Hydrothermal stability of some manganese oxides

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Abstract. Hydrothermal phase reaction studies in the systems β - MnO_2 - H_2O , γ - Mn_2O_3 - H_2O and γ - MnO_2 - H_2O have been carried out. Based on the experimental data and the reported phase diagrams in Mn_2O_3 - H_2O and MnO - H_2O systems, hydrothermal stability temperature of some of the manganese oxide minerals has been defined.

Keywords. Hydrothermal stability; manganese oxide.

1. Introduction

Several forms of manganese-oxygen compounds are known to occur as natural minerals or as synthesized manganese oxides. The phase relations of manganese oxides under differing conditions of temperature and pressure are particularly interesting since many of the manganese oxide deposits are metamorphosed manganese-containing sediments. Earlier studies were mainly confined to the stability conditions of manganese oxides, either as a function of Eh and PH, as in the systems Mn - H_2O , Mn - CO_2 - H_2O , Mn - S - CO_2 - H_2O at 25°C and one atmosphere pressure (Hem 1972) or at elevated temperatures and one atmosphere in air or oxygen (Faulring *et al* 1960; Hahn and Muan 1960; Lima-da-Faria and Lopes Vieira 1964; Ukai *et al* 1959). A review of the literature shows reports of equilibria diagrams of the systems MnO - H_2O , Mn_2O_3 - H_2O (Klingsberg and Roy 1959) and KMnO_4 - H_2O (Endo *et al* 1974). The present study pertains to the hydrothermal phase equilibria of β - MnO_2 - H_2O , γ - MnO_2 - H_2O and γ - Mn_2O_3 - H_2O systems and from the available data the sequence of stability of manganese minerals has been correlated for different starting compounds. Since the stellite vessels used for all the runs were sufficiently old and the pressurising fluid water reacts with the walls of the vessel to generate hydrogen which permeate through the platinum tubes. This corresponds to an oxygen fugacity comparable to Ni - NiO buffer (Eugster and Wones 1962).

2. Experimental method

The starting compounds used in the present study were β - MnO_2 , γ - MnO_2 and γ - Mn_2O_3 . β - MnO_2 (pyrolusite) used was the commercially available AR grade powder. γ - MnO_2 compound was from Union Carbide India Ltd. (battery grade material) prepared by electrolytic process. γ - Mn_2O_3 was prepared by hydrolyzing

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manganese chloride with 1M NaOH solution and the precipitate was aged on hot water bath for a few hours before it was filtered and dried in hot air-oven at 150°C. All the hydrothermal runs were carried out with tittle type stellite reactors by charging the starting compounds in platinum ampoules (5 cm × 0.5 mm dia with 0.1 mm wall thickness). The starting compounds were the respective oxides (100–200 mg) and double distilled water (6–7 drops), thus $P_{\text{total}} = P_{\text{H}_2\text{O}}$. The ampoules were sealed by arc welding and checked for any leakage by extended heating at 100°C in hot air oven and noting the weight differences if any. The ampoules showing any weight loss were discarded. The vessel with the charge was first pressurised with water medium and then introduced into the preheated furnace. After attaining the desired pressure and temperature, it was allowed for 60–80 h of uninterrupted run. At the end of the run the reaction was arrested by quenching the vessels with compressed air blast, until the ambient temperature was achieved. The remaining pressure was then vented out. The products were identified by the X-ray powder method. The accuracy of temperature and pressure controls was within $\pm 5^\circ\text{C}$ and ± 10 bars respectively.

3. Results

The phase diagram for $\beta\text{-MnO}_2\text{-H}_2\text{O}$ is given in figure 1. The sequence of decomposition of $\beta\text{-MnO}_2$ with increasing temperature is as follows

The phase boundaries between different oxide fields have steep positive slopes, which decrease as we go towards the field of lower oxides indicating that these are more and more pressure-dependent. The boundary with almost 45° positive slope

Figure 1. Phase diagram for $\beta\text{-MnO}_2\text{-H}_2\text{O}$ system.

suggests an almost equal dependence of temperature and pressure. This behaviour of change of slope was also observed by Endo *et al* (1974).

In the case of $\gamma\text{-MnO}_2\text{-H}_2\text{O}$ system, few isobaric (1 kbar) runs were carried out to understand the sequence of reactions. The $\gamma\text{-MnO}_2$ changes to $\beta\text{-MnO}_2$ at 220°C and then appears as lower oxides in the same sequence as in $\beta\text{-MnO}_2\text{-H}_2\text{O}$ system.

