



Original articles

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The conditions for the solid state synthesis of solid solutions in zirconia and hafnia systems with the oxides of rare earth elements

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Abstract

The goal of this work was to study the specific features of obtaining $(\text{Zr,Hf})_{1-x}\text{R}_x\text{O}_{2-0.5x}$ solid solutions through solid-phase sintering and to analyse the correctness of the existing variants of phase diagrams for $(\text{Zr, Hf})\text{O}_2\text{-R}_2\text{O}_3$ zirconia and hafnia systems with the oxides of rare earth elements.

We analysed the existing data on the duration of annealing used to study phase equilibria in zirconia and hafnia systems with the oxides of rare earth elements. The “annealing time logarithm – reciprocal temperature” dependences were constructed. It was shown that the effective diffusion coefficient upon annealing was at least 200 kJ/mol. The time of annealing required for the achievement of equilibrium at 1300 °C was no less than 6 months. The annealings for one year did not allow receiving reliable information on phase equilibria in these systems with temperatures lower than 1250 °C. All the data on phase diagrams presented in earlier studies for lower temperatures did not characterise the equilibrium state of systems. Apart from low-temperature phases of variable compositions presented in phase diagrams, among the characteristics of non-equilibrium states there were violations of the Hume–Rothery rule and observations of diffusionless processes of ordering of solid solutions, including those occurring upon “fluorite-pyrochlore” solid state transitions. Probable schemes of low temperature phase equilibria in the $\text{ZrO}_2\text{-Er}_2\text{O}_3$ and $\text{HfO}_2\text{-Eu}_2\text{O}_3$ systems were presented taking into account the third law of thermodynamics.

The obtained results are fundamental and will be useful for the assessment of the stability of thermal barrier coatings and fuel cells based on zirconium and hafnium oxides with the oxides of rare earth elements.

Keywords: Zirconia, Hafnia, Zirconium oxide, Hafnium oxide, Oxides of rare earth elements, Solid solutions, Ordering, Phase diagrams, Sintering

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1. Introduction

Solid solutions of R_2O_3 rare earth elements oxides in high-temperature cubic modifications of zirconium and hafnium dioxides with a general formula of $(Zr,Hf)_{1-x}R_xO_{2-0.5x}$ are among the most refractory oxides with a melting temperature of over 2700 °C [1, 2]. The materials based on them are widely used as crystals for jewellery (fianites) [3, 4] as well as refractory and corrosion resistant ceramics [5–9]. The high anionic conductivity of these solid solutions is combined with low thermal conductivity [10]. These conditions allow using the corresponding materials in electrochemical devices (fuel cells and oxygen sensors) [11–13] and as thermal barrier coatings [14, 15]. In both areas the materials are used as films and require continuous work with increased temperatures (up to 30,000 hours at 800 °C and higher).

Cubic solid solutions of $(Zr,Hf)_{1-x}R_xO_{2-0.5x}$ are obviously thermodynamically unstable at low temperatures. However, negligibly small coefficients of cation diffusion [16] prevent the decomposition of solid solutions, which makes the corresponding materials stable for an indefinitely long period of time at ambient temperatures. Still, what happens with an increase of temperature up to 800–1000 °C has been studied insufficiently [17].

To present the final scenario of the expected evolutions of the material based on zirconium and hafnium oxides stabilised by the oxides of rare earth elements upon a prolonged exposure to increased temperatures, it is advisable to know the phase T-x diagrams of the corresponding systems. Enormous efforts were needed to construct such phase diagrams (see, for instance, [18–35]), but the results of these studies cannot be considered satisfactory.

The main issues were associated with the achievement of equilibrium in the corresponding systems as the time required for the achievement of equilibrium increased exponentially with a decrease in temperature [36, 37]. The researchers from Tokyo Institute of Technology (M. Yashima, N. Ishizaawa, M. Yoshimura, etc.) showed that in some works the annealing was insufficient [25, 33]. In particular, it turned out that the temperature of the eutectoid decomposition

of the solid solution based on the medium temperature tetragonal modification in the ZrO_2 – Er_2O_3 system identified in [30] was understated by approximately 500 °C [25].

