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Abstract

Full Text

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PHASE RELATIONS IN THE SYSTEM SCANDIUM OXIDE–ALUMINUM OXIDE

The synthesis and phase studies of scandium silicates carried out in our work ([1,2]) showed that, by a number of characteristics, these compounds are analogues of the silicates of the rare-earth elements, the results of whose study have been published in a series of communications ([3–5]). Therefore the study of scandium aluminates also constituted an essential stage in further extensive work on the aluminates of the rare-earth elements, which represent a new and very little-studied class of chemical compounds stable at very high temperatures. Up to the present time no systematic studies have been carried out on the binary system scandium oxide–aluminum oxide. The literature contains only descriptions of individual syntheses carried out in this system. Thus, in 1925 the suggestion was made ([6]) of the existence of solid solutions of limited concentration between the components of the system. In 1961, in the system, within the range 63-42 mole % Sc_2O_3, the stability region of a crystalline phase of rhombohedral symmetry, called a solid solution, was established ([7]).

Fig. 1. Phase diagram of the Sc_2O_3–Al_2O_3 system

In our work a phase diagram of the entire system as a whole was constructed. For the synthesis, scandium oxide (99.5% Sc_2O_3) and chemically pure alumina (99.5% Al_2O_3) were used. Mixtures of the oxides in prescribed proportions were subjected to thorough grinding and mixing in an agate mortar; from them, samples were then formed in the form of small cylinders, which were fired in a silite furnace and then melted in a laboratory vacuum electric furnace of the F. Ya. Galakhov system. To determine the phase states in various regions of the system, the methods of annealing and quenching were used.

The specimens subjected to heat treatment at various temperatures were studied in polished sections with a metallographic microscope, in immersion preparations with an ordinary polarizing microscope, by X-ray diffractometry, and by infrared spectroscopy.

Fig. 3. X-ray diffraction patterns of samples of the Sc_2O_3-Al_2O_3 system, quenching temperature 1800°C. a –Sc_2O_3; –$Sc_2O_3 \cdot Al_2O_3$; –30 mol.% Sc_2O_3 and 70 mol.% Al_2O_3; –20 mol.% Sc_2O_3 and 80 mol.% Al_2O_3; –α-Al_2O_3

Figure 2: Fig. 3. X-ray diffraction patterns of samples of the Sc_2O_3-Al_2O_3 system, quenching temperature 1800°C. a –Sc_2O_3; –$Sc_2O_3 \cdot Al_2O_3$; –30 mol.% Sc_2O_3 and 70 mol.% Al_2O_3; –20 mol.% Sc_2O_3 and 80 mol.% Al_2O_3; –α-Al_2O_3

As a result of the investigation, the phase diagram shown in Fig. 1 was constructed. In the system, the existence of a binary compound of composition $Sc_2O_3 \cdot Al_2O_3$, or $ScAlO_3$, was found, as well as a region of formation of homogeneous crystals of variable composition occupying the central part of the phase diagram of the system. The boundaries of this region, which may be defined as the zone of primary separation of the variable-composition phase, vary with temperature as shown in Fig. 1. The invariant points of the Sc_2O_3–Al_2O_3 system are given in Table 1.

Fig. 3. X-ray diffraction patterns of samples of the Sc_2O_3–Al_2O_3 system, quenching temperature 1800°C.
a –Sc_2O_3; –$Sc_2O_3 \cdot Al_2O_3$; –30 mol.% Sc_2O_3 and 70 mol.% Al_2O_3; –20 mol.% Sc_2O_3 and 80 mol.% Al_2O_3; –α-Al_2O_3.

