
**PHASE EQUILIBRIA IN INORGANIC SYSTEMS:
THERMODYNAMICS AND MODELING**

High-Temperature Mass Spectrometric Study of the Vaporization of Oxycarbide MAX Phase Ceramics

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Abstract—The vaporization of the carbide materials with the chemical compositions Ti_2SiC , Ti_3SiC_2 , Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 containing MAX phases and of oxycarbide systems based on these materials with hafnia additives was examined by Knudsen effusion mass spectrometry at temperatures up to 2200 K. Atomic aluminum was identified as the major vapor species over the Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 samples at 1500 K. The silicon-containing samples were less volatile than the aluminum-containing carbide materials; they vaporized observably at temperatures above 1900 K to form Si, Si_2 , SiC_2 , and Si_2C vapor species. The addition of hafnia to the carbides under study led to the formation of oxygen-containing vapor species, particularly Al_2O and SiO , and to a decrease in total vapor pressure over the systems formed. The least volatile materials were samples of the Ti_2SiC – HfO_2 oxycarbide system, and among the aluminum-containing oxycarbide systems, samples of the Zr_2AlC – HfO_2 system containing up to 10 mol % hafnia and samples of the Ti_2AlC – HfO_2 system with a higher HfO_2 content.

Keywords: Knudsen effusion mass spectrometry, vaporization, carbide MAX phases, vapor pressure

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INTRODUCTION

The high-temperature behavior of carbon materials containing MAX phases and of the oxycarbide systems based on them with addition of hafnia has been studied. MAX phases are layered compounds with a hexagonal structure, having the general chemical formula $M_{n+1}AX_n$, where M is a *d* metal, A is a *p* element, X is carbon or nitrogen, and $n = 1, 2$ or 3 [1–3]. In this work, we chose to study vaporization of samples whose chemical composition corresponded to $M_{n+1}AX_n$ MAX phases with M = Ti or Zr, A = Si or Al, X = C, and $n = 1$ or 2 .

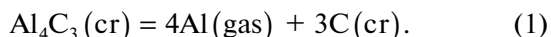
The MAX phases are known for their unique combination of physical and chemical properties, promising for materials design [1–3]. Carbide MAX phases, for example, retaining the advantages of transition-metal carbides, such as high thermal and electrical conductivity, refractoriness, high elastic stiffness, and low thermal expansion coefficients [2], are distinguished by enhanced damage tolerance and resistance to oxidation and corrosion [4–6]. Therefore, MAX phases can be used as high-temperature ceramics or additives to enhance the stability of highly refractory materials based on zirconium/hafnium borides in oxygen-containing environments at temperatures above 2273 K [5]. The electrochemical, thermal, and catalytic properties of MAX phases are notable, facilitating

the development of, respectively, ohmic contacts, heat exchangers, and oxidation and hydrogenation catalysts on their basis [3]. The MAX phases are precursors for other promising nanomaterials, namely MXenes [5, 6]. Due to their resistance to oxidation, corrosion, and ionizing radiation, MAX phases are of particular interest for use in the nuclear industry [3, 4], e.g., as materials for the cladding of fuel elements of nuclear reactors [7–9]. The carbide material based on the Zr_2AlC MAX phase and an oxycarbide system, containing zirconium oxide and Zr_2AlC , have shown high resistance in a prototype corium melt at temperatures up to 2773 K, thereby opening up wide opportunities for their application as elements of the core of nuclear reactors [10]. Additives of refractory oxides to carbon phases can further increase the refractory properties and oxidation resistance of the materials [11], which makes it relevant to study oxycarbide MAX phase systems.

As mentioned above, however, many MAX phase materials are prepared or perform at high temperatures, which can lead to selective vaporization of their most volatile components and, as a consequence, to an uncontrolled change in their physical and chemical properties. Thus, for the successful use of carbide MAX phases and oxycarbide MAX phase systems, it is necessary, as a first stage, to study their stability at high

temperatures in order to identify their temperature limits of thermal stability and the products that vaporize under heating.

There is information in the literature on an experimental study of the vaporization of pure carbides, summarized in Kazenas and Tsvetkov's monograph [12]. Pure aluminum carbide, when vaporized from graphite effusion cells, transfers into vapor in the form of atomic aluminum while the condensed phase becomes enriched in carbon [13]:



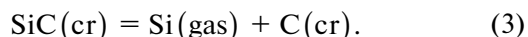
Hereafter, the physical state of the substance in chemical equations is indicated in parentheses: "(cr)" stands for a solid, and "(gas)" for a gas.

The vapor pressure of atomic aluminum over the $\text{Al}_4\text{C}_3 + \text{C}$ system in the temperature range 1321–1607 K is described by the equation

$$\log p(\text{Al}) [\text{Pa}] = -\frac{18000}{T} + 11.74, \quad (2)$$

where $p(i)$ is the partial pressure of the i th vapor species and T is absolute temperature.

According to Drowart et al. [14], the vapor over pure silicon carbide when it is vaporized from a graphite effusion cell consists of atomic silicon Si, its dimer Si_2 , and silicon carbides SiC_2 and Si_2C :



The temperature-dependent partial vapor pressures for Si, Si_2 , SiC_2 , and Si_2C vapor species over silicon carbide in the range 2149–2316 K are described by the following equations, respectively:

$$\log p(\text{Si}) [\text{Pa}] = -\frac{29339 \pm 157}{T} + (13.98 \pm 0.07), \quad (4)$$

$$\log p(\text{Si}_2) [\text{Pa}] = -\frac{37783 \pm 1667}{T} + (15.16 \pm 0.75), \quad (5)$$

$$\log p(\text{SiC}_2) [\text{Pa}] = -\frac{35561 \pm 2063}{T} + (15.84 \pm 0.93), \quad (6)$$

$$\log p(\text{Si}_2\text{C}) [\text{Pa}] = -\frac{35395 \pm 1641}{T} + (15.64 \pm 0.74). \quad (7)$$

In the Ti–C system, a TiC_x solid solution was identified, referred to as the δ phase. The highest amount of carbon in the δ phase TiC_x depends on temperature and does not exceed 49.2 mol %. At a higher carbon content, $\delta\text{-TiC}_x + \text{C}$ two-phase equilibrium occurs over a wide temperature range: 300–2800 K [15]. TiC_x vaporizes incongruently [16, 17] with selective transfer of titanium into vapor as atomic titanium. In addition, the vapor over the TiC_x vaporized from tungsten or tantalum Knudsen cells features the following species

(in the decreasing order of partial pressures): C_3 , C, C_2 , TiC_2 , C_5 , C_4 , and TiC_4 [16, 18]. The temperature-dependent partial pressure of atomic titanium over the $\text{TiC}_x\text{-C}$ system in the range 2518–2790 K is described by the following equation [18]:

$$\log p(\text{Ti}) [\text{Pa}] = -\frac{28950}{T} + (11.28 \pm 0.74). \quad (8)$$

However, information on the vaporization of carbide MAX phases and oxycarbide MAX phase systems has not been found in the literature. Therefore, the purpose of this work was a mass-spectrometric study of the vaporization of carbide materials of chemical composition Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , Zr_3AlC_2 , Ti_2SiC , and Ti_3SiC_2 containing MAX phases, and (for the first time) of oxycarbide systems based on the specified samples with additives of hafnia, which is one of the most thermally stable oxides. We should mention the following. Firstly, the Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , Zr_3AlC_2 , Ti_2SiC , and Ti_3SiC_2 formulae are used here to denote the desired chemical compositions of samples, without taking into account the actual phase composition of the material. For example, the notation " Ti_2SiC " indicates that the amounts of reagents during the synthesis of the sample were selected in such a way as to ensure the ratio of mole fractions of elements as Ti : Si : C = 2 : 1 : 1, but it does not imply that the synthesis would yield a pure MAX phase Ti_2SiC , which is not thermodynamically stable and has not yet been synthesized [19, 20]. The identified phase compositions of samples will appear below in the section "Experimental." Secondly, aluminum carbide is the most volatile of the pure carbides discussed above. Therefore, those who study the high-temperature behavior of aluminum-containing carbide and oxycarbide systems should expect selective vaporization of aluminum to occur at temperatures below 1600 K.