The systems ZrO_2 – R_2O_3 were studied by different groups of researchers. The reports were presented in [18, 19]. The results obtained for various rare earth elements did not correspond well with one another. There is an array of data for the systems HfO_2 – R_2O_3 which were obtained in the Materials Science Institute (Kyiv, L. M. Lopato, A. V. Shevchenko, E. R. Andrievskaya, etc.) in the course of studies conducted in accordance with one method, and the plotted phase diagrams showed natural changes for the motion along rare earth elements [18, 19].

The goal of this work was to study the specific features of obtaining $(Zr,Hf)_{1-x}R_xO_{2-0.5x}$ solid solutions through solid-phase sintering and to analyse the correctness of the existing variants of phase diagrams for the $(Zr, Hf)O_2$ – R_2O_3 systems.

2. Analysis methodology

As we showed before [36], there is a linear dependence of the annealing time logarithm (τ) on the reciprocal temperature upon the achievement of equilibrium during sintering. Indeed, Fick's diffusion equation shows that

$$X^2 \sim D\tau \quad (1)$$

where X is the thickness of the diffusion layer, D is the effective diffusion coefficient, and τ is time. In its turn, the diffusion coefficient exponentially depends on temperature

$$D = D_0 \exp(-E/kT), \quad (2)$$

where E is the diffusion activation energy, T is the absolute temperature, k is the Boltzmann constant. Therefore, the following linear dependence is valid in case of the same dispersion of the sintered particles

$$1/\tau = A \exp(-E/kT), \quad (3)$$

where A is a constant, and from the tangent of the slope of the line in coordinates $\lg \tau \sim 1/T$ it is possible to determine the activation energy of the limiting stage of the sintering process:

$$E = 206 \operatorname{tg} \alpha [\text{k}/\text{mol}] = 1.99 \operatorname{tg} \alpha [\text{eV}]. \quad (4)$$

3. Results and discussion

Fig. 1 presents some previous data on the thermal processing modes used for the study of phase equilibria in zirconia and hafnia with the oxides of rare earth elements. It supplements the information that was earlier presented graphically in [36, 37]. The data on the systems with zirconia and hafnia are seldom studied together, which corresponds to the first stage of the analysis.

Fig. 1 shows that there is a great scatter of data. It is obvious that in many works the duration of synthesis was insufficient. The use of the following protocol seemed quite reasonable: 10 hours at 1900 °C, 30–60 hours at 1600 °C, 1200 hours at 1300 °C. Pascual and Duran [20] annealed the samples for 3 hours at 2000 °C, for 10 hours at 1800 °C, and for 385 hours at 1450 °C, which seems acceptable. However, the 8 months of annealing at 800 °C used in this work were definitely insufficient. Apparently Yashima et al. [25] achieved the most correct results. They annealed the samples in the $ZrO_2-Er_2O_3$ system at 1690 °C for 48 hours and 8 months at 1315 °C. A linear dependence plotted in accordance with these data (angle α_1 on Fig.1) corresponded to the diffusion activation energy $E = 360$ kJ/mol, which reasonably corresponded to the value of 391 kJ/mol obtained in [16] for bulk interdiffusion of cations within the range of 1584–2116 °C. Other variants of the approximation relationships presented such values as $E = 260$ kJ/mol (angle α_2 on Fig. 1) and $E = 200$ kJ/mol (angle α_3 on Fig.1). These values are closer to the values obtained by Glushkova and her colleagues [23, 38].

It can be seen that with a decrease in the temperature, the required duration of the experiments quickly exceeded laboratory capabilities and reached the time of about a year at 1250 °C. Since all real laboratory experiments described in previous works did not exceed the duration of 8 months, the results obtained for temperatures below 1300 °C cannot be considered as those associated with the state of equilibrium. It is also true for many published variants of phase diagrams. However, the inverse proposition is wrong: not all research results associated with high temperatures can be considered as equilibrium.

