Chemistry

Yu. A. Korneev, V. F. Balakirev, Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov

1964

SovietRxiv

Fig. 1. Dependence of the lattice parameter of solid solutions $MgAl_{2-x}Fe_xO_4$ on their composition.

Figure 1: Fig. 1. Dependence of the lattice parameter of solid solutions $MgAl_{2-x}Fe_xO_4$ on their composition.

Fig. 2. Equilibrium oxygen pressure during dissociation of $MgAl_{0.25}Fe_{1.75}O_4$ at different degrees of reduction at 1000°C.

Figure 2: Fig. 2. Equilibrium oxygen pressure during dissociation of $MgAl_{0.25}Fe_{1.75}O_4$ at different degrees of reduction at 1000°C.

Abstract

Full Text

Chemistry

Yu. A. Korneev, V. F. Balakirev, Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov

PHASE RELATIONS IN THE SPINEL REGION OF THE SYSTEM Mg–Al–Fe–O

In the present study, data have been obtained on the equilibrium conditions in the system Mg–Al–Fe–O–H; the reduction by hydrogen of magnesium ferroaluminate of composition $MgAl_{0.25}Fe_{1.75}O_4$ at 1000°C has been studied, as well as the change in the crystal-lattice parameter of the spinel type $MgAl_{2-x}Fe_xO_4$ over a wide range of compositions $0 \leq x \leq 2$.

Solid solutions of compositions $x = 0$; 0.25; 0.5; 0.75; 1.0; 1.25; 1.50; 1.75; 2.0 were obtained by a ceramic sintering method in air from the corresponding mixtures of MgO, Fe_2O_3, and $Al(OH)_3$ at 1350° for 30 hours, followed by a 5-hour hold at 1000° and quenching in water in order to preserve the degree of inversion of the spinel structure corresponding to the experimental temperature.

X-ray structural analysis of the solid solutions and of the products of their reduction was carried out by the Debye method in Fe–K_α radiation, in a chamber 57.3 mm in diameter with asymmetric loading of the film.

Fig. 1. Dependence of the lattice parameter of solid solutions $MgAl_{2-x}Fe_xO_4$ on their composition.

Fig. 2. Equilibrium oxygen pressure during dissociation of $MgAl_{0.25}Fe_{1.75}O_4$ at different degrees of reduction at 1000°C.

From the experimentally obtained dependence of the crystal-lattice parameter of $MgAl_{2-x}Fe_xO_4$ on composition (Fig. 1), it follows that in these solid solutions

Fig. 3. Change in the crystal-lattice parameters of the spinel ($a_{Me_3O_4}$), wüstite (a_{MeO}), and metallic (a_{Me}) phases with the degree of reduction of magnesium ferroaluminate $MgAl_{0.25}Fe_{1.75}O_4$

Figure 3: Fig. 3. Change in the crystal-lattice parameters of the spinel ($a_{Me_3O_4}$), wüstite (a_{MeO}), and metallic (a_{Me}) phases with the degree of reduction of magnesium ferroaluminate $MgAl_{0.25}Fe_{1.75}O_4$

Vegard' s rule (^{1}) is not fulfilled: two linear regions are observed in the intervals $0 \leq x \leq 1$ and $1 \leq x \leq 2$. This occurs in cases where a continuous series of solid solutions is formed by spinels with different degrees of inversion. In the solutions under consideration, $MgAl_2O_4$ is a normal spinel, while $MgFe_2O_4$ at 1000° is an intermediate spinel (^{1}).

Reduction of $MgAl_{0.25}Fe_{1.75}O_4$ was carried out in a vacuum circulation apparatus according to the procedure described in (^{3}). The degree of reduction was determined from the loss in weight of the specimen and from the consumption of hydrogen. Reduction to $MgAl_2O_4$, MgO was taken as 100%.

The equilibrium oxygen pressure over the solid solutions was calculated from the equation

$$P_{O_2}^{1/2} = \frac{P_{H_2O}}{P_{H_2}} K_{H_2O},$$

where P_{H_2O}/P_{H_2} is determined experimentally from the equilibrium composition of the gas phase at different degrees of reduction; K_{H_2O} is the equilibrium constant of the water-vapor dissociation reaction at 1000° (^{4}). The results of the calculation of P_{O_2} are given in Fig. 2. The complex character of the change in the oxygen partial pressure reflects the changing nature of the solid phases during reduction.

Fig. 3. Change in the crystal-lattice parameters of the spinel ($a_{Me_3O_4}$), wüstite (a_{MeO}), and metallic (a_{Me}) phases with the degree of reduction of magnesium ferroaluminate $MgAl_{0.25}Fe_{1.75}O_4$

X-ray analysis showed that after 33.3% reduction the products contain a spinel phase of constant composition with a crystal-lattice parameter of 8.085 ± 0.005 Å, corresponding to magnesium aluminate $MgAl_2O_4$ (8.080 ± 0.005 Å) (Fig. 1); a wüstite phase of variable composition, whose crystal-lattice parameter changes from 4.285 ± 0.003 Å at 35.2% to 4.247 ± 0.003 Å at 87.0% reduction; and a metallic phase of constant composition with a crystal-lattice parameter of 2.867 ± 0.002 Å, corresponding to pure iron (Fig. 3).

