

Possibilities of Using Composite Track Membranes with Nitride Coating for Fractionation of Microelements in Natural Water

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Abstract—A plasma chemical procedure was developed for preparing composite track membranes with a conducting coating of titanium nitride particles having a complex hierarchic structure. Owing to oxynitride deposition on the surface of a poly(ethylene terephthalate) track membrane, the membrane channels become asymmetrical and the membrane strength is enhanced. The pore opening size in composite membranes can be varied in a wide range by varying the synthesis parameters. The possibilities of directly using composite track membranes for electron-microscopic imaging of the form and composition of nonconducting mineral and biological substances and for qualitative and quantitative size fractionation of microelements in natural water by ultrafiltration were demonstrated by the example of a series of macro- (C, Al, Si, Mg, Fe, P) and microelements (Sr, U, Th).

Keywords: composite track membranes, conducting coatings, microelement fractionation

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Determination of the fractional composition is an important aspect of speciation studies of microelements in natural water. Fractionation furnishes primary information on the ratio of suspended, colloidal, and molecular-ionic fractions of elements in solution, which allows estimation of their migration ability. Among fractionation methods, filtration methods play an important role. With membrane filtration materials, it is possible to determine the boundaries of the existence of colloidal and suspended microelement fractions of definite size in their inorganic and bioorganic constituents [1–3].

The available membrane materials, their preparation procedures, and fields of application are diverse [4–6]. An important place among membrane materials with supramolecular pore size is occupied by polymeric track membranes (PTMs). Their advantages are mechanical strength, chemical stability, narrow pore-size distribution, and wide range of commercially available membrane materials with respect to the pore

diameter [7, 8]. Thanks to these characteristics, PTMs are widely used in pharmaceuticals, medicine, and microelectronics [4–6]. The consumer properties of PTMs are determined by the chemical composition and the molecular and macroscopic structure of polymers from which they were prepared [4–10], and improvement of these properties is possible both by the development of new polymeric compounds as a base of membrane materials and by physicochemical modification of the existing PTMs [10]. One of efficient ways to improve the filtration properties of PTMs is making the membrane channels asymmetric, which considerably decreases their hydrodynamic resistance, with the permeability and working life preserved [5, 9, 11, 12]. Physicochemical modification of polymeric membranes is made by applying onto the PTM working surface chemical coatings, e.g., by grafting of a copolymer or oxidative treatment of the surface with cold plasma. However, the composite membranes prepared by this procedure are characterized by nonuniform

modification of the membrane material because of weak adhesion, and treatment of filtration channels in their depth is impossible [10].

Therefore, it seems appropriate to look for new approaches to improving the service properties of the existing track membrane materials. One of possible routes is the development of composites prepared by applying onto a PTM surface inorganic chemically stable and mechanically strong coatings by ion plasma sputtering. Technical problems in implementation of this approach are caused by the need to ensure prolonged contact of PTM with cold plasma below the crystallization point and are compensated by advantages of composite membranes with asymmetric structure of pores and by the possibility of precision control of the "effective" pore size in the course of coating growth in the pore opening zone. Wide range of physicochemical properties of inorganic materials available for ion plasma deposition allows coatings exhibiting, along with the required chemical and mechanical properties, also increased electrical and thermal conductivity to be prepared already now. It would expand the possible applications of composite PTMs, which will not be restricted to fractionation of suspensions and colloids and can also include direct (without additional deposition of a conducting layer [13]) nondestructive analysis of the phase, elemental, and morphological compositions of nonconducting fractions of important constituents of artificial and natural aquatic systems: minerals and biota [14].

The goal of this study was to experimentally assess the above-discussed potential advantages of track membranes prepared by ion plasma sputtering of titanium (oxy)nitride surface layers, when used for fractionation of microelements and radionuclides in natural water.

EXPERIMENTAL

The procedure for preparing composite membranes was based on an installation for electric arc ion plasma sputtering of coatings onto polymeric track membranes, developed by some of the authors [15]. As experimental material for the coating we chose TiN owing to combination of high mechanical strength, electrical and thermal conductivity, simple synthesis, and wide range of chemical and physical homogeneity of coatings obtained [16].

