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VAPOR PRESSURE AND EVAPORATION RATE OF CERTAIN HEAT-RESISTANT COMPOUNDS IN A VACUUM AT HIGH TEMPERATURES

A. S. Bolgar, T. S. Verkhoglyadova, G. V. Samsonov

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16. Abstract

The vapor pressure and evaporation rate of borides of titanium, zirconium, and chrome, as well as of strontium and carbides of titanium, zirconium, and chrome, molybdenum silicide, and nitrides of titanium, niobium, and tantalum in a vacuum are studied. It is concluded that all subject compounds evaporate by molecular structures except AlB_{12}, which dissociates, losing the aluminum.

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The development of high-temperature technology requires /142* that we find materials which can be used in a vacuum at high temperatures, whose chemical composition does not significantly change under these conditions, and which have the lowest vapor pressures and evaporation rates.

The most promising materials of this type are heat-resistant compounds: borides, carbides, nitrides, and silicides of metals in the IV-VI groups in the periodic system (titanium, zirconium, hafnium, vanadium, tantalum, chrome, molybdenum, tungsten), as well as certain non-metallic heat-resistant compounds, such as carbides and nitrides of boron and silicon, and boron-silicon and boron-aluminum alloys. However, the behavior of these materials in a vacuum at high temperatures has not been adequately studied and this creates considerable problems in selecting them for practical uses.

Old data on this problem, obtained for nitrides of heat-resistant transient metals, is referenced in monographs [1, 2].

Little has been added to this data in recent years. Reference [3] determines rhenium silicide dissociation pressure by effusion method, reference [4] tantalum silicide dissociation. Data has been obtained on silicon[5] and boron[6] nitride dissociation pressure, as well as on the pressure of saturated vapors of boron itself[7]. The results of this research, presented in table 1, show that there is virtually no data on the most interesting and important classes of heat-resistant compounds -- carbides and borides, which have the highest melting points[8], chemical stability[9], and mechanical strength at high

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*Numbers in the margin indicate pagination of the original.

temperatures[10]. In particular, Campbell feels that borides of transient metals should be considered the most promising materials for use as refractories in a vacuum at temperatures above 2500°.

This article reviews vapor pressure and evaporation rate of borides of titanium, zirconium, and chrome, as well as of strontium and carbides of titaniun, zirconium, and chrome; molybdenum silicide, and nitrides of titanium, niobium, and tantalum in a vacuum. Evaporation rate was calculated using Langmore's method[1], based on measuring the decrease in weight of the subject material over a unit of time from a unit of surface. Vapor pressure was calculated with the formula,

$$\rho,\ \text{mm Hg} = (17.14\omega/\alpha A\tau)(\sqrt{T/M})$$

where ω is the change in weight, g; α is the accommodation factor, about 1; A is the sample's surface, cm^2; τ - holding time, sec, at temperature T°, K; M is molecular weight taking into account that the molecular weights of the vapor and compound are equal, i.e. it is assumed that there is no dissociation. This data was then used to calculate evaporation heat.

The unit for calculating evaporation rate is designed on the basis of a retort-type laboratory vacuum furnace[11] and is depicted in figure 1. Heater 3, made of molybdenum or tungsten wire wound into a 25-mm-diameter coil, is fastened between two live, water-cooled contacts, 2 and 6. The heater is protected by two small double screens 4 and one large screen 1 made of molybdenum plate. The sample, in the form of a pressed pellet, is placed into a molybdenum cup 5, attached to a substrate at the bottom of live contact 6. This unit could be used for /143
experiments at temperatures from 1100 to 1900°. A vacuum was provided by a VH-461 initial vacuum pump and a V-15 mercury diffusion pump. Temperature was measured with an optical pyrometer, taking into account appropriate measuring errors.

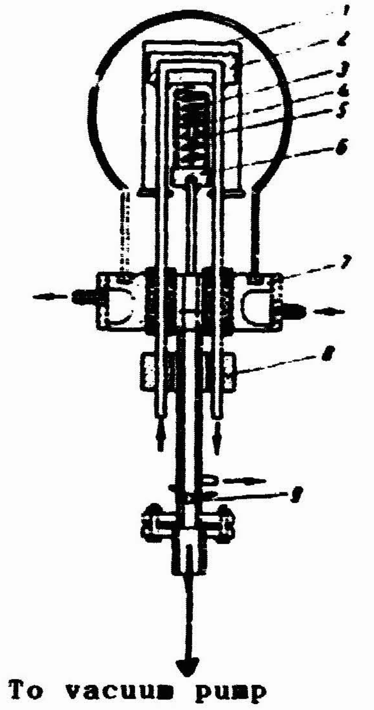

Figure 1. Unit for measuring evaporation rate of heat-resistant compounds:
1 - large screen; 2 - upper electrode; 3 - molybdenum coil; 4 - small screens; 5 - cup with sample; 6 - lower electrode;
7 - water-cooled plate;
8 - live contact; 9 trap cooled by liquid nitrogen.

