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Magnetic Resonance Imaging of Water Absorption by Highly Porous Ceramic Materials

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Abstract—A nontrivial character of water absorption in highly porous ceramic materials has been demonstrated for the first time by magnetic resonance imaging: a phenomenon of hygroscopic memory has been detected consisting in the concentration of adsorbed water in certain areas inside the sample, repeated during subsequent wetting with water. It has been shown that hydrophobization of the material by applying fluoro paraffin coatings to oxide fibers using the method of dissolution of fluoropolymers in supercritical CO_2 has a significant impact on the transport of water into products and can be considered an efficient means of protecting porous materials from moisture. The results demonstrate the capabilities of the MRI method in studying the water absorption and identifying water migration pathways in highly porous materials.

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Magnetic resonance imaging (MRI) has received enormous use in modern medicine due to its nondestructive nature and high information content; however, its application in the field of materials science is largely limited due to certain technical difficulties. Only in recent years, as a result of the accumulation of necessary experience, has there been a steady growth in materials science MRI applications. The method is especially promising in the study of composite [1, 2] and porous materials [3], which are widely used, for example, as heat and fire resistant materials in the production of various filters in catalytic systems. TZMK (based on SiO_2 fibers) and VTI (based on Al_2O_3) highly porous ceramic materials (HPCMs) with a porosity of up to 90–95% [4] developed at the All-Russian Research Institute of Aviation Materials are noteworthy. Due to the low thermal conductivity (0.05–0.07 W/(m K)) and high thermal stability, the materials were used as a heat-shielding coating for the Buran spacecraft. With a large number of advantages HPCMs have limitations, the key of them being hydrophilicity. Due to the high porosity, moisture absorption in the material can reach 2000%, which significantly complicates the manufacture, storage, and operation of ceramic articles. Water, having a high thermal conductivity, not only deteriorates the thermophysical properties of the material, but also at high temperatures can react with oxides, disturbing their structure and composition, and at negative temperatures, turning into ice, can destroy the integrity of the article. Due to the latter, these materials are not applicable in the Arctic, combining high humidity and low temperatures. Hence, the extreme importance of the hydrophobization of HPCMs is obvious. Hydrophobization can be achieved using organosiloxane fluids or by vapor deposition of products based on methyltriethoxysilane on the surface of oxide fibers [4]. Fluoropolymer materials exhibit good hydrophobic properties [5], for which, in the case of HPCMs, technologies of supercritical fluids have been developed: hydrophobic coatings of fluoro paraffins dissolved in sc-CO_2 are deposited on the fiber surface [6, 7].

In the overwhelming majority of cases, water absorption by porous materials has been studied by a gravimetric method based on weight measurement. This method and some others used to study adsorbed water (IR spectroscopy, dielectrometry, resonance methods) are integral and somewhat inefficient, because they provide information on the amount and state of water in the material regardless of its local distribution. In order to obtain information on the spatial distribution of water inside HPCMs and the ways of its migration, we used the MRI method for the first time. In addition to the water-repellent samples (with fluoro paraffins applied to oxide fibers), pristine samples were also studied. A series of TZMK-25 specimens

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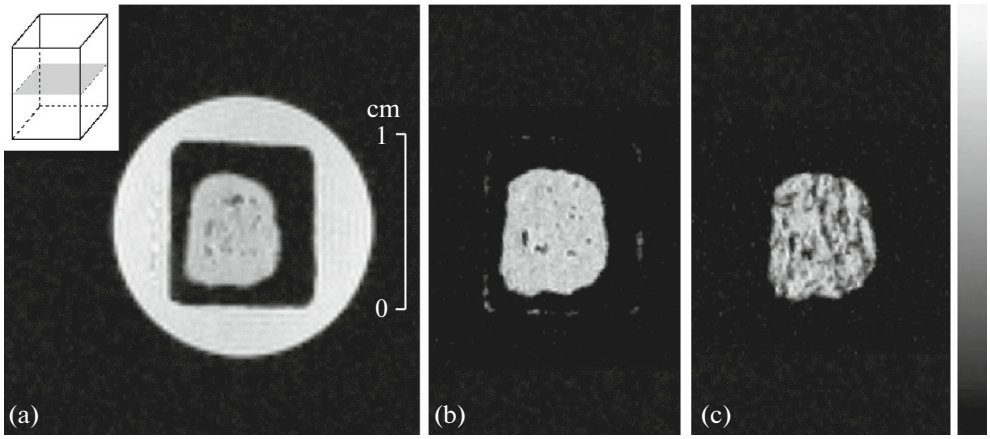

