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Mesostructure of Hydrated Hafnia Xerogels

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The process of hydrothermal synthesis based on treatment of aqueous solutions of metal salts at temperatures above 100°C and pressures above 1 atm have been widely used in recent years to produce advanced oxide materials [1, 2]. The mechanism of formation of nanoparticles under these conditions is rather complex from the physicochemical standpoint comprising at least several consecutive steps, in particular, the step of formation of amorphous metal hydroxides [3, 4]. It should be emphasized that the microstructure of final oxide materials is largely predetermined by the structure of intermediate amorphous compounds.

Of particular interest is analysis of the fractal structure of amorphous metal hydroxides. It is well known that aggregation of colloidal particles in aqueous solutions to give fractal clusters occurs rather often [5]. In some studies it was shown that xerogels and aerogels formed upon removal of the solvent from metal hydroxide gels retain the fractal properties inherent in colloid clusters in solutions [6]. Nevertheless, analysis of the effect of preparation conditions of metal hydroxide hydrogels and xerogels on their fractal dimension can hardly been found in the literature.

Therefore, in this communication, we present the results of the first study of the effect of acidity (pH) of the medium on the mesostructure (in particular, the fractal structure) of amorphous xerogels of hydrated hafnia.

The xerogels $HfO_2 \cdot nH_2O$ were prepared by adding an aqueous solution of ammonia (2.7 mol/l) to an aqueous solution of $HfO(NO_3)_2$ (0.25 mol/l) until a specified pH value was attained (3, 4, 6, 7, 8, and 9). The precipitates formed were washed and dried in air at 60°C for 6 h. A series of $ZrO_2 \cdot nH_2O$ xerogels were prepared in a similar way.

The xerogels were analyzed by small-angle neutron scattering (SANS). The measurements were carried out on a SANS-2 setup (GKSS Research Centre, Germany) operating at the neutron wavelength $\lambda = 5.8$ Å $\left(\frac{\Delta\lambda}{\lambda} = 20\%\right)$. Neutron scattering was recorded in the range of transmitted pulses of $2.5 \times 10^{-3} < q < 2.5 \times 10^{-1}$ Å^{-1} by a two-dimensional position-sensitive ^{3}He detector. The initial spectra were corrected by the standard procedure and reduced to absolute values by normalizing to the vanadium incoherent scattering cross-section with allowance for detector efficiency [7].

Figure 1 shows typical dependences of the SANS cross-section $\left(\frac{d\Sigma(q)}{d\Omega}\right)$ (after subtracting the incoherent scattering background on hydrogen atoms) for amorphous $HfO_2 \cdot nH_2O$ xerogels obtained at different pH values on the transmitted pulse. It can be seen that an increase in the precipitation pH results in a clear increase in the SANS intensity, indicating a decrease in the homogeneity of the xerogels in the nuclear density on 10–1000 Å scale.

The scattering curves of all samples comprise two q ranges in which the scattering patterns are sharply different; in the region $q < q_c \approx 0.025$ Å^{-1}, the value $\frac{d\Sigma(q)}{d\Omega}$ for all samples obeys the power law q^{-n}. The power index n varies from 3.38 to 3.95, which corresponds, according to [8], to scattering on fractal surfaces with dimensions $2.05 \le D_s = 6 - n < 2.62$ and is in good agreement with the results of [9] devoted to the structure of xerogels $ZrO_2 \cdot nH_2O$. Therefore, analysis of scattering in the range $q < q_c$ is further carried out using a two-phase structure model (solid phase–pore) with a fractal interface [8].

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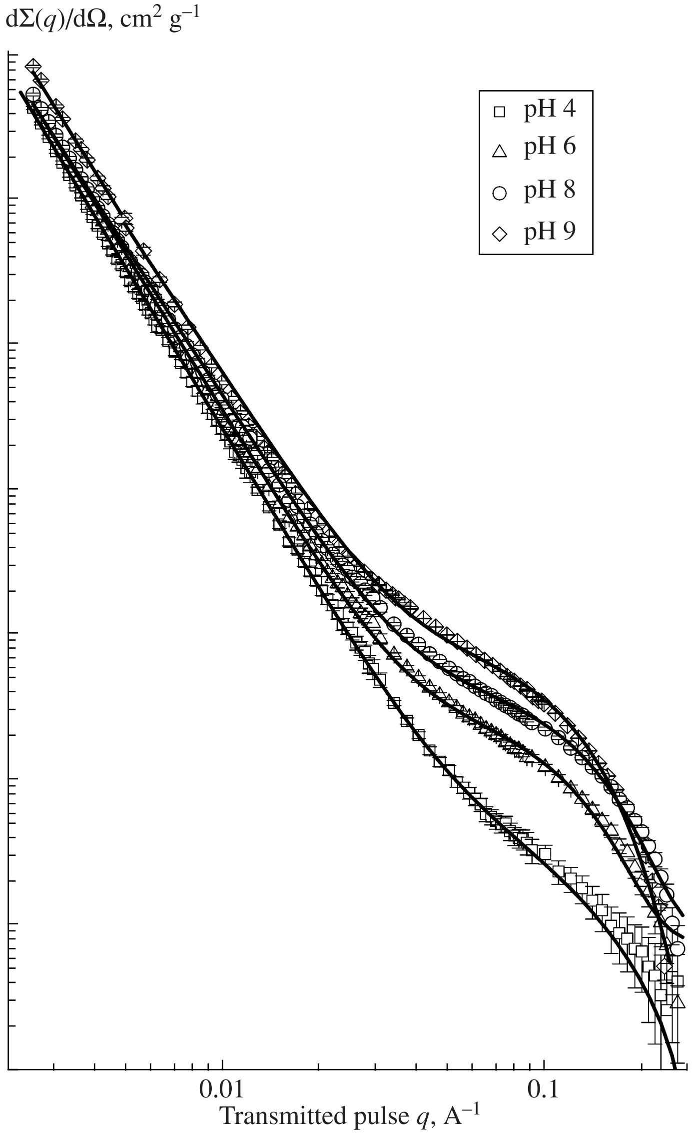

