

Preparation of high purity manganese oxide by pyrolysis of solution extracted from ferromanganese dust in AOD process

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The high purity manganese oxides were made from the dust, generated in AOD process that produces a medium-low carbon ferromanganese and collected in the bag filter. Manganese oxide content in the dust was about 90%, and its phase was confirmed as Mn_3O_4 . In the extraction of manganese, because of remaining amorphous MnO_2 , the dust was reduced to MnO by roasting with charcoal. The pulp density of the reduced dust can control pH of the solution more than 4 and then Fe ion is precipitated to a ferric hydroxide. Because a ferric hydroxide co precipitates with Si ion etc, Fe, Si ion was removed from the solution. Heating made water to be volatilized and nitrates was left in reactor. Then nitrates were a liquid state and stirring was possible. Among the nitrates in reactor, only the manganese nitrate which have the lowest pyrolysis temperature pyrolyzed into β - MnO_2 powder and $NO_{2(g)}$ at the temperature less than 200°C. When the pyrolysis of manganese nitrate has been completed about 90%, injection of water stopped the pyrolysis. Nitrates of impurity dissolved and the spherical high purity β - MnO_2 powders were obtained by filtering and washing. Mn_2O_3 or Mn_3O_4 powder could be manufactured from β - MnO_2 powder by controlling the heating temperature. Lastly, a manufactured manganese oxide particle has 99.97% purity.

Keywords: High purity, Manganese oxide, Nitric acid, Pyrolysis

Introduction

The high purity Mn_3O_4 powder is mainly consumed in manufacturing of Mn-Zn ferrite. The known manufacturing methods are an oxidizing electrolytic manganese powder in solution¹⁾ or a precipitating the extracted manganese into a manganese carbonate and calcining it²⁾. The latter is difficult to control of purity and the former is able to cost too much due to electrolysis.

This work presents another method for a manufacturing of high purity manganese oxide powder. A raw material is the dust generated in AOD process that produces a medium-low carbon ferromanganese.

Nitric acid extraction is able to make nitrates of metal elements in solution. Heating the extracted solution, nitrate will be pyrolyzed to a metal oxide. But the metal oxide will form a lump and cannot have high purity.

This method uses that the manganese nitrate which will be gotten as oxide has the low melting point, in order to stirring, and has the lowest pyrolysis temperature among nitrates in reactor.

In case of heating the extracted solution in the reactor, water vaporized and, after that, nitrate pyrolyzed. Because manganese nitrate has the lowest pyrolysis temperature

among nitrates in reactor, firstly it pyrolyzes into β - MnO_2 powder and $NO_{2(g)}$. So, if we heat and stirring the solution at temperature less than 200°C, high purity manganese oxide will be gotten and other nitrates will remain as it was and be removed by washing.

And, when a manganese nitrate pyrolyze, because the all nitrates is a liquid state, stirring is possible and a partial temperature rise is prevented. So, a fine and spherical manganese oxide powder can be gotten.

The phase of the pyrolyzed manganese oxide is β - MnO_2 and roasting can convert it into Mn_2O_3 or Mn_3O_4 .

Experiment and Result

1. Sample

This work applied the dust to the raw material, which is generated in AOD process that produces a medium-low carbon ferromanganese from a high carbon ferromanganese and collected in the bag filter. Table 1 show the composition of the raw material. The dust contain 63% Mn and a little Fe, Ca, Mg, K, Si, etc.

It is revealed by the XRD that the crystal in the dust mainly is Mn_3O_4 , as shown in Fig 1. It is supposed that

Table 1. Chemical composition of the dust.

Element	Mn	Fe	Ca	Mg	Na	K	Si
wt.%	63.07	2.36	0.49	0.12	0.11	0.60	0.14

Mn exist as Mn_3O_4 , the grade of Mn_3O_4 in the dust is about 90%. In case of extracting manganese from Mn_3O_4 by a nitric acid, $\frac{2}{3}$ of Mn is extracted and amorphous MnO_2 remain³⁾. So, in order facilely to extract Mn, we mixed the dust and 5% activated charcoal and roasted the mixture for 1 hour at the temperature 750°C.

