TRANSLATION

VAPORIZATION OF PURE-OXIDE CERAMICS AT HIGH TEMPERATURES

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FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

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VAPORIZATION OF PURE-OXIDE CERAMICS
AT HIGH TEMPERATURES

Ye. S. Lukin and D. N. Poluboyaninov
(Chemical Technological Institute named after D. I. Mendeleyev)

The use of pure-oxide ceramics at high temperatures in different inert gases and deep vacuum is limited in many cases by the significant vapor pressure of the ceramics, leading to significant weight loss.

The behavior of pure-oxide ceramics at high temperatures can be fully characterized in a calculation of all the parameters affecting vaporization. The most important of these are the nature of the oxides and their purity, the temperature of service, the surrounding gaseous medium and its parameters, the state of the surfaces of samples, their density, peculiarities of structure, etc.

This article is devoted to an investigation of the vaporization of pure-oxide ceramics at different temperatures in a vacuum of $10^{-4}$ mm Hg and in helium at positive pressure of 0.2 atm. This investigation was conducted to study quantitative vaporization as a technical property so that we could characterize one ceramic in specific conditions of vaporization at high temperatures. In connection with such problems the composition of the products of vaporization were not determined.
A significant number of works are devoted to the study of vaporization of oxides, a determination of the composition of the gaseous phase and the thermodynamic characteristics of the gas-like components. However, the vaporization of ceramics from MgO, BeO, ZrO$_2$, Al$_2$O$_3$, and their compounds MgO·Al$_2$O$_3$ and 3Al$_2$O$_3$·2SiO$_2$, at high temperatures has been insufficiently studied.

Vaporization was studied on samples of ceramics from pure oxides MgO, Al$_2$O$_3$, BeO, CaO, ZrO$_2$, MgO·Al$_2$O$_3$, 3Al$_2$O$_3$·2SiO$_2$, which contained about 0.5% impurities. The test samples were prepared according to the technology accepted for the corresponding oxides. The samples had a diameter of 12 - 13 mm, a thickness of 1 - 2 mm, and a weight of 1.0 - 1.5 g. Table 1 gives the characteristics of the samples.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content of impurities</th>
<th>Temperature</th>
<th>Density</th>
<th>Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.3</td>
<td>1710</td>
<td>3.82</td>
<td>4.5</td>
</tr>
<tr>
<td>BeO</td>
<td>0.3</td>
<td>1950</td>
<td>2.65</td>
<td>5.6</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;1.0</td>
<td>1750</td>
<td>3.03</td>
<td>9.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.3</td>
<td>1710</td>
<td>3.42</td>
<td>4.5</td>
</tr>
<tr>
<td>ZrO$_2$-MgO</td>
<td>0.5</td>
<td>1710</td>
<td>5.32</td>
<td>4.6</td>
</tr>
<tr>
<td>ZrO$_2$-CaO</td>
<td>0.5</td>
<td>1710</td>
<td>5.29</td>
<td>5.5</td>
</tr>
<tr>
<td>MgO·Al$_2$O$_3$</td>
<td>0.5</td>
<td>1710</td>
<td>3.44</td>
<td>3.9</td>
</tr>
<tr>
<td>3Al$_2$O$_3$·2SiO$_2$</td>
<td>0.3</td>
<td>1710</td>
<td>3.04</td>
<td>2.2</td>
</tr>
</tbody>
</table>

1. ZrO$_2$ - MgO: specially pure ZrO$_2$ stabilized by 10 molar \% MgO.
2. ZrO$_2$ - CaO: specially pure ZrO$_2$ stabilized by 10 molar \% CaO.

The spinel (proposed by I. P. Galkina) is synthesized by sintering from pure magnesium oxide and alumina of brand G-00. Mullite (proposed by Ye. B. Krol') is preliminarily synthesized from chemically pure Al$_2$O$_3$ and SiO$_2$ of an analytical grade at 1550°C with final sintering at 1710°C. The impurity content in pure MgO is shown without calculating for the calcium oxide; the quantity of CaO is about 9.7\%.

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Vaporization was studied at temperatures up to 2300°C in a high-temperature furnace with tungsten heaters. The construction of the furnace and the placement diagram of samples are shown on Fig. 1.

