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Investigation of High-Purity Metallic Scandium

Until now researchers have had at their disposal extremely limited quantities of high-purity metallic scandium. This is connected with the exceptional difficulty of the process of obtaining it ([1–12]), which is due to the combination in this metal of a high melting point (1539°), a low specific gravity (3.0), low vapor pressure up to 1500°, and high chemical activity. To obtain metallic scandium, calcium-thermal reduction of ScF_3 or anhydrous $ScCl_3$ is usually used in an atmosphere of argon or helium at a temperature of 850—900°. After separation of the slag by one method or another and melting of the metal in an arc furnace, an ingot of scandium is obtained that contains a significant quantity of impurities. Analysis of such a product is not given in works ([3–9]).

We have shown that, as a result of the reduction of anhydrous $ScCl_3$ with metallic calcium, after removal of the slag by washing with a series of solvents and melting of the metal in an arc furnace, the purity of the metallic scandium ingot is 97—97.5% ([12]). The main impurity in such metal is oxygen (up to 0.9% calculated as the element, or up to 2.6% calculated as Sc_2O_3). The only method of purification of metallic scandium described in the literature ([3–5,7–9]), and already used by us ([12]), is its sublimation in high vacuum (10^{-5}—10^{-6} mm Hg) at 1500—1650°. However, until now only work ([9]) has reported the preparation by this method of relatively significant quantities (10 g) of compact metallic scandium of purity $> 99\%$.

In the present work, metallic scandium of 99.5% purity was also obtained by the sublimation method. The process was carried out in an apparatus whose scheme is shown in Fig. 1. Evaporation of scandium was performed from a tantalum crucible (1) 30 mm in diameter, into which another tantalum crucible (2), of slightly smaller diameter, was tightly inserted. Tantalum crucible (3) served as a support for crucible (1) and at the same time as a radiation shield for the tungsten-rhenium thermocouple (VR 10/20). Heating was carried out by high-frequency currents.

Samples of molten scandium of purity 85 and 97—97.5% were subjected to sublimation. Dirtier samples required preliminary degassing in vacuum for several hours. The main mass of scandium (up to 70%) during sublimation condenses on the lower part of crucible (2), i.e., on the surface whose temperature is only 300—350° lower than the sublimation temperature. This leads to the result that,

owing to diffusion, the condensed scandium is substantially contaminated with tantalum. Therefore, when separating the sublimate from the tantalum substrate, it is necessary to file off the boundary layer contaminated with tantalum, 0.2—0.3 mm thick. The sublimed scandium obtained in this way is a compact silver-colored metal with a characteristic yellow tint. According to analysis carried out by the hydrogen method, it contains 99.5 wt.% metallic scandium. The oxygen content in the sublimate does not exceed 0.1%, and tantalum 0.05%. A total of 2 g of sublimed scandium was obtained; the yield was 95%.

In the course of sublimation, a considerable part of the scandium (up to 30%) evaporates through the opening in the bottom of crucible (2) and condenses on a water-cooled quartz bell jar. In this case, the scandium also condenses in the most

To the article by A. A. Men' kov, L. N. Komissarova, V. V. Karelin, Yu. A. Priselkova, An. N. Nesmeyanov, and Vikt. I. Spitsyn, p. 122

Fig. 2. Microstructure of fused metallic scandium of 97-97.5% purity. Photographed: **a** —in unpolarized light, **b** —in polarized light. 120×

Fig. 3. Microstructure of metallic scandium annealed in vacuum. Photographed: **a** —in unpolarized light, **b** —in polarized light. 120×

in the hot zone and can easily be separated from the quartz. Metallic scandium condensed on quartz is also a product of rather high purity (98.5% with respect to hydrogen). However, analysis showed that it contains 0.3% silicon and up to 0.3% oxygen. Apparently, a reaction reducing SiO_2 by scandium proceeds on the surface of the quartz. This is also confirmed by the fact that after a series of experiments the surface of the quartz becomes roughened.

It should be noted that the production of high-purity metallic scandium (>99%) by sublimation, especially in significant quantities, presents great experimental difficulties. Therefore the problem of isolating high-purity metal cannot yet be regarded as finally solved. The microstructures of cast metallic scandium of 97-97.5% purity, as well as of sublimed metal, are shown in Figs. 2 and 3 (insert to p. 112). The specimens were not annealed. Polishing was carried out using an aqueous suspension of chromium oxide. No etchant was used. In microphotographs of cast scandium the grain boundaries are clearly visible both in polarized and in nonpolarized light. Despite the fact that the metal contains up to 0.9% oxygen (up to 2.6% calculated as Sc_2O_3), no distinct separation of a second phase is observed. This indicates the probability of some solubility of scandium oxide in the metal. The grains of the sublimed metal appear only in polarized light, which indicates the high purity of the specimen. The effect of the purity of metallic scandium on its mechanical properties was noted in ([12]).

