Reports of the Academy of Sciences of the USSR

CHEMISTRY

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 158, No. 5

CHEMISTRY

V. F. Balakirev, M. I. Simonova, Corresponding Member of the Academy of Sciences of the USSR
G. I. Chufarov

EQUILIBRIUM CONDITIONS AND THE MECHANISM OF REDUCTION BY HYDROGEN OF SOLID SOLUTIONS IN THE Fe–Cr–O SYSTEM

The phase diagram of the Fe–Cr–O system at 1300° (^{1}) and the dependence of the crystal-lattice parameter of the spinel phase $FeCr_{2-x}Fe_xO_4$ on its composition—the ratio of iron and chromium cations (^{2},^{3})—indicate the complex nature of the functional property-composition relationship in these solid solutions. It has been established (^{4}) that the products of reduction of stoichiometric iron chromite $FeCr_2O_4$ are chromium oxide and iron.

In the present work, data are presented on equilibrium in the Fe–Cr–O and Fe–Cr–O–H systems at 1000°, and the reduction at this temperature of solid solutions over a broad composition interval $0 \leq x \leq 2$ has also been investigated.

The initial solid solutions of compositions $x = 0$; 0.7; 1.5; 1.8 were obtained by the ceramic method by sintering the corresponding mixtures of the oxides Cr_2O_3, Fe_2O_3, and FeO at 1300° for 10 hours in an atmosphere of purified argon. Wüstite was obtained by reduction of Fe_2O_3 in closed containers made of Armco iron at 900° for 30 hours, followed by quenching in a cooling mixture (−30°). Solid solutions of other compositions were obtained by reducing the initial samples. X-ray diffraction analysis of the solid solutions and of the products of their reduction was carried out by the Debye method in Cr–K_α radiation, in a camera of diameter 57.3 mm. An asymmetric film loading was used. The lattice parameters of the phases were determined by graphical extrapolation according to Bradley and Jay (^{5}).

The equilibrium compositions of the gas phase during reduction of the solid solutions were found by the static method in a closed vacuum apparatus with continuous circulation of the H_2+H_2O mixture. The water-vapor pressure in the system was maintained constant and equal to the saturated vapor pressure at 0° or −21.2°. After equilibrium had been established, the sample was removed from the furnace and quenched, the water vapor was frozen out in a trap immersed in liquid nitrogen, and the partial pressure of hydrogen was measured.

Attainment of equilibrium was effected both from the reduction side and from the oxidation side, and the mean value of the hydrogen pressure was taken as the equilibrium value. The degree of reduction was determined from the consumption of hydrogen and the loss in weight of the sample; complete removal of oxygen was taken as 100%. The dissociation pressure of oxygen over the solid solutions was calculated from the equation

$$P_{\mathrm{O2}}^{1/2} = \frac{P_{\mathrm{H2O}}}{P_{\mathrm{H2}}} \cdot k_{\mathrm{H2O}},$$

where $\frac{P_{\mathrm{H2O}}}{P_{\mathrm{H2}}}$ was obtained experimentally, and k_{H2O}—the equilibrium constant of the water-vapor dissociation reaction at the same temperature—was calculated by the formula of D. Chipman and A. Samarin ([6]). The compositions of the solid solutions formed during reduction were calculated from the phase composition and the known degree of reduction, and a comparison was made of the values of the para-

of their crystal lattices with the dependence, specially obtained for this purpose, of the spinel lattice parameter on its composition (Fig. 1). The experimental and calculated data are given in Table 1.

The oxygen potential in a system containing solid solutions of compositions $1.04 \leq x \leq 2$ is greater than the oxygen potential upon dissociation of wüstite to iron. This ensures the coexistence of wüstite in equilibrium with solid solutions of the indicated compositions, while the phase of metallic iron is not formed during reduction. The equilibrium hydrogen pressure remains lower than the corresponding value for the reduction of wüstite.

For the composition of the solid solution corresponding to $x = 1.04$, all three solid phases are in equilibrium: spinel, wüstite, and metallic. According to the phase rule, the system in this case, at the given temperature, is invariant. Therefore the equilibrium oxygen pressure, within experimental error, remains constant and equal to the potential of wüstite dissociation. This is observed in the reduction interval of the initial specimen $FeCr_{0.5}Fe_{1.5}O_4$ from 11.9% to 45.1%. The process proceeds through reduction of the previously accumulated wüstite. As reduction proceeds, the intensity of the diffraction lines of wüstite on the X-ray diffraction patterns decreases, while the intensity of the diffraction lines of iron increases. The intensity of the diffraction lines of the spinel phase and the parameter of its crystal lattice remain unchanged within the limits of measurement error, which indicates a constant composition of the solid solution. An analogous phenomenon was noted at 1300° ([1]).