Fig.1 show XRD results of the dust and the reduced dust. From this, we know that the crystal in the dust is Mn_3O_4 and the reducing roasting convert Mn_3O_4 into MnO.

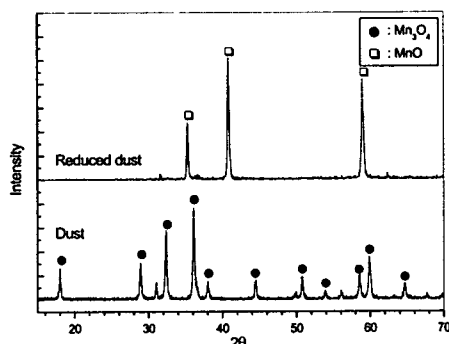


Fig. 1. XRD patterns of the dust and the reduced dust. (Cu $K\alpha 1$)

2. Preparation of the extracted solution

Extraction was undertaken with 4N nitric acid and for 1 hour at room temperature in terms of the pulp density of the reduced dust. Table 2 shows concentrations of the extracted ion in solution. Adding the reduced dust in nitric acid, a temperature of solution and pH was increased.



In proportion to increasing the pulp density from 130g/L to 150g/L, pH was increased and concentration of Fe, Si decreased. This may be explained from precipitation of $Fe(OH)_3$. Because iron hydroxide, $Fe(OH)_3$, is a colloidal state and has very large a specific surface and a adsorptive power, it can co precipitate with suspended solids and ions, etc. Decrease of concentration of Si may be

explained by it, and this property of $Fe(OH)_3$ has been applied in many part⁴⁾. Because Mn exist Mn^{2+} ion and it is stable at less than pH 7, Mn^{2+} ion don't be lost except a small quantity co precipitated with $Fe(OH)_3$.

So, adding the 150g/L reduced dust in 4N nitric acid and stirring for 1 hr, pH of solution increase more than 4 and Fe, Si are removed in solution and concentrate of Mn is about 10%.

3. Pyrolysis of the extracted solution

Heating the extracted solution in the reactor, water volatize and nitrates of the manganese and impurities remain. Because a melting point of the manganese nitrate is 25.8°C, nitrates in the reactor is a liquid state. And among nitrates in the reactor, only the manganese nitrate which have the lowest pyrolysis temperature pyrolyzed into β - MnO_2 powder and $NO_{2(g)}$ at temperature less than 200°C.

Fig.2 show TG-DTA result of the $Mn(NO_3)_2 \cdot 6H_2O$. At the temperature 25.8°C on the DTA curve, ① means that $Mn(NO_3)_2 \cdot 6H_2O$ is converted from a solid state into a liquid state. At the temperature 30~150°C, a 35% loss in TG, ② means that 5.5 mole H_2O in $Mn(NO_3)_2 \cdot 6H_2O$ volatize and $Mn(NO_3)_2 \cdot \frac{1}{2}H_2O$ is generated. ③ at the temperature 189°C is the endothermic peak that $Mn(NO_3)_2 \cdot \frac{1}{2}H_2O$ pyrolyze to $MnO_2 \cdot \frac{1}{2}H_2O$ and $NO_{2(g)}$. ④ at the temperature 195°C seem to be peak due to pyrolysis of $MnO_2 \cdot \frac{1}{2}H_2O$ into β - MnO_2 and steam.

Table. 2 Concentration of leached elements by nitric acid on addition amount of the reduced dust. (Unit : mg/L)

pulp density (g/L)	pH	Mn	Fe	Si	Ca	Mg	Na	K
130	0.53	112800	2649	11.49	418	238	59	176
135	0.85	101700	2176	27.66	407	280	66	198
142	3.00	104300	1.8	18.91	513	267	81	204
145	3.82	110900	0.1	1.87	564	292	74	205
150	4.11	106600	0.1	0.67	557	294	73	207