On the basis of these data, the reduction process of the initial magnesium ferroaluminate by more than 33.3% may be described in general form by the following equation:

$$(\mathrm{MgAl_2O_4})_{0.125}(\mathrm{MgFe_2O_4})_{0.875}+m\mathrm{H_2} = 0.125\mathrm{MgAl_2O_4}+(3.5-m)\mathrm{Mg}_{\frac{0.875}{3.5-m}}\mathrm{Fe}_{\frac{2.625-m}{3.5-m}}\mathrm{O}+(m-0.875)\mathrm{Fe}+m\mathrm{H_2O},$$

where m is a quantity proportional to the degree of reduction (at 100%, $m = 2.625$).

From the compositions of the solid solution MgO–FeO calculated from this equation at 35.2, 41.3, 44.0, 57.3, 72.5, and 87% reduction, and from the crystal-lattice parameters of the wüstite phase for the same degrees of reduction, a dependence of the parameter of the wüstite solution on composition was obtained that satisfies Vegard' s rule, which is in agreement with work (^{5}). By extrapolation, the lattice parameters for MgO and FeO were found to be 4.218 ± 0.003 Å and 4.320 ± 0.003 Å, respectively. The value obtained

of the parameter of the hypothetical wüstite is evidently due to the fact that the solid solution MgO–FeO, formed during reduction, has a composition close to stoichiometric MeO (^{6}).

On the basis of the dependence of the crystal-lattice parameter of the MgO–FeO solution on composition, the concentrations of its components (Table 1) were determined in samples reduced by less than 33.3%, assuming that, in equilibrium of the wüstite solution with the spinel phase, its defectiveness is likewise insignificant (^{3}).

After 33.3% the process $(\mathrm{FeO})_{\mathrm{soln}} + \mathrm{H_2} = \mathrm{Fe} + \mathrm{H_2O}$ takes place, and only the composition of the wüstite phase changes (Table 1). It becomes depleted in Fe^{2+} cations, which leads to a decrease in its parameter. The oxygen elasticity, however, decreases comparatively little. The experimental data on the equilibrium composition of the gas phase are in agreement with the work (^{7}).

Table 1

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

Reduction, %	Spinel phase	Wüstite phase	Metal	$P_{\mathrm{H_2}}$, mm Hg
1.4	$0.963\,(\mathrm{MgAl_2O_4})_{0.13}(\mathrm{MgFe_2O_4})_{0.80}(\mathrm{Fe_3O_4})_{0.07}$	$0.111\,(\mathrm{Mg_{0.96}Fe_{0.04}})\mathrm{O}$	—	0.038
6.5	$0.829\,(\mathrm{MgAl_2O_4})_{0.15}(\mathrm{MgFe_2O_4})_{0.59}(\mathrm{Fe_3O_4})_{0.26}$	$0.513\,(\mathrm{Mg_{0.75}Fe_{0.25}})\mathrm{O}$	—	0.092
10.35	$0.728\,(\mathrm{MgAl_2O_4})_{0.17}(\mathrm{MgFe_2O_4})_{0.45}(\mathrm{Fe_3O_4})_{0.38}$	$0.816\,(\mathrm{Mg_{0.67}Fe_{0.33}})\mathrm{O}$	—	0.258
14.8	$0.611\,(\mathrm{MgAl_2O_4})_{0.20}(\mathrm{MgFe_2O_4})_{0.29}(\mathrm{Fe_3O_4})_{0.51}$	$1.167\,(\mathrm{Mg_{0.60}Fe_{0.40}})\mathrm{O}$	—	0.380
20.1	$0.472\,(\mathrm{MgAl_2O_4})_{0.26}(\mathrm{MgFe_2O_4})_{0.08}(\mathrm{Fe_3O_4})_{0.66}$	$1.584\,(\mathrm{Mg_{0.53}Fe_{0.47}})\mathrm{O}$	—	0.435
22.4	$0.412\,(\mathrm{MgAl_2O_4})_{0.30}(\mathrm{Fe_3O_4})_{0.70}$	$1.764\,(\mathrm{Mg_{0.51}Fe_{0.49}})\mathrm{O}$	—	0.50
23.9	$0.373\,(\mathrm{MgAl_2O_4})_{0.33}(\mathrm{Fe_3O_4})_{0.67}$	$1.881\,(\mathrm{Mg_{0.47}Fe_{0.53}})\mathrm{O}$	—	0.68
27.8	$0.270\,(\mathrm{MgAl_2O_4})_{0.46}(\mathrm{Fe_3O_4})_{0.54}$	$2.190\,(\mathrm{Mg_{0.42}Fe_{0.58}})\mathrm{O}$	—	1.22
29.3	$0.231\,(\mathrm{MgAl_2O_4})_{0.54}(\mathrm{Fe_3O_4})_{0.46}$	$2.307\,(\mathrm{Mg_{0.39}Fe_{0.61}})\mathrm{O}$	—	2.35

