

## PHYSICOCHEMICAL MATERIALS RESEARCH

### PHASE DIAGRAMS OF REFRACTORY OXIDE SYSTEMS AND MICROSTRUCTURAL DESIGN OF MATERIALS

E. V. Dudnik,<sup>1,2</sup> S. N. Lakiza,<sup>1</sup> Ya. S. Tishchenko,<sup>1</sup> A. K. Ruban,<sup>1</sup>  
V. P. Red'ko,<sup>1</sup> A. V. Shevchenko,\* and L. M. Lopato\*

UDC 541.1:621.762

*It is shown that the phase diagrams of refractory oxide systems based on  $ZrO_2$ ,  $HfO_2$ ,  $Al_2O_3$ , and rare earth oxides underlie the microstructural design of various high-performance materials. Process steps to produce coarse-grained ceramics in the  $HfO_2$ - $ZrO_2$ - $Y_2O_3$ ,  $ZrO_2$ - $Y_2O_3$ - $Sc_2O_3$ ,  $HfO_2$ - $ZrO_2$ - $Sc_2O_3$ ,  $Y_2O_3$ - $Er_2O_3$ ,  $Y_2O_3$ - $ZrO_2$ ,  $Y_2O_3$ - $HfO_2$ ,  $Y_2O_3$ - $Al_2O_3$ ,  $Y_2O_3$ - $SiO_2$ , and  $Y_2O_3$ - $La_2O_3$  systems to perform at temperatures up to 2200°C are designed. Process steps to produce high-performance fine-grained composites in the  $HfO_2$ - $ZrO_2$ - $Y_2O_3$  ( $Ln_2O_3$ ) ( $Ln$ -Dy, Ho, Er, Tm, Yb),  $ZrO_2$ - $Y_2O_3$ - $Sc_2O_3$ ,  $ZrO_2$ - $Y_2O_3$ - $Sc_2O_3$ ,  $Al_2O_3$ - $Zr(Hf)O_2$ - $Ln(Y)_2O_3$  ( $Ln$ -La, Nd, Sm, Gd, Er, Yb), and  $ZrO_2$ - $Y_2O_3$ - $CeO_2$ - $Al_2O_3$  systems are designed as well.*

**Keywords:**  $ZrO_2$ ,  $HfO_2$ ,  $Al_2O_3$ , rare earth oxides, phase diagrams of refractory oxide systems, high-performance materials, mechanical properties.

#### INTRODUCTION

Fundamental research efforts in physical and colloidal chemistry, solid state physics and chemistry, and materials science are aimed at creating composites with unique characteristics to allow their application in harsh and extreme conditions (power, chemical, aerospace, and other industries, mechanical engineering, electronics, and medicine). Zirconium dioxide ( $ZrO_2$ ) and hafnium dioxide ( $HfO_2$ ) possess excellent mechanical characteristics and are among the leading materials for structural, functional, and medical ceramics. These oxides are not used in pure form because they undergo martensitic transformation from tetragonal to monoclinic structure when cooled down after sintering. This transformation causes expansion and destruction of the products. That is why all advances in the materials science of  $ZrO_2$  and  $HfO_2$  are associated with the stabilization of their high-temperature polymorphic modifications to room temperature using oxides of elements in group II (Mg, Ca) and group III (REM) of the

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\*Deceased.

<sup>1</sup>Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, Ukraine.

<sup>2</sup>To whom correspondence should be addressed; e-mail: dudnikelena@ukr.net; dep25@ipms.kiev.ua.

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Translated from Poroshkovaya Metallurgiya, Vol. 53, No. 5-6 (497), pp. 67-78, 2014. Original article submitted January 15, 2014.

Periodic Table. Hence, fundamental data sources on interactions in the systems formed by these oxides and oxides of elements in groups II and III are needed for successful production of materials from completely or partially stabilized  $ZrO_2(HfO_2)$ . Phase diagrams represent these data sources [1].

The phase diagrams of refractory oxide systems determine the meaning and content of the first link in the basic physicochemical analysis chain: composition  $\rightarrow$  structure  $\rightarrow$  particle size  $\rightarrow$  properties [2]. In accordance with the concept of structural engineering [3], reasoned choice of composites, knowledge of basic laws behind phase transitions of starting components with increasing temperature, and selection of optimal process steps allow directional microstructural design of materials with required properties.

