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Thermal Stability of Aluminum Oxocarbides

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Abstract—The composition of vapor over Al_2OC and $2Al_2O_3 \cdot Al_2OC$ aluminum oxycarbides was determined. The thermal stability of the oxycarbides increases in the series Al_2OC–$2Al_2O_3 \cdot Al_2OC$–Al_2O_3.

Aluminum carbides and oxycarbides are formed in the reaction of carbon with aluminum oxide phases. The reactions of aluminum oxide with carbon were studied extensively [1–7].

By now we confirmed the fact that stable aluminum oxycarbides, Al_4O_4C and Al_2OC, can form in a high-temperature reaction of aluminum oxide, Al_2O_3, with carbon and Al_4C_3-type carbides [5, 6]. Aluminum monoxycarbide Al_2OC is unstable on heating and seems to dissociate with vaporization of gaseous compounds. Elyutin *et al*. [4] believe that aluminum monoxycarbide has a high volatility at the temperatures of the synthesis. Lihrmann *et al*. [8] suggested that vaporization of aluminum monoxycarbide is accompanied by its decomposition to simpler compounds (Al, Al_2O, and CO). No unambiguous conclusions about the thermal stability of monoxycarbide can be found in the literature.

We have found [5, 6] that a phase with the spinel structure is formed in a high-temperature reaction in the Al_2O_3–C system. This phase resembles aluminum oxynitrides (γ-AlON or $x\text{AlN} \cdot Al_2O_3$) [9] in its structural characteristics. Taking into account the known structural similarity of Al_2OC and AlN [10], and also the absence of nitrogen-containing compounds in our experiment, we have good grounds to believe that the resulting spinel phase is a solid solution of the composition $xAl_2OC \cdot Al_2O_3$. We also synthesized a single-phase sample of this phase of the composition Al_6O_7C or $Al_2OC \cdot 2Al_2O_3$.

The aim of this work was to study the thermal stability of aluminum oxycarbide α-Al_2OC and of the phase with the spinel structure $Al_2OC \cdot 2Al_2O_3$, since their formation in the condensed phase is possible on high-temperature heating of such important composite refractory materials as Al_2O_3–SiC, Al_2O_3–TiC, and Al_2O_3–C. The determination of the temperatures at which these compounds begin to vaporize and the study of the vaporization dynamics and the composition of the gaseous products will allow prediction of the stability of properties of the above-listed composite materials.

In this work we studied the vaporization of Al_2OC obtained in the reaction of aluminum oxide with carbon in the molar ratio of 1 : 3 (1750°C, 8 h) and a single-phase sample of the spinel phase of the composition $Al_2OC \cdot 2Al_2O_3$ obtained in the reaction of aluminum oxide with carbon in the molar ratio of 1 : 1 (1750°C, 1 h).

Vaporization of Al_2OC. In the mass spectrum of vapor over aluminum oxycarbide in the temperature range 1620–1755 K, we found peaks of Al^+ and Al_2O^+ ions; their intensity ratio depended on temperature. To determine the nature of these ions, we measured their appearance potentials by the method of vanishing ion current. We used gold as a reference substance with well-known ionization potential of 9.22 eV [11]. The appearance potentials (eV, ±0.3) were 6.2 (Al^+) and 7.8 (Al_2O^+). These values almost coincide with the ionization potentials of atomic aluminum and Al_2O, respectively, which suggests their molecular origin.

The vapor mass spectra, the dependences of the ion currents on the vaporization temperature (T) and time (τ), and the appearance potentials of the ions in the mass spectrum suggest that, in the temperature range 1620–1755 K, aluminum oxocarbide vaporizes almost congruently with complete dissociation; the vapor consists of a mixture of Al_2O and Al, and, probably, of oxygen and carbon oxides. Quantitative measurements of the partial pressures of O_2, CO, and CO_2 are impossible because of the presence of N_2, CO, O_2, and CO_2 in the vacuum system of the mass spectrometer and, as a consequence, of strong background for

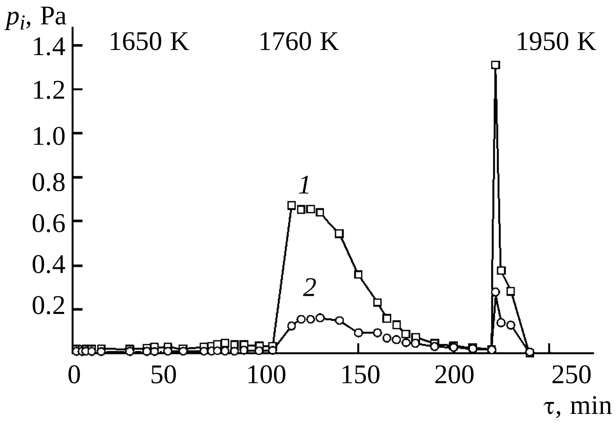

Fig. 1. Plot of partial pressures of the vapor components over Al_2OC vs. vaporization time. (*1*) Al_2O and (*2*) Al.

