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**Abstract**

**Full Text**

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### **CHEMISTRY**

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## **PREPARATION AND SOME PROPERTIES OF METALLIC SCANDIUM**

Metallic scandium has already been obtained in small quantities by many investigators (<sup>1-9</sup>), but its properties have so far been little studied. The present work is devoted to obtaining metallic scandium from its anhydrous chloride (<sup>10</sup>) and to studying some of its properties.

The starting compound in the work was spectrally pure scandium oxide, obtained from technical oxide by methods of rhodanide extraction and precipitation of scandium oxalate (<sup>11</sup>). Anhydrous scandium chloride was obtained by chlorinating a mixture of scandium oxide with sugar charcoal in a weight ratio of 3 : 1. The chlorination process was carried out in a quartz tube at 1000°; the scandium chloride formed was sublimed, condensing on the colder parts of the apparatus. Freshly prepared ScCl<sub>3</sub> was reduced with metallic calcium at 900° in an atmosphere of pure argon. The reaction mixture, containing a small excess of calcium (~ 5 wt. %), was placed in a tantalum crucible. The reaction products obtained, which usually contained impurities of Ca, CaO, ScCl<sub>3</sub>, and also Si, were ground to a powder with particle size < 0.2 mm and treated successively with water to dissolve CaCl<sub>2</sub>, Ca, CaO, and ScCl<sub>3</sub>, with a 10% solution of caustic soda in order to remove silicon, then again with water, and finally with methyl alcohol and ether. In all cases the solvents were separated by decantation. The resulting powdered metallic scandium was dried in air (10-15 min), and then in vacuum (10<sup>-4</sup> mm Hg) until the volatile impurities were completely removed (~ 30 min).

Melting of metallic scandium was carried out under reduced argon pressure (200 mm Hg) in an arc furnace with a water-cooled copper hearth and a movable tungsten electrode (<sup>7,8</sup>). Beforehand, the metal was pressed into pellets under a pressure of 100 kg/cm<sup>2</sup> and heated at 500-600° in high vacuum (10<sup>-5</sup>-10<sup>-6</sup> mm Hg).

Molten metallic scandium is a lustrous silver-colored metal with a characteristic yellow tint.

Fig. 1. Kinetics of oxidation of metallic scandium in air at 20°

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According to analysis carried out by the hydrogen method, the product contains 97-97.5 wt. % metallic scandium. Meanwhile, the total scandium content, which was determined by gravimetric and volumetric methods, is 98-99 wt. %. In the gravimetric determination, the sample was converted into solution, from which scandium hydroxide was then precipitated; the gravimetric form was  $\text{Sc}_2\text{O}_3$ . The volumetric determination was carried out by titration of trivalent scandium with Trilon B using murexide<sup>(12)</sup>. Gravimetric and volumetric analyses gave well-agreeing results. In most metal samples, the presence of small amounts of silicon (0.1 wt. %) and calcium (< 0.001 wt. %) was detected spectrally. In the case when scandium oxide of purity > 99% was used as the starting compound, the metal obtained contained traces of Zr, Th, Y, Yb, and Fe (in total < 0.1 wt. %). Chlorine was determined nephelometrically by reaction with  $\text{AgNO}_3$ . In some samples the oxygen content was established. The results of analysis\* of the fused metallic scandium are as follows (in percent): metallic scandium 97-97.5; total scandium content calculated as the element 98-99; chlorine < 0.05; calcium < 0.001; silicon 0.1; oxygen < 0.9; sum of Zr, Th, Y, Yb, Fe < 0.1.

\* Average values of analyses of different batches of metal are given here.

For further purification, the molten metallic scandium was sublimed in a high vacuum ( $10^{-5}$ – $10^{-6}$  mm Hg) from a tantalum crucible onto a tantalum plate at 1500-1600°. Heating was carried out by means of a high-frequency unit with a tube generator. The content of metallic scandium in the sublimate was > 99%. For the obtained samples of metallic scandium, the crystal structure, certain mechanical properties, stability in air, and also the kinetics of dissolution in hydrochloric acid were studied.