EXPERIMENTAL

A total of six samples of carbide materials (with the chemical compositions of Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , Zr_3AlC_2 , Ti_2SiC , and Ti_3SiC_2) and 18 samples of oxycarbide systems containing 10, 50, and 80 mol % HfO_2 were prepared (Table 1). The samples were synthesized using high-temperature sintering in a vacuum furnace and hot pressing from various precursor materials at various temperatures. The details of the syntheses of carbide materials containing MAX phases and oxycarbide systems based on them are described elsewhere [21–26]. The highest synthesis temperatures were 1773 and 2073 K. The chemical and phase compositions of the synthesized samples were studied by energy-dispersive electron probe microanalysis and X-ray powder diffraction. The Crystallographica Search Match software and the JCPDS database were used to identify compounds in X-ray powder diffrac-

Table 1. Elemental compositions of carbide and oxycarbide materials containing MAX phases synthesized in this work, as obtained by energy-dispersive electron probe microanalysis

Sample No.	Desired chemical composition, mol %	As-analyzed contents of elements, at %						
		Ti	Si	C	Al	Zr	Hf	O
1	Ti ₂ SiC	42.6	21.8	35.6	—	—	—	—
2	Ti ₃ SiC ₂	50.5	11.8	37.7	—	—	—	—
3	Ti ₂ AlC	54.5	—	27.8	17.8	—	—	—
4	Ti ₃ AlC ₂	45.7	—	39.9	14.3	—	—	—
5	Zr ₂ AlC	—	—	66.2	11.9	21.9	—	—
6	Zr ₃ AlC ₂	—	—	39.5	28.4	32.1	—	—
7	90Ti ₂ SiC–10HfO ₂	35.6	18.1	23.5	—	—	2.1	20.7
8	50Ti ₂ SiC–50HfO ₂	24.7	11.7	19.1	—	—	14.5	30.0
9	20Ti ₂ SiC–80HfO ₂	17.0	—	16.4	—	—	30.8	36.8
10	90Ti ₃ SiC ₂ –10HfO ₂	36.2	11.2	36.5	—	—	1.2	14.9
11	50Ti ₃ SiC ₂ –50HfO ₂	31.1	7.6	27.9	—	—	10.5	22.8
12	20Ti ₃ SiC ₂ –80HfO ₂	19.1	—	20.3	—	—	26.1	34.5
13	90Ti ₂ AlC–10HfO ₂	31.4	—	14.0	13.6	—	2.4	38.6
14	50Ti ₂ AlC–50HfO ₂	23.1	—	18.0	12.6	—	13.8	32.5
15	20Ti ₂ AlC–80HfO ₂	14.3	—	12.2	8.8	—	25.6	39.2
16	90Ti ₃ AlC ₂ –10HfO ₂	39.7	—	20.8	13.6	—	1.6	24.3
17	50Ti ₃ AlC ₂ –50HfO ₂	25.7	—	36.3	8.1	—	10.0	19.9
18	20Ti ₃ AlC ₂ –80HfO ₂	17.0	—	14.0	7.4	—	24.4	37.2
19	90Zr ₂ AlC–10HfO ₂	—	—	45.6	10.8	20.5	2.7	20.4
20	50Zr ₂ AlC–50HfO ₂	—	—	20.4	10.5	22.2	14.6	32.2
21	20Zr ₂ AlC–80HfO ₂	—	—	20.7	6.6	12.4	25.4	34.9
22	90Zr ₃ AlC ₂ –10HfO ₂	—	—	14.4	16.4	16.2	11.0	42.0
23	50Zr ₃ AlC ₂ –50HfO ₂	—	—	25.5	15.8	14.3	1.9	42.5
24	20Zr ₃ AlC ₂ –80HfO ₂	—	—	20.6	9.9	10.1	23.3	36.0

tion patterns. The phase compositions were quantified in the Crystallographica Search Match software suite by the least squares analysis of the difference between the calculated (theoretical) and measured profiles and intensities of X-ray diffraction peaks. The results of phase analysis of samples synthesized at 1773 and 2073 K appear in Table 2. The increasing synthesis temperature brings about a change in phase composition of the product, in particular, a decrease in the content of MAX phases and the preferential formation of binary oxides and carbides, such as Al₂O₃, HfO₂, HfTi₂O, and SiC, TiC, ZrC, and HfC. Therefore, it was proposed to compare the vapor composition over the samples in the MAX phase–HfO₂ system synthesized at different temperatures, in order to identify the sensitivity of the vaporization process to the phase composition of the samples.

The investigation method used was Knudsen effusion mass spectrometry [27, 28] on an MS-1301 mass spectrometer. Samples were vaporized from graphite twin Knudsen cells. The diameters of the effusion orifices in both compartments of the effusion cell were 0.6 mm; the diameters of the vaporization surfaces were 6 mm. Thus, the design of the effusion cell ensured the conditions of dynamic equilibrium between the condensed phase and vapor inside each compartment of the cell. The effusion cells were placed in a metal casing made of sheet molybdenum, as electron bombardment was used to heat the cells. The other parameters of the equipment used did not differ from standard ones and were described previously [29, 30]. The effusion cell temperature was measured on an EOP-66 optical pyrometer. The molecular beam effusing from the Knudsen cell was ionized in an ion source by slow electrons with energy of 30 eV to

Table 2. Phase compositions of carbide and oxycarbide materials containing MAX phases synthesized in this work at maximum temperatures of 1773 and 2073 K, as obtained by X-ray powder diffraction

Sample No.	Desired chemical composition, mol %	$T = 1773 \text{ K}$		$T = 2073 \text{ K}$	
		phase	content, mol %	phase	content, mol %
1	Ti ₂ SiC	Ti ₃ SiC ₂	33.83	Ti ₃ SiC ₂	3.03
		TiC	66.17	TiC	96.97
2	Ti ₃ SiC ₂	Ti ₃ SiC ₂	29.40	Ti ₃ SiC ₂	1.55
		TiC	70.60	TiC	98.45
3	Ti ₂ AlC	Ti ₂ AlC	40.11	Ti ₂ AlC	4.86
		TiC	59.89	TiC	95.14
4	Ti ₃ AlC ₂	Ti ₃ AlC ₂	21.37	Ti ₃ AlC ₂	4.19
		TiC	78.63	TiC	95.81
5	Zr ₂ AlC	Zr ₂ AlC	18.52	Zr ₂ AlC	7.41
		ZrC	81.48	ZrC	92.59
6	Zr ₃ AlC ₂	Zr ₃ AlC ₂	12.90	Zr ₃ AlC ₂	4.06
		ZrC	87.10	ZrC	95.94
7	90Ti ₂ SiC–10HfO ₂	Ti ₃ SiC ₂	7.85	SiC TiC	10.78 89.22
		TiC	29.98		
		TiO _x	29.87		
		HfO ₂	21.53		
		HfSiO ₄	10.76		
8	50Ti ₂ SiC–50HfO ₂	Ti ₃ SiC ₂	7.60	SiC TiC HfTi ₂ O	10.81 70.65 18.54
		TiC	13.09		
		TiO _x	13.99		
		HfO ₂	65.33		
9	20Ti ₂ SiC–80HfO ₂	TiC	13.93	TiC HfTi ₂ O	9.28 90.72
		HfO ₂	86.07		
10	90Ti ₃ SiC ₂ –10HfO ₂	Ti ₃ SiC ₂	1.43	SiC TiC	10.45 89.55
		TiC	26.39		
		TiO _x	49.87		
		SiC	11.46		
		HfO ₂	10.84		
11	50Ti ₃ SiC ₂ –50HfO ₂	Ti ₃ SiC ₂	6.62	SiC TiC HfO ₂ HfO ₂ ^{cubic}	4.97 35.38 27.07 32.58
		TiC	10.92		
		TiO _x	26.43		
		HfO ₂	56.03		
12	20Ti ₃ SiC ₂ –80HfO ₂	TiC	10.88	TiC HfO ₂ HfO ₂ ^{cubic}	41.63 18.10 40.28
		TiO _x	18.32		
		HfO ₂	48.32		
		HfO ₂ ^{cubic}	22.49		
13	90Ti ₂ AlC–10HfO ₂	Ti ₂ AlC	19.64	TiC HfO ₂ Al ₂ O ₃	68.43 26.56 5.01
		TiC	39.30		
		TiO _x	13.86		
		HfO ₂	20.01		
		Al ₂ O ₃	7.18		

Table 2. (Contd.)

