International Journal of Thermal Sciences 122 (2017) 124–132

Contents lists available at ScienceDirect

International Journal of Thermal Sciences

journal homepage: www.elsevier.com/locate/ijts

Kinetics of water freezing in mesopores determined by differential scanning calorimetry

Marcin Koniorczyk*, Piotr Konca

Department of Building Physics and Building Materials, Lodz University of Technology, Poland

ARTICLE INFO

Article history:
Received 21 October 2016
Received in revised form
17 August 2017
Accepted 18 August 2017

Keywords:
Kinetics
Mesopores
Water phase change
Calorimetry

ABSTRACT

The manuscript considers the kinetics of water freezing in mesopores of gamma aluminum oxide with the average pore diameter equal to 7.8 nm, investigated using differential scanning calorimetry. Four cooling rates: 1.0, 3.0, 5.0 and 10.0 °C/min are tested. The series of experiments are performed in order to determine the reaction kinetics, which appears to be independent of the cooling rate. The isoconversional method is used to determine the activation energy. The pre-exponential factor and reaction model are estimated using the methodology proposed by Málek. The Šesták–Berggren model gives the most reliable approximation of the conversion function. Additionally we apply the procedure proposed lastly by Arshad and Maaroufi to confirm the proper selection of the kinetic model. We also find the relation between parameters of empirical Šesták–Berggren model and phenomenological Johnsom-Mehl-Avrami model. Moreover, we perform very slow cooling and heating test assuming that the temperature rate is equal to 0.1 °C/min. For such a slow test we could assume that ice grows much faster than temperature changes, therefore the equilibrium between ice and water exists at any temperature. Based on the results obtained for the slowest test and applying Gibbs-Thompson equation we estimate the pore distribution.

1. Introduction

Most of solid materials contain voids, e.g. stone, concrete, brick, etc., which are usually filled with air, water or additionally various contamination dissolved in water. It is observed that in a confined geometry, i.e. pore system, the melting temperature of ice is depressed when compared with the melting temperature of bulk ice [1–3]. Cyclic water freezing in porous materials leads to microstructure damage and degradation of physical properties. Such a phenomenon is observed when saturation degree exceeds 92%. It is one of the most severe damage, which concerns porous materials existing or exploiting in the temperate and frigid zone [4–6].

Most of research devoted to frost damage of porous materials are developed assuming that temperature changes very slowly, when compared to water solidification. Consequently at any temperature the arbitrary mass of ice fills the pores [7,8]. However, it might happen that temperature fluctuates very fast, e.g. during fire in cold climate, when the turbulent heat and gas flow occurs. In such condition material might experience very rapid temperature changes. The frequency of sudden temperature variation will increase due to climate warming. The negligence of the kinetic effect associated with water solidification might lead to the substantial errors and therefore no longer can be justified.

The dynamic nonequilibrium freezing-melting of water in porous materials is deeply discussed in Refs. [9,10]. Based on the Dedoner's concept of the second law of thermodynamics Setzer investigated the affinity of the water-ice system in porous materials during heating and freezing as the main thermodynamic forces, which pushes the system towards equilibrium. The mathematical model and the numerical code of heat and mass transfer in the porous materials concerning the kinetics of water solidification was firstly developed by Bronfenbrenner [11,12]. A simple kinetic model introducing the characteristic time of water solidification process was applied. He also made an experimental observation of thermal effects associated with the kinetics of water solidification [13]. Koniorczyk et al. [14,15] developed more sophisticated mathematical model, which allows to investigate the durability of porous materials exposed to frost attack. Applying the kinetic model of water phase change he is able to calculate the strain in the solid skeleton and the propagation of damage parameter induced by cyclic water freezing.

* Corresponding author.
E-mail address: marcin.koniorczyk@p.lodz.pl (M. Koniorczyk).

http://dx.doi.org/10.1016/j.ijthermalsci.2017.08.015
1290-0729/

The main objective of the manuscript is the analysis of the water freezing kinetics in mesopores of gamma aluminum oxide. Differential scanning calorimetry (DSC) test was performed for water saturated material to investigate the kinetics of water solidification. The calculations are based on four experimental DSC data sets under constant cooling rate conditions (1.0, 3.0, 5.0 and 10.0 $^{o}Cmin^{-1}$). The activation energy is estimated using isoconversional methods, i.e. differential Friedman method and integral Starink method for freezing program. Then, applying the procedure proposed by Málek [16] we select the most appropriate kinetic model and determine its parameters. Additionally, we investigate the $h(\alpha)$ function introduced by Arshad and Maaroufi [17,18] to confirm the selection of the best fitted reaction model. Moreover, using their method we search for the relation between various kinetic models. The previous study shows that the rapid growth of ice from the overcooled water is evident when cooling procedure starts at the temperature above 0 °C. Such effects are of stochastic nature, unable to determine the reliable relation between the ice content and overcooling temperature. We propose the procedure how to overcome this difficulty and get the reliable experimental data. Moreover, we analyze the experimental results considering the equilibrium state. Using the Gibbs-Thompson equation and its approximation we investigate the mean pore diameter of the material both for cooling and heating program with the temperature rate equals 0.1 $^{o}Cmin^{-1}$. The method for analyzing the material microstructure based on the DSC test results is well known as the thermoporometry.