Fig. 1. Kinetics of oxidation of metallic scandium in air at 20°

The study of the structure of metallic scandium is of interest because the existence of its cubic modification ( $a = 4.5$  kX)<sup>(6,13)</sup> has not been definitively established. The X-ray diffraction study was carried out on a sample of metal sublimed in vacuum. The X-ray photographs were taken on an electron tube with a copper anode. The results of the X-ray diffraction analysis are presented in Table 1\*. All 29 lines of the photograph are well indexed

Table 1

Results of the X-ray diffraction study of metallic scandium

Line No.	Intensity	$hkl$	$1/d^2, \text{ kX}^{-2}$			No.	Intensity	$hkl$	$1/d^2, \text{ kX}^{-2}$		
			found	cal- labeled*	$\left( \frac{1}{d_{\text{found}}^2} - \frac{1}{d_{\text{calc}}^2} \right)$				found	cal- labeled*	$\left( \frac{1}{d_{\text{found}}^2} - \frac{1}{d_{\text{calc}}^2} \right)$
1	4	100	0,1234	0,1223	+0,0011	16	2	114	0,9449	0,9462	-0,0013
2	2	002	0,1458	0,1448	+0,0010	17	2	212	1,001	1,001	0
3	5	101	0,1602	0,1585	+0,0017	18	1	105	1,027	1,027	0
4	4	102	0,2677	0,2671	+0,0006	19	1	204	1,070	1,068	+0,002
5	4	110	0,3690	0,3669	+0,0021	20	3	300	1,101	1,101	0
6	4	103	0,4488	0,4481	+0,0007	21	4	213	1,182	1,182	0
7	2	200	0,4898	0,4892	+0,0006	22	4	302	1,245	1,245	0
8	4	112	0,5129	0,5117	+0,0012	23	1	006	1,301	1,303	-0,002
9	4	201	0,5267	0,5254	+0,0013	24	2	205	1,393	1,394	-0,001
10	2	004	0,5810	0,5793	+0,0017	25	3	214	1,434	1,435	-0,001
11	2	202	0,6333	0,6340	-0,0007	26	3	220	1,467	1,467	0
12	2	104	0,7018	0,7016	+0,0002	27	2	310	1,590	1,590	0
13	3	203	0,8158	0,8150	+0,0008	28	3	222	1,611	1,612	-0,001
14	1	210	0,8555	0,8560	-0,0005	29	5	311	1,625	1,626	-0,001
15	5	211	0,8940	0,8922	+0,0018						

\*  $a = 3.302 \text{ kX}$ ,  $c = 5.255 \text{ kX}$ .

in a hexagonal lattice of the magnesium type with  $a = 3.302 \pm 0.005 \text{ kX}$  and  $c = 5.255 \pm 0.005 \text{ kX}$ ,  $c/a = 1.591$ ;  $Z = 2$ . The X-ray density is equal to  $2.992 \text{ g/cm}^3$ ; pycnometrically, a value of  $3.0 \text{ g/cm}^3$  was found. Comparing the obtained results with the literature data <sup>(8,9)</sup>, it may be concluded that scandium crystallizes only in the hexagonal lattice. The cubic phase observed by Meisel <sup>(13)</sup> and Achard <sup>(6)</sup> was probably due to significant contamination of the metal, most likely by scandium nitride ScN, which crystallizes in the cubic system with  $a = 4.44 \text{ kX}$  <sup>(14)</sup>.

\* The authors express their gratitude to Yu. P. Simanov for valuable advice in discussing the results of the X-ray analysis of metallic scandium.

To characterize the mechanical properties of metallic scandium, the microhardness and tensile strength were studied. The microhardness measurements were carried out on an instrument with a diamond pyramid. The microhardness of 97-97.5% metallic scandium is  $145 \pm 10 \text{ kg/mm}^2$ ; for a sample of purity  $> 99\%$ , this same value decreases to  $75 \pm 5 \text{ kg/mm}^2$ , i.e., almost by a factor of 2. The microhardness value obtained by us for metallic scandium of purity  $> 99\%$  agrees well with the literature data <sup>(15)</sup>.

To determine the tensile strength, specimens of definite shape with a working-part diameter of 2 mm were machined from fused metallic scandium. It should be noted that metallic scandium is readily machined on a lathe. The tensile

Figure 2: Oxidation curve of metallic scandium upon heating in air

Figure 2: Figure 2: Oxidation curve of metallic scandium upon heating in air

Figure 3: Schematic of apparatus

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strength measurements were carried out on a tensile-testing machine at an average loading rate of  $3 \text{ kg/sec} \cdot \text{mm}^2$ . The tensile strength of 97-97.5% scandium is  $25\text{-}30 \text{ kg/mm}^2$ . With a higher content of nonmetallic impurities, the tensile strength of the metal is greatly reduced.