Fig. 1. Tomographic images of the TZMK specimen (a) after 2-h exposure to water, (b) immediately after removal from water, and (c) after 24 h of exposure to open air. The cross section of a tomographic slice with a thickness of (a) 1 and (b, c) 0.5 mm relative to the geometry of the specimen is shown.

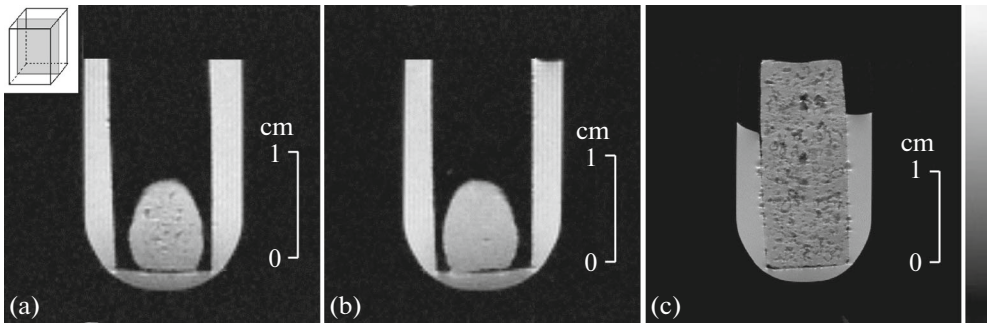

Fig. 2. Tomographic images of the TZMK specimen within (a) 5 min and (b) 14 days after the second dipping into water and (c) a specimen subjected to preliminary heating. The cross section of a tomographic slice with a thickness of 1 mm relative to the geometry of the specimen is shown.

made in the form of a 10 × 10 × 20 mm parallelepiped and VTI-17 specimens treated with PPU-90 perfluorinated powder accelerators (manufactured by GaloPolimer, Kirovo-Chepetsk) in sc-CO_2 were used. The specimens were saturated with water in a glass ampoule at room temperature (22°C). The MRI visualization of the water absorption process was performed using a Bruker Avance DPX 200 NMR spectrometer (200.13 MHz for ^{1}H), equipped with a MRI accessory that provides the maximum amplitude of the magnetic field gradient of 1 T/m.

The tomographic images of a TZMK specimen immersed in water for 2 h demonstrate the formation of an internal region filled with water the molecules of which have a high local mobility as compared to that of liquid water molecules (Fig. 1). It can be seen that the dimensions of the area with adsorbed water (6 × 7 × 9 mm) are substantially smaller than the dimensions of the specimen itself. In the peripheral part of the specimen, the signal is not detected, which is due to the absence of absorbed water. Images recorded using a special technique that allows the visualization of media with short spin–spin relaxation times have confirmed the absence of even immobile (bound to the fiber surface) water.

The relatively free state of water molecules in the TZMK matrix leads to its rapid evaporation from the accumulation region without noticeable redistribution inside the porous specimen (Fig. 1). Full evaporation of the absorbed water occurs after 100 h, which suggests that the specimen has returned to its original state. Repetition of the experiment, i.e., placing the dried specimen into water, leads to the same character of water absorption, which lasts for 5 min. Water penetrates into the same volume that it occupied during the primary absorption and does not enter in other areas of the specimen; the formation of the impregnation front characteristic of porous media is not observed either (Fig. 2). Moreover, further exposure of the TZMK specimen to water for 14 days does not change the contour of the water-containing zone.