The Department for Physics & Chemistry and Technology of Refractory Materials at the Frantsevich Institute for Problems of Materials Science, which was headed by Doctor of Chemical Sciences, Professor Lidiya Lopato, from its establishment in 1983 and up to 27 April 2012, conducts systematic research of phase equilibria in two- and three-component systems formed by Zr, Hf, Al, and REM oxides over a wide range of compositions and temperatures (to 3000°C). More than 70 binary and 50 ternary phase diagrams have been constructed:  $ZrO_2(HfO_2)-Y_2O_3$ ,  $ZrO_2(HfO_2)-Sc_2O_3$ ,  $HfO_2-ZrO_2$ ,  $HfO_2-CeO_2$ ,  $ZrO_2-Al_2O_3$ ,  $HfO_2-Al_2O_3$ ,  $HfO_2-TiO_2$ ,  $ZrO_2-TiO_2$ ,  $HfO_2-Eu_2O_3$ ,  $ZrO_2-Sc_2O_3$ ,  $HfO_2-Sc_2O_3$ ,  $ZrO_2-Y_2O_3-La_2O_3$ ,  $ZrO_2-Y_2O_3-Sc_2O_3$ ,  $HfO_2-Ln_2O_3(Y_2O_3, Sc_2O_3, Pr_2O_3, Nd_2O_3)$ ,  $HfO_2-Sm_2O_3(Gd_2O_3, Tb_2O_3, Dy_2O_3)$ ,  $HfO_2-Y_2O_3(Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3)$ ,  $HfO_2-ZrO_2-Sc_2O_3$ ,  $HfO_2-ZrO_2-Al_2O_3$ ,  $ZrO_2(HfO_2)-Sc_2O_3-Y_2O_3$ ,  $HfO_2-ZrO_2-Y_2O_3$ ,  $HfO_2-ZrO_2-Y_2O_3(Ln_2O_3)$ ,  $ZrO_2-Y_2O_3-Al_2O_3$ ,  $Al_2O_3-ZrO_2-Ln(Y)_2O_3$ ,  $Al_2O_3-ZrO_2(HfO_2)-Y_2O_3$ , and other  $ZrO_2(HfO_2)$  systems. The long-standing creative union of Doctors in Chemical Sciences, L. M. Lopato and A. V. Shevchenko (a unique expert in constructing phase diagrams of high-refractory multicomponent oxide systems, developing high-refractory oxide materials and methods to synthesize nanocrystalline oxide powders, and producing high-performance composites from these powders for various industrial and medical applications) formed the scientific foundation for directional creation of new ceramic materials by the Department.

The materials developed in the systems in question can be divided into two classes: coarse-grained for application at temperatures to 2200°C and fine-grained with improved mechanical characteristics. For successful production of such materials, new technologies are required to design their structure already when the starting powders are obtained.

The objective here is to ascertain that the phase diagrams of refractory oxide systems form the physicochemical basis for designing new materials with desired properties.

**COARSE-GRAINED COMPOSITES IN THE  $HfO_2-ZrO_2-Y_2O_3$ ,  $ZrO_2-Y_2O_3-Sc_2O_3$ ,  
 $HfO_2-ZrO_2-Sc_2O_3$ ,  $Y_2O_3-Er_2O_3$ ,  $Y_2O_3-ZrO_2$ ,  $Y_2O_3-HfO_2$ ,  $Y_2O_3-Al_2O_3$ ,  
 $Y_2O_3-SiO_2$ , AND  $Y_2O_3-La_2O_3$  SYSTEMS**

The high melting points and unique thermomechanical properties of  $ZrO_2$ ,  $HfO_2$ , and  $Y_2O_3$  allow the associated materials to be recommended as refractories for melting and casting of chemically active metals and alloys, special cermet composites for high-temperature vacuum applications, and heat-resistant alloys for ceramic oxide heaters to perform in oxidizing environments up to 2000°C.

The study of phase equilibria in the  $ZrO_2-HfO_2-Y_2O_3$  system showed that cubic solid solutions of fluorite type (F) occupied great primary solidification fields on the liquidus surface and formed wide single-phase regions at 1250–1900°C [4–7]. The regions of these solid solutions become narrower with decreasing temperature; hence, materials with smoothly varying properties can be produced. These materials can be used in a wide temperature range, their phase composition remaining stable. This is essential in the development of cermet composites for vacuum melting of refractory metals and alloys and for production of oxide heating resistors (Fig. 1a). Principles behind the formation of fragmented microstructure and effective surface of cermet composites produced from F-type  $Zr(Hf)O_2$  and tungsten solid solutions were identified to promote high-performance multiuse evaporators for nickel (Fig. 1b), which show high heat resistance and do not interact with the metal melt up to 2000°C. The high-refractory and heat-resistant  $HfO_2-ZrO_2-Y_2O_3-W$  materials can serve as a matrix to be combined with other

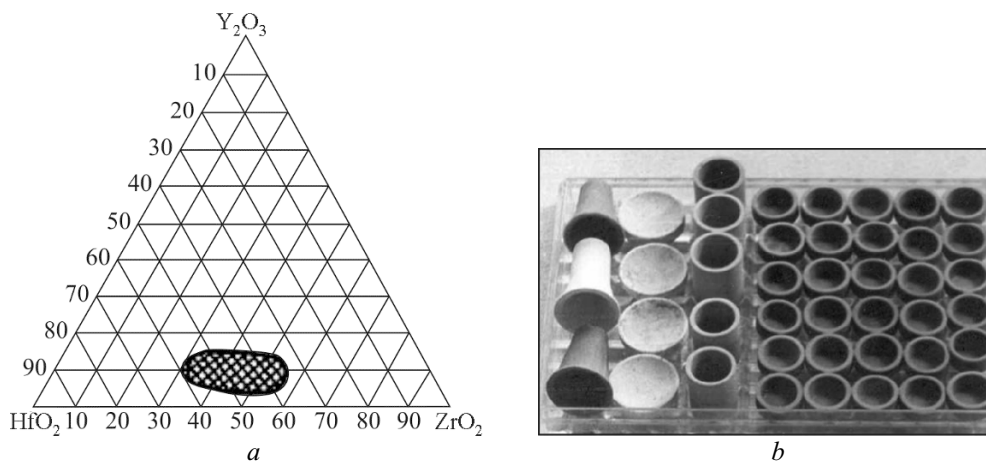


Fig. 1. Region of solid solutions in the  $ZrO_2$ - $HfO_2$ - $Y_2O_3$  phase diagram (a) of compositions promising for high-refractory materials and melting crucibles from these materials (b) [1]