The high-temperature furnace consists of the following basic parts: the body, the upper dome and the heater. The bottom 1, body 2 and cover 9 are equipped with water jackets. Water-cooled copper tubing 3, supported by large copper holders 4, enters the furnace through the bottom. The heater 6, made from molybdenum plates 0.5 - 0.7 mm and tungsten foil 0.2 mm thick, is fastened to the holders by screws. The diameter of the assembled heater is about 20 mm, the height is about 50 - 60 mm. Molybdenum screens 7 are set up around the heater to reduce heat losses. In the center of the heater and screens at one level there is an opening 1.5 - 2 mm in diameter for measuring the temperature of sample 5 by an optical tyrometer, "Pyrolux," with a disappearing thread. It can measure up to 3000°C.

Weight losses during vaporization of ceramic samples were determined on quartz scales of direct weighing. The quartz scales were introduced in the upper dome 10. The samples were suspended on a tungsten or molybdenum wire 8 with a diameter of 0.2 mm. For this the samples had a hole. The length of the wire was 300 - 350 mm. The change in the weight of a sample was determined from the position of the calibrating screw of the quartz coil 11 by a KM-6 cathetometer 12. The accuracy of weighing was 0.0001 g.

During the tests in a vacuum the sample was lowered on the wire to the center of the heater opposite the opening for measuring temperature. When vaporization was determined in helium the sample was lowered into a zirconium dioxide crucible, which prevented the
Fig. 1. Diagram of a high-temperature furnace for determining weight losses in a vacuum.

deposition of tungsten from the heater onto it. Also, next to the hanger we lowered a molybdenum wire 2 - 3 mm in diameter so that the products of vaporization, rising upwards, would condense not on the hanger, but on this wire, which had a surface considerably larger than that of the hanger.

Before and after the tests the samples were weighed on analytical scales with accuracy up to 0.0001 g. In determining weight loss in a vacuum we introduced a correction for vaporization of the hanger. It was determined in a dry run. The divergence in total weight loss of samples during vaporization, determined by weighing before and
after the tests and by direct weighting with a cathetometer, did not exceed 0.0005 g (0.3%).

As a result of these investigations we determined the dependence of vaporization of oxide ceramics on temperature in a vacuum and in helium (Fig. 2), and also the rate of vaporization at different temperatures. The vaporization of different types of ceramics depends on the nature of the initial oxide. For all oxides we can set the temperature of the start of noticeable vaporization (1 g/cm² 10⁻³ or ≈ 0.2% by weight). Pure magnesium oxide starts to vaporize at 1700°C; spinel, at 1800°C; Al₂O₃, at 1900°C; zirconium dioxide stabilized with CaO; at 2000°C; BeO and ZrO₂ stabilized with MgO, at 2100 - 2150°C.

Alumina, spinel, zirconium dioxide and beryllium oxide vaporize significantly less than pure magnesium oxide. The vaporization of oxides is significantly less in helium at 0.2 atm than in a vacuum. The temperatures of noticeable vaporization move into a region of higher, more curved dependences of vaporization on temperature with a flatter slope in helium than in a vacuum. Such a course of curves can be explained by the difference in the processes in vaporization in helium and in a vacuum. In a vacuum the products of vaporization are gradually drawn off during vaporization, which greatly stimulates the removal of molecules from the surface of the sample. In helium the removal of molecules of the material is determined by their diffusion into the gaseous phase, and also by the convection that takes place at high temperatures.
Fig. 2. Dependence of vaporization of oxide ceramics on temperature: a) in a vacuum of $10^{-4} \text{ mm Hg}$; b) in helium at 0.2 atm; 1) MgO; 2) MgO·Al₂O₃; 3) Al₂O₃; 4) ZrO₂ stabilized by CaO; 5) ZrO₂ stabilized by MgO; 6) BeO.
For a number of oxides our obtained results fully coincide with
the literary data. As a result of a study of the behavior of
refractory oxides in a vacuum of $10^{-4}$ mm Hg, the following temperatures
of vaporization were obtained [2]: for ZrO$_2$, 2300°C; for MgO, 1600°C;
for BeO, 2100°C.