1.1. Material and testing procedure

For the experiments we use distilled water. The following properties are assumed: the melting point of a bulk ice $T_0 = 273.15\ K$, heat of fusion is given by the equation [19,20]:

$$\Delta H_f = 334.1 + 2.119(T - T_0) - 0.00783(T - T_0)^2 \quad (1)$$

Water and ice density are described by the following empirical equations [20]:

$$\rho_l = -7.1114 + 0.0882T - 3.1959\cdot 10^{-4}T^2 + 3.8649\cdot 10^{-7}T^3 \quad (2)$$

$$\rho_i = 0.917\left(1.032 - 1.17\cdot 10^{-4}T\right) \quad (3)$$

Gamma aluminum oxide produced by Norton Chemical Process Products Corp., Akron was applied as a porous material. The chemical composition (% wt) of the material used in the experiments, according to the information delivered by producer, is as follow: aluminum oxide (99.7–99.9), silicon dioxide (0.1–0.2), ferric oxide (0.1). The manufacturer declares the mean pore diameter equal to 7.3 nm (for the mercury intrusion porosimetry test) and the porosity equals 0.56 ml/g. We performed two kinds of test in order to investigate the microstructure of gamma aluminum oxide. The first one is the nitrogen adsorption/desorption test, see Fig. 1a,b, which is performed using Micromeritics ASAP 2020. The specific surface area analysis is based on BET model of N_2 low temperature adsorption. Size and volume of pores between 3.36 nm and 100 nm diameter were determined using BJH desorption cumulative volume of pores and BJH desorption average pore diameter. The shape of adsorption-desorption isotherms is presented in Fig. 1a. It exhibits the typical type IV isotherm with a hysteresis loop from $p/p^{\circ} = 0.65$. The isotherms have a clear capillary condensation step and an evaporation step. That observation confirms regular microstructure of the sample, which framework consists of pores with similar diameters. The specific surface area equals 190 m^2/g, the total pore volume is equal to 0.58 ml/g and the average pore diameter equals 7.78 nm. The second microstructural analysis is the mercury intrusion porosimetry test (MIP). It provides additional information concerning the connectivity between pores. Applying pressure up to 400 MPa allows us to investigate the microstructure with pore diameter down to 3 nm. Both parameters declared by the manufacturer varied no more than 1%. The results of MIP test is presented in Fig. 2.

It can be noticed that the gamma aluminum oxide under investigation contains the pores with one dominant pore diameter equals 7.3 nm. The following parameters were determined during the MIP test: the pore volume equal to 0.56 ml/g, the bulk density

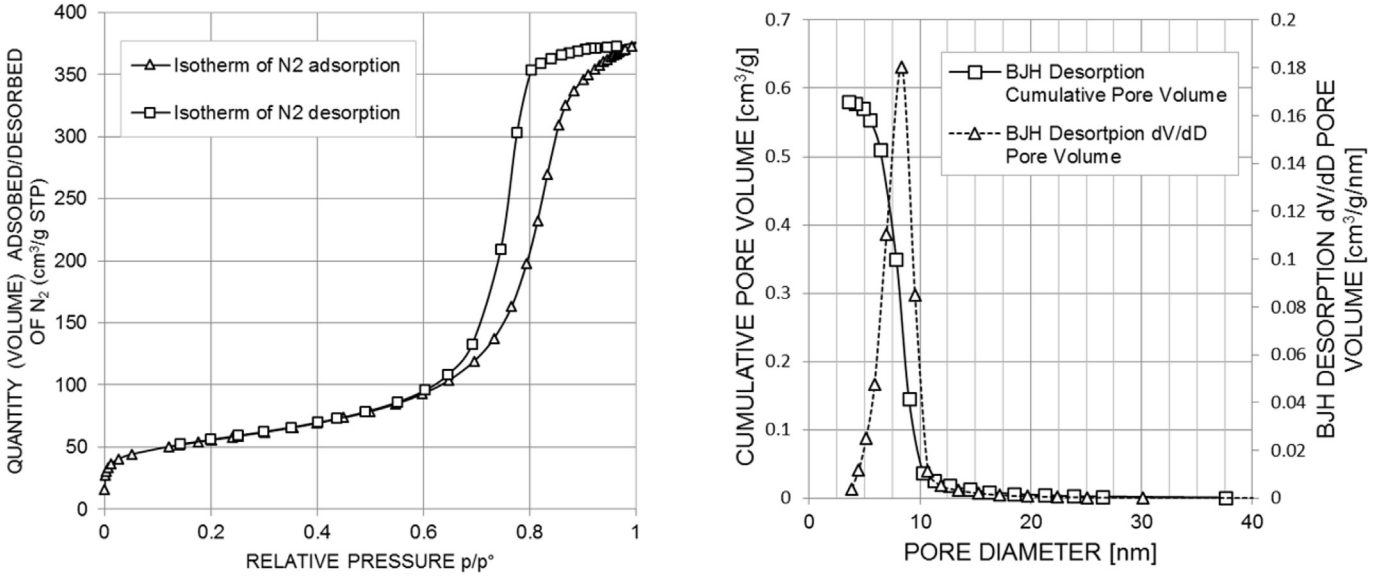

Fig. 1. a) Nitrogen adsorption/desorption isotherms of the sample and b) pore size distribution obtained by nitrogen desorption.