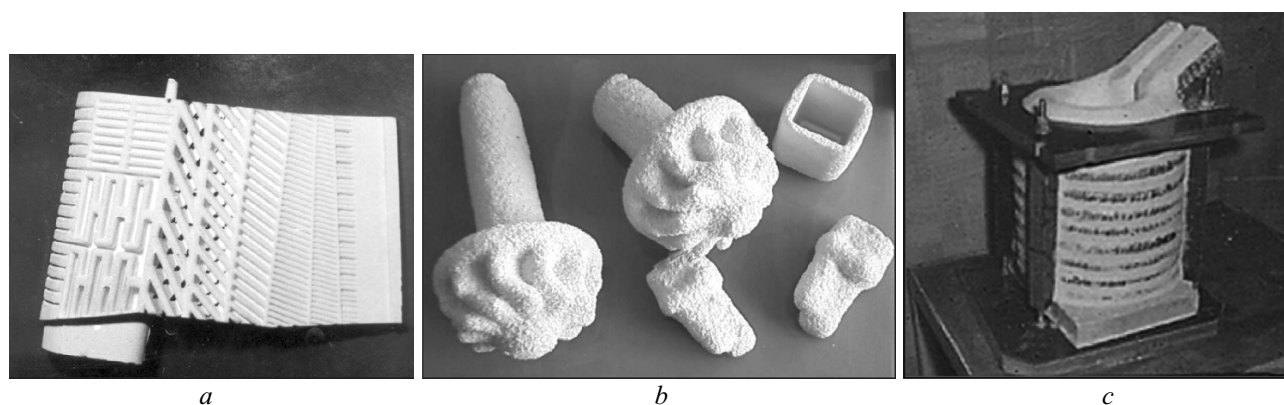


Fig. 2. High-refractory ware: rod and shell ceramics in the  $Y_2O_3$ - $La_2O_3$  (a) and  $Y_2O_3$ - $SiO_2$  and  $Y_2O_3$ - $Al_2O_3$  (b) systems and general view of the melting crucible ( $Y_2O_3$ - $ZrO_2$  and  $Y_2O_3$ - $HfO_2$  materials) (c)

refractory compounds (zirconium, hafnium, and titanium borides and nitrides) for developing new refractory composites in the  $HfO_2$ - $ZrO_2$ - $Y_2O_3$ -W-(Ti, Zr, Hf borides and nitrides) system [1, 4-7].

Materials that perform in contact with refractory metal melts are primarily required to have high heat resistance (above  $2000^\circ C$ ) and thermodynamic stability, show no chemical interaction with the melt, and be produced from available starting materials. Yttrium oxide satisfies these requirements to the greatest extent. The technology of producing high-refractory  $Y_2O_3$  ceramics relies on the data from analysis of binary phase diagrams, both well-known ( $Y_2O_3$ - $Al_2O_3$ ,  $Y_2O_3$ - $SiO_2$ ) [8] and specially examined or refined in the development of refractories ( $Y_2O_3$ - $La_2O_3$  [9],  $Y_2O_3$ - $Er_2O_3$  [10],  $Y_2O_3$ - $ZrO_2$  [11], and  $Y_2O_3$ - $HfO_2$  [12]). Lanthanum, erbium, zirconium, and hafnium oxides, which are the second components in the above systems, were added to  $Y_2O_3$  to adjust process and some other properties (thermal conductivity, thermal expansion coefficient (TEC), strength, sinterability) of refractory materials for the production of ceramic articles. These data were used to develop and test the following high-refractory ware (Fig. 2): rod ceramics in the  $Y_2O_3$ - $La_2O_3$  system [13-16], crucible ceramics in the  $Y_2O_3$ - $ZrO_2$ ,  $Y_2O_3$ - $HfO_2$ , and  $Y_2O_3$ - $Er_2O_3$  systems [17, 18], and shell ceramics in the  $Y_2O_3$ - $SiO_2$  and  $Y_2O_3$ - $Al_2O_3$  systems [19]. The structure, phase composition, and mechanical properties of cast alloys from active metals were analyzed to show that the metal melted in prefabricated crucibles only slightly differed from arc-melted metals in impurity content and plasticity. The combined molds show unique properties, making their application universal in various casting conditions: from equiaxed solidification to directional growth of single-crystalline preforms. The high compliance of combined molds allows alloys characterized by increased volume shrinkage during solidification