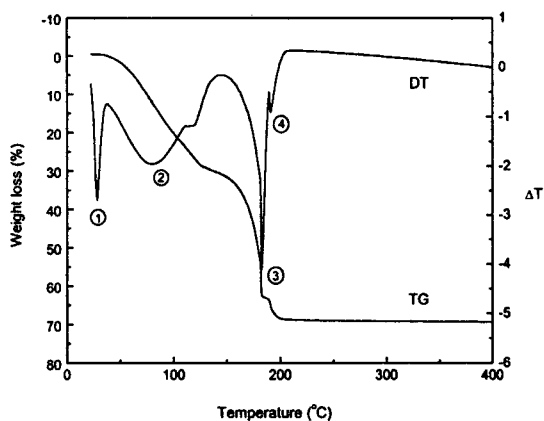


Fig. 2. TG-DTA curves for manganese nitrate. $(\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$

In order to manufacturing of manganese oxide, pyrolysis of the extracted solution was undertaken in a 2L, 5 necked, round-bottomed flask and it was equipped with a heating mantle, stirrer, thermometer and connected to a water-circulating packed tower for absorbing NO_2 gas evolved during reaction.

The 1L-extracted solution was added in the reactor and heated. First, water volatilized and the quantity of the solution decreased (Shown ② in Fig. 2). After that time, a temperature was increased and solution evolved a red NO_2 gas and was altered black due to generation of the manganese oxide powder. (Shown ③ in Fig. 2)

During the pyrolysis of the manganese nitrate, abruptly bubbles and boiling of the solution was shown. This phenomenon seems that 0.5mole H_2O vaporize and β - MnO_2 powder are generated. (Shown ④ in Fig. 2) At this time, 500mL pure water is added in the flask and reaction is terminated. After that, mixture of the β - MnO_2 powder and solution is filtrated.

The receipt rate of Mn was about 85~95%, which is estimated from quantity of β - MnO_2 powder and the extracted solution.

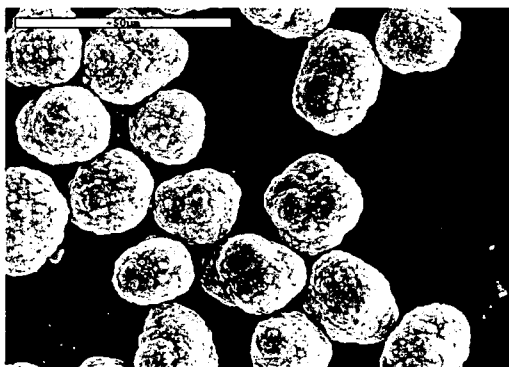


Fig. 3 SEM of the manganese oxide (MnO_2).

Fig.3 is a SEM photograph of the above-manufactured β - MnO_2 powder. The manganese oxide powder has a spherical shape and particle size is 20~30 μm . And XRD result show that manganese oxide is β - MnO_2 . (Fig.5)

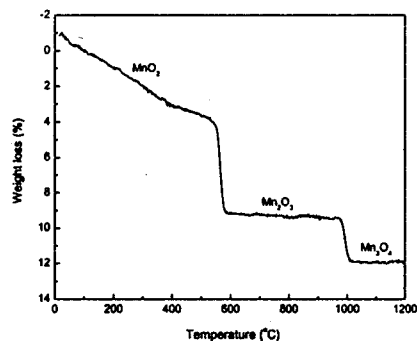


Fig. 4 TG graph of the manganese oxide.

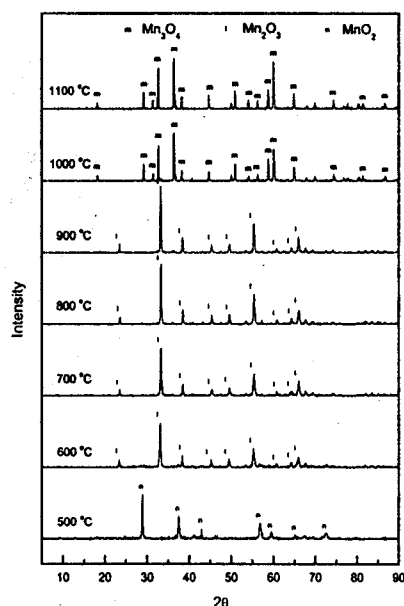


Fig. 5 XRD patterns of manganese oxides.