The composite membranes were prepared with a Bulat ion plasma sputtering installation by evaporation

of a titanium cathode onto poly(ethylene terephthalate) PTM specimens (Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna) 20 μm thick with the pore diameter of 0.1, 1.0, and 3.0 μm . The Ti ion deposition was performed in an N_2 medium with continuous monitoring of the support temperature and working gas pressure in the chamber.

To evaluate the filtration characteristics of membranes, we used methods based on microscopy, contactless ultrasound magnetic and phase spectroscopy, measurements of permeability to gases and liquids, and liquid porosimetry [16–21].

We performed several series of syntheses to assess the reproducibility of the results. For certification of composite track membranes (CTMs) and determination of the coating composition and morphology, we used X-ray photoelectron spectroscopy (XPES) [22, 23], scanning and transmission electron microscopy (SEM, TEM), scanning probe microscopy (SPM) [24–26], water porosimetry [27], and kinetic microindentation [28].

One of the most important characteristics of membrane materials is the pore size. Because of diversity and complexity of processes that accompany filtration, by the pore diameter is meant the effective pore diameter, i.e., the size directly participating in the filtration process. In this study we determined the effective pore diameter of composite track membranes with different times of conducting coating deposition by comparing the results of the analysis of SEM and SPM images with the results of experiments on the permeability of the composite membranes with the coating to distilled water. The advantage of this approach is that the membranes are characterized directly under the conditions of filtration processes [14]. The mechanical strength of composite track membranes was measured with a kinetic microindentation installation of the Institute of Engineering Science, Ural Branch, Russian Academy of Sciences.

Elemental analysis of samples of bottom water and filtrates after the fractionation was performed with a Spectromass 2000 mass spectrometer in the RapiQuant mode. More than 30 macro- and microelements in samples were monitored [29].

The SEM and SPM images were processed and analyzed using Scan Master and Photoshop software. The calculations, plotting, and statistical processing of the results were performed using Sigma Plot and Statistica software.

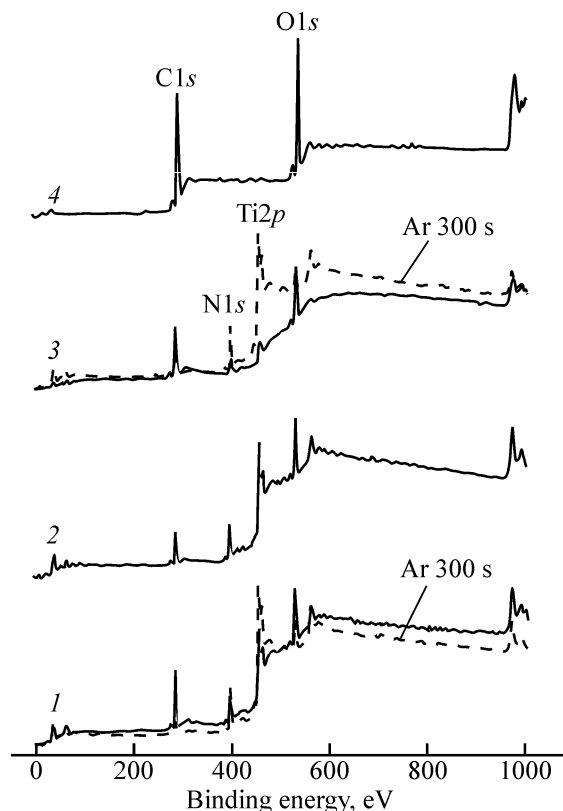


Fig. 1. Total XPE spectra of the CTM surface and titanium oxynitride films on the membrane. Deposition time, s: (1) 20, (2) 120, and (3) 450 s. For samples corresponding to spectra 1 and 3, the spectra recorded after ion etching with an argon beam are also shown.

RESULTS AND DISCUSSION

Figure 1 shows a typical total XPE spectrum of a composite membrane specimen with a deposited titanium nitride layer. An XPE study of inner electron levels of the main elements of the system (Ti, O, N, C) on the surface and in surface layers of the composites showed that the deposited layer consisted of titanium oxynitride coated with a layer of titanium dioxide. The film composition only slightly depended on the deposition time, and after the Ti(N,O) deposition for 450 s the membrane structure of the polymer film did not change noticeably, preserving the formed density of track holes (Fig. 2). According to SPM data, the surface of TiON films has a complex structure, with parent nitride phase particles combined in aggregates forming a hierarchic size structure. The finest aggregates of the “primary” coating are uniformly packed particles of the mean size close to 30 nm. Two levels

