Chemistry

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1965

SovietRxiv

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Abstract

Full Text

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On the Phase Equilibrium and Mechanism of Reduction of Solid Solutions of Manganese Ferrite and Chromite

The mechanism of reduction by hydrogen of manganese ferrochromite of composition $MnCr_{0.25}Fe_{1.75}O_4$ at 1000° has been investigated, and the equilibrium composition of the gas and solid phases at various degrees of reduction has been determined; the concentration dependence of the crystal-lattice parameter of the spinel-type solid solution $MnCr_xFe_{2-x}O_4$ has been established in the interval $0 \leq x \leq 2$ at $\Delta x = 0.25$.

The initial samples were obtained by the ceramic method, by sintering mixtures of chemically pure oxides Cr_2O_3, Fe_2O_3, MnO at 1200° for 15 hours in an atmosphere of purified nitrogen, followed by cooling in the furnace.

Analysis of the solid solutions and of the products of their reduction was carried out radiographically by the Debye method in $Cr{-}K_\alpha$ radiation with asymmetric placement of the film in a chamber of diameter 57.3 mm and with the use of graphical extrapolation to determine the lattice parameters of the crystalline phases ([1]). Figure 1 presents the change in the crystal-lattice parameter of solid solutions of manganese ferrite with manganese chromite as a function of composition. It is known ([2],[3]) that the lattice parameter of solid solutions of spinel phases with the same degree of inversion obeys Vegard' s law ([4]). Manganese chromite is a spinel with a normal distribution of cations ([2]), while in manganese ferrite the degree of inversion is 20% ([5]). Therefore one may expect some deviation from a linear course of the dependence $a(x)$, but Fig. 1 shows that this deviation is insignificant and lies within the accuracy limits of the method used (±0.005 Å).

Fig. 1. Dependence of the lattice parameter of solid solutions $MnCr_xFe_{2-x}O_4$ on their composition.

The solid solution of composition $MnCr_{0.25}Fe_{1.75}O_4$ was reduced in a vacuum circulation apparatus, and the equilibrium composition of the gas phase P_{H_2O}/P_{H_2} was determined by the procedure described in (^{6}). The degree of reduction was monitored from the loss in sample weight and the consumption of hydrogen. Reduction to $MnCr_2O_4$, MnO, Fe was taken as 100%.

The oxygen pressure over the solid solutions was found from the equation

$$P_{O2}^{1/2} = \frac{P_{H_2O}}{P_{H_2}} \cdot K_{H_2O},$$

in which P_{H_2O}/P_{H_2} was obtained experimentally, and K_{H_2O} is the equilibrium constant of the dissociation reaction of water vapor (at 1000°, $\lg K_{H_2O} = -7.2878$). The results of the calculation are presented in Fig. 2.

The character of the change in P_{O_2} indicates the formation, during reduction, of solid solutions of variable composition, which is also confirmed by X-ray phase analysis (Fig. 3).

On the curve of the dependence of P_{O_2} on the degree of reduction, three regions are clearly distinguished: 0–25%, 25–33%, and more than 33% reduction, each of which is characterized by its own law of decrease of the equilibrium oxygen pressure with increasing degree of reduction.

X-ray studies of specimens reduced by less than 33% revealed the following (Fig. 3): a spinel phase, whose crystal-lattice parameter decreases sharply from 8.505 ± 0.005 Å for the initial composition to 8.443 ± 0.005 Å at 31.6% reduction, and a monoxide phase with a parameter decreasing from 4.394 ± 0.003 Å at 14.2% to 4.360 ± 0.003 Å at 31.6% reduction.

Fig. 2

Fig. 3

Fig. 2. Change in oxygen fugacity during reduction of $MnCr_{0.25}Fe_{1.75}O_4$

Fig. 3. Change in the parameters of the crystal lattices of the spinel ($a_{Me_3O_4}$), monoxide (a_{MeO}), and metallic (a_{Me}) phases as a function of the degree of reduction of $MnCr_{0.25}Fe_{1.75}O_4$

After 33%, the reduction products contain three phases (Fig. 3): a spinel phase of constant composition with a crystal-lattice parameter 8.440 ± 0.005 Å, corresponding to $MnCr_2O_4$ (Fig. 1); a monoxide phase of variable composition, whose crystal-lattice parameter increases from 4.359 ± 0.003 Å at 34.6% to 4.408 ± 0.003 Å at 89.7% reduction; and a metallic phase with a crystal-lattice parameter 2.866 ± 0.002 Å, corresponding to pure iron.

On the basis of the foregoing, the composition of the monoxide phase that is in equilibrium after 33% reduction of $MnCr_{0.25}Fe_{1.75}O_4$ can be calculated from the following equation:

$$\mathrm{MnCr_{0.25}Fe_{1.75}O_4} + m\mathrm{H_2} = 0.125\,\mathrm{MnCr_2O_4} +$$

$$+(3.5-m)\,\mathrm{Mn}_{\frac{0.875}{3.5-m}}\mathrm{Fe}_{\frac{2.625-m}{3.5-m}}\mathrm{O} + (m-0.875)\,\mathrm{Fe} + m\mathrm{H_2O}, \qquad (1)$$

where

$$m = \frac{(\%\text{ reduction})\cdot 2.625}{100}.$$

The chemistry of the process in this region is reduced to the reduction of wüstite dissolved in the monoxide phase:

$$(\mathrm{FeO})_{\mathrm{soln}} + \mathrm{H_2} \rightleftharpoons \mathrm{Fe} + \mathrm{H_2O}.$$

As a result, the lattice parameter of the monoxide phase increases, since it is enriched with larger Mn^{2+} cations. The equilibrium oxygen pressure changes only slightly, in agreement with the results of the study of the solid solution MnO—FeO (^{7}).