A comparison of the magnitudes of vaporization shows that certain
oxides are rather stable at high temperatures. Thus, the temperature
of noticeable vaporization of MgO in air [2] is 1900°C, BeO, 2400°C,
Al$_2$O$_3$, 1750°C, CaO, 1700°C. In the opinion of a number of authors,
beryllium oxide is stable up to 2000°C; other investigators [3] claim
BeO does not volatilize in a vacuum up to 2200°C. However, in the
presence of water vapors BeO vaporizes intensely at 1300 - 1500°C [3].

From the results of our work we conclude that BeO is fully stable in
a vacuum of $10^{-4}$ mm Hg up to 2000°C. Upon heating above 2100 - 2150°C
the samples start to vaporize noticeably; at 2200°C about 10% by
weight (the weight of a BeO sample was about 1.5 g) vaporizes in 1 hr;
at 2300°C in the same conditions approximately 35% by weight vaporizes
in 1 hr. In helium vaporization of BeO samples is not observed up to
2200°C; insignificant weight losses occur at 2300°C.

In spite of the stability of beryllium ceramics in helium up to
high temperatures, their use in thermal shocks in service at tempera-
tures above 200°C encounters great difficulties. This is because
in the interval of 2160 - 2300°C BeO undergoes polymorphous transfor-
mation accompanied by an increase in linear dimensions of articles
up to 4%. Even small BeO discs and cylinders, heated to 2300°C, are
completely destroyed upon sharp cooling. The literature also makes
reference to the polymorphous transformation of beryllium oxide [4,7].

The rate of vaporization (Fig. 3) of samples from Al$_2$O$_3$, BeO,
ZrO$_2$ stabilized by MgO and CaO, at 2000°C in a vacuum are within limits of $1 \times 10^{-5} - 2 \times 10^{-5}$ g/cm$^2$·min. The rate of vaporization of spinel (MgO·Al$_2$O$_3$) at 2000°C is one order greater, and that of pure magnesium oxide is two orders greater than the stated oxides.

Fig. 3. The rate of vaporization of pure-oxide ceramics in a vacuum depending upon temperature: 1) MgO; 2) MgO·Al$_2$O$_3$; 3) Al$_2$O$_3$; 4) ZrO$_2$ stabilized with CaO; 5) ZrO$_2$ stabilized with MgO; 6) BeO; 7) 3Al$_2$O$_3$·2SiO$_2$.

As the temperature is increased the rate of vaporization of all oxides increases, especially strongly for ceramics from MgO and BeO. An increase in the rate of vaporization by two orders (from $10^{-5}$ to $10^{-3}$) is observed for MgO in the interval of 1700 - 2000°C, and for BeO in the interval of 2000 - 2300°C. The weight losses for MgO samples at 2000°C in a vacuum are about 40%, for BeO samples at 2300°C about 35%.

The rate of vaporization of ZrO$_2$ stabilized with CaO at temperatures up to 2300°C is somewhat higher than that zirconium dioxide stabilized with MgO. Evidently, this is mostly explained by technological factors. The stabilization of ZrO$_2$ by introducing calcium oxide proceeds
through the formation of zirconates, which in turn give solid solutions with zirconium dioxide. A determination of the rate of vaporization of calcium zirconate itself shows intensive volatilization somewhat above 1800°C. Also, the radius of the Ca\(^{2+}\) ion (1.06) is somewhat larger than the radius of the Zr\(^{4+}\) ion (0.87). When a calcium ion is introduced into the ZrO\(_2\) grid some distortion of the structure occurs and the grid constant is increased in comparison with the Mg\(^{2+}\) ion (0.78), which evidently can also affect vaporization of zirconium dioxide. We should note that at 2200°C and higher in a vacuum and in helium samples of zirconium dioxide become black with a metallic shine.

The literature [1] states that at high temperatures ZrO\(_2\) is depleted of oxygen and the ratio between O and Z decreases from 2.0 to 1.97 - 1.96, and the free zirconium evidently forms a solid solution with zirconium dioxide. This change in stoichiometry in no way affects the refractory properties of ZrO\(_2\) ceramics. The temperature of the start of deformation under load of such a ZrO\(_2\) sample, preliminarily heated in a vacuum to 2300°C, is not different from the temperature of softening of ordinary ceramics from zirconium dioxide. The process of vaporization of stabilized ZrO\(_2\) is rather complex and is evidently connected with joint vaporization of the stabilizer and the zirconium dioxide itself.