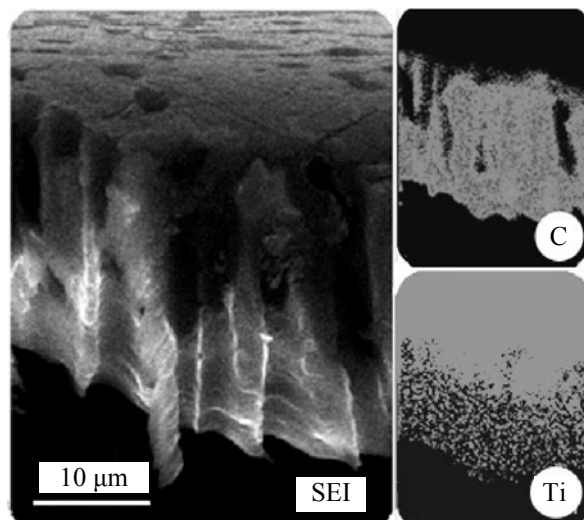


Fig. 2. Typical image of a section of a composite track membrane with the initial pore diameter of 3 μm and maps of Ti and C distribution on this image. JEOL JSM 6390 LA electron microscope, EDX attachment, accelerating voltage 20 kV. Diffuse distribution of Ti throughout the thickness of the track membrane channel is seen.

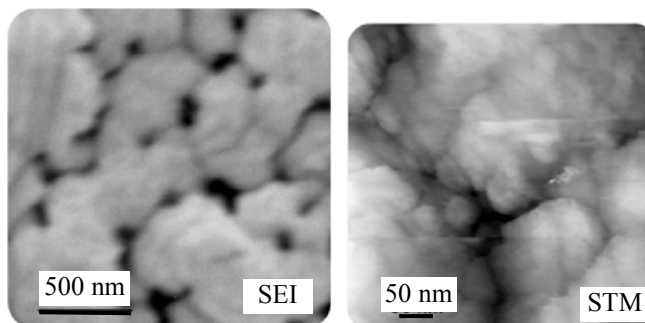


Fig. 3. Image of the composite membrane surface at various magnifications (SEM, SPM).

of aggregates (daughter forms relative to primary particles) exist with the size of approximately 100 and 300 nm (Fig. 3).

A study of the pore cross section profile in modified membranes by atomic force microscopy (AFM) (Fig. 2) revealed no changes in the morphology of the initial PTMs and pores on the back (opposite to titanium oxynitride coating) side of the composite membranes. Because the pore opening size in composite membranes decreased appreciably, we concluded that the initially cylindrical pores became asymmetric after the coating deposition. This is confirmed by the results of the quantitative determination of the pore diameter from the water permeability. In the first step of the measurements, we experimentally determined the applicability limits of the Darcy filtration law in relation

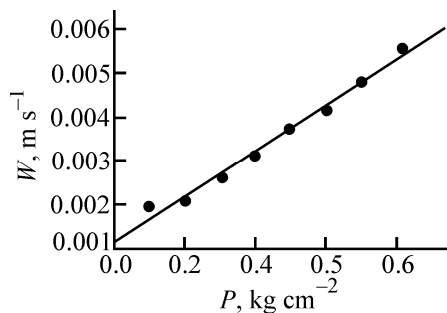


Fig. 4. Example of the dependence of the filtration rate on the applied pressure for a membrane with a pore diameter of 1 μm .

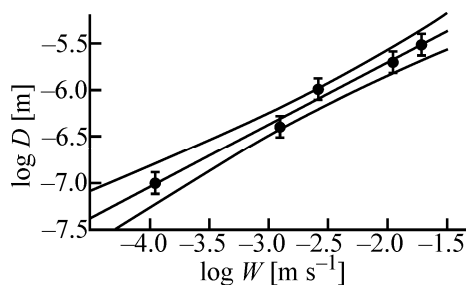


Fig. 5. Empirical correlation between the effective pore size in CTM (D) and linear velocity of water filtration (W), used for determining the pore size in composite membrane materials with Ti(O,N) coating. Results of statistical processing by the equation $\log D = a + b \log W$: correlation coefficient $R = 0.987$, linearization uncertainty $S_r = 0.11 \pm 0.02$, $a = 6.46 \pm 0.60$, $b = 1.48 \pm 0.09$.