From equation (1), using the values of m at 34.6; 51.8; 73.7; 89.6% reduction, a dependence of the crystal-lattice parameter of the monoxide phase on composition satisfying Vegard' s law was obtained; by extrapolation, the parameters of FeO and MnO were found to be, respectively, 4.319 ± 0.003 and 4.439 ± 0.003 Å. Apparently, the monoxide solid solution that forms has only a very small deviation from the stoichiometric composition MeO, which explains the increased value of the lattice parameter of wüstite (FeO) present in the solution.

Using the concentration dependence of the crystal-lattice parameter of the MnO—FeO solid solution, it is easy to determine the contents of MnO and FeO in the monoxide phase of samples reduced by less than 33%, assuming that the defectiveness of the monoxide solution in contact with the spinel phase of variable composition is also insignificant.

The process of reduction of the initial manganese ferrochromite up to 33% is described by the scheme:

$$\mathrm{MnCr_{0.25}Fe_{1.75}O_4} + m\mathrm{H_2} =$$

$$= (1-m)\left[(\mathrm{MnCr_2O_4})_{\frac{0.125}{1-m}}(\mathrm{MnFe_2O_4})_{\frac{0.875-3mz}{1-m}}(\mathrm{Fe_3O_4})_{\frac{m(3z-1)}{1-m}}\right] +$$

$$+3m\,\mathrm{Mn}_z\mathrm{Fe}_{1-z}\mathrm{O} + \mathrm{H_2O}. \qquad (2)$$

From the known composition of the monoxide phase (z) and the given degree of reduction (m), the composition and amount of the spinel phase were calculated (Table 1).

Table 1

Composition of the equilibrium solid and gas phases at $P_{H_2O} = 4.579$ mm Hg

No.	Percent reduction	Spinel phase	Monoxide phase	Metal	P_{H_2}, mm Hg
1	0	$(MnCr_2O_4)_{0.125}(MnFe_2O_4)_{0.875}$	–	–	–
2	0.1	$MnCr_{0.25}Fe_{1.75}O_4$	Present	–	0.07
3	14.2	$0.625\,(MnCr_2O_4)_{0.20}(MnFe_2O_4)_{0.26} \times (Fe_3O_4)_{0.54}$	$1.099\,Mn_{0.64}Fe_{0.36}O$	–	0.61
4	19.8	$0.481\,(MnCr_2O_4)_{0.26}(MnFe_2O_4)_{0.12} \times (Fe_3O_4)_{0.62}$	$1.559\,Mn_{0.53}Fe_{0.47}O$	–	0.94
5	25.4	$0.333\,(MnCr_2O_4)_{0.37}(MnFe_2O_4)_{0.11} \times (Fe_3O_4)_{0.52}$	$2.001\,Mn_{0.42}Fe_{0.58}O$	–	1.42
6	26.4	$0.307\,(MnCr_2O_4)_{0.41}(MnFe_2O_4)_{0.10} \times (Fe_3O_4)_{0.49}$	$2.079\,Mn_{0.41}Fe_{0.59}O$	–	1.63
7	27.5	$0.277\,(MnCr_2O_4)_{0.45}(MnFe_2O_4)_{0.07} \times (Fe_3O_4)_{0.48}$	$2.069\,Mn_{0.39}Fe_{0.61}O$	–	1.95
8	31.0	$0.185\,(MnCr_2O_4)_{0.68}(MnFe_2O_4)_{0.01} \times (Fe_3O_4)_{0.31}$	$2.045\,Mn_{0.36}Fe_{0.64}O$	–	4.63
9	31.6	$0.171\,(MnCr_2O_4)_{0.73}(MnFe_2O_4)_{0.01} \times (Fe_3O_4)_{0.26}$	$2.087\,Mn_{0.35}Fe_{0.65}O$	–	6.81
10	34.6	$0.125\,MnCr_2O_4$	$2.601\,Mn_{0.34}Fe_{0.66}O$	0.024 Fe	7.27
11	51.8	$0.125\,MnCr_2O_4$	$2.140\,Mn_{0.41}Fe_{0.59}O$	0.485 Fe	8.97
12	73.7	$0.125\,MnCr_2O_4$	$1.566\,Mn_{0.56}Fe_{0.44}O$	1.059 Fe	10.83
13	89.6	$0.125\,MnCr_2O_4$	$1.148\,Mn_{0.76}Fe_{0.24}O$	1.477 Fe	11.90

From a comparison of the data in Table 1 and Fig. 2 it follows that, as reduction proceeds, the content of manganese ferrite steadily decreases; it disappears in the ternary solid solution at 33% reduction, while the concentration of magnetite first increases to 62% at 19.8% reduction and then falls to zero at 33%, and the spinel solid solution is converted into $MnCr_2O_4$. In other words, in the region considered the spinel phase is depleted both in manganese cations and in iron-

iron; but at the beginning of reduction the predominant process is the transition of manganese cations from the spinel phase into the wüstite phase, which is formed on the basis of MnO. This is accompanied by a sharp decrease in the crystal-lattice parameter of the spinel phase. The iron cations entering the wüstite phase also reduce the parameter of its crystal lattice. Beginning at approximately 20–25%, magnetite is mainly reduced, or, more precisely, it is chiefly iron cations that pass from the spinel phase into the wüstite phase.

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Received
16 IX 1964

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