The investigation of 3Al\(_2\)O\(_3\)·2SiO\(_2\) at 1700 – 1900°C has established a comparatively low rate of vaporization. However, at 1800 – 1900°C the rate of vaporization of mullite is somewhat higher than that of alumina. The vaporization of mullite is evidently connected with partial disassociation into elements and volatilization of SiO and Al\(_2\)O\(_3\) [1, 5]. The rate of vaporization of spinel in a vacuum at all
temperatures is approximately one order less than the rate of vaporization of pure magnesium oxide.

The rate of vaporization of oxide ceramics is less in helium than in a vacuum (Table 2).

Table 2. Rates of Vaporization of Oxide Ceramics in a Vacuum and in Helium at Different Temperatures, g/cm²·min

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Temperature, °C</th>
<th>1000</th>
<th>2200</th>
<th>2300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In vacuum</td>
<td>In helium</td>
<td>In vacuum</td>
<td>In helium</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.75·10⁻⁴</td>
<td>1.45·10⁻⁴</td>
<td>1.5·10⁻⁴</td>
<td>1.2·10⁻⁴</td>
</tr>
<tr>
<td>MgO</td>
<td>1.9·10⁻⁴</td>
<td>1.5·10⁻⁴</td>
<td>1.7·10⁻⁴</td>
<td>1.4·10⁻⁴</td>
</tr>
<tr>
<td>MgO·Al₂O₃</td>
<td>1.9·10⁻⁴</td>
<td>1.5·10⁻⁴</td>
<td>1.7·10⁻⁴</td>
<td>1.4·10⁻⁴</td>
</tr>
<tr>
<td>ZrO₂·CaO</td>
<td>1.4·10⁻⁴</td>
<td>1.1·10⁻⁴</td>
<td>1.6·10⁻⁴</td>
<td>1.3·10⁻⁴</td>
</tr>
<tr>
<td>ZrO₂·MgO</td>
<td>1.4·10⁻⁴</td>
<td>1.1·10⁻⁴</td>
<td>1.6·10⁻⁴</td>
<td>1.3·10⁻⁴</td>
</tr>
</tbody>
</table>

Figure 4 shows the rate of vaporization of MgO and MgO·Al₂O₃ depending upon the duration of heating at 2000 °C.

The vaporization of ceramics from pure magnesium oxide at 2000 °C is a whole order less in helium than in a vacuum. As the temperature is increased the rate of vaporization increases, but significantly less than in a vacuum at the same temperature gradient. The rate of vaporization of spinel at 2000 °C is approximately three times less. The rate of vaporization ZrO₂ stabilized with MgO and CaO, as that of BeO, is low even at 2300 °C: the weight losses of samples are about 1% in an hour.

During vaporization of MgO and MgO·Al₂O₃ ceramics in helium the products of vaporization condense on the cold portions in the form of thread-like crystals of magnesium oxide and spinel.

Thus, in a vacuum and in helium at all temperatures pure magnesium oxide ceramics vaporized most of all. However, in practice in many case for the production of articles we use MgO with additions of alumina, which particularly increases the thermal stability of ceramics.
An investigation of the vaporization of such samples in a vacuum and in helium at 2000°C showed that additions of alumina, even in comparatively small quantities (4 and 8%), significantly decreased vaporization. The addition of 4% of alumina in MgO decreased the rate of vaporization in a vacuum by more than two times (Table 3). Increasing the quantity of Al₂O₃ to 8% did not give a significant effect. In helium the rate of vaporization of samples with additions of Al₂O₃ is 25 - 30% less than that of pure magnesium oxide. The large difference in the effects of additions on vaporization in helium and in a vacuum is evidently explained by the character of processes of vaporization of magnesium oxide in these conditions.