Sample No.	Desired chemical composition, mol %	$T = 1773 \text{ K}$		$T = 2073 \text{ K}$	
		phase	content, mol %	phase	content, mol %
14	50Ti ₂ AlC–50HfO ₂	Ti ₂ AlC	10.69	TiC	42.44
		TiC	8.50	HfO ₂	25.00
		TiO _x	23.24	HfO ₂ cubic	23.47
		HfO ₂	52.41	Al ₂ O ₃	9.09
		Al ₂ O ₃	5.16		
15	20Ti ₂ AlC–80HfO ₂	Ti ₂ AlC	2.19	TiC	10.74
		TiC	9.26	HfO ₂	45.17
		TiO _x	6.08	HfO ₂ cubic	38.11
		HfO ₂	76.99	Al ₂ O ₃	5.99
		Al ₂ O ₃	5.48		
16	90Ti ₃ AlC ₂ –10HfO ₂	Ti ₃ AlC ₂	6.29	TiC	58.01
		TiC	60.77	HfO ₂ cubic	15.51
		TiO _x	19.51	Al ₂ O ₃	26.48
		HfO ₂	7.79		
		Al ₂ O ₃	5.64		
17	50Ti ₃ AlC ₂ –50HfO ₂	Ti ₃ AlC ₂	6.38	TiC	35.67
		TiC	6.97	HfO ₂	30.34
		TiO _x	38.52	HfO ₂ cubic	28.22
		HfO ₂	42.85	Al ₂ O ₃	5.77
		Al ₂ O ₃	5.27		
18	20Ti ₃ AlC ₂ –80HfO ₂	Ti ₃ AlC ₂	1.77	TiC	32.90
		TiC	7.34	HfO ₂	51.13
		TiO _x	7.74	HfO ₂ cubic	9.87
		HfO ₂	80.95	Al ₂ O ₃	6.10
		Al ₂ O ₃	2.20		
19	90Zr ₂ AlC–10HfO ₂	Zr ₂ AlC	9.92	ZrC	75.69
		ZrC	66.25	HfC	24.31
		HfO ₂	12.27		
		Al ₂ O ₃	11.56		
20	50Zr ₂ AlC–50HfO ₂	Zr ₂ AlC	10.35	ZrC	76.11
		ZrC	6.91	HfC	7.68
		HfC	27.60	HfO ₂	5.91
		HfO ₂	21.92	HfO ₂ cubic	8.16
		HfO ₂ cubic	19.22	Al ₂ O ₃	2.15
		Al ₂ O ₃	14.00		
21	20Zr ₂ AlC–80HfO ₂	ZrC	6.20	ZrC	23.64
		HfC	13.58	HfC	15.44
		HfO ₂	57.86	HfO ₂	13.72
		HfO ₂ cubic	20.06	HfO ₂ cubic	35.11
		Al ₂ O ₃	2.31	Al ₂ O ₃	12.09
22	90Zr ₃ AlC ₂ –10HfO ₂	Zr ₃ AlC ₂	9.02	ZrC	79.74
		ZrC	33.30	HfC	20.26
		HfO ₂	42.01		
		Al ₂ O ₃	15.67		

Table 2. (Contd.)

Sample No.	Desired chemical composition, mol %	$T = 1773 \text{ K}$		$T = 2073 \text{ K}$	
		phase	content, mol %	phase	content, mol %
23	50Zr ₃ AlC ₂ –50HfO ₂	Zr ₃ AlC ₂	10.81	ZrC	54.13
		HfC	41.02	HfC	39.25
		HfO ₂	41.79	HfO ₂ ^{cubic}	4.23
		HfO ₂ ^{cubic}	2.10	Al ₂ O ₃	2.40
		Al ₂ O ₃	4.28		
24	20Zr ₃ AlC ₂ –80HfO ₂	ZrC	7.30	ZrC	11.23
		HfC	17.55	HfC	44.56
		HfO ₂	60.56	HfO ₂	28.03
		HfO ₂ ^{cubic}	11.24	HfO ₂ ^{cubic}	13.63
		Al ₂ O ₃	3.34	Al ₂ O ₃	2.55

obtain a mass spectrum of the vapor over the samples under study.

The partial pressures of vapor species over the samples were determined by the ion current comparison method [27, 28]:

$$p(i) = p(s) \frac{I(i^+)T(i)\sigma(s)\gamma(s^+)f(s^+)}{I(s^+)T(s)\sigma(i)\gamma(i^+)f(i^+)}, \quad (9)$$

where the i and s indices refer to the sample under study and the pressure standard, respectively; $\sigma(i)$ is the ionization cross section of the i th vapor species; $\gamma(i^+)$ is the conversion factor of the secondary electron multiplier; and $f(i^+)$ is the isotopic abundance of the i^+ th ion in the mass spectrum of the vapor obtained by ionization of the i th vapor species.

To study vaporization, the sample under study was placed in one compartment of the effusion cell, and the pressure standard was placed in the reference compartment of the cell. When carbide samples containing MAX phases were studied, pure aluminum carbide or silicon carbide, for which the temperature dependences of the partial pressures of vapor species had been previously determined, were used as pressure standards. For oxycarbide MAX phase–HfO₂ systems, the pressure standards used were respective carbide samples with the chemical compositions Ti₂AlC, Ti₃AlC₂, Zr₂AlC, Zr₃AlC₂, Ti₂SiC, and Ti₃SiC₂, the partial pressures of vapor species over which were determined in this work. It should be mentioned that when determining partial pressures of vapor species by the ion current comparison method, as a rule, gold is used as the pressure standard since the temperature dependence of the Au partial vapor pressure over gold was recommended by the International Union of Pure and Applied Chemistry [31]. However, gold is known to form thermally stable compounds with carbon [12]. Its activity decreases as a result, causing data distortion. It was for this reason that we chose pure carbides to be pressure standards. In addition, one should take

account of the fact that partial vapor pressures over the samples under study were determined during vaporization from graphite cells under the settings where reaction with carbon at high temperatures could occur, which could shift the composition of the condensed phase. For this reason, in order to gain correct Knudsen effusion mass spectrometry data, it was necessary to provide identical vaporization conditions for carbide phases under study and for pure carbides; in this work, we accomplished this by simultaneously vaporizing samples from different compartments of the same graphite effusion cell in one experiment. Alternate measurements of ion current intensities in the vapor mass spectra over the studied sample and over the pure carbide made it possible to identify quantitative differences in the nature of vaporization between carbide materials based on MAX phases and Al₄C₃ or SiC.

The atomic aluminum partial pressures over aluminum-containing carbide materials based on MAX phases were determined by modified Eq. (9):

$$p(\text{Al}) = p_s(\text{Al}) \frac{I(\text{Al}^+)}{I_s(\text{Al}^+)}, \quad (10)$$

where the Al partial vapor pressure over pure carbide Al₄C₃ ($p_s(\text{Al})$) was found by Eq. (2).

A relation similar to Eq. (10) was used to determine Si partial vapor pressures over silicon-containing samples. The partial pressures of Si₂, SiC₂, and Si₂C vapor species over the studied materials containing MAX phases were determined by the following relation:

$$p(i) = p_s(\text{Si}) \frac{I(i^+)T(i)\sigma_s(\text{Si})\gamma_s(\text{Si}^+)f_s(\text{Si}^+)}{I_s(\text{Si}^+)T_s(\text{Si})\sigma(i)\gamma(i^+)f(i^+)}, \quad (11)$$

where $i = \text{Si}_2, \text{SiC}_2, \text{or Si}_2\text{C}$; the conversion factor of the secondary electron multiplier $\gamma(i^+)$ is taken to be proportional to the molecular mass of the ion: $1/\sqrt{M(i^+)}$; the ionization cross sections for atoms were

taken from [32]; the Si_2 ionization cross section was calculated using the Mayer and Lynch relation [33]; and the ionization cross sections of SiC_2 and Si_2C molecules were found by the additivity rule [28].

RESULTS AND DISCUSSION

Vaporization of Carbide Materials Containing the MAX Phases

In the vapor mass spectra over aluminum carbide Al_4C_3 and over aluminum-containing carbide materials with the Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 chemical compositions, Al^+ ions with an appearance energy of 6.0 eV were identified starting at ca. 1500 K. Comparison to the ionization energy of atomic aluminum [34] showed that those ions appeared in the mass spectrum as a result of direct ionization of the Al vapor species. The Ti^+ and C_3^+ ions appeared in the vapor mass spectra over studied samples at far higher temperatures (1870 and 2300 K, respectively). This indicates that selective vaporization of atomic aluminum occurred when samples of aluminum-containing carbide materials were heated up to 1500 K in vacuum (under a residual gas pressure of about 10^{-3} Pa), and carbon, as well as titanium or zirconium, accumulated in the condensed phase.

