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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Abstract

Full Text

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ON THE THERMAL STABILITY OF ScF_3 AND ITS INTERACTION WITH MgF_2

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Scandium fluoride may be used to obtain free scandium and its magnesium alloys by reduction with metallic magnesium. However, the literature data on the physicochemical properties of ScF_3 are very limited. It is known only that this compound is a stable crystalline substance with a melting point $> 1000°$ ([1]). It crystallizes in a rhombohedral (pseudocubic) lattice with parameters $a = 4.022 \pm 0.004$ Å and $d(\text{Sc—F}) = 2.01$ Å ([2]).

Fig. 1. Dependence of the change in weight of scandium fluoride: **a**—on temperature, **b**—on time at temperatures 700° (*1*), 800° (*2*), 900° (*3*)

Fig. 2. Debye patterns (Co anode): **a**—Sc_2O_3; **b**—partially hydrolyzed ScF_3; **c**—ScF_3; **d**—alloy with 64.01% ScF_3; **e**—alloy with 10.6% ScF_3; **f**—MgF_2

We have determined the melting point of ScF_3 and have studied its thermal stability and its interaction with magnesium fluoride in the molten state. The work used scandium fluoride obtained from spectrally pure scandium oxide by treatment with a 40% solution of hydrofluoric acid of "chemically pure for analysis" grade. The precipitate of scandium fluoride was washed with water and absolute alcohol and dried for 4 hours at a temperature of 450°. Chemical analysis of the preparation showed that its composition corresponded exactly to the formula ScF_3. Magnesium fluoride was obtained by reacting magnesium carbonate of "chemically pure"grade likewise with a 40% solution of hydrofluoric acid. The investigation of the thermal stability of scandium fluoride was carried out using continuous-weighing balances in the interval 20–1000°. The heating rate averaged 5 deg/min. The weighed sample of the preparation under study was ~0.2 g.

Figure 1a gives a typical curve of the change in weight of ScF_3 with temperature. The slight decrease in the weight of the preparation upon heating in air-

···in air is already observed at about 400°; above 650° a sharp change in weight occurs, ending at 950°. Samples of scandium fluoride whose weight had decreased, respectively, by 5, 10, 20, 25, and 32.3% were subjected to X-ray phase

Fig. 3. Heating and cooling curves: a –ScF_3; b –alloy with 64.01% ScF_3; c –alloy with 9.57% ScF_3; d –MgF_2

Figure 2: Fig. 3. Heating and cooling curves: a –ScF_3; b –alloy with 64.01% ScF_3; c –alloy with 9.57% ScF_3; d –MgF_2

Fig. 4. Phase diagram of the ScF_3–MgF_2 system

Figure 3: Fig. 4. Phase diagram of the ScF_3–MgF_2 system

analysis. In the debyegrams obtained, lines were found corresponding only to scandium fluoride and oxide. The formation of oxyfluorides, as might have been expected by analogy with the rare-earth elements (^{3}), is not observed in this case: as a result of hydrolysis, scandium fluoride is converted directly into the oxide. The intermediate products are mixtures of scandium oxide and fluoride (Fig. 2). The rate of the process of transformation of ScF_3 into Sc_2O_3 depends to a considerable extent on temperature. In Fig. 1b the isotherms of hydrolysis of scandium fluoride are given, from which it is seen that at 900°, for complete completion of the process, 2.5 h is sufficient; at 800°, 5.3 h; and at 700°, as much as 11 h is required.

Fig. 3. Heating and cooling curves: **a** –ScF_3; **b** –alloy with 64.01% ScF_3; **c** –alloy with 9.57% ScF_3; **d** –MgF_2

The melting temperature was determined by the method of thermal analysis from heating curves (Fig. 3a), recorded on a Kurnakov pyrometer. Carrying out the experiment was complicated by the slight thermal stability of ScF_3 in air at temperatures above 400°. Therefore the substance was placed in a platinum crucible, tightly closed with a lid that had an opening for the thermocouple. Temperature was measured with a platinum-platinum-rhodium thermocouple. The samples were melted in a vertical silite furnace at a heating rate of 105°/min, i.e., a temperature of 1600° was reached within 15 min.

