COMPLEX INVESTIGATION OF THE THERMAL AND ELECTROPHYSICAL PROPERTIES OF REFRACTORY OXIDES IN THE LIQUID AND SOLID PHASES*

É. É. Shpil'rain, D. N. Kagan, L. S. Barkhatov, L. I. Zhmakin, and V. V. Koroleva

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Results of an experimental investigation of the enthalpy and specific electrical conductivity of aluminum and scandium oxides in the 1570-3100°K range and also of the heats of fusion of these oxides are presented.

The thermophysical and electrophysical properties of aluminum and scandium oxides were investigated in specimens not less pure than 99.9%. Heating was performed in high-temperature resistance furnaces with tungsten heaters in a highly pure argon atmosphere or in a vacuum. The temperature was measured by optical pyrometers of ÉOP-66 type. The length-to-diameter ratio of the blackbody model was not less than 10 in all cases. A correction for optical system absorption was introduced by computation on the basis of a preliminary calibration.

According to IUPAC data [1], the recommended value of the melting point of Al_2O_3 is 2323 ± 4°K. On the basis of an analysis of the data in [2-6], we take the melting point of scandium oxide at 2762 ± 20°K.

The enthalpy of the aluminum and scandium oxides was measured by the mixing method by using a calorimeter with an evaporating fluid. The quantity of heat introduced by the ampule with the substance being investigated into the calorimeter was determined by the increase in the weight of the evaporating calorimetric fluid during the calorimetrization.

Six molybdenum and four tungsten ampules of 18-20-mm diameter and 60-65-mm height were used to investigate the aluminum oxide, and two tungsten ampules of analogous dimensions were used for the scandium oxides. All the ampules were sealed. Welding was performed by electron-beam apparatus in a high vacuum; hence, the substance being investigated was under the pressure of its own vapors.

Data on the enthalpy and integrated emissivity of molbydenum were taken from [7,8]. Jointly processed results [9] and data in good agreement [10,11] were used for the tungsten enthalpy. Information about the emissivity of tungsten was borrowed from [12].

The results of an experimental investigation of the enthalpy of aluminum oxide in the 2000-3100°K temperature range are presented in Table 1. They permit the determination of the heat of fusion of Al_2O_3, equal to 25.7 ± 1.2 kcal/mole for T_m = 2323 ± 4°K. Also present in Table 1 are data on the enthalpy of scandium oxide in the solid and liquid states. The heat of fusion of Sc_2O_3 turned out to equal 24 ± 2 kcal/mole for T_m = 2762 ± 20°K.

To reduce the enthalpy results to 298.15°K, a correction $H_{373.15} - H_{298.15}$ was introduced according to data on the low-temperature enthalpy of the aluminum [13] and scandium [14] oxides. The confidence interval for the maximal relative error in determining the enthalpy is 0.8-1.6%, and for the enthalpy of scandium oxide was 1.1-1.8%.

Data obtained on the enthalpy of solid phase Al_2O_3 agree well with the results in [15-18]. It should be noted that the data are somewhat exaggerated in a narrow premelting region in [18]. The reason for this phenomenon should be sought in the inadequate purity of

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TABLE 1. Enthalpy of Aluminum and Scandium Oxides

Aluminum oxides: $M_{Al_2O_3}=101.96$; $T_m=2323\pm 4°K$

T, °K	$H_T-H_{298.15}$ kcal/mole
Solid phase	
2068	52102
2142	55018
2152	55028
2200	56955
2218	57823
2223	57667
2301	60852
Liquid	
2323	86530
2331	87100
2339	87832
2356	89030
2370	90035
2379	90130
2382	90678
2384	91045
2393	91130
2414	91633
2460	93432
2489	94330
2500	96033
2715	104988
2808	109530
2831	111310
2994	118030
3100	123330

