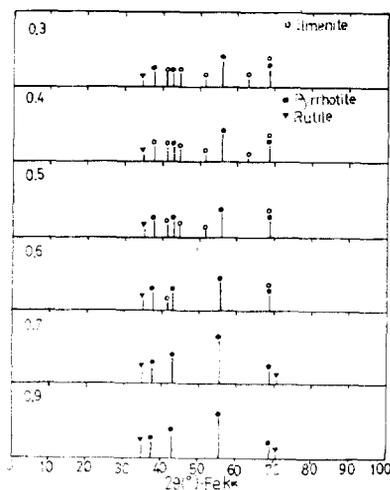


Fig. 6. X-Ray Diffraction Pattern at various Amount of Carbon

and 70 min. But after these durations, the conversion ratio tended to decrease. The cause of this phenomenon is the same as the above-mentioned case.

Fig. 6 shows the diffraction patterns of the products obtained by changing the weight ratio of added carbon at 800°C, for 1hr in a sulfur dioxide stream(100 cm³/min).

The x-ray diffraction patterns showed ilmenite, pyrrhotite and rutile in every case within a range of 0.3 to 0.6, but the diffraction pattern of ilmenite didn't appear above 0.7.

Consequently from the above mentioned results, it is sufficient that the weight ratio of added carbon to titaniferous magnetite be 0.7.

3-3-3. Effect of the reaction time

In the before-mentioned experiment, when the reaction temperature was kept at 800°C, the weight ratio of added carbon to titaniferous magnetite was at 0.7, the particle size of the sample was at 150 mesh and the sulfur dioxide flow-rate was at 100 cm³/min, the author examined the effect of the reaction time on the conversion ratio. The results are

shown in Fig. 7.

The x-ray analysis of the products in the boat showed rutile and pyrrhotite together with ilmenite for the cases where the reaction time was between 30 min to 50 min, and only rutile and pyrrhotite appeared between 60 min and 70 min of the reaction time but ilmenite appeared again after 80 min. This tendency agrees with the phenomenon that the conversion ratio reaches its maximum between 60 min and 70 min, and decreases after 70 min. This, as before, is due to the dual functions of sulfur dioxide which is both an oxidizing agent and a reducing agent. Namely, at the early stage of the reaction, sulfur dioxide contributes to the conversion of iron oxide in the titaniferous magnetite to pyrrhotite, as a reducing agent, together with elemental sulfur which is produced by the reduction of sulfur dioxide by the carbon. But, after arriving at the possible maximum ratio which is obtainable under specified reaction conditions, a small amount of pyrrhotite is converted to iron oxide by the oxidizing function of sulfur dioxide. These results agree well with the results of Montilo's²⁰⁾ or Diev's²¹⁾.

Consequently, it can be concluded from these results that the best reaction time is 1hr under the above-mentioned conditions.

3-3-4. Effect of the sulfur dioxide flow-rate

Fig. 8 shows the conversion ratio of products obtained by heating the mixture of titaniferous magnetite(3.0g) and carbon(2.10g) at 800°C for various lengths of time in a sulfur dioxide stream whose flow-rate changed within a range of 20cm³/min to 120 cm³/min. In this case, reactor size is 28 mm ID and 1000 mm in length.