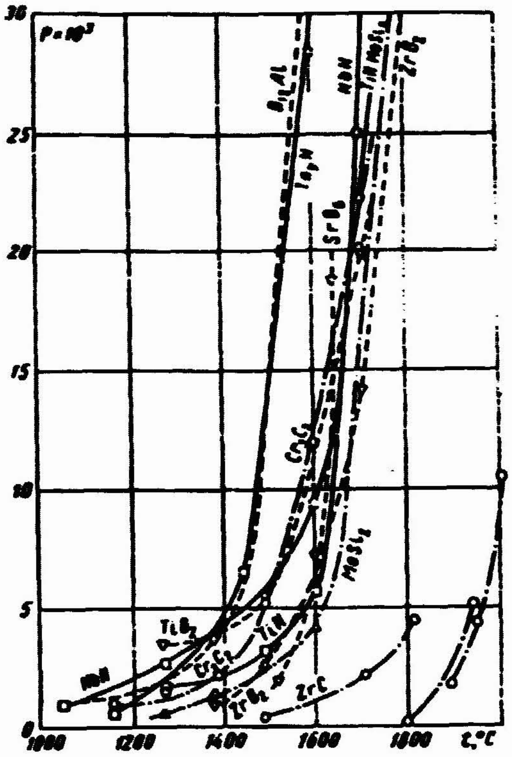

Figure 2. Vapor pressure of heat-resistant compounds as a function temperature (two outer curves represent NbC and HfC respectively.

The results are given in table 2 and shown in figure 2. Table 3 presents comparative data on the change in chemical composition of the samples before and after heating in a vacuum at 1700°.

It follows from this data (given the limited accuracy of chemical analysis) that none of the compounds except AlB_{12} undergoes dissociation at the temperatures studied, i.e. evaporation takes place in molecular structures. However, since mass-spectrometry did not reveal the existence of, for example, TiC in a gas phase[11], we can hypothesize that, during heating, dissociation takes place in a gas phase on the edge of the sample's surface. In other words, the samples' surfaces disintegrate with gradual detachment and elimination of molecular structures.

Data in table 2 for hafnium and niobium carbides, as well as for strontium hexaboride, was used to set up equations for vapor pressures:

$$\lg P_{HfC}(\text{mm Hg}) = 8.6 - (30\,555/T)(1900\text{-}2000^\circ C)$$
$$\lg P_{NbC}(\text{mm Hg}) = 10.6 - (36\,666\ /T)(1800\text{-}2000^\circ C)$$
$$\lg P_{SrB_6}(\text{mm Hg}) = 6.36 - (21\,428/T)(1500\text{-}2000^\circ C)$$

Table 1. Equations for Dissociation Pressure for Certain Heat-Resistant Compounds

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Compound	Dissociation Equation	Dissociation pressure equation, p, mm Hg	Source
Re_3Si	$Re_3Si_{(TB)} \underset{*}{=} 3Re_{(TB)} + Si_{r}$ **	$\lg p = 5.953 - \frac{24040}{T}$	[3]
$ReSi$	${}^{3}/_{2}ReSi_{(TB)} = {}^{1}/_{2}Re_3Si_{(TB)} + Si_{(r)}$	$\lg p = 7.444 - \frac{25800}{T}$	[3]
$ReSi_2$	$ReSi_{2(TB)} = ReSi_{(TB)} + Si_{(r)}$	$\lg p = 7.518 - \frac{25610}{T}$	[3]
$Ta_{4.5}Si$	$Ta_{4.5}Si_{(TB)} = 4.5Ta_{(TB)} + Si_{(r)}$	$\lg p = 9.5 - \frac{28600}{T}$	[4]
Ta_2Si	${}^{9}/_{5}Ta_2Si_{(TB)} = {}^{10}/_{3}TaSi_{(TB)} + Si_{(r)}$	$\lg p = 9.8 - \frac{28000}{T}$	[4]
$TaSi_{0.6}$	$10TaSi_{0.6(TB)} = 5Ta_2Si_{(TB)} + Si_{(r)}$	$\lg p = 9.1 - \frac{25000}{T}$	[4]
$TaSi_2$	${}^{5}/_{7}TaSi_{2(TB)} = {}^{5}/_{7}TaSi_{0.60(TB)} + Si_{(r)}$	$\lg p = 7.35 - \frac{25550}{T}$	[4]
Si_3N_4	$Si_3N_{4(TB)} = 3Si_{(TB)} + 2N_{2(r)}$	$\lg p = 8.54 - \frac{19250}{T}$	[5]
BN	$2BN_{(TB)} = 2B_{(TB)} + N_{2(r)}$	$\lg p = 4.0 - \frac{6450}{T}$	[6]
B ***	$B_{(TB)} = B_{(r)}$	$\lg p = 10.48 - \frac{22129}{T}$	[7]

* TB = Solid

** r = Gas

***Evaporation.

Table 2. Temperature Relationship between Vapor Pressures and Evaporation Rates of the Compounds Studied*