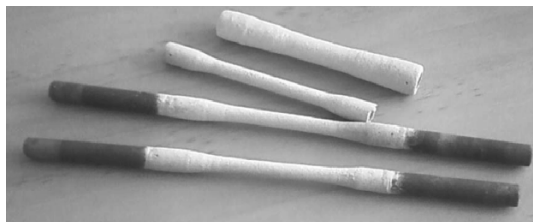


Fig. 3. High-temperature oxide heaters in the  $ZrO_2-Y_2O_3-Sc_2O_3$  and  $HfO_2-ZrO_2-Y_2O_3(Sc_2O_3)$  systems for multiple use in oxidizing environments at temperatures to 2000°C

to be cast. Shell molds have low thermal conductivity and thus can be adequately filled. This is especially important for casting of thin-walled articles (wall thickness to 1 mm). These articles are used for melting and casting of uranium, vanadium, and titanium [1].

The ionic conductivity of cubic solid  $ZrO_2$  ( $HfO_2$ ) solutions, being close to unity, remains in a wide range of oxygen partial pressures and temperatures [20, 21]. The ranges of optimal compositions of materials with high oxygen ion conductivity and low TEC were determined in the ternary  $ZrO_2-Y_2O_3-Sc_2O_3$  and  $HfO_2-ZrO_2-Y_2O_3(Sc_2O_3)$  systems to underlie the development of high-temperature oxide heaters intended for repeated use in oxidizing environments. The heaters are advantageous in that they contain no platinum group metals and can replace lanthanum chromite heaters ( $La(Ca)CrO_3$ ) without redesign of the furnaces (SVK type). Heating resistors (Fig. 3) possess high heat resistance in the range 1300–1700°C [22–25].

**FINE-GRAINED MATERIALS IN THE  $HfO_2-ZrO_2-Y_2O_3(Ln_2O_3)$  (LN—DY, HO, ER, TM, YB),  
 $ZrO_2-Y_2O_3-Sc_2O_3$ ,  $ZrO_2-Y_2O_3-Sc_2O_3$ ,  $Al_2O_3-ZR(HF)O_2-LN(Y)_2O_3$   
(LN—LA, ND, SM, GD, ER, YB), AND  $ZrO_2-Y_2O_3-CEO_2-AL_2O_3$  SYSTEMS**

Modern fine-grained materials represent oxide composites intended to perform different functions and having complex chemical and phase composition.

Unlike conventional ceramics, optically transparent polycrystalline materials show virtually porousless perfect microstructure without a glassy phase; thus, they are exceptionally resistant to corrosive environments. As distinct from most glasses, they possess high refractory and mechanical properties. Optically transparent ceramic material based on C-type  $Y_2O_3$  was produced in the  $HfO_2-ZrO_2-Y_2O_3$  system. It is characterized by high optical transmission in the visible and near-infrared region with wavelength ranging from 0.3 to 8.5  $\mu m$ . Its composition was chosen from the regions close to univariant equilibrium in  $HfO_2-ZrO_2-Y_2O_3$  to produce ceramics with increased transparency in the visible and infrared region [1, 4–7]. There are extensive regions of solid solutions based on C-type  $Ln_2O_3$  ( $HfO_2(ZrO_2)-Ln_2O_3$  systems, where Ln is Gd, Dy, Ho, Er, Tm, Yb, Lu) in more complex systems formed by  $HfO_2(ZrO_2)$  with oxides of yttrium-subgroup lanthanides. The ceramic matrix in these systems is a solid solution of  $HfO_2(ZrO_2)$  in  $Ln_2O_3$ ; this obeys one of the fundamental principles for producing transparent ceramic material—it has to consist of a single phase. These efforts became a peculiar algorithm for making transparent ceramics from C-type solid solutions of yttrium-subgroup lanthanide oxides. Transparent ceramics have been produced (Fig. 4) from C-type pure oxides of lanthanides (Gd, Dy, Ho, Er, Tm, Yb, Lu) and their solid solutions with  $Y_2O_3$  in the  $HfO_2-ZrO_2-Y_2O_3(Ln_2O_3)$  system [1, 26].

Tubular and flat-plate electrolytes have been developed in the  $ZrO_2-Y_2O_3-Sc_2O_3$  system for ‘self-supporting’ fuel cells (Fig. 5). The size of ‘self-supporting’ fuel cell assemblies, with the electrolyte consisting of consecutively connected tubular elements, can be easily varied. The apparent advantage of the flat-plate configuration is that each individual cell and the entire cell stack can be tested (for electrical characteristics, integrity, compliance with geometric dimensions) prior to final assembly [1].