Measurement of the ion current intensities in vapor mass spectra over the studied carbide materials containing the MAX phases served to determine the temperature-dependent partial pressures of atomic aluminum over samples 3–6 (Table 1) of the Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 compositions, respectively, in the temperature range 1500–1700 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{25038 \pm 505}{T} + 15.68 \pm 0.32, \quad (12)$$

$$\log p(\text{Al}) [\text{Pa}] = -\frac{26483 \pm 934}{T} + 17.09 \pm 0.59, \quad (13)$$

$$\log p(\text{Al}) [\text{Pa}] = -\frac{26120 \pm 14529}{T} + 15.83 \pm 0.90, \quad (14)$$

$$\log p(\text{Al}) [\text{Pa}] = -\frac{29234 \pm 857}{T} + 18.16 \pm 0.54. \quad (15)$$

The temperature-dependent partial vapor pressures over Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 carbide materials containing the MAX phases are presented in Fig. 1 and in Tables S1–S4 in the attachment. Ti_2AlC has the highest thermal stability in the Al_4C_3 , Ti_2AlC , and Ti_3AlC_2 series. The atomic aluminum partial vapor pressures over Al_4C_3 and Ti_3AlC_2 match each other within the determination error, but their ratio decreases as temperature rises. The Zr_3AlC_2 sample is less volatile than titanium-containing phases are, although above 1550 K, the Al partial vapor pressures over Ti_2AlC and Zr_3AlC_2 become undistinguish-

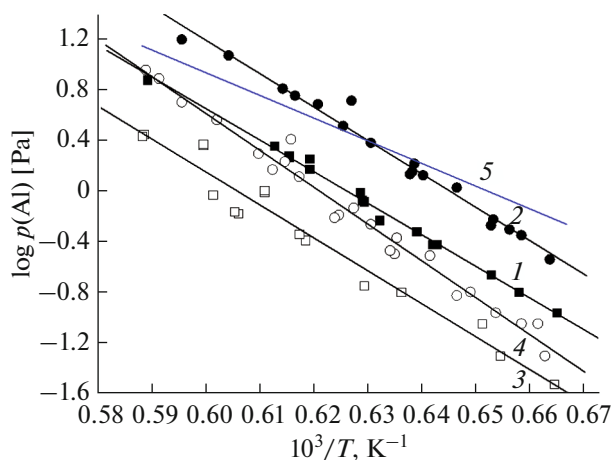


Fig. 1. Temperature-dependent Al partial vapor pressures over carbide materials with the chemical composition of (1) Ti_2AlC , (2) Ti_3AlC_2 , (3) Zr_2AlC and (4) Zr_3AlC_2 , as determined by Knudsen effusion mass spectrometry in this work, against the respective data for (5) Al_4C_3 according to Eq. (2) [13].

able within the experimental error. Zr_2AlC is the least volatile of the tested aluminum-containing carbides. Thus, the volatilities of the studied MAX phase-containing carbide materials with aluminum increase in the following order: $\text{Zr}_2\text{AlC} < \text{Zr}_3\text{AlC}_2 < \text{Ti}_2\text{AlC} < \text{Ti}_3\text{AlC}_2$.

In vapor mass spectra over the carbide samples of the SiC , Ti_2SiC , and Ti_3SiC_2 chemical compositions, the Si^+ , Si_2^+ , SiC_2^+ , and Si_2C^+ ions were identified starting at 1900 K. Some difficulties arose from the overlap of ions in the vapor mass spectrum over the studied samples with the signals from the ionization of residual gases of the vacuum system. A reliable quantitative measurement of Si^+ ion current intensity at a mass-to-charge ratio of 28 (for the most abundant silicon isotope) failed because of the high ion current intensities from nitrogen N_2^+ and carbon monoxide CO^+ . Therefore, measurements of Si^+ ion current intensities could only be carried out at a mass-to-charge ratio of 30, for a silicon isotope with a molecular mass of 30, the content of which is 3.12%. The SiC^+ ion with a molecular mass of 40 overlaps with a high Ar^+ background signal at the corresponding mass-to-charge ratio. Due to the low SiC content in the vapor over silicon carbide [14], it is not possible to measure the SiC^+ ion current at mass-to-charge ratios of 41 and 42. It should be mentioned here that the MS-1301 mass spectrometer has an electrical shutter and a mechanical shutter designed to separate the “useful” ionic current intensities associated with the studied sample from the background signal. However, they shut off not only the Si^+ and SiC^+ ion currents, but

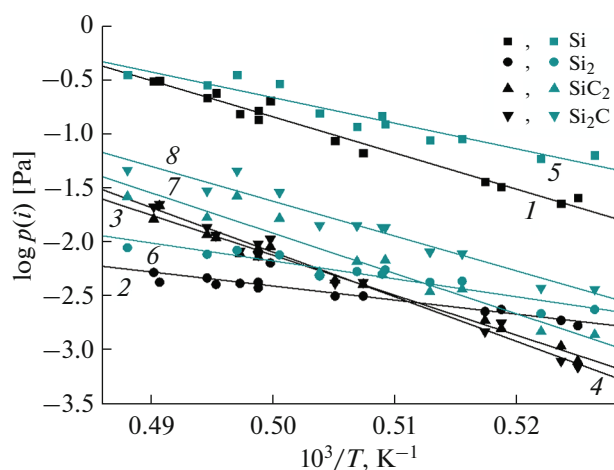


Fig. 2. Temperature-dependent partial vapor pressures of (1, 5) Si, (2, 6) Si₂, (3, 7) SiC₂, and (4, 8) Si₂C over samples **1** and **2** (Table 1) of composition (1–4) Ti₂SiC and (5–8) Ti₃SiC₂ according to Eqs. (16)–(23), determined by Knudsen effusion mass spectrometry in this work.

also part of the N₂⁺ + CO⁺ and Ar⁺ background signals, which interfered with the quantitative results.

The above-listed ions (Si⁺, Si₂⁺, SiC₂⁺, and Si₂C⁺) identified in vapor mass spectra over carbide samples with the SiC, Ti₂SiC, and Ti₃SiC₂ chemical compositions are all molecular ions [14]. The Ti⁺ and C₃⁺ ions were detected in vapor mass spectra over samples **1** and **2**, whose chemical compositions were Ti₂SiC and Ti₃SiC₂, respectively (Table 1), at 2330 K. The data obtained imply that above 1900 K the vapor over the studied silicon-containing carbide materials consists of a mixture of atomic silicon, Si₂, SiC₂, and Si₂C.

Using the ion current comparison method, measurements of temperature-dependent ion current intensities of the Si⁺, Si₂⁺, SiC₂⁺, and Si₂C⁺ ions enabled determination of the temperature dependences of the partial pressures of Si, Si₂, SiC₂, and Si₂C vapor species over sample **1** (Eqs. (16)–(19)) and sample **2** (Table 1; Eqs. (20)–(23)) in the range 1900–2050 K:

$$\log p(\text{Si}) [\text{Pa}] = -\frac{33677 \pm 1528}{T} + (16.01 \pm 0.77), \quad (16)$$

$$\log p(\text{Si}_2) [\text{Pa}] = -\frac{13095 \pm 1626}{T} + (4.14 \pm 0.82), \quad (17)$$

$$\log p(\text{SiC}_2) [\text{Pa}] = -\frac{37240 \pm 1297}{T} + (16.50 \pm 0.65), \quad (18)$$

$$\log p(\text{Si}_2\text{C}) [\text{Pa}] = -\frac{41500 \pm 1600}{T} + (18.66 \pm 0.81), \quad (19)$$

$$\log p(\text{Si}) [\text{Pa}] = -\frac{23852 \pm 2417}{T} + (11.27 \pm 1.23), \quad (20)$$

$$\log p(\text{Si}_2) [\text{Pa}] = -\frac{16688 \pm 1817}{T} + (6.17 \pm 0.92), \quad (21)$$

$$\log p(\text{SiC}_2) [\text{Pa}] = -\frac{37539 \pm 3536}{T} + (16.86 \pm 1.79), \quad (22)$$

$$\log p(\text{Si}_2\text{C}) [\text{Pa}] = -\frac{32428 \pm 2543}{T} + (14.60 \pm 1.30). \quad (23)$$

The thus-calculated partial pressures of vapor species over samples **1** and **2** (with the Ti₂SiC and Ti₃SiC₂ chemical compositions, respectively) are shown in Fig. 2 and in Tables S5 and S6; their values indicate that Ti₂SiC has the least total vapor pressure in the SiC, Ti₂SiC, and Ti₃SiC₂ series. Therefore, Ti₂SiC is the least volatile carbide material of those studied in this work.

Vaporization of Oxycarbide MAX Phase–HfO₂ Systems

When the vaporization of MAX phase–HfO₂ systems was studied, a sample of the oxycarbide system being studied was vaporized from one compartment of the twin effusion cell, and the corresponding carbide material containing the MAX phase was vaporized from the reference compartment, as mentioned in the Section “Experimental”.