Fig. 1. SANS cross-sections $\frac{d\Sigma(q)}{d\Omega}$ for amorphous $HfO_2 \cdot nH_2O$ xerogel samples obtained at pH 4, 6, 8, and 9 vs. transmitted pulse q. Continuous lines correspond to description of experimental data by formula (1).

In the $q > q_c$ range, the scattering curves show a so-called shoulder, indicating the presence of minor monodisperse inhomogeneities with the effective gyration radius r_g.

The observed scattering picture implies that all samples have two types of scattering inhomogeneities differing considerable in the characteristic scale. It can be concluded that $HfO_2 \cdot nH_2O$ xerogels are composed of aggregates with developed surface build of the initial small monodisperse monomeric species.

The absence of the Guinier region in the scattering curves at low q's means that the upper limit of self-similarity exceeds the maximum size of inhomogeneities $R_{\max}$ scattering on which can be detected by the given instrument resolution. In turn, the lower limit of self-similarity is determined by the size of monodisperse inhomogeneities r_0, which is usually in the range from $2r_g$ to $3r_g$ (for spheres, $2.6r_g$) [10].

Scattering by amorphous xerogels $HfO_2 \cdot nH_2O$ was analyzed over the whole q range studied using the relation [9, 10]:

$$\frac{d\Sigma(q)}{d\Omega} = \frac{A_1(D_s)}{q^n} + A_2\exp\left(-\frac{q^2 r_g^2}{3}\right), \tag{1}$$

where $A_1(D_s)$ and A_2 are free parameters, the first one depending on the fractal dimension [10] and the second one being directly proportional to the product of the

Mesostructure parameters of amorphous $HfO_2 \cdot nH_2O$ xerogels from SANS data

Parameter	pH					
	3	4	6	7	8	9
$A_1 \times 10^{-6}$, cm^2/g	0.4 ± 0.2	2.5 ± 0.5	4.1 ± 1.4	12.3 ± 0.5	52 ± 3	74 ± 20
D_s	2.05 ± 0.02	2.05 ± 0.04	2.17 ± 0.05	2.35 ± 0.05	2.53 ± 0.04	2.62 ± 0.04
$A_2 \times 10^{-1}$, cm^2/g	0.52 ± 0.05	0.57 ± 0.05	2.71 ± 0.06	4.08 ± 0.07	4.32 ± 0.07	5.3 ± 0.08
r_g, Å	17.7 ± 1.1	17.4 ± 0.9	16.2 ± 0.8	14.5 ± 0.8	14.4 ± 0.7	13.6 ± 0.9
S_0, m^2/g	3.7 ± 0.2	4.3 ± 0.2	8.4 ± 0.4	27 ± 2	45 ± 3	78 ± 4

number of monodiperse inhomogeneities in the scattering volume and the amplitude density ρ of the neutron scattering on them [11].

The final results were obtained by convolution of expression (1) with a setup resolution function approximated with the Gaussian function. The experimental dependences $\frac{d\Sigma(q)}{d\Omega}$ were treated by the least-squares method over the whole range of q studied. The results of analysis are presented in Fig. 1 and in the table.

In porous materials composed of two homogeneous phases, the parameter $A_1(D_s)$ is known to be related to the interface surface area as [10]

$$A_1(D_s) = \pi\frac{\rho^2}{\rho_0}\Gamma(5-D_s)\sin\left[(D_s-1)\left(\frac{\pi}{2}\right)\right]N_0, \qquad (2)$$

where Γ is the gamma-function, ρ_0 is the density of the solid phase, and ρ for a molecule containing several elements is found as

$$\rho = \sum_i b_i N_i \frac{\rho_0 N_A}{M}, \qquad (3)$$

where N_A is the Avogadro number, M is molar mass, b_i is the scattering length of element i in the molecule, and N_i is the number of atoms of this element. The constant N_0 is related to the fractal surface area as $S_0 = N_0 r^{2-D_s}$, where r^{2-D_s}, is determined by the scale of measurements. For smooth surfaces $D_s = 2$ and $N_0 = S_0$. The estimate of S_0 was obtained using the procedure we used previously [9] and shown in Fig. 2 and in the table.