Scandium oxides: $M_{Sc_2O_3}=137.91$; $T_m=2762\pm 20°K$

T, °K	$H_T-H_{298.15}$, kcal/mole
Solid phase	
1570	38710
1590	39396
1774	46697
1972	50344
2137	56127
2332	61432
2346	62119
2368	62333
2409	65034
2480	66978
2484	68051
2585	73965
2608	76149
2628	76652
2699	80617
2748	84865
2759	86387
Liquid	
2773	113737
2791	112245
2793	108934
2820	115339
2842	112484
2867	119253
2886	116293
2930	118798

the oxide being investigated: under operating conditions with unsealed ampules, the use of a graphite heater afforded a possibility of graphitization of the aluminum oxide as well as the insertion of other contaminants. An indirect verification of this circumstance is the fact that the melting point quantity obtained in [18] for Al_2O_3 turned out to be below the corresponding results of other researchers. At temperatures above the melting point of the aluminum oxide, the object for comparison can only be papers [18,19] in a quite limited temperature range (to 2740°K [19]). Because of the reasons considered earlier, the results of [18] differ somewhat from the data of [19], which are in good agreement with those presented in Table 1, in its turn.

All the above also refers to the heat of fusion of Al_2O_3, which is 28 ± 0.55 [18] and 25.8 ± 1.3 kcal/mole [19].

We know of just two papers where the enthalpy of scandium oxide has been investigated [20,21] to 1610 and 1800°K, respectively. Our data are in good agreement with [20,21] in this temperature range. There is no information about the enthalpy of Sc_2O_3 above 1800°K in the literature.

The specific electrical conductivity of the aluminum and scandium oxides in the liquid and solid phases was measured by a contact method by using two-electrode coaxial cells. One of the electrodes of these cells was a cylindrical crucible and the other was a coaxially disposed small-diameter rod capable of being moved along the crucible axis. Tungsten cells with the following parameters were used to measure the Sc_2O_3 electrical conductivity: crucible inner diameter 20 mm, crucible height 60-65 mm, central electrode diameter 3 mm.

The electrical conductivity of the Al_2O_3 was determined in both tungsten and molybdenum cells, where the latter had different geometrical characteristics (30-mm crucible diameter, 1.2-mm central electrode), and were used only to 2600°K. The mass of the oxides in the cell crucibles was 40-90 g. All the measurements were performed by a resonance method using audio-frequency alternating current. The experimental data presented below for the electrical conductivity of Al_2O_3 and Sc_2O_3 were obtained at a 5-kHz resonance frequency; a change in resonance frequency between 1-10 kHz limits did not affect the results of experiments.

Data on the specific electrical conductivity of liquid Al_2O_3 and Sc_2O_3, obtained at

TABLE 2. Specific Electrical Conductivity of Aluminum and Scandium Oxides

Aluminum oxides		Scandium oxides	
T, °K	$\varkappa$, $\Omega^{-1}\cdot m^{-1}$	T, °K	$\varkappa$, $\Omega^{-1}\cdot m^{-1}$
Solid phase		Solid phase	
2059	$2{,}21\cdot10^{-2}$	2361	2,07
2102	$3{,}99\cdot10^{-2}$	2449	2,65
2161	$7{,}07\cdot10^{-2}$	2518	4,11
2214	$8{,}45\cdot10^{-2}$	2583	6,05
2240	$1{,}32\cdot10^{-1}$	2615	10,70
2245	$1{,}48\cdot10^{-1}$	2678	12,70
2256	$1{,}37\cdot10^{-1}$	2751	18,60
2268	$1{,}33\cdot10^{-1}$		
Liquid		Liquid	
2342	269	2782	1670
2383	312	2826	1796
2408	336	2840	1815
2465	406	2854	1847
2512	477	2867	1818
2537	502	2895	1805
2554	560	2909	1924
2559	545	2932	1914
2579	603	2953	1942
2598	620	2982	1961
2681	742	3014	2020
2697	769	3056	2088
2747	861		
2835	1013		
2891	1075		
2935	1152		
2991	1251		
3008	1266		

temperatures to 3000 and 3100°K, respectively, are presented in Table 2. It should be noted that the growth in the electrical conductivity of the melts with temperature, as well as the noticeable polarization effect at the cell electrodes which was detected in dc measurements, indicate indirectly the primarily ionic nature of the conductivity of these oxides in the liquid phase.