Preliminary experiments showed that carbide materials containing MAX phases with aluminum are far more volatile than oxycarbide samples are. Therefore, it was impossible to conduct experiments by the differential mass spectrometric method where the cell compartments with the studied sample and pressure reference would be alternately moved onto the optical axis of the mass spectrometer without changing the temperature. On the one hand, at low temperatures (~1500 K), at which materials containing MAX phases with aluminum vaporize, the ion current intensities in vapor mass spectra over oxycarbide samples, as a rule, are at the sensitivity threshold of the mass spectrometer. On the other hand, there are two factors limiting the measurements for the sample and standard at high temperatures, at which the vapor mass spectra over oxycarbide systems are recorded reliably. Firstly, the atomic aluminum partial pressure over a carbide material containing the MAX phase under the specified conditions significantly exceeds the upper limit of pressure measurements by the Knudsen method (13 Pa). Secondly, at high temperatures, the selective vaporiza-

tion of aluminum from the carbide sample changes the composition of the condensed phase, which does not allow the experimentally obtained values to be attributed to the initial composition of the material. Therefore, in this work, we first measured the Al⁺ ion current intensity in the vapor mass spectrum over a carbide material containing the MAX phase at the temperature at which the oxycarbide sample vaporization was not observed. Then, the vaporizer with the effusion cell was moved to the position to measure the ion current intensities in the vapor mass spectrum over the MAX phase–HfO₂ system, and the cell temperature was increased in order to measure the temperature-dependent ion current intensities in the vapor mass spectrum over the studied oxycarbide sample. To determine the partial pressures of vapor species over the MAX phase–HfO₂ system, the Al⁺ ion current intensity in the vapor mass spectrum over the carbide sample was recalculated using Eqs. (12)–(15) to refer it to the temperature at which the Al⁺ intensity in vapor mass spectra over the oxycarbide sample was measured.

It should be especially noted that numerous ions generated by the ionization of highly volatile organic substances, CO, and CO₂ were identified in the vapor mass spectrum during the initial heating of the effusion cells with test samples. For this reason, the vacuum system of the mass spectrometer did not cope with pumping off residual gases to a high vacuum, so after each incremental increase in temperature we had to wait for some time for the vacuum to be restored to a value that would keep the device's protective system from triggering.

In vapor mass spectra over aluminum-containing MAX phase–HfO₂ systems, Al⁺ and Al₂O⁺ ions with an appearance energies of 6.0 and 7.7 eV, respectively, were identified starting at 1600 K. Comparison to the ionization energies of Al and Al₂O vapor species [34] showed that the identified ions were direct ionization products. Noteworthy, the vapor mass spectra over carbide materials containing MAX phases with aluminum also featured an Al⁺ ion, and not Al₂O⁺. The atomic aluminum partial pressures over MAX phase–HfO₂ oxycarbide systems were determined by Eq. (10), where the Al partial vapor pressure over aluminum-containing carbide samples ($p_s(\text{Al})$) was determined by Eqs. (12)–(15). The Al₂O partial pressures over the studied oxycarbide systems were determined by the relation below, which is an analogue of Eq. (11):

$$p(\text{Al}_2\text{O}) = p_s(\text{Al}) \frac{I(\text{Al}_2\text{O}^+) \sigma_s(\text{Al}) \gamma_s(\text{Al}^+)}{I_s(\text{Al}^+) \sigma(\text{Al}_2\text{O}) \gamma(\text{Al}_2\text{O}^+)}, \quad (24)$$

where the aluminum ionization cross sections were taken from [32], and Al₂O ionization cross sections were calculated as for a dialuminum oxide molecule. The dialuminum ionization cross section is $1.8 \times \sigma(\text{Al})$ [28], and the dialuminum oxide ionization cross

section can be calculated as $0.65 \times \sigma(\text{Al}_2) = 1.17 \times \sigma(\text{Al})$. The calculated values appear in Table S7; they were used to estimate the coefficients of temperature-dependent partial pressures of vapor species over the studied oxycarbide samples.

In the Ti₂AlC–HfO₂ system, temperature-dependent Al and Al₂O partial vapor pressures were determined over the following samples:

– 90 mol % Ti₂AlC–10 mol % HfO₂ in the temperature range 1600–1795 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{23715 \pm 988}{T} + 14.52 \pm 0.36, \quad (25)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{25675 \pm 790}{T} + 15.28 \pm 0.32, \quad (26)$$

– 50 mol % Ti₂AlC–50 mol % HfO₂ in the temperature range 1627–1821 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{32906 \pm 2480}{T} + 18.17 \pm 1.435, \quad (27)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{30168 \pm 2419}{T} + 16.00 \pm 1.38, \quad (28)$$

– 20 mol % Ti₂AlC–80 mol % HfO₂ in the temperature range 1632–1821 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{24380 \pm 1330}{T} + 12.79 \pm 0.43, \quad (29)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{25084 \pm 806}{T} + 12.85 \pm 0.47. \quad (30)$$

The total Al and Al₂O vapor pressure over the samples of the Ti₂AlC–HfO₂ oxycarbide system is far lower than the Al partial vapor pressure over sample 3 (Ti₂AlC chemical composition according to Table 1). The partial vapor pressure of the Al vapor species over the Ti₂AlC–HfO₂ system decreases as the HfO₂ content increases. The Al₂O fraction in the total vapor pressure increases, as temperature rises, over the 90 mol % Ti₂AlC–10 mol % HfO₂ and 20 mol % Ti₂AlC–80 mol % HfO₂ samples, and decreases over the 50 mol % Ti₂AlC–50 mol % HfO₂ sample.

In the Ti₃AlC₂–HfO₂ system, temperature-dependent Al and Al₂O partial vapor pressures were determined over the following samples:

– 90 mol % Ti₃AlC₂–10 mol % HfO₂ in the temperature range 1501–1615 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{27109 \pm 1767}{T} + (17.00 \pm 1.14), \quad (31)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{29897 \pm 1907}{T} + (18.40 \pm 1.23), \quad (32)$$

— 50 mol % Ti_3AlC_2 –50 mol % HfO_2 in the temperature range 1699–1815 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{28595 \pm 654}{T} + 15.94 \pm 0.37, \quad (33)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{24576 \pm 1257}{T} + 13.05 \pm 0.72, \quad (34)$$

— 20 mol % Ti_3AlC_2 –80 mol % HfO_2 in the temperature range 1729–1835 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{24238 \pm 2281}{T} + 13.19 \pm 1.28, \quad (35)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{27658 \pm 1160}{T} + 14.63 \pm 0.65. \quad (36)$$

The total Al and Al_2O vapor pressure over the samples of the Ti_3AlC_2 – HfO_2 oxycarbide system is far lower than the Al partial vapor pressure over sample 4 (with the Ti_3AlC_2 chemical composition according to Table 1). The Al_2O fraction in the total vapor pressure increases, as temperature rises, over the 90 mol % Ti_3AlC_2 –10 mol % HfO_2 and 20 mol % Ti_3AlC_2 –80 mol % HfO_2 samples and decreases over the 50 mol % Ti_3AlC_2 –50 mol % HfO_2 sample. The Ti_3AlC_2 – HfO_2 system has a higher volatility compared to that of the Ti_2AlC – HfO_2 system.

In the Zr_2AlC – HfO_2 system, temperature-dependent Al and Al_2O partial vapor pressures were determined over the following samples:

— 90 mol % Zr_2AlC –10 mol % HfO_2 in the temperature range 1685–1777 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{28535 \pm 1229}{T} + 16.63 \pm 0.71, \quad (37)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{32198 \pm 1410}{T} + 18.01 \pm 0.81, \quad (38)$$

— 50 mol % Zr_2AlC –50 mol % HfO_2 in the temperature range 1699–1824 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{27154 \pm 1492}{T} + 15.05 \pm 0.84, \quad (39)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{19387 \pm 1482}{T} + 9.96 \pm 0.84, \quad (40)$$

— 20 mol % Zr_2AlC –80 mol % HfO_2 in the temperature range 1725–1844 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{27136 \pm 641}{T} + 14.72 \pm 0.36, \quad (41)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{29249 \pm 1029}{T} + 15.40 \pm 0.58. \quad (42)$$

The total Al and Al_2O vapor pressure over the samples of the Zr_2AlC – HfO_2 oxycarbide system is far lower than the Al partial vapor pressure over sample 5 (with the Zr_2AlC chemical composition according to Table 1). The Al_2O fraction in the total vapor pressure increases, as temperature rises, over the 90 mol % Zr_2AlC –10 mol % HfO_2 and 20 mol % Zr_2AlC –80 mol % HfO_2 samples and decreases over the 50 mol % Zr_2AlC –50 mol % HfO_2 sample.

