Acid Digestion of Thermally Reduced Manganese Dioxides*

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As one of the methods of crystal phase transformation, manganese dioxides were thermally reduced and then digested with acid solutions. It has been known that the manganese dioxide is formed, for instance, by the following reaction. $\text{Mn}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{MnO}_2 + \text{MnSO}_4 + \text{H}_2\text{O}$. The products were α - or γ - MnO_2 according to the treating conditions.

This paper deals chiefly with the effects of the treating conditions on the crystal structures of the products and the yield of manganese dioxide.

The original manganese dioxides were for the most parts artificial ones. β - MnO_2 was prepared by the thermal decomposition of $\text{Mn}(\text{NO}_3)_2$, $\alpha(1)$ - MnO_2 by the decomposition of KMnO_4 with $\text{HCl}^{(1)}$, and $\alpha(2)$ - MnO_2 by autoclaving of γ - MnO_2 with KCl solution⁽²⁾. The products were examined by chemical analysis, electron micrographs, electron and X-ray diffraction methods.

Results obtained were as follows :

(1) While hot or after cooling, the thermally reduced original dioxides were poured into the boiling acid solutions, and the boiling was kept for 30 minutes. In Table 1, characteristics of the products were indicated.

Table 1 Properties of the Products

Sample No.	Original Oxides	Heating Temp.(°C)	Temp.*1 of Mn_2O_3	Composition of Acid Soln.	x in Formula MnO_x	Yield	Crystal Types*2		
							Electron Micrograph	Electron Diffraction	X-ray Diffraction
1-1	β - MnO_2	600	C	5:1 H_2SO_4	1.94	—	α	$\alpha(+\gamma)$	γ
1-2	"	700	"	5:1 H_2SO_4	1.93	50.7	α	α	α
1-3	"	600	"	10:1 HNO_3	1.92	—	γ	γ	γ
1-4	"	600	"	"	—	—	$\gamma(+\alpha)$	γ	γ
1-5	"	600	H	5:1 H_2SO_4	1.92	46.9	$\gamma+\alpha$	α	$\alpha[+\gamma]$
1-6	"	600	"	20:1 H_2SO_4	1.95	48.4	$\gamma+\alpha$	$\gamma[+\alpha]$	γ
1-7	"	600	"	1:1 HNO_3	1.96	47.9	$\gamma(+\alpha)$	$\gamma[+\alpha]$	γ
1-8	"	600	"	15:1 HNO_3	1.96	49.4	γ	γ	γ
1-9	"	700	"	5:1 H_2SO_4	1.95	44.1	$\alpha(+\gamma)$	α	α
1-10	"	700	"	20:1 H_2SO_4	1.94	46.6	$\alpha(+\gamma)$	$\gamma(+\alpha)$	γ
1-11	"	700	"	1:1 HNO_3	1.95	47.9	$\gamma[+\alpha]$	γ	γ
1-12	"	700	"	15:1 HNO_3	1.94	48.9	γ	$\gamma[+\alpha]$	γ
1-13	"	700	"	20:1 H_2SO_4 +33% $\text{K}_2\text{Cr}_2\text{O}_7$	1.94	53.9	$\gamma+\alpha$	$\alpha(+\gamma)$	α
1-14	"	700	"	20:1 H_2SO_4 +10% K_2SO_4	1.79	59.8	$\alpha+\gamma$	α	α
1-15	"	700	"	15:1 HNO_3 +10% KNO_3	1.93	48.5	$\gamma(+\alpha)$	$\gamma[+\alpha]$	γ
1-16	$\alpha(1)$ - MnO_2	650	"	5:1 HNO_3	—	—	α	α	α
1-17	"	750	"	"	—	—	α	α	α
1-18	$\alpha(2)$ - MnO_2	700	"	5:1 H_2SO_4	1.94	51.3	$\gamma+\alpha$	$\gamma+\alpha$	$\gamma+\alpha$
1-19	"	700	"	20:1 H_2SO_4	1.94	53.3	$\gamma(+\alpha)$	$\gamma(+\alpha)$	γ
1-20	"	700	"	1:1 HNO_3	1.96	51.7	$\gamma(+\alpha)$	$\gamma[+\alpha]$	γ
1-21	"	700	"	15:1 HNO_3	1.95	52.4	$\gamma(+\alpha)$	$\gamma[+\alpha]$	γ