The ternary  $Al_2O_3-ZrO_2(HfO_2)-REM$  oxide systems are of special interest in the development of high-performance materials. Aluminum hardly interacts with zirconium and REM oxides in these systems. We have revealed that the systems have a great number of binary and ternary eutectic points. Directional solidification of



Fig. 4. Transparent ceramics based on C-type pure lanthanide oxides

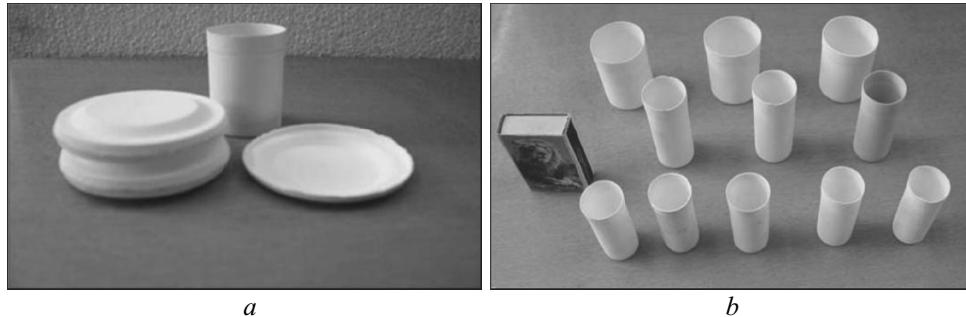


Fig. 5. Flat-plate (a) and tubular (b) electrolytes in the  $ZrO_2$ - $Y_2O_3$ - $Sc_2O_3$  system for ‘self-supporting’ fuel cells

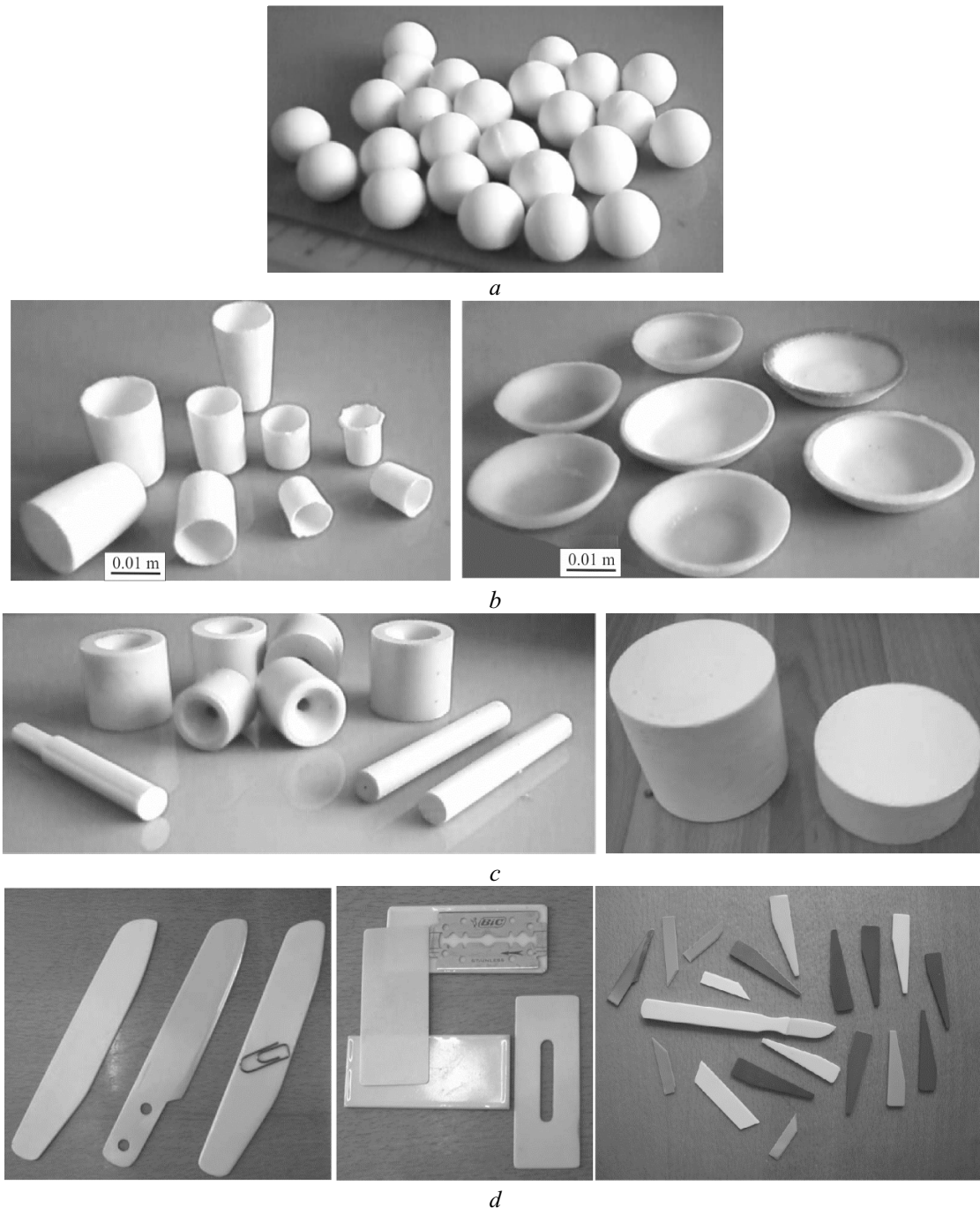
ternary eutectics in  $Al_2O_3$ -rich regions in  $Al_2O_3$ - $Zr(Hf)O_2$ - $Ln(Y)_2O_3$  offers an opportunity to create new high-temperature materials. Directionally solidified eutectics are an example of composites whose properties depend on solidification conditions. They combine the thermodynamic stability and beneficial properties of composites, especially *in situ* ones. Operating temperature of these materials can reach  $1600^\circ C$ . The  $Al_2O_3$ - $Zr(Hf)O_2$ - $Ln(Y)_2O_3$  systems are promising for the development of materials for thermal barrier coatings, solid electrolytes, and refractories [27–31].

