THEORETICAL ANALYSIS OF FORMATION OF DEFECTS IN HAFNIA

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Hafnia is very attractive due to its superhigh melting temperature of \((3193 \pm 20) \text{ K}\) and a high chemical resistance to acids and alkalis. Its high radiation resistance and capacity to withstand high temperatures (up to 2100 K) without polymorphic transformation are of great interest. Two modifications of \(\text{HfO}_2\) are known, namely, monoclinic and tetragonal or, respectively, low-temperature and high-temperature [1, 2]. An admixture of \(\text{ZrO}_2\) decreases the temperature of the phase transformation [2].

Additives of some elements of the second and third groups in an amount of \(10^{-3} - 30\) mol.% stabilize the cubic phase of hafnia and widen the range of its use to a temperature of about 3000 K. Such solid solutions with ionic conduction are used in systems of high-temperature fuel elements and in high-temperature pick-ups for determination of the presence and amount of oxygen in metal and alloy melts. Much attention is devoted to hafnia in fields where chemical resistance at especially high temperatures is required, for example, in fabrication of crucibles for melting some metals and alloys or electrodes for open-cycle MHD generators.

Published data on the properties of \(\text{HfO}_2\) determined by defects are quite scarce [3], although the special features of technical use and the variation of the properties of hafnia, especially at high temperatures, are caused by its structural defects.

Study of the nature of ionic conduction of \(\text{HfO}_2 - \text{Y}_2\text{O}_3\) solid solutions and the x-ray and pycnometric density shows that vacancies in the anion sublattice of impurity origin predominate in stabilized cubic hafnia [4, 5].

In addition, vacancies can be introduced into the anion sublattice in annealing of powder at a temperature of 2200 K and a low partial pressure of oxygen. An increase in the temperature of the tetragonal-monoclinic transformation by 250 K indicates the appearance of oxygen vacancies in the system. The authors of [6] studied the dependence of the electrical conductivity (direct current) on the pressure of oxygen in the range of \(1 - 10^{-8}\) atm \((10^2 - 10^{-3}\) Pa\) in the range of 1100 - 1600 K and showed that at an oxygen pressure of \(10^{-3}\) atm \((10^2\) Pa\) \(\sigma \sim P_{\text{O}_2}^{1/6}\). The latter is assumed to indicate the presence of a doubly ionized oxygen vacancy \(\left[V\text{O}^{+}\right]\). The authors of [6] also pointed out that the electrical conductivity does not depend on the oxygen pressure in the range of \(10^{-6} - 10^{-8}\) atm \((10^{-1} - 10^{-3}\) Pa\).

\(\text{HfO}_2\) polycrystals were studied in more detail in [7] in the range of 1300 - 1800 K. Here the authors determined dependences of the electrical conductivity on the temperature, the sign of the differential thermo-e.m.f., and the change in the mass as a function of the oxygen pressure. At oxygen pressures ranging from 1 to \(10^{-4}\) atm \((10^5 - 10^1\) Pa\) \(\sigma \sim P_{\text{O}_2}^{-1/4}\), and at \(10^{-4} - 10^{-8}\) atm \((10 - 10^{-3}\) Pa\) the dependence assumes the form \(\sigma \sim P_{\text{O}_2}^{+1/5}\). Here the thermo-e.m.f. remains positive, and the change in the mass obeys the dependence \(\Delta m \sim P_{\text{O}_2}^{-1/5}\) for the entire studied pressure range. An analysis of the results allowed the authors...
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...to conclude that the cation sublattice is characterized by some disorder, namely, there are hafnium vacancies ionized to the maximum degree \([V_{Hf}'']\).

However, Kofstad [3] rejects this interpretation on the basis of data obtained for \(\text{ZrO}_2, \text{Ta}_2\text{O}_5\), etc. and assumes that \(\text{HfO}_2\) is an oxide with a deficit of oxygen with a predominance of anion vacancies in the structure. With a high stability for \(\text{HfO}_2\) and a correspondingly high enthalpy of formation of point defects their natural concentration at pressures close to atmospheric should be low and should depend on the content of impurities. However, Kofstad stresses that the validity of the suggested model should be checked experimentally.

We see that the presented data are contradictory and scarce and do not inform researchers on all the possible kinds of defects and their number densities. Therefore, we thought it expedient to obtain data on the kind and number density of point defects in oxides in general and in hafnia in particular.