*1 C: Cold, H: Hot

*2 (): small amount, []: very small amount

(2) As shown in sample 1-1, the electron diffraction pattern of the product showed the lines of α - MnO_2 , while the X-ray diffraction pattern showed those of γ - MnO_2 . This product was treated with 1:1 HCl at 70°C for about 1 minute, and then the electron diffraction pattern, same as the X-ray diffrac-

* Studies on Manganese Dioxide for Dry Cells (Part 3)

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The original written in Japanese can be seen in J. Electrochem. Soc. Japan, 27, 221 (1959)

Fig. 1 Electron diffraction patterns

were determined by flame photometry and several results were indicated in Table 2. These values were less than the values previously reported⁽³⁾, and sample 1-5 showed an especially small value. From these results, as already reported in our former paper⁽²⁾, it may be supposed that the alkali metal ions or other cations are not always necessary to form α - MnO_2 structure.

Table 2 Alkali Metals Content in the Products

Sample No.	K(%)	Na(%)	Mn(%)	K/Mn (mol ratio)	Na/Mn (mol ratio)	Cryst. Types
1-14	3.03	0.15	58.9	0.072	0.006	α
1-16	4.40	0.15	58.5	0.106	0.006	α
1-18	1.82	0.16	60.4	0.043	0.006	α
1-5	0.07	0.18	59.6	0.002	0.007	$\alpha[\gamma]$
1-15	0.75	0.15	61.0	0.017	0.005	γ

(6) Treating the $\alpha(1)$ - MnO_2 , the products were the same α - MnO_2 , as shown in sample 1-16, 17 in Table 1. While, on treating the $\alpha(2)$ - MnO_2 , whose alkali metal content was less than the $\alpha(1)$ - MnO_2 , the products were γ - MnO_2 , as shown in sample 1-18, 21. Therefore it can be said that the manganese dioxides, rich in alkali metal contents, cannot be changed to γ - MnO_2 by this treatment.

(7) This treatment was applied to natural β - MnO_2 ore (Pirica) for the purpose of activating of

Table 3 Discharge Results of UM-5 Made with Various Manganese Dioxides
(Test Temp. 20°C, 40 Ω Continuous Discharge, Cut Off Voltage 0.85 V)

Sample No.	Original dioxides	Weight of Black Mix. (g)	After 2 days				After 3 Months			
			Open Cir. Volt. (V)	Short Cir. Cur. (A)	Closed Cir. Volt. (V)	Service Hours (min.)	Open Cir. Volt. (V)	Short Cir. Cur. (A)	Closed Cir. Volt. (V)	Service Hours (min.)
4-1	Pirika Ore	2.58	1.53	2.30	1.48	154	1.46	1.76	1.40	111
4-2	Pirika Ore Treated by HNO_3	2.20	1.77	2.48	1.71	233	1.58	1.50	1.51	213
4-3	Pirika Ore Treated by H_2SO_4	1.95	1.80	2.08	1.73	307	1.55	1.10	1.48	240
4-4	Electrolytic Dioxide	2.55	1.63	2.73	1.59	342	1.54	2.27	1.50	300
4-5	Ohira Ore (Natural)	2.55	1.60	2.68	1.55	223	1.52	2.15	1.48	156

1-1

1-14

1-1-HCl

1-19

1-3

2-5

Photographs

depolarizer for dry cells. The original ore was converted to γ - MnO_2 . In Table 3 and Fig. 2, discharge characteristics of the dry cells made with these treated dioxides, and the other artificial and natural ones, were indicated. Remarkable improvements of the cell characteristics were indicated in comparison with the original ore.

Fig. 2 Discharge curves of UM-5 after 3 months storage

(Received 17th, January 1959)

Literature :

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