The violations of the third law of thermodynamics are among the indications of

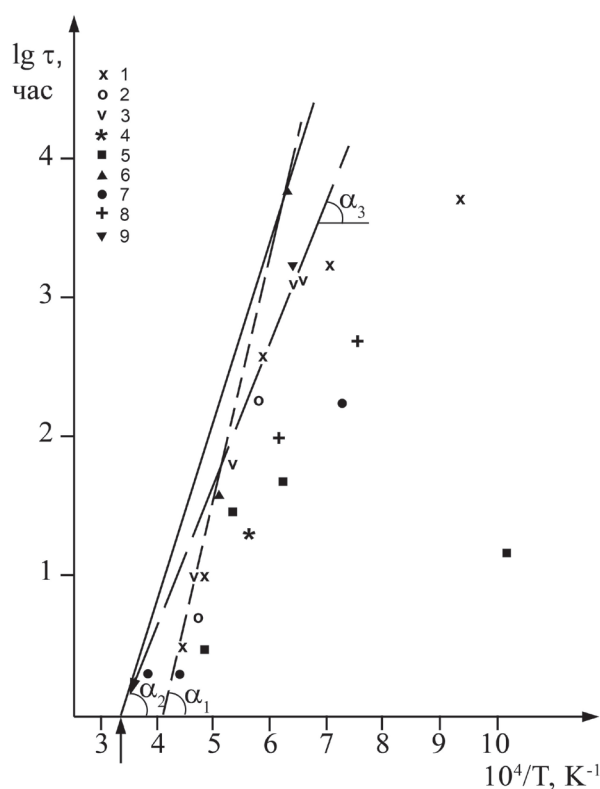


Fig. 1. The duration of annealing for the synthesis of samples in systems $(Zr, Hf)O_2-R_2O_3$ depending on the reciprocal synthesis temperature according to 1 – Pascual, Duran, 1983 [20]; 2 – Scott, 1978 [21]; 3 – Meister et al., 1991 [22]; 4 – Krzhizhanovskaya, 1990 [23]; 5 – Schedecker e.a., 1977 [24]; 6 – Yashima e.a., 1991 [25]; 7 – Ruh e.a., 1977 [26]; 8 – Thornber, e.a., 1970 [27]; 9 – Stubican e.a., 1984 [28]. The arrow shows the melting point of zirconium dioxide

thermodynamic incorrectness of the plotted phase diagrams. According to the consequence of this law, when the temperature tends to absolute zero, all phases of variable compositions in quasi-equilibrium processes disappear through decomposition or contraction of compositions to those stoichiometric [37]. The second important thermodynamic condition is the so-called Hume-Rothery rule, according to which the region of existence of a disordered phase sharply narrows when an ordered phase with a narrow region of homogeneity appears [39]. This rule is regularly violated when a solid phase ordering of heterovalent fluorite solid solution with phase separation of the pyrochlore structure is shown in the $(Zr, Hf)O_2-R_2O_3$ systems [18, 19].

The use of the correction method for phase diagrams with extrapolation of phase equilibria to

absolute zero seems promising for the $(\text{Zr, Hf})\text{O}_2\text{-Er}_2\text{O}_3$ systems. This method has been successfully applied in a number of binary systems in our works [40–42].

Fig. 2 shows corrections in the data on phase equilibria in the $\text{ZrO}_2\text{-Er}_2\text{O}_3$ system while Fig. 3 shows corrections in the $\text{HfO}_2\text{-Eu}_2\text{O}_3$ system [18]. The $\text{ZrO}_2\text{-Er}_2\text{O}_3$ system is among the most well-studied systems of this group with the duration of annealing up to 8 months [25, 31]. The basis (Fig. 2a) was the diagram plotted in [31]. The region of low concentrations of erbium oxide was corrected according to the data from [25] (the temperature of the eutectoid decomposition of the tetragonal phase was increased by approximately 500 °C). Accordingly, the temperature of the eutectoid decomposition of the cubic solid solution, with account of the data from [25], was presumably targeted at 600 ± 100 °C. The thin dashed line indicates a metastable extension of the curve of the maximum concentration of this solid solution (the solvus curve). This curve must pass through the origin of the coordinates and have a vertical tangent at this point. This condition can be fulfilled only if there is a point

of inflexion on the solvus curve (in this case, on the metastable part of this curve). Such inflexion points are typical for all heterovalent solid solutions based on compounds with the fluorite structure [43], which is associated with diffuse phase transitions in fluorite matrices [44]. In the region of high concentrations of erbium oxide, the correction has a significant effect on the decrease in the homogeneity region of the ordered phase, which must shrink to its ideal composition $\text{Er}_6\text{ZrO}_{11}$ when the temperature decreases. It also affects the position of the decomposition curve of a solid solution based on the cubic modification of erbium oxide, which must come to the point of the pure component at $T = 0$ K.