Ceramic composites designed to perform at relatively low temperatures are based on various multiphase  $ZrO_2$ - $Y_2O_3$ - $CeO_2$ - $Al_2O_3$  composites. These composites mostly consist of a matrix (T- $ZrO_2$  and M- $ZrO_2$  solid solutions) and fine  $\alpha$ - $Al_2O_3$  particles. Their properties in this system are determined by the properties of materials in the bounding binary and ternary systems. The four-component  $ZrO_2$ - $Y_2O_3$ - $CeO_2$ - $Al_2O_3$  phase diagram is still to be constructed, but the phase diagrams of the bounding binary and ternary systems are available. Our analysis of the available phase diagrams shows that aluminum oxide hardly dissolves in  $ZrO_2$  solid solutions in these systems; i.e., the four-component system can be regarded as a two-component one:  $ZrO_2$ - $Al_2O_3$ -based solid solution.

For microstructural design of high-performance materials in this system, transformation hardening should be employed to the extent possible because it is one of the main mechanisms of improving the strength of  $ZrO_2$ -based ceramics. This is promoted by a well-reasoned choice of both the starting nanocrystalline powders and the methods of their consolidation to promote optimum microstructure of the composites [32].

In developing  $ZrO_2$  materials, it is very important to retain metastable T- $ZrO_2$ , tending to transformation under applied load. This can occur even if the following basic requirements are met:

- the starting powders for synthesis are optimally doped with insoluble additions, being homogeneously distributed in  $ZrO_2$ ;
- samples (not necessarily of high density) with ‘regular’ unstrained microstructure, with evenly distributed pores over volume, are produced by compaction, the size of these pores is to be commensurable with those of starting powder particles;
- heat treatment conditions are selected so that the compacts are sintered in a narrow temperature range, commonly at temperatures not higher than  $1200$ – $1300^\circ C$ , to limit abnormal grain growth, promote the diffusion of doping additions and admixtures to their boundaries, and form ‘pure’ grain boundaries with low concentration of potential defects (silicate films, gas inclusions, cracks, etc.).



*Fig. 6.* Articles from nanocrystalline powders in the  $ZrO_2-Y_2O_3-CeO_2-Al_2O_3$  system: grinding balls for mills (*a*); crucibles for physicochemical research (*b*); rolls and bushings (*c*); targets for deposition of thermal barrier coatings (*d*); cutting tools for various applications (*e*)

If these conditions are satisfied, materials with minimum possible residual stresses, causing defects during operation, are produced [33].

The properties of powders are determined by the method of their production. There is no universal method of making starting nanocrystalline powders. Soft chemical methods have been widely applied to produce oxide powders; they involve the synthesis of nanostructures from aqueous salt solutions at 200–300°C. We have developed several options of hydrothermal synthesis, combining advantages of coprecipitation, sol–gel technology, and hydrothermal treatment [1, 32].

The microspherical morphology of starting nanocrystalline powders of complex composition and rounded 'soft' agglomerates of primary particles allow the production of homogeneous materials for different applications when certain molding and sintering operations are employed (Fig. 6).

The use of different approaches in microstructural design of materials leads to composites of different types.

Heterogeneous microstructure leads to self-reinforced and multilayer (laminar) materials. The  $ZrO_2$  solid-solution matrix is self-reinforced when nonisometric plate-like  $Al_2O_3$  grains form within it. The material is characterized by plastic fracture. It is reinforced through transformation hardening and crack deviation/branching, improving its strength. Microstructural design of multilayer materials is aimed at promoting uniform microstructure of individual layers and tight connection between them. These are heterophase materials with high concentration of interfaces, characterized by nonlinear three-dimensional distribution of composition and properties. These composites are hardened through a combined action of various mechanisms peculiar to  $ZrO_2$  materials. The microstructural design of fine-grained materials is intended to create regular microstructure.

Materials in the  $ZrO_2$ - $Y_2O_3$ - $CeO_2$  system exhibit increased resistance to ageing in the environment of a living organism. The composites with different microstructures are promising in creating structural ceramics for different applications [34].

To form a high-porous  $ZrO_2$  matrix with characteristics corresponding to human bone, one link has been changed in the production chain for fine-grained preforms: the preform with regular microstructure is replaced by a preform with a wide pore size distribution. Foamed implants were produced by impregnation using various polymer materials with appropriate pore size and developed permeable structure. To make foamed composites, aqueous suspensions are used and the polymer matrix is impregnated in a single step. The microstructural design of skeletal matrices involves shell molding [1] to produce dense or porous articles of complex shape. The strength and porosity of skeletal matrices are controlled by varying the number of layers, concentration of ethyl silicate binder, particle size of filling powder, and sintering temperature. As a result, porous composites with foamed and skeletal microstructures have been produced; they can be used for various implants [35]. The application of bioactive coatings for these materials will expand opportunities of reconstructive surgery.