Previously we showed that oxidation of powdered metallic scandium in air begins at 250° ([12]). For comparison, a study was made of the interaction of powdered scandium with oxygen and nitrogen (Table 1). In an atmosphere of oxygen, noticeable oxidation of the metal begins already at 200°, and in moist oxygen the

Fig. 1. Diagram of an apparatus for subliming metallic scandium in a high vacuum. 1 —evaporator, 2 —crucible-condenser, 3 —radiation shield for the thermocouple, 4 —tungsten-rhenium thermocouple, 5 —optical window for pyrometry, 6 —water-cooled quartz jacket, 7 —inductor, 8 —tungsten rods, 9 —molybdenum support, 10 —ceramic tube, 11 —flange, 12 —rubber gasket, 13 —brass transition to the diffusion pump, 14 —device for fastening the ceramic tube, 15 —holes in the brass transition for introducing thermocouples.

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reaction proceeds much more rapidly than in dry oxygen. As a result of studying the stability of powdered metal in an atmosphere of purified nitrogen, it was found that the reaction of scandium with N_2 begins practically above 600° and proceeds at a considerable rate at 800°*. In 20 h at 800° the nitriding reaction of scandium proceeds to 65%. X-ray examination established the formation under these conditions of scandium nitride of composition ScN ([13]).

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The study of the kinetics of the interaction of scandium with solutions of HCl, H_2SO_4, HNO_3, and NaOH** was carried out in a special apparatus, which

* The study of the interaction of scandium with nitrogen was carried out in the thermodynamics laboratory of Moscow State University on the apparatus of R. D. Shapovalova and I. A. Vasil' eva.
** The study of the interaction of scandium with solutions of acids and caustic soda was carried out with the participation of V. A. Stepanov.

Table 1

Interaction of powdered metallic scandium with oxygen and nitrogen.
Metal purity 97–97.5%, grain size < 0.2 mm, sample weight ~ 0.1 g

T, °C	Experimental conditions	Exposure, h	Gain, %
200	Dry oxygen[1]	20	0.4
200	Moist oxygen[2]	20	1.0
250	Dry oxygen	20	2.0
250	Moist oxygen	20	2.5
300	Dry oxygen	20	2.5
300	Moist oxygen	20	3.7
700	Dry nitrogen[3]	10	1.4
800	Dry nitrogen	10	20

[1] Oxygen was dried with concentrated sulfuric acid.
[2] The water-vapor pressure was 15.5–18.0 mm Hg.
[3] Nitrogen was dried with phosphorus pentoxide.

described in detail in (12). The volume of the solution was 1500 ml, whereas the loss in weight of the metal plate during the experiment did not exceed 10 mg. Therefore it may be assumed that the concentration of the initial solution is constant, and the dissolution of scandium proceeds as if in an infinite volume. Taking also into account that during the experiment the corroding surface of the metal practically does not change, the interaction of metallic scandium with acid and sodium hydroxide solutions under our conditions can be regarded as a zero-order reaction; therefore the reaction rate is independent of time and is equal to $V = KSN$, where V is the rate of dissolution of scandium, mg/min; S is the area of the corroding surface of the sample, cm^2; N is the normality of the acid, g-eq/l; K is the dissolution-rate constant at the given temperature, mg $\cdot$ l/cm^2 $\cdot$ min $\cdot$ g-eq. In the work, fused and sublimed metallic scandium was used, with purities of 97–97.5% and 99.5%. The results of the study are presented in Table 2 and in Fig. 4. As was established from the example of the interaction of high-purity scandium with 0.01 and 0.1 N H_2SO_4 solutions, the purity of the metal has no noticeable effect on the dissolution rate. The values of K for HCl and H_2SO_4 practically coincide. Using the values of the rate constants for three temperatures (25, 50, and 100°) and applying the known equation

$$\ln K = -\frac{\Delta E}{RT} + C,$$

we calculated the activation energy of the process, ΔE, which proved to be 9.0 ± 0.2 kcal/g-eq. The temperature coefficient of the reaction rate,

$$\gamma = \frac{K_{t^\circ+10}}{K_t},$$

is 1.5.

Fig. 4. Kinetics of the interaction of metallic scandium with aqueous H_2SO_4 solutions of various concentrations.
1 –0.1 N; $t = 25°$, $K = 0.70$;
2 –0.05 N; $t = 25°$, $K = 0.80$;
3 –0.02 N; $t = 25°$, $K = 0.75$;
4 –0.01 N; $t = 25°$, $K = 0.75$;
5 –0.05 N; $t = 50°$, $K = 2.6$;
6 –0.02 N; $t = 50°$, $K = 2.5$;
7 –0.01 N; $t = 50°$, $K = 2.5$.