Fig. 1. Crystal-lattice parameter of the solid solution $FeCr_{2-x}Fe_xO_4$

Fig. 1. Crystal-lattice parameter of the solid solution $FeCr_{2-x}Fe_xO_4$

Figure 1: Fig. 1. Crystal-lattice parameter of the solid solution $FeCr_{2-x}Fe_xO_4$

At $x < 1.04$, the equilibrium oxygen potential in the system is lower than that for wüstite dissociation. Therefore the continuous series of solid solutions is reduced directly to metallic iron, bypassing the wüstite phase. Naturally, the measured equilibrium hydrogen pressure in this range of compositions is greater than the corresponding value for the case of wüstite reduction.

Thus, an increase in the chromium content in the solid solutions decreases the equilibrium oxygen pressure in the system.

If the solid solutions in the Fe—Cr—O system are represented formally as a solution of magnetite Fe_3O_4 in iron chromite $FeCr_2O_4$, then in this case the process of reduction of the solid solutions is reduced to reduction of magnetite, and only after its disappearance does reduction of iron chromite begin.

The metallic phase detected in the solid reduction products has a parameter coinciding with the lattice parameter of pure iron, which remains constant up to the formation of ferrochrome ($x = 0$). This means that, during reduction of solid solutions of any composition under the conditions studied, all the chromium remains in the spinel phase, gradually enriching it, while ferrochrome is not formed.

The high value of the wüstite crystal-lattice parameter (4.310 Å) is due to the smallest number of vacancies in the metallic sublattice, which occurs when wüstite is in equilibrium with iron. When wüstite is in equilibrium with the spinel phase, the number of vacancies in the metallic sublattice increases sharply, which causes a significant decrease in the parameter (4.295 Å). In the limiting case, when wüstite is in equilibrium with magnetite ($x = 2$), the defectiveness of wüstite is greatest and the lattice parameter is smallest (4.282 Å) (^{7}).

Table 1

Equilibrium composition of the solid and gas phases

Composition of solid solution	Equilibrium composition of gas phase, P_{H_2O}, mm Hg	Equilibrium composition of gas phase, P_{H_2}, mm Hg	Dissociation pressure P_{O_2}, atm	Crystal-lattice parameters, Å: spinel	Crystal-lattice parameters, Å: wüstite	Crystal-lattice parameters, Å: iron	Note
FeO	4,579	6,337	$1,388 \cdot 10^{-15}$	—			
Fe_3O_4	4,579	0,982	$5,77 \cdot 10^{-14}$			—	

Composition of solid solution	Equilibrium composition of gas phase, P_{H_2O}, mm Hg	Equilibrium composition of gas phase, P_{H_2}, mm Hg	Dissociation pressure P_{O_2}, atm	Crystal-lattice parameters, Å: spinel	Crystal-lattice parameters, Å: wüstite	Crystal-lattice parameters, Å: iron	Note
$FeCr_{0,20}Fe_{1,80}O_4$	4,579	1,462	$2,602 \cdot 10^{-14}$	$8,392 \pm 0,005$	$4,295 \pm 0,003$	–	
$FeCr_{0,25}Fe_{1,75}O_4$	4,579	2,152	$1,203 \cdot 10^{-14}$	$8,393 \pm 0,005$	$4,295 \pm 0,003$	–	$FeCr_{0,20}Fe_{1,80}O_4$ reduced by 5%
$FeCr_{0,41}Fe_{1,59}O_4$	4,579	2,906	$6,593 \cdot 10^{-15}$	$8,385 \pm 0,005$	$4,297 \pm 0,003$	–	“” 12,7%
$FeCr_{0,50}Fe_{1,50}O_4$	4,579	4,169	$3,212 \cdot 10^{-15}$	$8,385 \pm 0,005$	$4,297 \pm 0,003$	–	
$FeCr_{0,96}Fe_{1,04}O_4$	4,579	5,658	$1,741 \cdot 10^{-15}$	$8,397 \pm 0,005$	$4,310 \pm 0,003$	weak lines $2,866 \pm 0,002$	$FeCr_{0,50}Fe_{1,50}O_4$ reduced by 11,9%
$FeCr_{0,96}Fe_{1,04}O_4$	4,579	5,848	$1,615 \cdot 10^{-15}$	$8,398 \pm 0,005$	$4,310 \pm 0,003$	$2,866 \pm 0,002$	“” 23,3%
$FeCr_{0,96}Fe_{1,04}O_4$	4,579	5,943	$1,574 \cdot 10^{-15}$	$8,401 \pm 0,005$	$4,309 \pm 0,003$	$2,866 \pm 0,002$	“” 31,8%
$FeCr_{0,96}Fe_{1,04}O_4$	4,579	6,042	$1,533 \cdot 10^{-15}$	$8,404 \pm 0,005$	$4,309 \pm 0,003$	$2,866 \pm 0,002$	“” 45,1%
$FeCr_{1,00}Fe_{1,00}O_4$	4,579	6,438	$1,339 \cdot 10^{-15}$	$8,405 \pm 0,005$	–	$2,866 \pm 0,002$	“” 50%
$FeCr_{1,30}Fe_{0,70}O_4$	4,579	6,539	$1,300 \cdot 10^{-15}$	$8,407 \pm 0,005$	–	$2,866 \pm 0,002$	
$FeCr_{1,43}Fe_{0,57}O_4$	4,579	6,743	$1,227 \cdot 10^{-15}$	$8,405 \pm 0,005$	–	$2,866 \pm 0,002$	$FeCr_{1,30}Fe_{0,70}O_4$ reduced by 9%
$FeCr_{1,58}Fe_{0,42}O_4$	4,579	10,827	$4,748 \cdot 10^{-16}$	$8,397 \pm 0,005$	–	$2,866 \pm 0,002$	“” 17%
$FeCr_{1,68}Fe_{0,32}O_4$	4,579	65	$1,303 \cdot 10^{-17}$	$8,394 \pm 0,005$	–	$2,866 \pm 0,002$	“” 23%
$FeCr_{1,83}Fe_{0,17}O_4$	4,579	148	$2,437 \cdot 10^{-18}$	$8,391 \pm 0,005$	–	$2,866 \pm 0,002$	“” 29%