4. Preparation of the Mn_3O_4

Fig.4 is TG graph of the above-manufactured MnO_2 . In order to confirm production, we roasted the above-manufactured MnO_2 for 2 hours in terms of the temperature. And Fig.5 shows XRD result of the product. From this, we know that Mn_2O_3 can be manufactured at the temperature more than 550°C and Mn_3O_4 more than 950°C from MnO_2 .

The Mn_3O_4 was made from the above-manufactured MnO_2 by roasting for 2 hours at the temperature 1000°C. Fig.6 is a SEM photograph of it. Sintering of particles did

Table 3. Chemical composition of manganese oxide(Mn_3O_4).

Element	Mn	Si	Fe	Ca	Mg	Na	K	Al	Cu	Pb	Zn
ppm	71.8 wt%	27.2	13.1	22.6	15.6	56	32.9	23.2	14.4	91	29.4

not occur and shape of particle remained. Irregularly, a crack is shown in the surface of particles. It seems to be caused that oxygen evolved in the inner particle or an internal and external reduction velocity of the particle is different.

An attrition mill was used to pulverizing the particles. Pulverization was undertaken in a 2L chamber and 1kg 3mm-diametered zirconium balls and 0.5kg sample and 500mL water was added in it and stirred at 200 rpm for 4 hours. Fig.7 is a SEM photograph of the pulverized Mn_3O_4 particles. As shown, particle size decreased to less than 5 μm . Before pulverization, a color of particles was black but afterward a color was dark brown.

Table 3 is composition of the above- manufactured Mn_3O_4 and this result indicates that the lastly manufactured Mn_3O_4 has 99.97% purity.

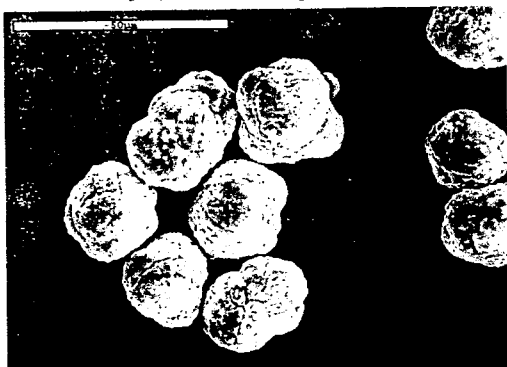


Fig.6 SEM of the manganese oxide (Mn_3O_4)



Fig.7 SEM of the pulverized manganese oxide (Mn_3O_4)

Conclusion

Another high purity manganese oxide manufacturing method was developed by pyrolysis of the extracted solution. Manganese was extracted from the dust, which generated in AOD process that produces a medium-low carbon ferromanganese and collected in the bag filter. The following conclusions were derived from the experiment.

1. Addition of the 150g/L reduced dust in 4N nitric acid and stirring for 1 hr increased pH of the solution more than 4. And, Fe and Si were co precipitated in the solution and concentrate of Mn was about 10%.
2. Heating and stirring of the extracted solution, the manganese nitrate pyrolyze into β - MnO_2 powder and $NO_2(g)$ but other nitrates remained. β - MnO_2 powder is black and spherical and particle size is 20~30 μm .
3. MnO_2 could be converted into Mn_2O_3 at the temperature more than 550°C and Mn_3O_4 more than 950°C. So, MnO_2 was roasted for 2 hours at the temperature 1000°C and pulverized by an attrition mill. A phase of it was Mn_3O_4 and particle was fine and dark brown.
4. The manufactured Mn_3O_4 has 99.97% purity.

Acknowledgment

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References

1. Korea patent "Application number: 90-20056"
2. Korea patent "Application number: 86-10796"
3. Gye Seung Lee, Gi Chun Han, Young Jun Song, Kang Ho Shin, Dong Sung Cho, 2000 "The extraction of manganese from the Medium-Low Carbon Ferromanganese dust with nitric acid" J. of The Korean Inst. of Resources Recycling Vol.9, No.1, 24
4. Jin Gun Sohn, Tae Bong Byeon, Jae Young Lee, Dae Young Kim, 1996 "Removal impurities from Waste Picking Acid in Ironmaking Industry" J. of The Korean Inst. of Resources Recycling Vol.5, No.2, 61