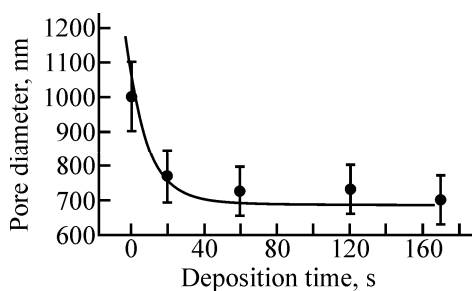


Fig. 6. Pore diameter in composite track membranes as a function of the time of depositing the titanium oxynitride coating. Initial pore diameter in the track membrane $D = 1000$ nm.

to the pore size and liquid filtration rate. Comparison of the experimentally found Reynolds numbers characterizing the water flow in the pore space of membranes with the tabulated values showed that, for the pore diameter larger than 2 nm, the filtration rate W is a linear function of the excess pressure applied to the porous medium P , which is characteristic of laminar flow of a

liquid in pores (Fig. 4). This fact allowed us to calculate the pore size in nanocomposite track membranes using an empirical $W(D)$ relationship, where D is the effective pore diameter. The parameters of this relationship were determined by the least-squares method for a series of commercial membranes with the certified pore size (confidence level 95%) (Fig. 5).

Using the regression equation obtained, we found the D values for a series of modified track membranes with titanium oxynitride coatings, which were subsequently used for studying the fractional composition of radionuclides in natural water.

The results of determining the physicochemical strength of composite track membranes in the range of the linear dependence of the membrane coating strain on the indenter load showed that deposition of the nitride coating onto PTM does not affect or improves (at a coating thickness exceeding 1 μm) the strength properties of the composite membranes.

Thus, plasma chemical deposition allows preparation of composite filtering materials based on track membranes and titanium oxynitride coating with the required pore size in the range from 10 nm and larger, reproducible within no more than 15% (Fig. 6). The coating formation is complete in 100–150 s, which does not lead to irreversible heat-induced changes in the support material owing to the procedure that we used to remove heat from the walls of the reactor with the material being sputtered. This allows the synthesis of composite filtering materials to be performed in the continuous sputtering mode. The possibility of decreasing the pore size in composite filtering materials below 10 nm is limited by metrological rather than technical problems, namely, by an increase in the uncertainty of effective pore size determination with a decrease in the filtration rate. Determination of the physicochemical properties of composite filtering materials prepared by this method and of their chemical stability is the goal of our further studies.

We used the composite track membranes with titanium nitride coating for estimating the fractional composition of microelements in natural water [14, 27]. Combination of membrane filtration with SEM and energy-dispersive analysis allowed us to separate suspended and colloidal fractions for a large number of microelements and to image their fractional composition in various size ranges. Quantitative fractionation of separate chemical elements using CTM with various pore sizes required correction of the filtration data in

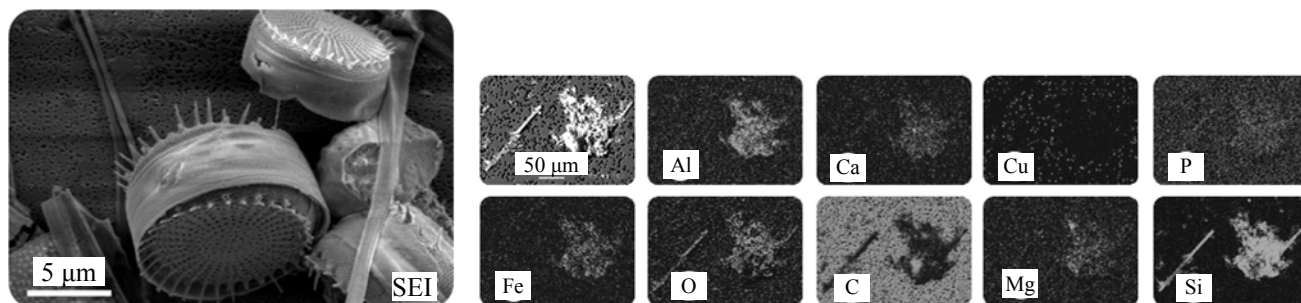


Fig. 7. SEM image of the mineral-biological fraction of particles of the linear size exceeding 1 μm on the CTM surface after filtration of water samples from Techa river and microelement distribution maps (EDX).