Reduction, %	Spinel phase	Wüstite phase	Metal	P_{H_2}, mm Hg
32.4	$0.150\,(MgAl_2O_4)_{0.834}(Fe_3O_4)_{0.166}$	$2.550\,Mg_{0.34}Fe_{0.66}O$	—	5.2
35.2	$0.125\,MgAl_2O_4$	$2.566\,Mg_{0.34}Fe_{0.66}O$	0.059 Fe	7.2
41.3	$0.125\,MgAl_2O_4$	$2.416\,Mg_{0.36}Fe_{0.64}O$	0.209 Fe	8.3
44.0	$0.125\,MgAl_2O_4$	$2.345\,Mg_{0.37}Fe_{0.63}O$	0.280 Fe	8.5
57.3	$0.125\,MgAl_2O_4$	$1.996\,Mg_{0.44}Fe_{0.56}O$	0.629 Fe	10.0
72.5	$0.125\,MgAl_2O_4$	$1.597\,Mg_{0.55}Fe_{0.45}O$	1.028 Fe	11.3
87.0	$0.125\,MgAl_2O_4$	$1.216\,Mg_{0.72}Fe_{0.28}O$	1.409 Fe	33.3

Upon reduction to 33.3%, the following equilibrium phases are found in the solid reduction products: a spinel of variable composition, whose crystal-lattice parameter changes from 8.362 ± 0.005 Å at 1.4% reduction to 8.085 ± 0.005 Å, and a wüstite phase of variable composition with a crystal-lattice parameter changing from 4.222 ± 0.003 Å to 4.285 ± 0.003 Å (Fig. 3).

The spinel phase in this case may be represented as a ternary solution of the type $(MgAl_2O_4)_{z_1}(MgFe_2O_4)_{z_2}(Fe_3O_4)_{1-z_1-z_2}$, and the reduction process described by the equation

$$MgAl_{0.25}Fe_{1.75}O_4+mH_2=(1-m)\left[(MgAl_2O_4)_{\frac{0.125}{1-m}}(MgFe_2O_4)_{\frac{0.875-3my}{1-m}}(Fe_3O_4)_{\frac{m(3y-1)}{1-m}}\right]+3mMg_yFe_{1-y}O+mH_2$$

From the known composition of the ferrous phase (y) at a given stage of reduction (m), the composition and amount of the spinel phase were calculated (Table 1).

The data of Table 1 show that, during reduction from 0 to 20.1%, the content of magnesium ferrite in the solid solution decreases. The concentration of magnetite in it increases, reaching a maximum value of 70%.

The decrease in the parameter of the spinel phase in the region considered from 8.362±0.005 Å to 8.328±0.005 Å is caused by its enrichment in $MgAl_2O_4$, which has a considerably smaller parameter in comparison with $MgFe_2O_4$ and Fe_3O_4, whose parameters are close (3). The increase in the amount of the wüstite phase

occurs at the expense of both MgO and FeO, and the concentration of ferrous oxide increases, causing an increase in the lattice parameter of the wüstite solid solution. The equilibrium oxygen pressure is determined by the process

$$(MgFe_2O_4)_{sol} \rightleftarrows (Fe_3O_4)_{sol} + Mg_yFe_{1-y}O + O_2$$

and decreases in this interval by more than 10^2 times.

After 20.1% reduction, magnetite is reduced in the binary solution $(MgAl_2O_4)_c(Fe_3O_4)_{1-c}$, and at 33.3% the spinel phase is transformed into magnesium aluminate. This also explains the sharp decrease in the crystal-lattice parameter of the spinel from 8.328 ± 0.005 Å to 8.085 ± 0.005 Å.

A further increase in the amount of the wüstite phase is provided only by ferrous oxide (with the absolute amount of MgO remaining constant), which leads to a distinctive change in the lattice parameter (Fig. 3).

The decrease in the oxygen elasticity in this region is due to the equilibrium

$$(\mathrm{Fe_3O_4})_{\mathrm{sol}} \rightleftarrows 3(\mathrm{FeO})_{\mathrm{sol}} + \frac{1}{2}\mathrm{O_2}.$$

In the transition region adjoining 20% reduction, where the chemistry of the process changes (the reduction of magnesium ferrite ends and the reduction of magnetite begins), a corresponding change in the dissociation elasticity is also observed.

Institute of Metallurgy
Sverdlovsk

Received
7 VII 1964

REFERENCES

1. L. Vegard, Zs. Phys., **5**, 393 (1921).
2. L. Weil, E. Bertaut, L. Bochirol, J. phys. et radium, **11**, 5, 208 (1950).
3. A. A. Shershketkin, L. G. Khromykh et al., DAN, **152**, No. 1, 124 (1962).
4. O. A. Esin, P. V. Gald, *Physical Chemistry of Pyrometallurgical Processes*, Part 1, Sverdlovsk—Moscow, 1950, p. 23.
5. H. Shenk, W. Pfaff, Arch. Eisenhüttenwesen, **32**, 11, 741 (1961).
6. H. J. Goldschmidt, Nature, **157**, 478 (1946).
7. A. V. Shashkina, Ya. I. Gerasimov, ZhFKh, **27**, 3, 399 (1953).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.