It follows from the presented data that both the fractal dimension D_s (Fig. 3) and the parameter $A_1(D_s)$ increase with increase in the pH for the xerogels under study. Note that the fractal dimension of the surface of xerogels obtained by precipitation at lower pH (3 and 4) is close to 2; i.e., in this case, monomeric species form practically nonfractal compact aggregates. Conversely, when the precipitation pH increases to 6 and above, the D_s values considerably increase, which is indicative of a sharp change in the type of monomer aggregation. It is of interest that a similar picture (Fig. 3) is observed for $ZrO_2 \cdot nH_2O$ xerogels prepared by a similar procedure [9]. The results are well correlated with a change in the specific surface area of samples S_0. As follows from Fig. 2, an increase in the precipitation pH results in a sharp (by about 1.3 orders of magnitude) increase in S_0, which indirectly attests to the formation of more branched aggregates.

In turn, the size of monodiperse inhomogeneities $r_0 = 2.6r_g$ corresponding to the lower limit of self-similarity of a surface fractal regularly changes from 47 to 35 Å following increase in the precipitation pH. Thus, precipitation conditions of $HfO_2 \cdot nH_2O$ xerogels affect both the fractal dimension of aggregates and the size r_0 of the monomers forming these aggregates.

The observed change in the mesostructure of $HfO_2 \cdot nH_2O$ and $ZrO_2 \cdot nH_2O$ xerogels confirms the Clearfield theory [12] according to which slow hydrolysis of zirconium and hafnium salts (in this case, taking place at low pH) gives rise to planar layers composed of tetrameric $M_4(OH)_8$ fragments, whereas an increase in the hydrolysis rate (e.g., in alkaline media) promotes polycondensation processes to give branched

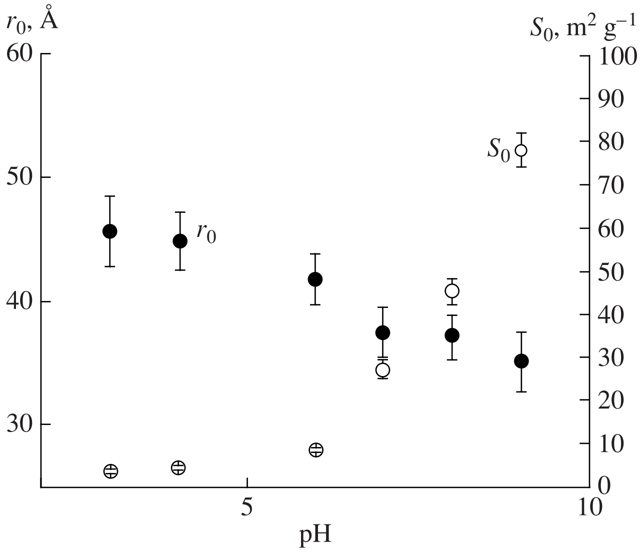

Fig. 2. Specific surface area S_0 and maximum monomer size r_0 for $HfO_2 \cdot nH_2O$ samples vs. pH.

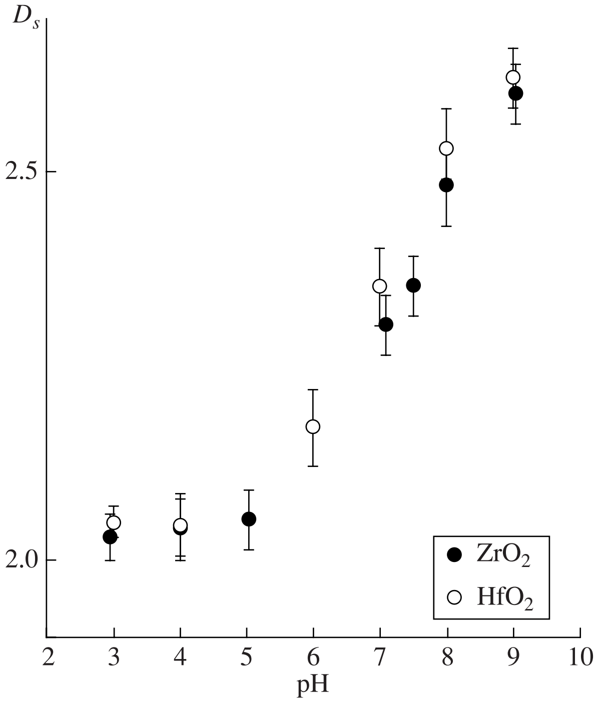

Fig. 3. Fractal dimension D_s for $HfO_2 \cdot nH_2O$ and $ZrO_2 \cdot nH_2O$ samples [9] vs. pH.

structures, which behave, as shown above, as surface fractals.

Thus, the effect of medium acidity (pH) on the structure of amorphous $HfO_2 \cdot nH_2O$ xerogels was established. It was shown for the first time that an increase in the precipitation pH from 3 to 9 entails transition from a porous structure with almost smooth boundaries ($D_s \approx 2$) to a structure consisting of aggregates with a highly developed fractal surface (D_s = 2.62) with simultaneous decrease in the size and increase in the concentration of the monomeric species forming the aggregates.

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