International Journal of Heat and Mass Transfer 126 (2018) 32–38

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

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

Surface tension driven flow forming aluminum oxide microtubes

Isabela T. Coutinho, A.A.R. Neves, G. Sombrio, J.A. Souza *

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil

ARTICLE INFO

Article history:
Received 9 February 2018
Received in revised form 3 May 2018
Accepted 4 May 2018

Keywords:
Microtubes
Metallic nanoparticles
Oxidation process
Al_2O_3
Hollow materials

ABSTRACT

Aluminum oxide microtubes decorated with metallic nanoparticles were produced through thermal oxidation method by using metallic aluminum microwire above its melting point, i.e., in the liquid phase. The obtained translucent aluminum oxide microtubes have 66 μm of internal diameter, with a wall thickness of ~2 μm while the patterned Al metallic nanoparticles have diameter in the range 50–200 nm. Structural characterization indicated that the microtube wall is formed by amorphous oxide phase which coexist with crystallized metallic one. Heat treatment at T = 1050 °C leads to the crystallization into Al_2O_3 phase. During the fabrication process, a thin oxide layer was formed first on the molten liquid surface establishing a solid oxide tube with a liquid inner core. The formation and growth of a spherical droplet, at the microwire's end, draw the molten aluminum inner core, acting as a driving force for the liquid mass transfer movement and microtube formation. The capillary effect and surface tension driven flow effect plays an important role towards the microtube formation.

1. Introduction

Hollow structures have attracted great attention as an important group of functional materials. This high interest is due to their unique characteristics such as high surface area, low density and high load capacity [1]. These properties are exploited in a large variety of applications including micro and nano reactors [2], catalysis [3], composites [4], microwave adsorption [5], energy storage [6], sensors [7], environmental [8] and biomedical applications [9,10]. For example, microtubes can have potential applications in hollow core waveguides due to their low-cost and high-power capability with high coupling efficiency [11]. Waveguides are applied in ophthalmology and dentistry for laser surgery as well as in photodynamic therapy [12]. Coherent fiber bundles have been applied to transmit high-resolution images, as in endoscopic medical imaging [13]. Silver coated hollow waveguide has also been applied to enhance the scintillation signal transmission while minimizing contamination from a standard dielectric fiber [14]. On the other hand, aluminum oxide presents excellent dielectric properties, good adhesions for many surfaces and chemical/thermal stability. As a consequence, in addition to mentioned above, this material can be applied as an insulator and protective barrier in the microelectronics [15,16]. Aluminum oxide can exist in several crystal phases, but the most stable is rhombohedral phase with *R*-3*cH* space group symmetry (known as α-phase). On the other hand, other metastable phases such as cubic spinel, tetragonal, and monoclinic can be found in nature [17].

The current methods to obtain hollow structures are a hard/soft templating method and self-templating method [18]. Hard templating methods consist in coating the template with the material of interest and then removing it. The soft templating method is very similar, but, due to the fluid nature of the template, almost in every case there is no need of a removal step. The hard-templating method is the simplest one, although soft templating method provides more control of internal and external properties. In a self-templating method, the structures are obtained directly, without the need of a template, in a process of creating voids in the solid structure due to ions diffusion. Fabrication techniques of metallic microtubes use polymers as templates. A metal layer is enrolled as part of the hybrid polymer/metal tube which after pyrolysis the polymeric material is removed [19]. In some cases, structural phase transition along with the application of an electrical current play an important role to fabricate hollow materials in micrometer scale [20]. In this work, we have discovered a unique method to fabricate hollow microtubes which are formed due to metal liquid mass transfer movement. This approach, which is completely different from those discussed above, is simple, fast, and the final hollow structure free of external agent.

Microtubes in the presence of liquid exhibit capillarity phenomenon which can move the liquid up and down inside the hollow channel [21]. The tendency of wetting liquids to move into the confined space of a narrow tube is associated with capillarity effect and surface tension. It also includes physical phenomena in which

* Corresponding author.
E-mail address: joseantonio.souza@ufabc.edu.br (J.A. Souza).

https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.026
0017-9310/

Nomenclature

a, *b*, *c*	lattice constants, Å
Al	aluminum
Cu	copper
$K\alpha_1$	K Alpha 1 beam
P_{Air}	atmospheric pressure, Pa
P_C	capillary pressure, Pa
P_{Metal}	pressure in the droplet, Pa
R	droplet radius, m
r	capillary radius, m
T	temperature, °C
T_M	melting point temperature, °C
Greek symbols	
θ	contact angle, °
ΔP	pressure difference at the droplet surface, Pa
σ	surface tension, N/m

a curved liquid–gas interface forming a meniscus is observed. The theory of capillarity involving the Young-Laplace equation describes the pressure drop across a curved interface in which a certain surface tension can be associated. In general, when the overall size of structures is reduced, capillarity effect becomes more relevant, because forces on the surface dominate over bulk forces. It is very interesting that, in this work, we use capillarity and surface tension effects not to study the liquid confinement inside the microtubes, but to fabricate them.