In this experiment, although the flow-rate

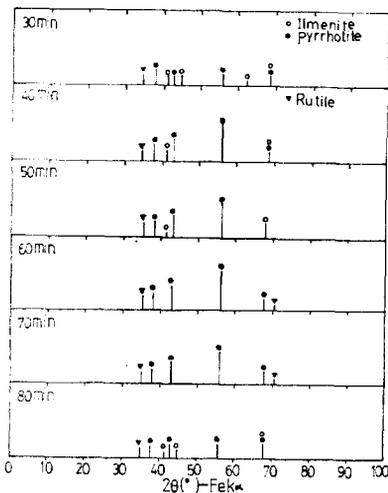


Fig. 7. X-Ray Diffraction Pattern at various Reaction Time

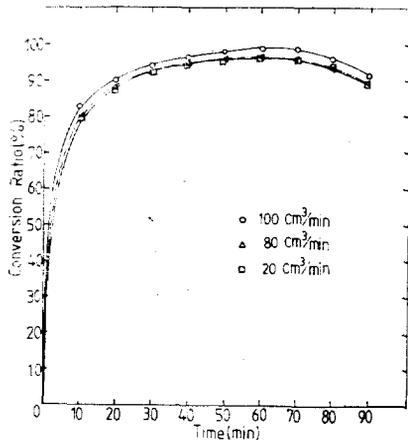


Fig. 8. Effect of Sulfur Dioxide Flow-Rate on the Sulfidization Reaction of Titaniferous Magnetite

of the sulfur dioxide stream changed in a range between 20 cm³/min and 120 cm³/min, the conversion ratio and the reaction rate showed a similar tendency. Though the maximum conversion ratio obtained was only 94% for 1hr in a sulfur dioxide stream of 80 cm³/min, it was 98.8% for 1 hour in a sulfur dioxide stream over 100 cm³/min.

Fig. 9 shows the results of an X-ray ana-

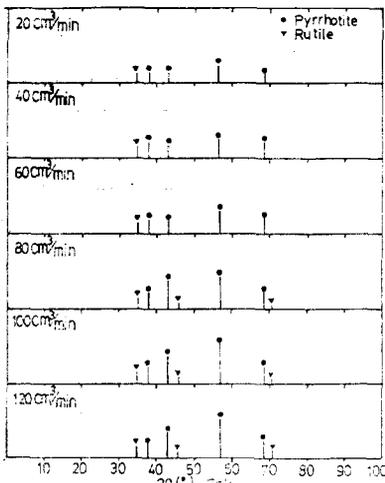


Fig. 9. X-Ray Diffraction pattern at various Sulfur Dioxide Flow-Rate

lysis on the products obtained by heating for 1 hour.

In all ranges, the x-ray diffraction pattern shows only rutile and pyrrhotite. But the diffraction-pattern of rutile newly appeared at 46° and 71° in a sulfur dioxide stream over 80 cm³/min, and especially the diffraction-pattern of pyrrhotite was prominent in a sulfur dioxide stream over 100 cm³/min. Comparing the above-mentioned results of Fig. 8 with the results of the x-ray analysis, there is little difference in the conversion ratio within the range of 20 cm³/min to 120 cm³/min, but the diffraction-pattern of rutile and pyrrhotite was more prominent than in any other cases in a sulfur dioxide stream over 100 cm³/min. Consequently, for this reason, the proper sulfur dioxide flow-rate is considered as 100 cm³/min for the effectual separation of titanium oxide and iron oxide.

3-3-5. Effect of the particle size of titaniferous magnetite

Fig. 10 and Table. 2 show the effect of the particle size on the conversion ratio.

As the particle size became smaller, the reaction rate and the conversion ratio increa-

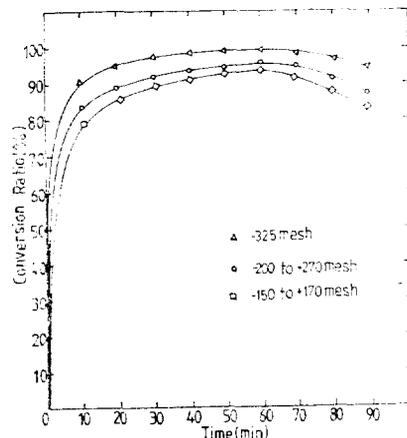


Fig. 10. Effect of Particle Size on the Sulfidization Reaction of Titaniferous Magnetite

Table 2. Effect of Particle Size

Particle Size(mesh)	Weight Loss(%)	X-Ray Diffraction Pattern	Ws*(g)	Conversion Ratio(%)
-150 to +170	32.1	Pyrrhotite, Rutile	2.1	94.3
-200 to +270	33.2	Pyrrhotite, Rutile	2.9	96.1
-325	33.7	Pyrrhotite' Rutile	3.1	99.3

*Ws: Amount of Sulfur obtained outside Heating Zone

sed. Especially there was a distinct difference in the conversion ratio. The maximum conversion ratio was displayed as 94.3% in the case of -150 to +170 mesh, 96.1% in the case of -200 to +270 mesh, and 99.3% in the case of -325 mesh.