Scandium monoaluminate $ScAlO_3$ melts congruently at $1870^\circ \pm 20^\circ$. This compound is stable only within a limited temperature interval between 1870° and 1730°. Above the upper limit the crystals melt, and below 1730° decomposition into crystals of scandium oxide and crystals of the described phase of variable composition occurs. However, the monoaluminate in the metastable state can crystallize from supercooled melts at a lower temperature as well. In specimens corresponding in composition to the monoaluminate, obtained by solid-phase reactions at 1500°, only crystals of scandium oxide and of the phase of variable composition were found. Investigation of the homogeneity region, located in the central part of the phase diagram, showed that its limits decrease with increasing temperature from 34.5–18 mol.% Sc_2O_3 at 1650° to 31–22 mol.% Sc_2O_3 at 1790°. A photomicrograph of crystals of this phase is given in Fig. 2,c. (see insert, p. 1344). X-ray diffraction patterns obtained on the diffractometer of the Institute of Crystallography, USSR Academy of Sciences, are given in Fig. 3,c,d.

Consideration of the infrared spectra from the homogeneity region likewise indicates a regular shift of the absorption-spectrum bands; this is confirmed by the microscopic and X-ray diffraction data.

Investigation of microhardness also showed a rectilinear character of the change in microhardness of crystals of the phase of variable composition as a function of their composition. Special attention in our study was paid to the influence

of small additions of scandium and aluminum oxides to each of the components. Crystallo-optical and X-ray diffraction studies showed, however, that even with small additions of the second oxide (of the order of 1–3 mol.%) separation of a second phase is observed in the crystallization products, which contradicts the definitions of other authors ([7]). Apparently the point is that the crystallo-optical method used by us proves to be more sensitive in such cases. No formation of solid solutions based either on Sc_2O_3 or on α-Al_2O_3 was found in the system.

Fig. 4. Plot of the dependence of microhardness on the composition of crystals of the phase of variable composition in the system $Sc_2O_3 - Al_2O_3$

Table 1

Invariant points of $Sc_2O_3 - Al_2O_3$

Phases	Process	Composition, wt.% Sc_2O_3	Composition, wt.% Al_2O_3	Composition, mol.% Sc_2O_3	Composition, mol.% Al_2O_3	Temp., °C
Sc_2O_3 + S* + Al_2O_3	Eutectic	63.2	36.8	56	44	1820 ± 20
$Sc_2O_3 \cdot Al_2O_3$ + liquid	Congruent melting	57.5	42.5	50	50	1870 ± 20
Sc_2O_3 + S* + $Sc_2O_3 \cdot Al_2O_3$	Decomposition in the solid phase	57.5	42.5	50	50	1730 ± 20
$Sc_2O_3 \cdot Al_2O_3$ + S* + liquid	Eutectic	41.0	58.9	33.3	66.6	1790 ± 20
$Sc_2O_3 \cdot Al_2O_3$ + S* + liquid	Reaction	37.8	62.2	31	69	1790 ± 20
S + α-Al_2O_3 + liquid	Peritectic point	28.2	71.8	22.5	77.5	1850 ± 20
S + α-Al_2O_3 + liquid	Reaction	25.9	74.1	20.5	79.5	1850 ± 20

* S —region of formation of homogeneous crystals of variable composition.

In studying preparations from the scandium oxide—aluminum oxide system (Fig. 4), we encountered very great difficulties caused by the high rate of crystallization and the impossibility of obtaining the preparations in the form of glass, as well as by the considerable chemical resistance of the preparations with respect to a number of acids, alkalis, and salt solutions. This greatly hampered the possibility of revealing the structure by means of chemical etching. Therefore we used a special procedure, consisting in remelting a series of specimens with the addition of 5 mol.% silica in order to obtain a matrix which, after etching, would make it possible to reveal more clearly the phase relations in the samples under study. And indeed, the siliceous matrix obtained, as can be seen in Figs. 2b, c, made it possible to observe in clearer form the phase relations in the most critical part of the phase diagram of the system.

X-ray diffraction and infrared investigation showed that the principal phases crystallizing here are identical with those which we obtained in pure preparations of the scandium oxide–aluminum oxide system.

Comparison of the phase diagram obtained by us with that recently studied for the scandium oxide–gallium oxide system also constitutes indirect confirmation of our results, since the trivalent gallium ion is crystallochemically very close to the trivalent aluminum ion (8).

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