This result is evidence that the porous specimen has hygroscopic memory, which causes the existence of the zone of preferred accumulation of adsorbed

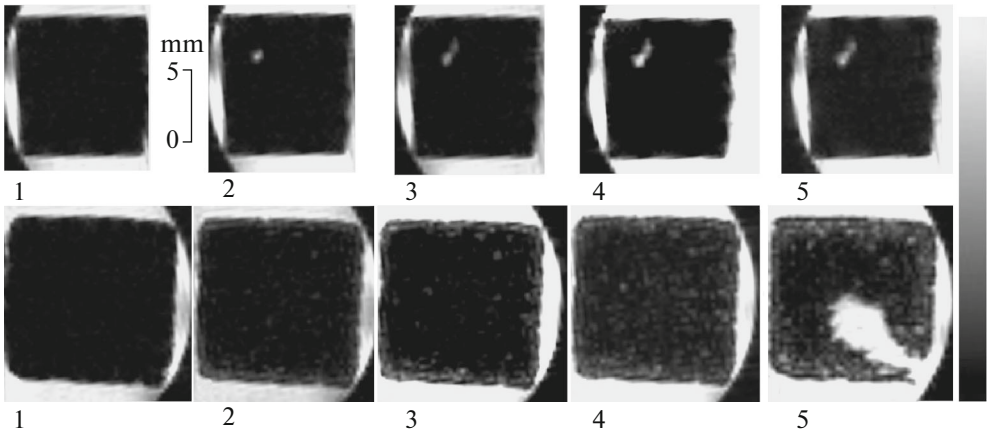

Fig. 3. Upper row: tomographic images of the TZMK + PPU-90 specimen within (1) 5 min, (2) 24, (3) 120, (4) 192, and (5) 312 h after dipping into water. Lower row: tomographic images of the VTI + PPU-90 specimen within (1) 5 min, (2) 120, (3) 192, (4) 312, and (5) 456 h after dipping into water. The cross section of a tomographic slice with a thickness of 1 mm relative to the geometry of the specimen is analogous to that shown in Fig. 1.

water. It is likely that, in the course of fabrication of a specimen, a spatial structure of oxide material fibers formed that had a certain combination of physical and chemical properties (wettability of the fiber surface with water, local geometry of the pore space, diameter of capillaries and their connection with each other, etc.). This results in that water migration inside the specimen deviates from classical laws describing motion of liquids in capillary-porous bodies under the action of their own capillary pressure [8]. Thus, an area with adsorbed water is formed only where the necessary parameters are present (the desired combination of viscosity, surface tension, contact angle, etc.).

The faster filling of the marked region with water in repeated experiments is explained by the fact that the surface of peripheral fibers through which the primary water transport into the filling region occurred retains a thin layer of adsorbed water molecules, which are not detected in the experiment. This layer does not disappear upon drying at room temperature and, when in contact with water, promotes faster transport of water so that it occupies the same volume as previously. After additional heating of the highly porous specimen at 150°C for 2 h, the tomographic image of the second water uptake radically changes (Fig. 2c): within 5 min after immersion, impregnation of the entire specimen, rather than separate zones, is observed. It can be argued that heating completely destroys the hygroscopic memory of the specimen. It is obvious that special heating makes it possible to regulate the sorption properties of HPCMs and the character of water adsorption.

Studying the interaction of water with HPCM specimens treated with fluoro paraffins in sc-CO_2 revealed a significant difference in the character of water adsorption as compared with the pristine specimens. Prolonged exposure to water of the TZMC + PPU-90 specimen does not lead to the formation of internal regions with a high content of adsorbed water. Only after 24 h can one detect on tomographic images the presence of water traces in the form of local areas less than 1 mm in size (Fig. 3). Over time, their size does not increase; the formation of new zones of water concentration is also not observed, and the total volume of absorbed water remains constant. Water transport to these local areas seems to occur along certain paths with lower hydrophobicity (for example, along fibers that are not coated or only partially coated with a hydrophobic agent), which is due to random technological factors.