The x-ray diffraction pattern of each product showed only rutile and pyrrhotite. From the above-mentioned results, it is considered that a particle size of -150 mesh for titaniferous magnetite is sufficient, because the conversion ratio is more than 94.3% in the case of -150 to +170 mesh, and from an economic view point, the power consumption for pulverizing of the sample must be accounted for.

3-4. Leaching experiments of the the reaction product

From the results of the above experiments, the optimum reaction conditions for sulfidization of titaniferous magnetite were determined. Thus, leaching experiments of the products obtained by heating the mixture at the optimum conditions were examined.

Table. 3 shows the components of the residues obtained after leaching. The residues were found to consist of 82.15% of TiO₂. As the starting materials contained approximate 8% gangue, which was presumably metal oxide, it was not absolutely soluble in 1M hydrochloric acid.

In addition the residues were analyzed by the x-ray diffraction and the x-ray diffraction pattern showed only rutile.

Table 3. Chemical Analysis of Residues

Comp.	Total Fe	TiO ₂	MnO	SiO ₂	MgO	V ₂ O ₅	CaO	Cr ₂ O ₃
%	8.18	82.15	1.05	0.46	2.67	0.62	0.90	0.0089

*leaching solution: 1M HCl

A tentative flowsheet for upgrading of titaniferous magnetite by the sulfidization is shown in Fig. 11.

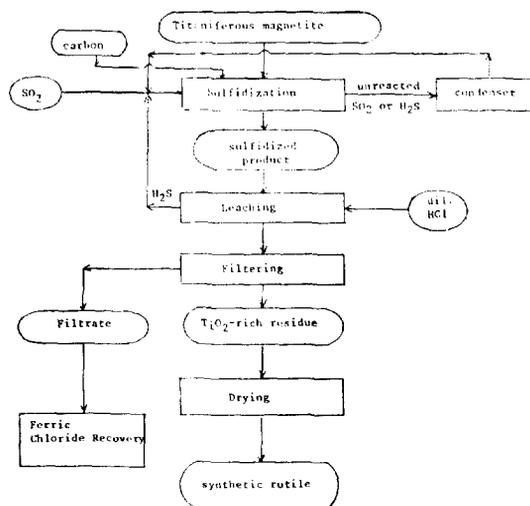


Fig. 11. Flow sheet for upgrading of titaniferous magnetite by the sulfidization.

4. Conclusions

In view of all the results so far achieved conclusions for the sulfidization of titaniferous magnetite are as follows:

- 1) The maximum conversion ratio is obtained at 800°C, for 1hr. At the temperatures higher than 800°C, however the maxim

- um conversion ratio could be obtained in less than 1hr.
- 2) It is sufficient that the weight ratio of added carbon to titaniferous magnetite be 0.7. In this case the maximum conversion ratio is obtained at 800°C, for 1hr. Increasing the weight ratio of carbon above 0.7 doesnot increase the maximum conversion. ratio.
 - 3) The proper reaction time is 1hr with a reaction temperature at 800°C, and the weight ratio of carbon at 0.7. Under these conditions, the maximum conversion ratio is obtained, but the conversion ratio is decreased after that lapse of the time.
 - 4) A 100cm³/min sulfur dioxide flow-rate (reactor size: 28 mm ID, 1000 mmL) is suitable because the maximum conversion ratio is similarly obtained above this flow-rate, and the diffraction pattern of rutile and pyrrhotite appear more striking than in any other cases.
 - 5) As the particle size of the sample becomes finer, the conversion ratio increases. When the particle size is under 150 mesh, a 98.8% conversion ratio is obtained.
 - 6) The analysis of the residues left after the leaching of the product obtained at the above-mentioned optimum conditions shows that the content of TiO₂ is 82.15% and the x-ray diffraction pattern showed only rutile.
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