The error in measuring the electrical conductivity of the Al_2O_3 and Sc_2O_3 melts is estimated at 4-6% for a 95% confidence.

A comparison of the experimental data on the electrical conductivity of fused Al_2O_3 obtained in this paper with those published earlier [22-26] exhibits a significant discrepancy between the data of different authors. The possible causes for this discrepancy are examined in [27]. The results of our paper are in good agreement just with the data of Fay [23] at 2400°K. There is no information about the specific electrical conductivity of a scandium oxide melt in the literature.

The specific electrical conductivity of aluminum and scandium oxides in the solid phase is measured from the melting point to 2000°K (Al_2O_3) and 2300°K (Sc_2O_3). To this end, the central electrode of the cell was dropped a definite depth into the oxide melt, and after its solidification the cell resistivity was measured as a function of the temperature. Corrections were introduced for the leakage of current through the gas phase and for diminution of the volume of oxide in the crucible during melt solidification at the melting point. The error in measurement was 15-20%.

The results of the present paper on the specific electrical conductivity of Al_2O_3 in the solid phase agree satisfactorily with the experimental data of other authors obtained on polycrystalline oxide specimens in a neutral medium and published in [28] and in [29]. However, it should be noted that the electrical conductivity of Al_2O_3 in these papers was investigated to temperatures not exceeding 2030°K [28] and 2100°K [29].

Comparing our data on the electrical conductivity of Sc_2O_3 with those available in the literature is difficult since they are obtained only to 1800°K [30,31]. The ratio between the electrical conductivities of the liquid and solid phases of the aluminum and scandium oxides at the melting points is $1.04 \cdot 10^3$ for Al_2O_3 and $0.90 \cdot 10^2$ for Sc_2O_3.

NOTATION

T_m, melting point of the oxide; H_T, enthalpy of the oxide at the temperature T, °K; M, molecular weight of the oxide; $\varkappa$, specific electrical conductivity.

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THERMOPHYSICAL PROPERTIES OF SCANDIUM–TITANIUM ALLOYS

Zh. M. Tomilo

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We present the results of measurements of the specific heat capacity of scandium–titanium alloys in the 4.2-12°K range and their electrical resistivity in the 4.2-300°K range.

Since the use of scandium as a structural material (melting point 1812°K, density 3 g/cm^3, chemical and corrosion stability) [1,2] is limited today (because of its high cost), we must investigate the properties of alloys of scandium with other metals. Thus, e.g., scandium–titanium alloys have higher strength and plasticity than metallic scandium at room temperature, and even at higher temperatures [2].

The literature supplies no information on the heat capacity of scandium–titanium alloys and only very limited information concerning their electrical resistivity [2].

In order to obtain scandium–titanium alloys, we used scandium containing 0.6% O, 0.06% H, 0.025% Cu, <0.004% Ca, 0.035% Fe, and 0.002% Mo (by mass), with an electrical resistivity at 300°K that was twice the electrical resistivity at 4.2°K. The titanium contained 0.006% Fe, 0.01% C, 0.0025% Ni, <0.01% Mg, <0.005% Mn, <0.01% Si, <0.02% Al, and <0.01% Cr by mass. The alloys were obtained by the method of electric-arc melting with a permanent electrode in an argon atmosphere.

The low-temperature heat capacity of Sc, Ti, and Sc–Ti alloys was measured in an adiabatic calorimeter by a step method [3,4]. The sensor used was a gold–copper thermocouple (the gold containing an added 0.035 at. % iron); the thermocouple was calibrated by means of the VNIIFTRI's germanium resistance thermometer. The mean deviation of the experimental points from the smoothed curve was ±4% over the entire range investigated (4.2-12°K), which did not exceed the error in the measurement of the heat capacity. The results of the heat-capacity measurements are shown in Table 1.

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