Fig. 4. Rate of vaporization:
a) in a vacuum; b) in helium;
1) MgO; 2) MgO·Al₂O₃
Specific gravity and porosity change in the process of vaporization of samples of certain oxides (Table 4). Of all the tested oxides open porosity was revealed after tests at high temperatures only in samples of MgO and BeO. This indicates that vaporization in a vacuum occurs not only from the surface, as in helium, but additionally from within the sample. The specific gravity of samples of other oxides increased somewhat, which is evidently connected with some additional sintering at higher temperatures than during their first kilning. In helium closed porosity was retained by all samples and their specific gravity increased somewhat. Samples of MgO and MgO·Al₂O₃ were glazed after tests in helium.
Preliminary investigations of the vaporization of ceramics from oxides with total porosity of 50 - 70% have shown that samples from \( \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{BeO} \) and \( \text{MgO} \), prepared by burning out additions and by the foam method, vaporized in a vacuum approximately 1.5 - 2 times more by weight than dense samples of the corresponding oxides.

In our investigation of vaporization we weighed the samples on a tungsten or molybdenum wire 0.2 mm in diameter, which allowed us to establish the character of their interaction at high temperatures. In a vacuum and in helium we observed no interaction on the contact of the hanger from W and Mo with samples of \( \text{Al}_2\text{O}_3, \text{MgO}, \text{Al}_2\text{O}_3 \) up to 2000°C, from mullite up to 1900°C, from BeO and specially pure, stabilized \( \text{ZrO}_2 \) up to 2300°C. Interaction of tungsten and molybdenum with magnesium oxide was noted at temperatures above 1800°C, when its intenses vaporizations started. The greatest interaction of W and Mo occured with calcium oxide. In connection with this we should note the peculiarity of the behavior of CaO in a vacuum and in helium at high temperatures. Calcium oxide evidently absorbs the tungsten vaporized from the heater from the gaseous phase very intensely. In a vacuum a sample increased in weight by approximately \( \frac{x}{x} \) from 1200 to 2000°C. At 2000°C a sample usually breaks due to the very intensive reaction at the contact with a W or Mo hanger. All CaO samples became black after testing. The measures taken to protect the sample from deposition of tungsten did not give a positive result. The same thing also occured in helium.

The applied method investigation is essentially the method of vaporization from an open surface in a Langmuir vacuum. Proceeding from this and knowing the products of a gaseous phase, from the rate of vaporization we can calculate the vapor pressure of the
corresponding materials according to the formula [6]:

\[ G = \alpha P \sqrt{\frac{M}{2\pi RT}} \]

where \( G \) is the rate of vaporization, \( g/cm^2\cdot sec \); \( P \) is the vapor pressure, dyne/cm\(^2\); \( \alpha \) is the coefficient of accommodation; \( M \) is the molecular weight of the vapor; \( R \) is the gas constant, erg/deg·mole; \( T \) is the absolute temperature, °K.

In our investigation we did not determine the composition of the gaseous phase during vaporization; the literature contains very contradictory data about its composition above the vaporizing oxides at high temperatures. Therefore, in most cases it was not possible to calculate vapor pressure and compare it with the literature data without determining the composition of the gaseous phase in the specific conditions of our task. Let us give the results of calculating the vapor pressure of BeO during vaporization of beryllium ceramics according to our tests at 2000°C proceeding from the assumption that molecules of beryllium oxide are vaporizing:

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature, °C</th>
<th>Vapor pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our tests</td>
<td>2000</td>
<td>8.15 \times 10^{-9}</td>
</tr>
<tr>
<td>[3]</td>
<td>2000</td>
<td>8.30 \times 10^{-9}</td>
</tr>
<tr>
<td>[3]</td>
<td>1969</td>
<td>7.50 \times 10^{-9}</td>
</tr>
</tbody>
</table>

Conclusions

The developed method of investigating vaporization allowed us to study the behavior of widely applied oxide ceramics at temperatures up to 2300°C in a vacuum and in helium.

At such temperatures all oxides vaporize, but in different manners depending upon their nature and the test conditions. One should look for the causes of the different vaporization of oxides...
in the crystalline structure of the substance itself, because vaporization depends on the type of crystalline grid and its energy and, consequently, is determined by the strength of the bond between atoms or ions of the substance.

REFERENCES