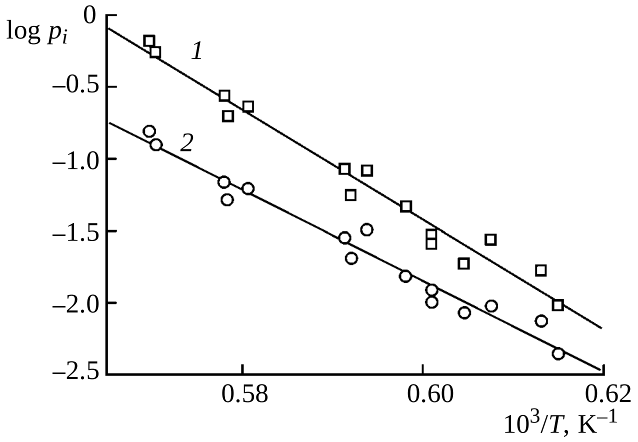

Fig. 2. Plot of the logarithms of partial pressures of the vapor components over Al_2OC vs. reciprocal temperature. (*1*) Al_2O and (*2*) Al.

m/z 28, 32, and 44. Nevertheless, the deterioration of the vacuum inside the mass spectrometer on heating of the sample and the ion peaks corresponding to O_2^+ and CO^+, which are partially eliminated with a shutter, suggest the presence of these gases in the vapor over the sample. The intensities of the ion currents of CO_2^+, which are proportional to the partial pressures of carbon dioxide over the samples, are low and remain almost unchanged during the experiment. We determined the partial pressures of atomic aluminum and Al_2O by the procedure of comparing the ion currents by Eq. (1):

$$p_1 = \frac{p_2 I_1 T_1 \sigma_2 \gamma_2 a_2}{I_2 T_2 \sigma_1 \gamma_1 a_1}. \qquad (1)$$

Here p_i is the partial pressure of *i*th vapor component; I_i, intensity of the ion current; σ_i, full ionization cross section of the molecules; γ, conversion coefficient of the secondary electron multiplier of the mass spectrometer; and a_i, natural abundance of an isotope. The indices 1 and 2 refer to the substance under study and a reference substance, respectively. The ionization cross sections were determined by the additivity rule using atomic cross sections from [12]. The dependence of Al_2O and Al partial pressures on the vaporization time and temperature is shown in Fig. 1.

At 1650–1800 K, the partial pressures of Al and Al_2O and their ratio remain almost unchanged during the whole time of vaporization. The vapor pressure of Al_2O is higher than the vapor pressure of aluminum in this temperature range, and their ratio depends on temperature. Only at the end of the experiment, on passing to the unsaturated vapor, the pressure of Al_2O decreases and becomes equal to the pressure of atomic aluminum. The measurements of the temperature dependences of the intensities of Al^+ and Al_2O^+ ion currents allowed us to derive temperature dependences (2), (3) of the partial pressures of the vapor components over the starting composition in the range 1626–1755 K.

$$Al_2O\text{: } \log p \text{ [Pa]} = -(38\,254 \pm 1882)/T + (21.53 \pm 1.12), \qquad (2)$$

$$Al\text{: } \log p \text{ [Pa]} = -(31\,564 \pm 1609)/T + (17.09 \pm 0.95). \qquad (3)$$

The dependences of the logarithms of Al and Al_2O partial pressures on reciprocal temperature are shown in Fig. 2. It is seen that, as the temperature increases, the relative content of Al_2O in the vapor increases, and the content of atomic aluminum decreases, which can be accounted for by an increase in the concentration of oxygen in the saturated vapor and by the shift of gas-phase equilibrium (4) to the left.

$$Al_2O(gas) \rightleftarrows 2Al(gas) + 1/2O_2(gas). \qquad (4)$$

Vaporization of the $2Al_2O_3 \cdot Al_2OC$ spinel phase. We have detected peaks of Al^+ and Al_2O^+ ions in the vapor mass spectrum starting from 1650 K. Examination of the vapor mass spectrum, its dependence on the vaporization time and temperature, and also the appearance potentials of ions show that the sample vaporizes incongruently. In the vapor there are aluminum oxide Al_2O, atomic aluminum (the ratio of their partial pressures changed during the experiment), and, presumably, O_2 and CO. The dependence of the partial pressures of Al and Al_2O on the vaporization time and temperature is shown in Fig. 3. It is seen that the pressures of Al_2O and atomic aluminum decrease during the whole experiment. This is characteristic for the vaporization of solid solutions or melts with components differing in their volatility. The vapor pressure of aluminum was higher than the vapor pressure of Al_2O in the vaporization temperature range. Only on increasing the temperature by 100–150 K for several minutes the pattern became opposite. After a short isothermal heating, p(Al) again became greater than $p(Al_2O)$. As the sample vaporizes, less volatile Al_2O_3 seems to accumulate in the condensed phase, vaporizing only above 2100 K. To check this assumption, we studied the vaporization of pure aluminum oxide from a molybdenum cell.