The correction of the phase diagram in the $\text{HfO}_2\text{-Eu}_2\text{O}_3$ system (Fig. 3) in the region of ordering of the fluorite solid solution with the release of a pyrochlore-type phase was conducted in accordance with the third law of thermodynamics (the homogeneity region of the pyrochlore phase contracted to the stoichiometric composition, two-phase “fluorite + pyrochlore” regions expanded with a decrease in temperature, and two eutectoid equilibria limiting the region

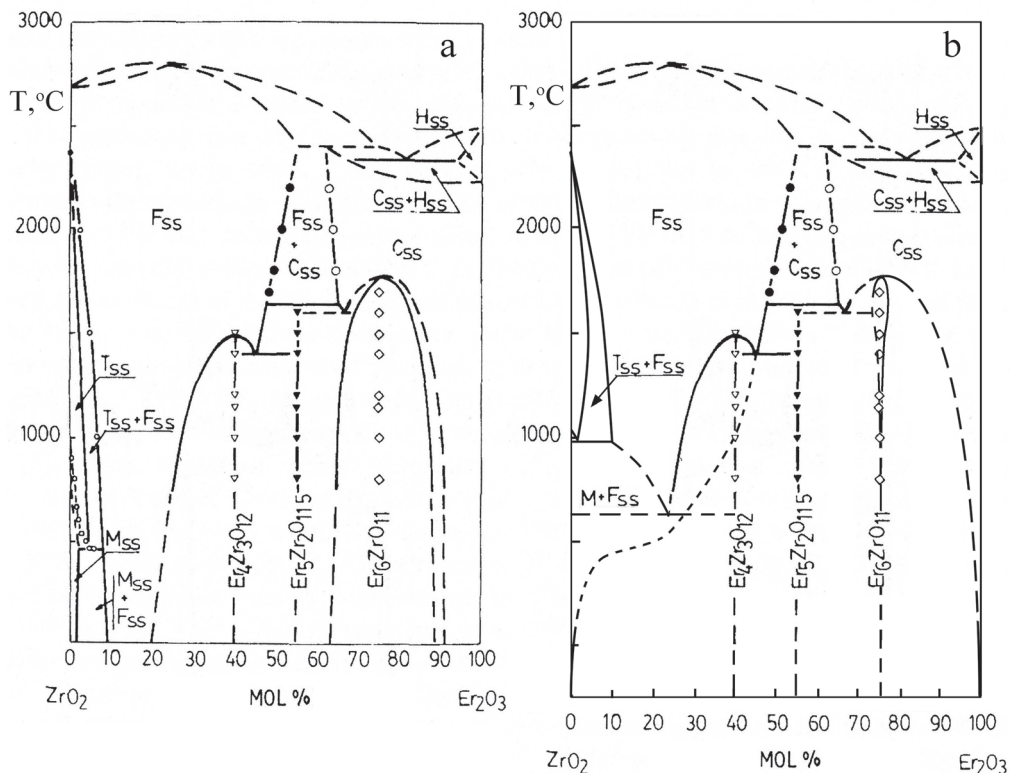


Fig. 2. Phase diagram of the $\text{ZrO}_2\text{-Er}_2\text{O}_3$ system according to [31] (a) and its correction with account of the requirements of the third law of thermodynamics (b)