In the Zr_3AlC_2 – HfO_2 system, temperature-dependent Al and Al_2O partial vapor pressures were determined over the following samples:

— 90 mol % Zr_3AlC_2 –10 mol % HfO_2 in the temperature range 1634–1765 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{27438 \pm 1293}{T} + 16.84 \pm 0.76, \quad (43)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{30297 \pm 2121}{T} + 18.05 \pm 1.24, \quad (44)$$

— 50 mol % Zr_3AlC_2 –50 mol % HfO_2 in the temperature range 1687–1785 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{25995 \pm 1217}{T} + 15.95 \pm 0.70, \quad (45)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{31377 \pm 2413}{T} + 18.67 \pm 1.38. \quad (46)$$

— 20 mol % Zr_3AlC_2 –80 mol % HfO_2 in the temperature range 1699–1805 K:

$$\log p(\text{Al}) [\text{Pa}] = -\frac{26223 \pm 1287}{T} + 15.64 \pm 0.83, \quad (47)$$

$$\log p(\text{Al}_2\text{O}) [\text{Pa}] = -\frac{31152 \pm 1881}{T} + 18.07 \pm 1.07. \quad (48)$$

The total Al and Al_2O vapor pressure over the samples of the Zr_3AlC_2 – HfO_2 oxycarbide system is far lower than the Al partial vapor pressure over sample 6 (with the Zr_3AlC_2 chemical composition in Table 1). The Al_2O fraction in the total vapor pressure increases, as temperature rises, over all studied Zr_3AlC_2 – HfO_2 samples. The Zr_3AlC_2 – HfO_2 system has a higher volatility compared to that of the Zr_2AlC – HfO_2 system.

In the vapor mass spectra over Ti_2SiC – HfO_2 and Ti_3SiC_2 – HfO_2 oxycarbide systems, Si^+ , SiC^+ , SiO^+ , Si_2^+ , SiC_2^+ , and Si_2C^+ ions were identified starting at ca. 1950 K. The determination of the molecular precursors of these ions showed that they are all products of

Table 3. Coefficients in the equation for the temperature-dependent decimal logarithm of SiC₂ and Si₂C partial vapor pressures over samples of Ti_{n+1}SiC_n–HfO₂ (*n* = 1 or 2) oxycarbide systems, determined by Knudsen effusion mass spectrometry in this work

HfO ₂ , mol %	Temperature range, K	log <i>p</i> (<i>i</i>) [Pa] = – <i>A</i> / <i>T</i> + <i>B</i>			
		SiC ₂		Si ₂ C	
		<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
The Ti ₂ SiC–HfO ₂ system					
0	1900–2050	37 240 ± 1297	16.50 ± 0.65	41 500 ± 1600	18.66 ± 0.81
10	1995–2115	39 294 ± 746	17.24 ± 0.36	41 789 ± 1000	18.52 ± 0.29
50	2004–2115	41 552 ± 949	18.37 ± 0.44	36 620 ± 1220	15.90 ± 0.61
80	2051–2135	38 954 ± 1211	16.84 ± 0.64	35 118 ± 850	15.02 ± 0.41
The Ti ₃ SiC ₂ –HfO ₂ system					
0	1900–2050	37 539 ± 3536	16.86 ± 1.79	32 428 ± 2543	14.60 ± 1.30
10	2016–2112	39 294 ± 1195	17.24 ± 0.54	41 789 ± 1620	18.52 ± 0.78
50	1995–2124	41 369 ± 1214	18.44 ± 0.40	38 971 ± 1430	17.58 ± 0.59
80	2011–2104	41 018 ± 1214	17.98 ± 0.40	37 575 ± 1430	16.60 ± 0.59

direct ionization. We should mention that the Si⁺, SiC⁺, and SiO⁺ ions overlap with the N₂⁺ + CO⁺, Ar⁺, and CO₂⁺ background signals. For this reason, the Si⁺, SiC⁺, and SiO⁺ ion current intensities were measured at the temperature at which useful signals (separated by the electrical shutter of the mass spectrometer) with mass-to-charge ratios of 28, 40, and 44 were in excess over the background signals. At a mass-to-charge ratio of 44, for example, in addition to a high background signal from the CO₂⁺ ion, there is an ion current separated by the electrical shutter that largely corresponds to the SiO⁺ ion. The appearance energy of this ion is 10.6 eV, which corresponds to the ionization energy of silicon monoxide [34], while the ionization energy of CO₂ is 13.8 eV [34]. Thus, the vapor over Ti₂SiC–HfO₂ and Ti₃SiC₂–HfO₂ systems in the temperature range 1950–2100 K consists of Si, SiO, SiC, SiC₂, Si₂, and Si₂C.

The determination of temperature-dependent Si⁺, SiO⁺, and SiC⁺ ion current intensities is difficult due to the fact that the electrical and mechanical shutters of the mass spectrometer both shut off not only the Si⁺, SiC⁺, and SiO⁺ ions of the vapor mass spectrum over the studied samples, but also part of the N₂⁺ + CO⁺, Ar⁺, and CO₂⁺ background signals. Therefore, the investigation of vaporization of the Ti₂SiC–HfO₂ and Ti₃SiC₂–HfO₂ systems was further reduced to the determination of the temperature-dependent partial pressures of the SiC₂ and Si₂C vapor species. The Si₂⁺ ion current intensity was at the sensitivity threshold of the mass spectrometer and, accordingly, was not measured quantitatively.

In the Ti₂SiC–HfO₂ system, the temperature-dependent partial vapor pressures of SiC₂ and Si₂C were determined over the 90 mol % Ti₂SiC–10 mol % HfO₂ sample in the temperature range 1995–2115 K, the 50 mol % Ti₂SiC–50 mol % HfO₂ sample in the temperature range 2004–2115 K, and the 20 mol % Ti₂SiC–80 mol % HfO₂ sample in the temperature range 2051–2135 K. The coefficients of equations for those temperature dependences of the partial pressures of vapor species over the samples in the Ti₂SiC–HfO₂ system are listed in Table 3.

The SiC₂ and Si₂C partial vapor pressures over the samples in the Ti₂SiC–HfO₂ oxycarbide system were far lower than over sample 1 (with the Ti₂SiC chemical composition in Table 1).

In the Ti₃SiC₂–HfO₂ system, the temperature-dependent partial vapor pressures of SiC₂ and Si₂C were determined over the 90 mol % Ti₃SiC₂–10 mol % HfO₂ sample in the temperature range 2016–2112 K, the 50 mol % Ti₃SiC₂–50 mol % HfO₂ sample in the temperature range 1995–2124 K, and the 20 mol % Ti₃SiC₂–80 mol % HfO₂ sample in the temperature range 2011–2104 K (Table 3).

The SiC₂ and Si₂C partial vapor pressures over the samples in the Ti₃SiC₂–HfO₂ oxycarbide system were far lower than over sample 2 (with the Ti₃SiC₂ chemical composition in Table 1). The sum of the SiC₂ and Si₂C partial vapor pressures over the Ti₃SiC₂–HfO₂ oxycarbide samples is several times the respective value over the Ti₂SiC–HfO₂ samples containing equal hafnia concentrations. We may conclude that the Ti₃SiC₂–HfO₂ system has a higher volatility than that of the Ti₂SiC–HfO₂ system.

Altogether, the Knudsen effusion mass spectrometric study of the MAX phases-containing carbide

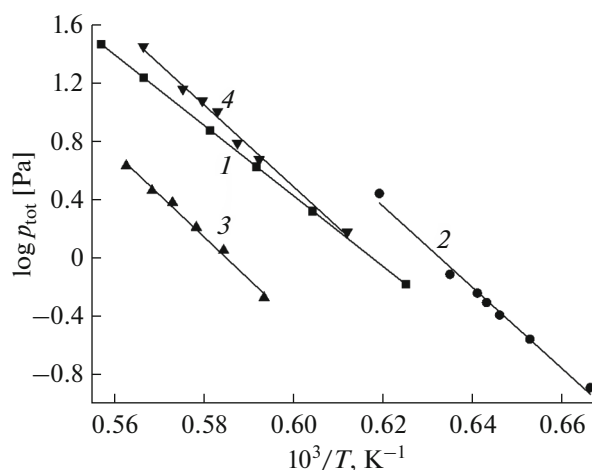


Fig. 3. Total vapor pressure as the sum of Al and Al₂O partial vapor pressures over samples **13**, **16**, **19**, and **22** (Table 1) with the following chemical compositions, mol %: (1) 90Ti₂AlC–10HfO₂, (2) 90Ti₃AlC₂–10HfO₂, (3) 90Zr₂AlC–10HfO₂, and (4) 90Zr₃AlC₂–10HfO₂.

materials with the Ti₂AlC, Ti₃AlC₂, Zr₂AlC, Zr₃AlC₂, Ti₂SiC, and Ti₃SiC₂ chemical compositions and their reaction products with hafnia implies that the samples containing titanium, silicon, and carbon are the least volatile and stable up to 1900 K. Of the SiC, Ti₂SiC, and Ti₃SiC₂ carbide materials, sample **1** (with the Ti₂SiC chemical composition in Table 1) has the least volatility. Hafnia additives decrease the partial pressures of the Si₂C and SiC₂ vapor species over the Ti₂SiC–HfO₂ system.