Replacing SiO_2 ceramic fibers by Al_2O_3 fibers leads to a change in the mechanism of water penetration into the material. The VTI + PPU-90 specimen demonstrates excellent stability during the first 3–4 days after contact with water: both bulk and local moisture content areas are absent (Fig. 3). However, further exposure of the specimen to water leads to the formation of the impregnation front characteristic of porous media, moving from the surface into the specimen. After 15–18 days of the experiment, as water accumulates in the near-surface areas and the impregnation front moves, a significant amount of water spontaneously penetrates into the specimen to form the area observed in the untreated specimen. For the appearance of this effect, it is necessary to achieve some critical moisture content in the material. The relatively slow water diffusion and capillary transport lead to a gradual change in the combination of physicochemical parameters of the medium, and once certain conditions (capillary pressure, local geometry of the porous space, degree of capillary filling with water, etc.) have been achieved, the character of mass transfer changes with the formation of the spatial structure of the waterways. This effect has the same nature as

the percolation transition observed during vapor adsorption by porous media [9]. In addition, the pore topology makes some routes of water movement more preferable, if they have been inefficiently treated with hydrophobic coatings; these areas become the "weak link" through which the water breaks through into the specimen.

In conclusion, it should be noted that here the nontrivial nature of the interaction of highly porous ceramic materials with water, revealed by MRI, has been demonstrated for the first time. By the example of specimens made of pristine oxide fibers and those treated with hydrophobic fluoro paraffins using the technology of their dissolution in sc-CO_2, a significant difference in the water absorption has been shown. In the TZMK specimens obtained from silica fibers, the phenomenon of hygroscopic memory has been discovered, consisting in the accumulation of adsorbed water in certain zones inside the specimen, repeated during subsequent wettings with water. The filling of the specimen volume occurs without the formation of the impregnation front or moisture content gradient. This factor can be eliminated by special heat treatment, which can be considered as a technological method that regulates the sorption properties of a highly porous material. Our studies have shown that the application of fluoro paraffin coatings to oxide fibers in order to make the material water-repellent is an effective means of protecting HPCMs from moisture. Our results demonstrate the capabilities of the MRI method in studying the patterns of water absorption and identifying water migration pathways in highly porous materials.

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REFERENCES

1. Morozov, E.V., Koptyug, I.V., and Buznik, V.M., *Aviats. Mater. Tekhnol.*, 2014, no. S1, pp. 17–29.
2. Avilova, I.A., Buznik, V.M., Volkov, V.I., Zhelezina, G.F., Morozov, E.V., Raskutin, A.E., and Falaleev, O.V., *Aviats. Mater. Tekhnol.*, 2014, no. S1, pp. 30–36.
3. Koptyug, I.V., Progr. *Nucl. Magnet. Reson. Spectrosc.*, 2012, vol. 65, pp. 1–65.
4. Kitaeva, N.S., Mukhanova, E.E., and Deev, I.S., *Aviats. Mater. Tekhnol.*, 2013, no. S1, pp. 125–130.
5. Buznik, V.M., *Aviats. Mater. Tekhnol.*,2013, no. 1, pp. 29–34.
6. Bespalov, A.S., Buznik, V.M., Grashchenkov, D.V., Nikitin, L.N., Ivanov, V.K., Lebed', V.O., and Chashchin, I.S., *Neorg. Mater.*, 2016, vol. 52, no. 4, pp. 431–437.
7. Bespalov, A.S., Kablov, E.N., Grashchenkov, D.V., Chashchin, I.S., Buznik, V.M., and Nikitin, L.N., RF Patent 2630523, *Byul.*, 2016.
8. Sahimi, M., *Flow and Transport in Porous Media and Fractured Rock: From Classical Methods to Modern Approaches*, 2nd ed., Weinheim: Wiley-VCH, 2011.
9. Parlar, M. and Yortsos, Y.C., *J. Colloid Interface Sci.*, 1988, vol. 124, no. 1, pp. 162–176.

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