The sequence of decomposition of $\gamma\text{-Mn}_2\text{O}_3$ in $\gamma\text{-Mn}_2\text{O}_3\text{-H}_2\text{O}$ system is:

The phase diagram of the above system is given in figure 2. It may be noted that $\gamma\text{-Mn}_2\text{O}_3$ was expected to decompose to MnO via the intermediate field of Mn_3O_4 . But due to difficulty in distinguishing between $\gamma\text{-Mn}_2\text{O}_3$ and Mn_3O_4 by X-ray powder data the Mn_3O_4 field could not be established. In fact, more often $\gamma\text{-Mn}_2\text{O}_3$ is quoted in the literature as pseudo-hausmannite (ASTM Card no. 18.803).

X-ray powder diffraction data of the stable phases in all the above systems are given in table 1.

4. Discussion

The hydrothermal study of the manganese oxide systems has brought out certain interesting features concerning the stability of the different manganese oxides. The stabilization of hydrous phases was not found in the hydrothermal systems $\beta\text{-MnO}_2\text{-H}_2\text{O}$, $\gamma\text{-MnO}_2\text{-H}_2\text{O}$ and $\gamma\text{-Mn}_2\text{O}_3\text{-H}_2\text{O}$, although some of the runs were carried out at very low temperatures ($\approx 150^\circ\text{C}$) and for durations as long as 200 h. Similarly, only the anhydrous phases like $\text{K}_2\text{Mn}_7\text{O}_{14}$ and $\text{KMn}_8\text{O}_{16}$ were reported in the low temperature regions of $\text{KMnO}_4\text{-H}_2\text{O}$ system (Endo *et al* 1974). In the $\text{MnO-H}_2\text{O}$ and $\text{Mn}_2\text{O}_3\text{-H}_2\text{O}$ systems, Klingsberg and Roy (1959) reported Mn(OH)_2 and MnOOH hydrous phases at low temperatures but their attempt to stabilize hydrohausmannite from Mn_3O_4 was unsuccessful.

The lower limit of the hydrothermal stability range of the manganese oxide mineral depends on the parent material from which the oxide is derived, while the

Figure 2. Phase diagram for $\gamma\text{-Mn}_2\text{O}_3\text{-H}_2\text{O}$ system.

Table 1. X-ray diffraction data.

$\gamma\text{-MnO}_2$		$\beta\text{-MnO}_2$		Mn_2O_3		$\gamma\text{-Mn}_2\text{O}_3$		Mn_3O_4		MnO	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
4.01	mw	3.480	w	3.849	ms	4.913	m	4.935	w	2.560	s
2.41	ms	3.120	vs	2.717	vs	3.087	s	3.085	m	2.214	vs
2.11	vs	2.410	s	2.359	mw	2.881	vw	2.883	w	1.567	s
1.62	ms	2.206	vw	2.214	vvw	2.770	s	2.762	s	1.339	mw
		2.115	m	2.114	vw	2.490	vs	2.560	vvw		
		1.972	w	1.840	m	2.368	mw	2.491	vs		
		1.830	vw	1.661	s	2.040	m	2.341	mw		
		1.626	ms	1.530	vw	1.830	vw	2.034	mw		
		1.558	m	1.418	m	1.796	mw	1.819	vw		
		1.431	w	1.414	vvw	1.699	vw	1.785	m		
		1.398	vvw			1.640	vw	1.701	w		
						1.575	mw	1.639	s		
						1.544	ms	1.570	m		
						1.436	vw	1.540	ms		
						1.380	vw	1.462	vw		
						1.343	w	1.442	mw

Figure 3. Stability temperatures of some manganese oxide minerals at 1 kbar water vapour pressure based on the hydrothermal phase reaction studies (Δ Klingsberg and Roy 1959; ● Endo *et al* 1974; *present work).

maximum stability temperature is the same irrespective of the parent material (figure 3). For instance, bixbyite stability ranges from 550 to 725°C when the parent material is pyrolusite, but when derived from manganite the formation of bixbyite is at 275°C. The stability of manganese oxide minerals also depends on several factors such as soluble ions like K, Ba, Na, etc. in the hydrothermal fluid. Work in this direction is currently in progress in this laboratory.

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