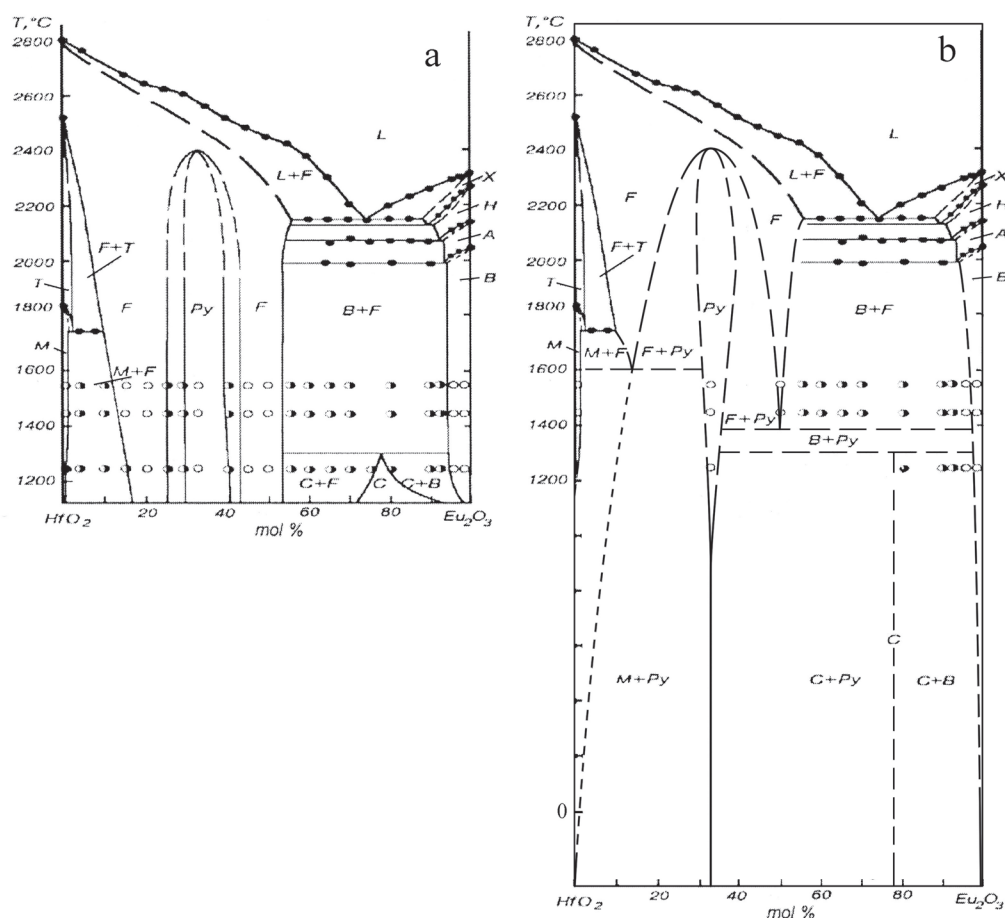


Fig. 3. Phase diagram of the $\text{HfO}_2\text{-Eu}_2\text{O}_3$ system according to [18] (a) and its correction with account of the requirements of the third law of thermodynamics (b)

of existence of the fluorite phase from below were implemented). It should also be noted that the region of phase equilibria near europium oxide was plotted in [18] assuming the existence of a low-temperature cubic modification of Eu_2O_3 . This assumption, which is a part of the polymorphism and morphotropy scheme in a row of oxides of rare earth elements plotted in accordance with the data from [45], turned out to be incorrect due to the hydroxyl contamination. A low-temperature cubic phase identified in this system in the region of ~ 75 mol% Er_2O_3 is probably another ordered fluorite-like phase that requires further studying.

4. Conclusions

Phase equilibria at low temperatures in systems with zirconia and hafnia are among the fundamental issues that still need solving. Since the time of achieving equilibrium, controlled by cationic diffusion, increases exponentially with decreasing temperature, the study of low-

temperature equilibria is a very difficult and often insoluble problem. Regions for which the time for establishing equilibrium by means of dry sintering is about 1 year can be considered as being low-temperature regions. For systems based on zirconium and hafnium oxides, this is no lower than 1250°C .

On numerous published $(\text{Zr,Hf})\text{O}_2\text{-R}_2\text{O}_3$ “phase diagrams” at temperatures below 1300°C , frozen states are depicted instead of equilibrium phase regions. The actual behaviour of materials in these systems upon cooling is determined mainly not by equilibrium phase transformations, but by diffusionless phase transitions. Accordingly, in some cases two-phase regions on phase diagrams are reduced, and instead of them we see the martensitic phase transformation lines. This is also true for the processes of “fluorite-pyrochlore” ordering.

It should be noted that the ordering processes in the systems with zirconia and hafnia have

not been studied well, see, for example, [47]. Important discoveries can be made in this area.

Thermodynamic modelling is not always reliable. In particular, the temperature of the eutectoid decomposition of the cubic phase in the ZrO_2 - Y_2O_3 system differed according to the data of different models by hundreds of degrees [48–50], while in [51] it was below absolute zero, which contradicted the third law of thermodynamics.

We need other methods to study low-temperature phase formation in the discussed systems in addition to simple sintering. It is reasonable to use the methods of synthesis involving a liquid phase. The use of hydrothermal synthesis for acceleration of achieving equilibrium allowed obtaining the most reliable data on ZrO_2 - R_2O_3 ($R = Er, Y, Sc$) and ZrO_2 - CeO_2 systems [33, 52, 53]. It can be expected that the use of salt melts will allow making progress in this matter.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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