Composition of solid solution	Equilibrium composition of gas phase, P_{H_2O}, mm Hg	Equilibrium composition of gas phase, P_{H_2}, mm Hg	Dissociation pressure P_{O_2}, atm	Crystal-lattice parameters, Å: spinel	Crystal-lattice parameters, Å: wüstite	Crystal-lattice parameters, Å: iron	Note
$FeCr_2O_4$	0,686	109	$1,053 \cdot 10^{-19}$	$8,383 \pm 0,005$	–	$2,866 \pm 0,002$	Cr_2O_3 is present

It is known that in a number of solid solutions of the spinel and wüstite types ($^{7-12}$) Vegard' s rule (^{13}) is obeyed. However, for the spinel solid solution $FeCr_{2-x}Fe_xO_4$, the dependence of the lattice parameter on composition has a complex nonmonotonic course (Fig. 1).

A dependence of this type is explained by the fact that, in the formation of solid solutions between normal iron chromite $Fe^{2+}[Cr_2^{3+}]O_4^{2-}$ and inverse magnetite $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}$, there occurs not only substitution of Cr^{3+} cations by Fe^{3+} cations, but also redistribution of Fe^{3+} and Fe^{2+} cations over the octahedral and tetrahedral sites of the spinel lattice; i.e., the degree of inversion λ increases from zero (stoichiometric iron chromite) to 0.5 (magnetite). The degree of inversion increases nonuniformly with increasing x. In the region $0 \leq x \leq 0.7$ the solid solution remains normal, and in the region $1.6 \leq x \leq 2$ it is inverse. The increase in the crystal-lattice parameter occurs as a result of the replacement of Cr^{3+} cations by the larger Fe^{3+} cations.

The sharp increase in λ in the interval $0.7 \leq x \leq 1.2$ leads to a decrease in the spinel lattice parameter, while at $1.2 \leq x \leq 1.6$ the growth of the parameter with changing composition is compensated by its decrease due to the increase in λ.

Institute of Metallurgy
Sverdlovsk

Received
16 VI 1964

REFERENCES CITED

1. A. V. Seybolt, *J. Electrochem. Soc.*, **107**, 3, 147 (1960).

2. H. J. Yearian, J. M. Kortright, R. H. Langenheim, *J. Chem. Phys.*, **22**, 1196 (1954).

3. W. D. Derbyshire, H. J. Yearian, *Phys. Rev.*, **112**, No. 5, 1603 (1958).
4. A. N. Morozov, I. A. Novokhatskii, *Izv. AN SSSR, OTN, Metallurgiya i toplivo*, No. 6, 3 (1962).
5. A. I. Brodii, A. H. Joy, *Proc. Phys. Soc.*, **44**, 563 (1932).
6. O. A. Esin, P. V. Gel' d, *Physicochemical Pyrometallurgical Processes*, vol. 1, Sverdlovsk–Moscow, 1950, p. 23.
7. E. R. Jette, F. Foote, *J. Chem. Phys.*, **1**, 29 (1933).
8. H. Schenk, W. Pfaff, *Arch. Eisenhüttenwesen*, **32**, No. 11, 741 (1961).
9. P. K. Foster, A. J. E. Welch, *Trans. Farad. Soc.*, **52**, 1636 (1956).
10. A. H. Jay, K. W. Andrews, *J. Iron and Steel Inst.*, **152**, 15 (1945).
11. V. N. Bogoslovskii, I. E. Startseva et al., *Fiz. met. i metalloved.*, **15**, No. 2, 181 (1963).
12. V. Montoro, *Gazz. Chim. Ital.*, **68**, 728 (1938); **70**, 145, 150 (1940).
13. L. Vegard, *Zs. Phys.*, **5**, 393 (1921).

Note: Figure translations are in progress. See original paper for figures.