## CONCLUSIONS

The successful microstructural design of new materials using  $ZrO_2$ ,  $HfO_2$ ,  $Al_2O_3$ , and REM oxides necessitates the use of data from the respective phase diagrams of refractory oxide systems and involves a scientifically sound choice of the chemical and phase composition of starting grained and nanocrystalline powders as well as determination of basic physicochemical laws by which the microstructure forms during production, heat treatment, molding, and sintering to create materials with required characteristics.

## REFERENCES

1. A. V. Shevchenko, *Phase Diagrams of Zirconium and Hafnium Oxides with Rare Earth Elements as Physicochemical Basis for New Materials* [in Russian], ScD Thesis, Kiev (2007), p. 531.
2. I. V. Tananaev, V. B. Fedorov, I. D. Morokhov, et al., "Physicochemical fundamentals of metastable ultrafine substances and prospects of their application," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **20**, No. 6, 1026–1033 (1984).
3. V. V. Skorokhod, "Hierarchy of structural levels and structural engineering of inorganic materials," in: *Inorganic Materials Science* [in Russian], Naukova Dumka, Kiev (2008). Vol. 1, 339–357.
4. A. V. Shevchenko, L. M. Lopato, T. V. Obolonchik, et al., "Liquidus surface of the  $HfO_2$ - $ZrO_2$ - $Y_2O_3$  system," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **23**, No. 3, 452–455 (1987).
5. A. V. Shevchenko, L. M. Lopato, V. D. Tkachenko, and A. K. Ruban, "Interaction of hafnium and zirconium dioxides," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **23**, No. 2, 259–263 (1987).
6. L. M. Lopato, V. P. Red'ko, G. I. Gerasimiyuk, and A. V. Shevchenko, "Synthesis of some REE zirconates (hafnates)," *Powder Metall. Met. Ceram.*, **29**, No. 4, 318–320 (1990).

7. T. V. Obolonchik, L. M. Lopato, G. I. Gerasimyuk, and A. V. Shevchenko, "Interaction in the  $\text{HfO}_2\text{-ZrO}_2\text{-Y}_2\text{O}_3$  system at 1250–1900°C," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **27**, No. 11, 2345–2349 (1991).
8. N. A. Toropov, V. P. Borzakovskii, V. V. Lapin, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems: Handbook* [in Russian], Nauka, Leningrad (1969), p. 435.
9. L. M. Lopato, B. S. Nigmanov, A. V. Shevchenko, and Z. A. Zaitseva, "Interaction between lanthanum and yttrium oxides," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **22**, No. 5, 771–774 (1986).
10. I. M. Maister, L. M. Lopato, A. V. Shevchenko, and B. S. Nigmanov, "The  $\text{Er}_2\text{O}_3\text{-Y}_2\text{O}_3$  system," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **20**, No. 3, 446–448 (1984).
11. S. N. Lakiza, L. M. Lopato, and A. V. Shevchenko, "Interactions in the  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$  system," *Powder Metall. Met. Ceram.*, **33**, No. 9–10, 486–490 (1994).
12. A. V. Shevchenko, L. M. Lopato, and I. E. Kiryakova, "Interaction of  $\text{HfO}_2$  with  $\text{Y}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Tm}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Lu}_2\text{O}_3$ ," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **20**, No. 12, 1991–1996 (1984).
13. A. K. Ruban, A. V. Shevchenko, and L. M. Lopato, "Ceramic rods for precision casting of low-doped chromium," in: *Structural Chromium Alloys* [in Russian], Naukova Dumka, Kiev (1986), pp. 104–109.
14. L. I. Lugin, L. M. Lopato, G. I. Gerasimyuk, and A. V. Shevchenko, "Phase relations in the  $\text{La}_2\text{O}_3\text{-CaO}$  and  $\text{Ce}_2\text{O}_3\text{-CaO}$  systems," *Ukr. Khim. Zh.*, **38**, No. 2, 143–148 (1972).
15. L. M. Lopato, G. I. Gerasimyuk, A. V. Shevchenko, and S. G. Tresvyatskii, "Phase equilibria in the  $\text{Dy}_2\text{O}_3\text{-CaO}$ ,  $\text{Y}_2\text{O}_3\text{-CaO}$ , and  $\text{Yb}_2\text{O}_3\text{-CaO}$  systems," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **9**, No. 3, 157–162 (1973).
16. A. V. Shevchenko, L. M. Lopato, and G. I. Gerasimyuk, *Refractory Material* [in Russian], USSR Inventor's Certificate 589235, IPC C0 4 B 35/20, No. 2182297/29-33; Bulletin No. 3; appl. October 17, 1975; publ. January 25 (1978), p. 7.
17. A. K. Ruban, A. V. Shevchenko, A. N. Rakitskii, et al., "Production of crucibles from rare earth oxides for melting of low-doped chromium in induction furnaces," in: *Structural Chromium Alloys* [in Russian], Naukova Dumka, Kiev (1986), pp. 120–128.
18. A. N. Rakitskii, T. L. Kuznetsova, I. L. Yakimenko, et al., "Induction melting of low-doped chromium alloys in yttrium oxide crucibles," in: *Structural Chromium Alloys* [in Russian], Naukova Dumka, Kiev (1986), pp. 115–120.
19. A. V. Shevchenko, A. K. Ruban, T. V. Obolonchik, et al., "Production of shell molds for shaped casting of low-doped chromium," in: *Structural Chromium Alloys* [in Russian], Naukova Dumka, Kiev (1988), pp. 110–114.
20. A. V. Zyrin, V. P. Red'ko, L. M. Lopato, and A. V. Shevchenko, "Ordered phases in the  $\text{ZrO}_2\text{-Sc}_2\text{O}_3$  and  $\text{HfO}_2\text{-Sc}_2\text{O}_3$  systems," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **23**, No. 8, 1326–1329 (1987).
21. A. V. Zyrin, A. V. Shevchenko, and L. M. Lopato, "Electrical properties of phases in the  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  system," *Powder Metall. Met. Ceram.*, **39**, No. 3–4, 146–150 (2000).
22. A. V. Shevchenko, I. M. Maister, L. M. Lopato, and V. D. Tkachenko, "Interaction in the  $\text{HfO}_2\text{-ZrO}_2\text{-Sc}_2\text{O}_3$  system at 1700–2850°C," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **25**, No. 6, 989–993 (1989).
23. A. V. Shevchenko, I. M. Maister, and L. M. Lopato, "Interaction in the  $\text{HfO}_2\text{-Sc}_2\text{O}_3$  and  $\text{ZrO}_2\text{-Sc}_2\text{O}_3$  systems at high temperatures," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **23**, No. 8, 1320–1324 (1987).
24. I. M. Maister, L. M. Lopato, Z. A. Zaitseva, and A. V. Shevchenko, "Interaction in the  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$  system at 1300–1900°C," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **27**, No. 11, 2337–2340 (1991).
25. A. V. Shevchenko, L. M. Lopato, and I. M. Maister, "Liquidus surface of the  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$  system," *Izv. Akad. Nauk SSSR. Neorg. Mater.*, **27**, No. 12, 2673–2676 (1991).
26. A. V. Shevchenko, V. A. Dubok, E. V. Dudnik, et al., "Transparent ceramics based on yttrium subgroup lanthanide, yttrium, and scandium oxides," *Powder Metall. Met. Ceram.*, **49**, No. 9–10, 537–545 (2010).