The stability of 97-97.5% metallic scandium in air was studied by two methods: isothermal at  $20^\circ$  and polythermal in the temperature range  $20\text{-}800^\circ$ . In the first case, oxidation of the metal was studied by the kinetic method on damping quartz balances with a sensitivity of  $1 \mu\text{g/division}^{(16)*}$ . The results of one of the experiments are presented in Fig. 1, from which it is seen that in 170 h the surface of the metal becomes covered with an oxide film of thickness  $\sim 600 \text{ \AA}$ , and the oxidation process of the metal practically ceases.

Fig. 2. Oxidation of metallic scandium upon heating in air (average heating rate  $3^\circ$  per minute)

Oxidation of 97-97.5% scandium upon heating in air was studied on continuous-weighing balances. The metal, in the form of powder ( $< 0.2 \text{ mm}$ ), was placed in a quartz cup, which was suspended from the balance on a platinum wire. The weight of the sample during heating was measured with an accuracy of  $\pm 0.5 \text{ mg}$ . A typical curve of the change in weight of the metal as a function of temperature is presented in Fig. 2 (average heating rate  $3^\circ/\text{min}$ ). Noticeable oxidation of metallic scandium in air begins at  $250^\circ$ . Starting from this temperature, the weight-change curve rises sharply upward. In the range  $20\text{-}200^\circ$ , however, the metal practically does not oxidize. Thus, holding powdered metallic scandium in air at  $200^\circ$  for 20 h does not lead to a change in the weight of the sample.

Fig. 3. Diagram of the apparatus for studying the interaction of metallic scandium with aqueous HCl solutions: 1 —reaction flask; 2 —glass thermostat; 3 —“spoon” with ground joint; 4 —magnetic stirrer; 5 —burette; 6 —stopcock for connecting the flask with the atmosphere; 7 —contact thermometer; 8 —funnel for bringing the pressure in the apparatus to atmospheric; 9 —heater; 10 —stirrer; 11 —thermometer

The kinetics of the interaction of metallic scandium with aqueous HCl solutions was studied at  $25 \pm 0.1^\circ$  on the apparatus whose diagram is shown in

\* The measurements were carried out at the Institute of Physical Chemistry, Academy of Sciences of the USSR, with the participation of V. A. Arslambekov.

Fig. 3\*. The specimens used were plates of molten metal with an apparent

Fig. 4

Figure 4: Fig. 4

surface area of 3–4 cm<sup>2</sup> and a weight of 0.3–0.5 g. The rate of dissolution of the metal was recorded from the amount of hydrogen evolved; the total amount of scandium dissolved over the entire duration of the experiment was also confirmed by the loss in weight of the specimen. Both determinations gave similar results. The data obtained in several experiments are presented in Fig. 4.

Fig. 4. Kinetics of the interaction of metallic scandium with aqueous HCl solutions of various concentrations:

- 1 –0.001 N,  $K < 5 \cdot 10^{-5}$  mg/cm<sup>2</sup> · min;
- 2 –0.005 N,  $K = 0.001$ ;
- 3 –0.01 N,  $K = 0.007$ ;
- 4 –0.02 N,  $K = 0.015$ ;
- 5 –0.05 N,  $K = 0.03$ ;
- 6 –0.1 N,  $K = 0.1$

For each HCl concentration, the dissolution-rate constant  $K$  (mg/cm<sup>2</sup> · min) was calculated graphically. The interaction of metallic scandium with aqueous HCl solutions proceeds rather rapidly at acid concentrations of 0.05–0.1 N and higher. As the HCl concentration is lowered, the rate of dissolution of the metal decreases sharply, and in 0.001 N HCl the dissolution constant of the metal is extremely small ( $< 5 \cdot 10^{-5}$  mg/cm<sup>2</sup> · min). Therefore it may be considered that dissolution of metallic scandium in 0.001 N HCl (pH 3), and still more so in water, practically does not occur.

The relatively high melting point of metallic scandium, 1539°<sup>(9)</sup>, its low specific gravity, considerable mechanical strength, and, under certain conditions, low chemical activity are very valuable properties that make it a promising material for a number of fields of modern technology.

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\* The study was carried out with the participation of V. A. Stepanov.

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

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