Compound	Temperature, °C										
	1100	1200	1300	1400	1500	1600	1700	1800	1900	1950	2000
TiC	—	0.832	—	5.869	—	6.172	7.078	7.680	31.130	—	—
	—	0.741	—	5.625	—	6.270	7.399	8.290	32.100	—	—
ZrC	—	—	—	—	0.065	0.302	0.280	0.562	—	—	—
	—	—	—	—	0.046	0.217	0.211	0.435	—	—	—
HfC	—	—	—	—	—	—	—	—	0.317	0.795	1.764
	—	—	—	—	—	—	—	—	0.184	0.467	1.037
NbC	—	—	—	—	—	—	—	0.023	0.594	0.634	—
	—	—	—	—	—	—	—	0.023	0.415	0.502	—
Cr_3C_2	—	0.200	0.303	0.423	0.968	2.169	3.865	4.166	—	—	—
	—	0.100	0.151	0.217	0.517	1.197	2.195	2.468	—	—	
SrB_6	—	—	—	—	0.336	2.128	3.250	17.250	—	—	188.900
	—	—	—	—	0.197	1.266	1.980	10.790	—	—	125.900
TiB_2	—	—	0.427	1.080	0.63	1.330	2.185	2.165	—	—	—
	—	—	0.350	0.890	0.545	1.162	1.985	1.967	—	—	—
ZrB_2	—	—	—	0.150	1.248	1.030	1.969	3.843	—	—	—
	—	—	—	0.100	0.834	0.720	1.417	3.227	—	—	—
CrB_2	—	2.890	4.520	4.760	1.450	7.680	—	4.980	—	—	—
	—	1.710	3.560	3.820	1.200	6.640	—	4.620	—	—	—
AlB_{12}	0.194	0.607	—	0.690	—	4.680	—	48.300	—	—	—
	0.098	0.314	—	0.380	—	2.720	—	29.900	—	—	—
TiN	—	—	0.219	—	0.349	0.599	2.480	—	—	—	—
	—	—	0.186	—	0.319	0.565	2.230	—	—	—	—
NbN	0.153	—	0.418	—	0.223	1.310	3.410	9.020	—	—	—
	0.092	—	0.272	—	0.155	0.940	2.510	6.850	—	—	—
Ta_2N	—	0.189	—	1.800	—	4.926	—	11.390	—	—	—
	—	0.061	—	0.648	—	1.845	—	4.630	—	—	—
$MoSi_2$	—	—	0.136	0.270	0.470	0.740	3.590	5.310	—	—	—
	—	—	0.070	0.150	0.270	0.419	2.030	3.360	—	—	—

*The top line represents evaporation rate, $v \cdot 10^7$, $g/cm^3 \cdot sec$; the bottom line -- vapor pressure, $p \cdot 10^5$ mm Hg.

These equations can be used to extrapolate approximated /145 boiling points of 5400, 4500, and 5100°C for HfC, NbC, and SrB_6 respectively. The boiling point of NbC correlates satisfactorily with published data[12].

Table 3. Change in Chemical Composition of Samples of Heat-Resistant Compounds after Heating in a Vacuum at 1700°

Compound	Metal/Non-metal Ratio		
	Before Experiment (A)	After Experiment (B)	B/A
TiC	4.06	4.12	1.010
ZrC	7.63	7.62	0.999
HfC	15.92	16.42	1.030
NbC	7.69	7.97	1.030
Cr_3C_2	6.50	6.44	0.995
TiB_2	2.21	2.09	0.995
ZrB_2	4.21	4.21	1.000
CrB_2	2.40	2.59	1.080
AlB_{12}	4.55	0.176	0.039
TiN	3.42	3.36	0.990
$MoSi_2$	1.72	1.79	1.030

Table 4 presents the heats of evaporation of the subject heat-resistant compounds.

Table 4. Heats of evaporation p of the heat-resistant Compounds Studied

Compound	ρ, Kcal/mole	Compound	ρ, Kcal/mole
TiC	38.08	ZrB_2	56.4
ZrC	52.20	CrB_2	41.2
HfC	139.64	AlB_{12}	45.7
NbC	167.00	TiN	62.3
Cr_3C_2	44.00	NbN	91.5
SrB_6	97.90	Ta_2N	42.0
TiB_2	45.70	$MoSi_2$	57.1

Conclusions. 1. Evaporation rates and vapor pressures for several heat-resistant compounds: TiC, ZrC, HfC, NbC, Cr_3C_2, TiB_2, ZrB_2, CrB_2. SrB_6, AlB_{12}, TiN, NbN, Ta_2N, and $MoSi_2$, were calculated with Langmore's method and the evaporation heats of these compounds were determined.

2. It is shown that, at the temperatures studied, all subject compounds evaporate by molecular structures, except AlB_{12}, which dissociates, losing the aluminum.

Institute of Metalloceramics
and Special Alloys
Academy of Sciences UKSSR

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