27. S. M. Lakiza and L. M. Lopato, "Stable and metastable phase relations in the system alumina–zirconia–yttria," *J. Am. Ceram. Soc.*, **80**, No. 4, 893–902 (1997).
28. S. M. Lakiza, "Directionally solidified eutectics in the  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--Ln}_2\text{O}_3$  systems," *Teor. Prakt. Metall.*, No. 4–5, 126–127 (2006).
29. S. M. Lakiza, J. S. Tyschenko, and L. M. Lopato, "Phase diagrams of the systems  $\text{Al}_2\text{O}_3\text{--Zr(Hf)O}_2\text{--Ln(Y)}_2\text{O}_3$  as a scientific base for creating new high-temperature structural ceramics," in: *Proc. Symp. J. Functional and Structural Ceramics and Ceram. Matrix Composites (September 15–19, 2008)*, Warsaw (2008), pp. 58–69.
30. S. M. Lakiza, J. S. Tyschenko, and L. M. Lopato, "Phase diagram of the  $\text{Al}_2\text{O}_3\text{--HfO}_2\text{--Y}_2\text{O}_3$  system," *J. Eur. Ceram. Soc.*, **31**, 1285–1291 (2011).
31. J. S. Tyschenko, S. M. Lakiza, and L. M. Lopato, "Phase diagram of the  $\text{Al}_2\text{O}_3\text{--HfO}_2\text{--Er}_2\text{O}_3$  system," *J. Am. Ceram. Soc.*, **95**, 4015–4020 (2012).
32. E. V. Dudnik, Physicochemical Fundamentals for Developing  $\text{ZrO}_2$ -Based Materials [in Russian], ScD Thesis, Kiev (2010), p. 403.
33. A. V. Shevchenko, E. V. Dudnik, A. K. Ruban, et al., "Hydrothermal synthesis of nanocrystalline powders in the  $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--CeO}_2$  system," *Powder Metall. Met. Ceram.*, **46**, No. 1–2, 18–24 (2007).
34. E. V. Dudnik, A. V. Shevchenko, A. K. Ruban, et al., "Microstructural design of  $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--CeO}_2\text{--Al}_2\text{O}_3$  materials," *Powder Metall. Met. Ceram.*, **49**, No. 9–10, 528–536 (2010).
35. A. V. Shevchenko, E. V. Dudnik, V. V. Tsukrenko, et al., "Microstructural design of bioinert composites in the  $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--CeO}_2\text{--Al}_2\text{O}_3\text{--CoC}$  system," *Powder Metall. Met. Ceram.*, **51**, No. 11–12, 724–733 (2012).