We analyzed the processes of defect formation in \(\text{HfO}_2\) in connection with the fact that this information is far from complete for oxides and in particular for \(\text{HfO}_2\). We made such an analysis for \(\text{ZrO}_2\) in [8]. The presented results of an analysis of the literature allow us to call the absence of an exhaustive theoretical analysis of the processes of defect formation the main cause of this situation, because there is no single opinion on the predominant kind of defects [3]. This is connected with the high valence of the cation in \(\text{HfO}_2\) and, as a consequence, with five probable degrees of ionization of vacancies or interstices of the cation, as well as with the presence of polymorphic modifications of \(\text{HfO}_2\) known at the present time.

We based our theoretical analysis on the previously employed [8, 9] method of quasichemical approximation, in which all the kinds of defects formed in a crystal are identified with the chemical components that participate in the chemical reactions. Similar approaches have been developed in [10, 11]. We proceeded from the assumption that if a crystal is in equilibrium with the ambient in correspondence with the reaction

\[
\text{MO}_{a/b} \pm \frac{x}{2} \text{O}_2 \rightarrow \text{MO}_{a/b}(x \pm y),
\]

the processes of defect formation can be described by ordinary chemical reactions.

It follows from the theoretical concepts developed that four basic kinds of defects of nonstoichiometric origin are equiprobable for any oxide, namely, \(V_o, V_m\) (vacancies in the oxygen and metallic sublattices) and \(O_i, M_i\) (interstitial positions of oxygen and the metal). Therefore, the problem of choosing the predominant kind of defect with the help of one or several experimental methods cannot be solved without an appropriate theoretical analysis of all possible kinds of defects.

Within the framework of the present work we suggest theoretical prerequisites for determination of the kind and number density of point defects that appear in \(\text{HfO}_2\) as a result of deviation of its composition from stoichiometric. Using quasichemical concepts, we derived phenomenological equations describing the processes of disordering in the electron and ion subsystems. The dependence of the concentration of point defects of nonstoichiometric origin on the partial pressure of oxygen for each kind of defect was obtained by the suggested method by solving systems of equations.

We considered equilibria between \(\text{HfO}_2\) and the ambient at high temperatures and associated a change in the composition with the process of disordering in the anion and cation sublattices in accordance with the Schottky, Frenkel, and anti-Frenkel representations. We also considered the processes of formation of defects in the electron subsystem. The adopted model considers the behavior of \(\text{HfO}_2\) at high temperatures under equilibrium conditions. Therefore, the chemical processes can be described by equilibrium constants of the appropriate form.

Table 1 presents a quasichemical and mathematical description of the process of disordering in \(\text{HfO}_2\) by the Schottky mechanism. The mechanism of formation of defects in \(\text{HfO}_2\) according to Schottky is described by nine quasichemical equations with ten unknowns, and hence the presented system of equations should be supplemented by one more equation chosen from the conditions of electroneutrality. After this the system of quasichemical equations can be transformed into an algebraic system whose tenth equation has the form

\[
\prod_{i=1}^{n} x_j a_j p_{O_2}^{z_j/m} = \beta_{ij}, \quad j = 1, \ldots, n,
\]

where \(x_j\) is the number density of defects of the electron charges, \(a_j\) are known rational coefficients, \(p_{O_2}\) is the partial pressure of oxygen, and \(\beta_{ij}\) is an equilibrium constant. Linearization of these equations and use of the Gauss method for solving a system of the linear equations allowed us to describe the number densities of electrons, holes, vacancies, and interstices in \(\text{HfO}_2\) in terms of available constants and the partial pressure of oxygen.

Theoretically, \(\text{HfO}_2\) can bear all kinds of defects and any mechanism of defect formation, namely, Schottky (oxygen vacancies and cation vacancies \(V_O, V_m\)), Frenkel (hafnium ions \(Hf^+\) with different degrees of ionization predominate in the interstices), and anti-Frenkel (the anion \(O_i\) predominates in the interstices).

However, for an individual pure oxide and given \(p_{O_2}\) and \(T\) one kind of defect of nonstoichiometric origin is predominant, as a rule, and its number density is a function of the temperature and the partial pressure of oxygen. Having found the form of this dependence experimentally, we will be