Vaporization of Al_2O_3. We have detected peaks of Al^+, Al_2O^+, AlO^+, $Al_2O_2^+$, MoO_2^+, and $MoO_3{}^+$ ions in the mass spectrum of the vapor over aluminum oxide at the ionizing voltage of 25 V. The $Al^+:Al_2O^+:AlO^+:Al_2O_2^+$ ratio in the temperature range 2220–2350 K is, on the average, 100 : 8.7 : 6.5 : 1.2. The appearance potentials (eV, ±0.3) are 6.2 (Al^+), 7.8 (Al_2O^+), 9.5 (AlO^+), 9.5 (MoO_2^+), and 12.0 (MoO_3^+). We have not measured the appearance potential of $Al_2O_2^+$ because of the low intensity of the ion current. The appearance potentials of ions in the mass spectrum of the vapor over Al_2O_3 coincide with the appearance potentials of the corresponding molecules [11] within the limits of the measurement error, suggesting that these ions are formed by the direct ionization of gaseous Al, Al_2O, AlO, Al_2O_2, MoO_2, and MoO_3. The main components of the vapor at 2220–2350 K are oxygen and atomic aluminum; the sum of the partial pressures of aluminum suboxides does not exceed 15% of the aluminum pressure [scheme (5)].

$$Al_2O_3(cr.) + Mo(cr.) \longrightarrow Al(gas) + O_2(gas)$$
$$+ Al_2O(gas) + AlO(gas) + MoO_2(gas) + MoO_3(gas). \quad (5)$$

From the measured intensities of the ion currents of Al^+, Al_2O^+, and AlO^+ and the partial pressures of Al, Al_2O, and AlO as functions of temperature in the range 2228–2352 K, we derived Eqs. (6)–(8) for the temperature dependences of the partial pressures of the vapor components over Al_2O_3.

$$\log p\ [Al,\ Pa] = -(25\,050 \pm 2000)/T + (10.9 \pm 0.9), \quad (6)$$

$$\log p\ [AlO,\ Pa] = -(27\,700 \pm 2700)/T + (10.9 \pm 1.2), \quad (7)$$

$$\log p\ [Al_2O,\ Pa] = -(27\,350 \pm 2500)/T + (10.7 \pm 1.1). \quad (8)$$

The results obtained allowed us to estimate the relative thermal stability of aluminum monoxycarbide Al_2OC, of the spinel phase Al_6O_7C, and of aluminum oxide Al_2O_3. Aluminum monoxycarbide is the most volatile in this series. On heating to 1700–1750 K, it vaporizes, dissociating completely to Al_2O, CO, atomic aluminum, and oxygen. Aluminum oxide is the most thermally stable. It begins to dissociate, with atomic aluminum and oxygen passing into vapor, above 2200 K. The data obtained support our assumption that the spinel phase is a solid solution of aluminum monoxycarbide in aluminum oxide of the composition $xAl_2OC \cdot Al_2O_3$. The thermal stability of the spinel phase seems to depend on the concentration of aluminum oxide and oxycarbide in it. The activity of aluminum monoxycarbide decreases with the formation of the spinel phase, which results in a decrease in the partial pressures of Al and Al_2O vapor and leads to an increase in the thermal stability of the phase.

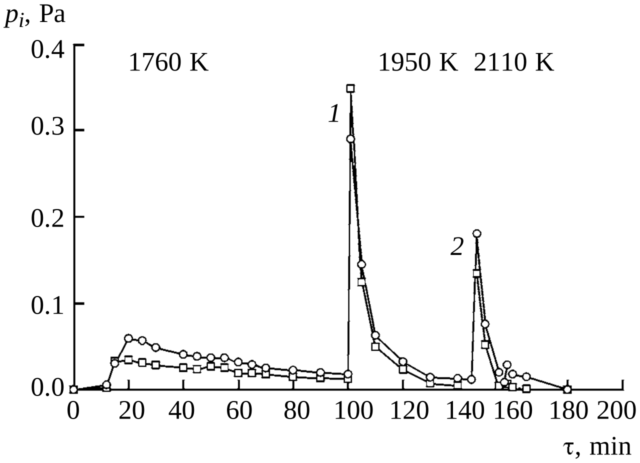

Fig. 3. Plot of partial pressure of vapor components over the Al_2O_3–Al_2OC system vs. vaporization time (starting composition of the condensed phase $2Al_2O_3 \cdot Al_2OC$). (*1*) Al_2O and (*2*) Al.

EXPERIMENTAL

The work was carried out on an MS-1301 mass spectrometer at an ionizing voltage of 25 V. We vaporized the samples from a molybdenum twin cell heated by electron bombardment. The temperature was measured with an EOP-66 optical pyrometer. The cell was first calibrated against the vapor pressure of gold and CaF_2 [13, 14]. We determined the partial pressures of the vapor components by comparing the ion currents. We used gold as internal and external reference of pressure, as recommended by IUPAC [13].

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