For the carbide materials containing the MAX phases with aluminum, the Al partial pressure increases in the following order: Zr₂AlC < Zr₃AlC₂ < Ti₂AlC < Ti₃AlC₂.

Sample **5** of the chemical composition Zr₂AlC has the least volatility in the range of temperatures studied. When doped with hafnia, the volatility order of the samples changes. Sample **19**, which also contains the Zr₂AlC phase, has the lowest sum of Al and AlO partial vapor pressures among the carbide systems containing 10 mol % HfO₂. The total vapor pressures over the 90 mol % Ti₂AlC–10 mol % HfO₂ and 90 mol % Zr₃AlC₂–10 mol % HfO₂ samples match each other within the determination error (Fig. 3). The thus-derived increasing order of volatilities is as follows: 90 mol % Zr₂AlC–10 mol % HfO₂ < 90 mol % Ti₂AlC–10 mol % HfO₂ ~ 90 mol % Zr₃AlC₂–10 mol % HfO₂ ≪ 90 mol % Ti₃AlC₂–10 mol % HfO₂.

In the systems containing 50 mol % HfO₂, the least sum of Al and AlO partial vapor pressures is over sample **14**, which contains the Ti₂AlC MAX phase. The total vapor pressure over sample **20** of composition 50 mol % Zr₂AlC–50 mol % HfO₂ (Table 1) at low temperatures (1700–1750 K) matches, within the experimental uncertainty, the total vapor pressure over

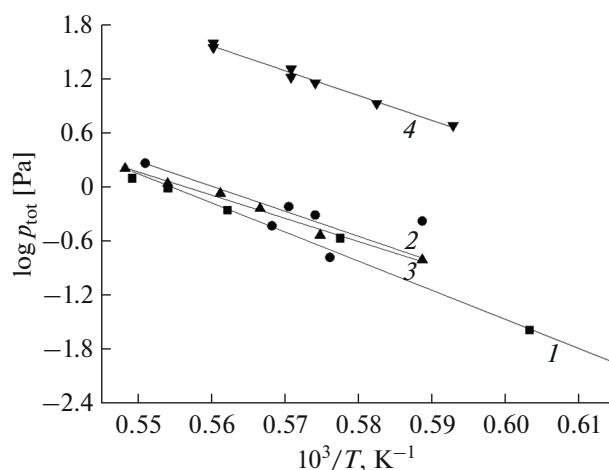


Fig. 4. Total vapor pressure as the sum of Al and Al₂O partial vapor pressures over samples **14**, **17**, **20**, and **23** (Table 1) with the following chemical compositions, mol %: (■, 1) 50Ti₂AlC–50HfO₂, (●, 2) 50Ti₃AlC₂–50HfO₂, (▲, 3) 50Zr₂AlC–50HfO₂, and (▼, 4) 50Zr₃AlC₂–50HfO₂.

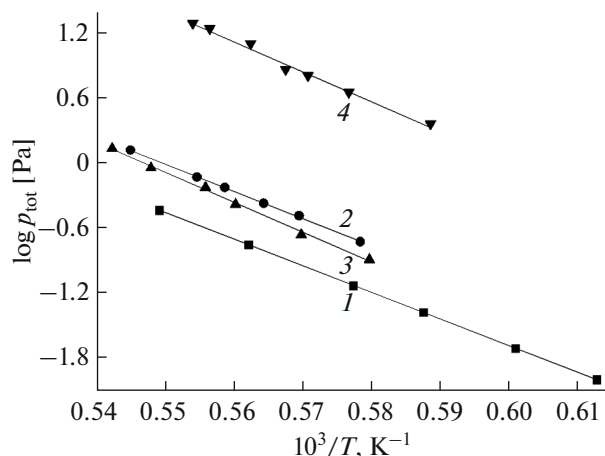


Fig. 5. Total vapor pressure as the sum of Al and Al₂O partial vapor pressures over samples **15**, **18**, **21**, and **24** (Table 1) with the following chemical compositions, mol %: (1) 20Ti₂AlC–80HfO₂, (2) 20Ti₃AlC₂–80HfO₂, (3) 20Zr₂AlC–80HfO₂, and (4) 20Zr₃AlC₂–80HfO₂.

sample **17** (with the chemical composition of 50 mol % Ti₃AlC₂–50 mol % HfO₂), and at higher temperatures (1790–1820 K), it corresponds to the total vapor pressure over sample **14** (with the chemical composition of 50 mol % Ti₂AlC–50 mol % HfO₂) (Fig. 4). Therefore, the volatility series will be the following: 50 mol % Ti₂AlC–50 mol % HfO₂ < 50 mol % Zr₂AlC–50 mol % HfO₂ < 50 mol % Ti₃AlC₂–50 mol % HfO₂ ≪ 50 mol % Zr₃AlC₂–50 mol % HfO₂.

In the 80 mol % HfO₂ system, the least sum of the Al and AlO partial vapor pressures is over carbide material **15**, which contains the Ti₂AlC MAX phase. In the temperature range 1720–1850 K, the total vapor

Table 4. Vapor mass spectra over sample **14** (with the chemical composition of 50 mol % Ti_2AlC –50 mol % HfO_2) synthesized at maximum temperatures of 1773 and 2073 K

T, K	Synthesis temperature, K			
	1773		2073	
	Ion current intensity, arb. units			
	Al^+	Al_2O^+	Al^+	Al_2O^+
1790	23	2.4	24	2.7
1813	38	6.6	37	6.3
1844	52	9.0	52	8.7
1779	21	2.0	22	2.1

pressure over sample **21** (with the chemical composition of 20 mol % Zr_2AlC –80 mol % HfO_2) is comparable (within the experimental uncertainty) with the total vapor pressure over sample **18** (with the chemical composition of 20 mol % Ti_3AlC_2 –80 mol % HfO_2) (Fig. 5). Therefore, the volatility series will be the following: 20 mol % Ti_2AlC –80 mol % $\text{HfO}_2 < 20$ mol % Zr_2AlC –80 mol % $\text{HfO}_2 \sim 20$ mol % Ti_3AlC_2 –80 mol % $\text{HfO}_2 \ll 20$ mol % Zr_3AlC_2 –80 mol % HfO_2 .

To conclude the work, we compared vaporization processes of the samples of oxycarbide systems, containing the MAX phase with aluminum, that have different maximum synthesis temperatures, namely, the Ti_2AlC – HfO_2 , Ti_3AlC_2 – HfO_2 , Zr_2AlC – HfO_2 , and Zr_3AlC_2 – HfO_2 systems. We should mention here that all the results presented above were obtained from samples synthesized at a maximum temperature of 2073 K. In the mass-spectrometric experiment, however, those samples vaporized at lower temperatures (starting from 1500–1600 K). Therefore, synthesis at 2073 K might be accompanied with selective vaporization of aluminum from the system and a change in the composition of the condensed phase. To check whether this might indeed occur, we carried out a comparative vaporization of samples synthesized at maximum temperatures of 1773 and 2073 K in systems containing aluminum and 50 mol % HfO_2 . It appeared that the vapor composition and partial pressures of Al and Al_2O vapor species over the samples synthesized at 1773 and 2073 K matched each other within the experimental uncertainty. An example of the vapor mass spectrum over sample **14** (with the chemical composition of 50 mol % Ti_2AlC –50 mol % HfO_2 according to Table 1) is presented in Table 4. The identical results obtained for samples synthesized at different temperatures indicate the following: a change in the maximum synthesis temperature of samples of the studied oxycarbide systems in the range 1773–2073 K does not change the vapor composition or the partial pressures of vapor species over the samples as determined by Knudsen effusion mass spectrometry.