In this work, we employ a sort of self-template method, based in thermal oxidation process, to obtain aluminum oxide microtubes using a metallic precursor in its liquid phase. Hollow aluminum oxide microstructures are obtained with inner diameter about 66 μm and as long as 10 mm. The wall of the as-grown microtubes is comprised of amorphous aluminum oxide decorated with metallic nanoparticles. Further heat treatment can both crystallize the Al_2O_3 phase into R-3cH space group symmetry and consume the remaining metallic part. The capillary driven pressure effect plays an important role towards the microtube formation, which is discussed through microfluidic dynamics involving Young–Laplace equation.

2. Experimental section

In order to obtain an aluminum oxides (Al_2O_3) microtubes, metallic aluminum microwires (63 μm diameter and 99.99% purity) were placed into a horizontal quartz furnace to be oxidized. A thermal oxidation process has been done at 750 °C in air atmosphere during 2 h. We have systematically studied the microtube formation in other temperatures (700 °C and 800 °C) and time (1 and 3 h). As we will shall see, the results revealed very small variation on the microtubes dimensions. An optical microscopy (LEIKA DM 2700M) was used to characterize the tubular structure of microtubes as well as scanning electron microscopy (JEOL SEM JSM-6010LA). X-ray diffraction measurements were performed using an X-ray diffractometer STADI-P in transmission geometry by using monochromatic radiation Cu $K\alpha_1$ (1.54056 Å; operating at 40 kV and 40 mA) selected by a curved germanium (1 1 1) at room temperature. Transmission electron microscopy (TEM) was employed for structural characterization using a LaB_6 electron thermionic emission. All images were collected by a transmission microscopy (Zeiss Libra 120) operated at 120 kV of acceleration voltage acquired by CCD camera (Olympus Cantega G2). Bright and dark field images were used to visualize particles morphologies and sizes while diffraction patterns were used to confirm the crystallographic phase. Electron energy loss spectroscopy (EELS) was applied to investigate elemental analysis and chemical bonds around aluminum and oxygen atoms.

3. Results and discussion

During an oxidation process, the well-understood steady-state diffusion of ions throughout the crystal structure is governed by Fick's law [22]. This means that the diffusion of ions and vacancies is induced by the difference in atomic concentration due to chemical potential gradient. The oxidation chemical reaction encompasses a process where a thin oxide layer is formed first on the metal surface, followed by simultaneous outward diffusion of metal ions through the oxide layer and inward diffusion of oxygen from the atmosphere into the core. Metal ions often diffuse outward faster than oxygen diffuses inward, which is consistent with the smaller ionic radius of cations than anions. In this work, we show that aluminum oxide microtubes decorated with metallic Al nanospheres have been obtained in a straightforward method involving thermal oxidation process. Al metallic microwires are used as a precursor. All the process takes place above the Al melting point, T_M = 660 °C. The furnace containing the microwires in a crucible is warmed up to a set point temperature of 750 °C at a rate of 12 °C/min and kept constant for 2 h. Afterwards, the system was allowed to cool down to room temperature. We have performed the process on both air atmosphere and in the presence of water vapor, which increased the oxidation layer on the surface of the metal. It is very interesting that even in the liquid phase the microwire keeps its cylindrical shape due to surface tension. During the chemical reaction, an aluminum oxide layer is formed first, which can also influence the wettability and adhesion/cohesive force of the Al liquid. The combined effects of the structural support provided by the solid Al_2O_3 layer, capillarity effects and the surface tension nature of the Al liquid in the core will provide the necessary conditions for the processing of our microtubes. Fig. 1(a) and (b) show some representative SEM images of the obtained samples after the oxidation process. It is very interesting that we have found out hollow structure morphology. Samples are comprised of an oxide tube along with the remaining metallic part where one can see, at the end or in the middle, the formation of large spherical droplet. The formation of these droplets along with capillarity effects are the driving forces for the liquid movement inside the tube. They have around 66 μm of internal diameter and a wall thickness of approximately 2 μm and length as long as 10 mm. Concerning the length of the microtubes, nanofluidic devices and lab-on-a-chip research have considered several millimeters as long enough for applications [23]. The current trend of miniaturization has brought forward applications relying on a lab-on-a-chip technologies, smaller microtubes would most likely be used. Analyzing the surface morphology through the optical and scanning electron microscopy imagens we can notice that they are uniform with the absence of porous. The microtubes are a little