As a result of the investigation carried out, it was established that scandium fluoride melts at a temperature of $1530 \pm 20°$ and undergoes a polymorphic transformation at $1350 \pm 20°$. Interactions in the ScF_3–MgF_2 system were studied by methods of thermal and X-ray phase analysis. Thermal analysis was carried out from cooling curves recorded on a Kurnakov pyrometer (Fig. 3). The mixtures of fluorides were placed in tightly closed platinum crucibles; heating was carried out in a silite furnace. The results of the investigation are presented in Table 1 and in Fig. 4.

Fig. 4. Phase diagram of the ScF_3–MgF_2 system

In the ScF_3–MgF_2 system, on the magnesium fluoride side there is a narrow region of solid solutions (not more than 5 mol.% ScF_3). The presence of the latter is confirmed by a lowering of the temperature of the polymorphic transformation of magnesium fluoride from 960° in MgF_2 to 840° in alloys containing more than 5 mol.% ScF_3. In addition, a decrease is observed in the lattice parameter of the solid phase based on MgF_2 with increasing concentration of ScF_3. For magnesium fluoride, the para-

parameters a and c, respectively, are 4.613 ± 0.005 kX and 3.081 ± 0.005 kX; an alloy with 3.6 mol.% ScF_3 has $a = 4.602 \pm 0.005$ kX and $c = 3.057 \pm 0.005$ kX. With a further increase in the concentration of scandium fluoride, saturation of the solid solution occurs and the lattice parameters remain constant; the parameters of the solid solution containing 10.6 mol.% ScF_3 are: $a = 4.595 \pm 0.005$ kX and $c = 3.041 \pm 0.005$ kX.

Scandium fluoride and the solid solution based on MgF_2 form a eutectic with one another. The composition of the eutectic point corresponds to 34 mol.% ScF_3, and the melting temperature of the eutectic mixture is 1095°.

No formation of intermediate phases is observed in the system, which is confirmed by the X-ray phase-analysis data. In Fig. 2 (b, c, d, e), for comparison, Debye diagrams are presented for magnesium fluoride, scandium fluoride, and fluoride alloys with 10.6 and 64.01 mol.% ScF_3. Both alloys consist of two components: scandium fluoride and a solid solution based on magnesium fluoride (the diffraction lines in the Debye diagrams shown for MgF_2—solid solution and pure MgF_2 practically coincide because of the small difference in the angle θ for the corresponding lines).

Table 1

Results of the investigation of the phase diagram of the ScF_3—MgF_2 system

No.	Content of ScF_3, mol.%	Liquidus temperature, °C	Eutectic temperature, °C	Temperature of polymorphic transformation: MgF_2	Temperature of polymorphic transformation: ScF_3
1	0	1255	–	960	–
2	4.72	1235	1085	840	–
3	9.57	1210	1090	840	–
4	20.37	1160	1100	840	–
5	26.00	1140	1100	840	–
6	33.70	1100	1095	840	–
7	39.42	1135	1100	840	–
8	48.60	1195	1095	840	–
9	58.76	1275	1095	–	–
10	64.01	1325	1100	–	–
11	70.03	1360	1095	–	–
12	74.33	1395	1095	–	–
13	80.02	1425	1095	–	1360

No.	Content of ScF_3, mol.%	Liquidus temperature, °C	Eutectic temperature, °C	Temperature of polymorphic transformation: MgF_2	Temperature of polymorphic transformation: ScF_3
14	84.14	1465	1100	–	1350
15	100.00	1530	–	–	1350

The polymorphic transformation of MgF_2, recorded by us at 960°, is traced in the alloys of the system up to 49 mol.% ScF_3, and its temperature decreases to 840°.

The polymorphism of scandium fluoride at 1350° appears throughout the entire concentration range and is marked by a slight bend in the liquidus curve.

Thus, the ScF_3–MgF_2 system belongs to type IV of phase diagrams according to Roozeboom.

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