CONCLUSIONS

This work is the first where the vaporization of the carbide materials of the Ti_2SiC , Ti_3SiC_2 , Ti_2AlC , Ti_3AlC_2 , Zr_2AlC , and Zr_3AlC_2 chemical compositions, containing the MAX phases, and MAX phase– HfO_2 oxycarbide systems was studied up to 2200 K by Knudsen effusion mass spectrometry. We have shown that carbide materials of as-batch chemical compositions Ti_2SiC and Ti_3SiC_2 are the least volatile and are stable up to 1900 K. Of the studied silicon-containing carbide materials (SiC , Ti_2SiC , and Ti_3SiC_2), the sample of as-batch chemical composition Ti_2SiC has the least total vapor pressure. The vapor over the samples with Ti_2SiC and Ti_3SiC_2 compositions at temperatures above 1900 K features Si, Si_2 , SiC , SiC_2 , and Si_2C species, just as over pure silicon carbide. In the vapor over materials containing the MAX phases with aluminum, atomic aluminum is the major vapor species at temperatures starting from 1500 K. The relative volatility of the studied aluminum-containing samples has been found to increase in the series $\text{Zr}_2\text{AlC} < \text{Zr}_3\text{AlC}_2 < \text{Ti}_2\text{AlC} < \text{Ti}_3\text{AlC}_2$.

We have found that hafnia additives to the carbide materials under consideration bring about a decrease in total vapor pressure over the formed oxycarbide systems and give rise to the appearance of oxygen-containing vapor species: SiO and Al_2O , which were not identified in this work over the carbide materials containing the MAX phases with silicon and aluminum, respectively. The increasing HfO_2 content in aluminum-containing oxycarbide samples changes the order of relative volatilities. When the doping level is 10 mol % HfO_2 , oxycarbide samples based on Zr_2AlC -containing materials have the least total vapor pressures, as was the case with the above-considered carbide samples. However, when the HfO_2 content increases to 50 mol % or more, the system whose chemical composition is described with the Ti_2AlC – HfO_2 formula becomes the least volatile system. Variations in the maximum synthesis temperature in the range 1773–2073 K for samples of the studied oxycarbide systems do not bring about a change in either the qualitative or the quantitative composition of the vapor over the oxycarbide material as determined by Knudsen effusion mass spectrometry.

SUPPLEMENTARY INFORMATION

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- M. W. Barsoum, *Prog. Solid State Chem.* **28**, 201 (2000). [https://doi.org/10.1016/S0079-6786\(00\)00006-6](https://doi.org/10.1016/S0079-6786(00)00006-6)
- M. Radovic and M. W. Barsoum, *Am. Ceram. Soc. Bull.* **92**, 20 (2013). <https://bulletin-archive.ceram-ics.org/is-cacheable/1605850406926/ucujko.pdf>
- J. Gonzalez-Julian, *J. Am. Ceram. Soc.* **104**, 659 (2021). <https://doi.org/10.1111/jace.17544>
- D. Y. Kovalev, M. A. Luginina, and S. G. Vadchenko, *Russ. J. Inorg. Chem.* **62**, 1638 (2017). <https://doi.org/10.1134/S0036023617120117>
- E. P. Simonenko, N. P. Simonenko, and I. A. Nagornov, *Russ. J. Inorg. Chem.* **67**, 705 (2022). <https://doi.org/10.1134/S0036023622050187>
- E. P. Simonenko, N. P. Simonenko, I. A. Nagornov, et al., *Russ. J. Inorg. Chem.* **67**, 1838 (2022). <https://doi.org/10.1134/S0036023622601222>
- E. N. Hoffman, D. W. Vinson, R. L. Sindelar, et al., *Nucl. Eng. Des.* **244**, 17 (2012). <https://doi.org/10.1016/j.nucengdes.2011.12.009>
- W. E. Lee, E. Giorgi, R. Harrison, et al., *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications* (John Wiley & Sons, Inc., Hoboken, 2014). <https://doi.org/10.1002/9781118700853.ch15>
- T. Galvin, N. C. Hyatt, W. M. Rainforth, et al., *Nucl. Mater. Energy* **22**, 100725 (2020). <https://doi.org/10.1016/j.nme.2020.100725>
- V. I. Almjashev, V. L. Stolyarova, E. V. Krushinov, et al., *Nucl. Propuls. React. Plants* **31**, 60 (2023). https://doi.org/10.52069/2414-5726_2023_1_31_60
- Z. Wen, Z. Tang, H. Meng, et al., *Corros. Sci.* **207**, 110574 (2022). <https://doi.org/10.1016/j.corsci.2022.110574>
- E. K. Kazenas and Yu. V. Tsvetkov, *Evaporation of Carbides* (Krasand, Moscow, 2017) [in Russian]. www.rf-br.ru/library/books/2620/.
- G. H. Rinehart and R. G. Behrens, *J. Chem. Thermodyn.* **12**, 205 (1980). [https://doi.org/10.1016/0021-9614\(80\)90038-5](https://doi.org/10.1016/0021-9614(80)90038-5)
- J. Drowart, G. De Maria, and M. G. Inghram, *J. Chem. Phys.* **29**, 1015 (1958). <https://doi.org/10.1063/1.1744646>
- Z. Cao, W. Xie, I. H. Jung, et al., *Metall. Mater. Trans. B: Process Metall. Mater. Process. Sci.* **46**, 1782 (2015). <https://doi.org/10.1007/s11663-015-0344-8>
- C. A. Stearns and F. J. Kohl, *Mass Spectrometric Determination of the Dissociation Energies of Titanium Dioxide and Titanium Tetracarbide* (NASA Technical Note D-5653 Cleveland, 1970).
- Y. L. Li and T. Ishigaki, *Mater. Sci. Eng., A* **345**, 301 (2003). [https://doi.org/10.1016/S0921-5093\(02\)00506-3](https://doi.org/10.1016/S0921-5093(02)00506-3)
- C. A. Stearns and F. J. Kohl, *High-Temperature Mass Spectrometry—Vaporization of Group 4-B Metal Carbides* (NASA Technical Note D-7613, Cleveland, 1974). <https://ntrs.nasa.gov/search.jsp?R=19740012680> (accessed March 24, 2020).
- V. J. Keast, S. Harris, and D. K. Smith, *Phys. Rev.* **80**, 214113 (2009). <https://doi.org/10.1103/PhysRevB.80.214113>
- D. Saucedo, P. Singh, A. R. Falkowski, et al., *npj Comput. Mater.* **7**, 6 (2021). <https://doi.org/10.1038/s41524-020-00464-7>
- S. N. Perevislov, T. V. Sokolova, and V. L. Stolyarova, *Mater. Chem. Phys.* **267**, 124625 (2021). <https://doi.org/10.1016/j.matchemphys.2021.124625>
- S. N. Perevislov, V. V. Semenova, and A. S. Lysenkov, *Russ. J. Inorg. Chem.* **66**, 1100 (2021). <https://doi.org/10.1134/S0036023621080210>
- S. N. Perevislov, I. E. Arlashkin, and A. S. Lysenkov, *Refract. Ind. Ceram.* **63**, 215 (2022). <https://doi.org/10.1007/S11148-022-00709-6>
- I. E. Arlashkin and S. N. Perevislov, *Materialovedenie* **6**, 16 (2023). <https://doi.org/10.31044/1684-579X-2023-0-6-16-21>
- I. E. Arlashkin, S. N. Perevislov, and V. L. Stolyarova, *Russ. J. Gen. Chem.* **93**, 881 (2023). <https://doi.org/10.1134/S107036322304014X>
- S. N. Perevislov, I. E. Arlashkin, and V. L. Stolyarova, *J. Am. Ceram. Soc.* **107**, 488 (2023). <https://doi.org/10.1111/jace.19419>
- K. Hilpert, *Rapid Commun. Mass Spectrom.* **5**, 175 (1991). <https://doi.org/10.1002/rcm.1290050408>
- J. Drowart, C. Chatillon, J. Hastie, et al., *Pure Appl. Chem.* **77**, 683 (2005). <https://doi.org/10.1351/pac200577040683>
- S. I. Lopatin, S. M. Shugurov, Z. G. Tyurnina, et al., *Glass Phys. Chem.* **47**, 38 (2021). <https://doi.org/10.1134/S1087659621010077>
- S. I. Lopatin, *Glass Phys. Chem.* **48**, 117 (2022). <https://doi.org/10.1134/S1087659622020055>
- R. C. Paule and J. Mandel, *Pure Appl. Chem.* **31**, 371 (1972). <https://doi.org/10.1351/pac197231030371>
- J. B. Mann, *J. Chem. Phys.* **46**, 1646 (1967). <https://doi.org/10.1063/1.1840917>
- R. T. Meyer and A. W. Lynch, *High Temp. Sci.* **5**, 192 (1973).
- S. G. Lias, J. E. Bartmess, J. F. Liebman, et al., *J. Phys. Chem. Ref. Data* **17**, Suppl. 1, 861 (1988).

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