When scandium interacts with nitric-acid solutions, the reaction proceeds with the formation of NH_4NO_3, while no gaseous products are evolved. The rate of dissolution of scandium at 25° in hydrochloric and sulfuric acids ($K = 0.75$) is 50 times greater than its rate of dissolution in nitric acid ($K = 0.015$).

Metallic scandium practically does not interact with sodium hydroxide solutions of concentrations up to 10% (2.8 N). In more concentrated sol–

Table 2

Kinetics of the interaction of metallic scandium with aqueous acid solutions. The values of V/S are averages from 4-5 experiments

H_2SO_4 **solutions**

$t = 25°C$; 97.5% Sc								
a	b	c	a	b	c	a	b	c
0.1	0.07	0.70	0.1	0.075	0.75	0.05	0.13	2.6
0.05	0.04	0.80	0.01	0.0075	0.75	0.02	0.05	2.5
0.02	0.015	0.75			$K_{avg} = 0.75$	0.01	0.025	2.5
0.01	0.0075	0.75						$K_{avg} = 2.5$
		$K_{avg} = 0.75$						

(continued)

$t = 100°C$; 97.5% Sc								
H_2SO_4 solutions	H_2SO_4 solutions	H_2SO_4 solutions	HCl solutions	HCl solutions	HCl solutions	HNO_3 solutions	HNO_3 solutions	HNO_3 solutions
a	b	c	a	b	c	a	b	c
0.05	0.80	16.0	0.1	0.080	0.80	5.0	0.085	0.017

H_2SO_4 solutions	H_2SO_4 solutions	H_2SO_4 solutions	HCl solutions	HCl solutions	HCl solutions	HNO_3 solutions	HNO_3 solutions	HNO_3 solutions
0.02	0.34	17.0	0.05	0.035	0.70	1.0	0.013	0.013
0.01	0.15	15.0	0.02	0.015	0.75	0.1	0.0015	0.015
		$K_{\text{avg}} =$ 16.0	0.01	0.007	0.70			$K_{\text{avg}} =$ 0.015
					$K_{\text{avg}} =$ 0.75			

Note: a—acid normality, g-equiv/l; b—V/S, mg/cm^2 · min.; c—K, mg · l/cm^2 · min. · g-equiv.

In NaOH solutions the metal dissolves slowly. The values of $\frac{V}{S}$ at 25° for 20, 30, and 40% sodium hydroxide solutions are, respectively, 0.0005, 0.001, and 0.003 mg/cm^2 min.

It should be noted that, whereas the physical properties of scandium (hardness, ductility, tensile strength, electrical resistivity, etc.) vary strongly depending on the purity of the metal within the range from 97 to 99.5%, its chemical properties (oxidation, dissolution in acids and alkalis, etc.) depend on the purity of the specimen to a considerably lesser extent.

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REFERENCES

1. W. Fischer, K. Brünger, H. Grineisen, Zs. anorg. u. allgem. Chem., **231**, 54 (1937).
2. H. Bommer, E. Hohman, Zs. anorg. u. allgem. Chem., **248**, 357 (1941).
3. F. Petrů, B. Hájek, V. Procházka, Chem. listy, **50**, 15, 2025 (1956).
4. F. Petrů, V. Procházka, B. Hájek, Chem. listy, **51**, 4, 672 (1957).
5. V. K. Iya, J. Rech. Centre Nat. Rech. Sci., **35**, 91 (1956).
6. J. C. Achard, P. Caro, J. Lories, C. R., **243**, 493 (1956).
7. Chem. Age, **82**, 2106, 742 (1959).

8. F. H. Spedding, A. H. Daane, Progr. in Nucl. Energy, Sec. 5, Metallurgy and Fuels, Ch. 5, 412 (1956).

9. F. H. Spedding, A. H. Daane, G. Warkefield, D. H. Dennison, Trans. Metallurg. Soc. AIME, **218**, No. 4, 608 (1960).

10. A. A. Men' kov, L. N. Komissarova, Yu. P. Simanov, Vikt. I. Spitsyn, DAN, **128**, No. 1, 92 (1959).

11. Metal Ind., London, 1961, p. 461.

12. Vikt. I. Spitsyn, L. N. Komissarova, A. A. Men' kov, DAN, **139**, No. 4, 903 (1961).

13. K. Becker, F. Ebert, Zs. Phys., **31**, 268 (1925).

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