estimation of the rejected substance fraction because of the fact that the use of rough vacuum led to evaporation of a part of the liquid phase in the course of filtration and to subsequent thickening of the sample. To take into account thickening, we suggested a procedure for determining the thickening factor from variations in the concentrations of macroelements that could be used as internal reference. We showed by methods of mathematical statistics that variations in the concentrations of Na, K, and Rb in the course of filtration are exclusively due to water thickening as a result of evaporation in the course of filtration through a porous medium and that these elements can be used as internal concentration reference in the solutions being studied. The averaged factor of the change in the concentration of these three elements in the inlet solution relative to the filtrate was used for correction of the filtrate volume and of concentration of the monitored elements in the filtrate after the fractionation, which allowed reliable determination of the fractional composition of the microelements from the results of filtration of natural water through CTMs with different pore sizes.

With freshly taken samples of Techa river water (Chelyabinsk oblast) as examples, we showed that a considerable part of the suspended material in the river water was of both organic and mineral origins (Fig. 7). The use of composite track membranes allowed us to visualize and determine the composition of fractions filtered off from the river water without any additional pretreatment. The presence of a sputtered conducting layer of titanium nitride ensured the charge leakage from the filtered-off suspended and colloidal fractions (including those of biological origin) on the surface of the composite, which, in turn, ensured high-quality imaging of poorly conducting objects.

The images presented show that the major mineral components of the suspended fraction are a complex Al–Mg–Si compound and Fe compounds; the organic

substances is primarily represented by diatomic algae coated with iron compounds. In Techa river water in sampling sites we revealed the presence of diatomic algae *Stephanodiscus hantzschii* Grun., diameters 13.5–4.5, 10.5–4.0, and 10.0–5.0 μm, and *Synedra ulna* (Nitzsch.) Ehr., 192.0–7.0 μm.

A quantitative fractional analysis of the suspended and colloidal fractions of U, Sr, and Th showed that, irrespective of the season, U, Sr, and Th mainly (20–80%) occur in water in the ionically dispersed state (Fig. 8).

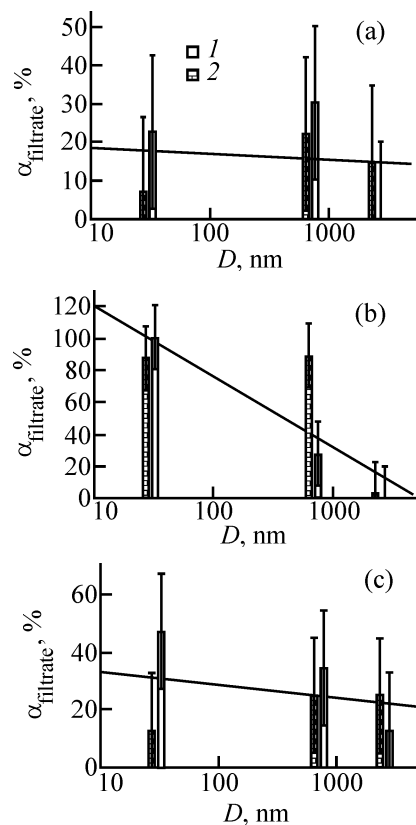


Fig. 8. Distributions of (a) Sr(II), (b) Th(IV), and (c) U(VI) in the suspended and colloidal fractions of freshly taken river water, sampled in the (1) spring and (2) autumn period in the region of Techa river issue.

The remaining fraction of Sr, U, and Th (up to 80–20%) in the river water can be transported in the adsorbed form on mineral magnesium aluminosilicates and iron hydroxides, and also on the surface of the silicate framework of diatomic algae [1].

Thus, the developed procedure for plasma chemical synthesis allows preparation of composite track membranes with a conducting layer of titanium oxynitride particles having a complex hierarchic structure. Owing to the oxynitride film deposition onto a track membrane (support), the composite membrane becomes asymmetrical. The pore opening size in composite membranes can be varied in a wide range by varying the synthesis parameters. The possibilities of directly using composite track membranes for electron-microscopic imaging of the form and composition of nonconducting mineral and biological substances and for qualitative and quantitative size fractionation of microelements in natural water by ultrafiltration were demonstrated by the example of a series of macro- (C, Al, Si, Mg, Fe, P) and microelements (Sr, U, Th).

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