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Development and optimization of thermal sprayed ceramic microfiltration membranes

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ABSTRACT

We prepared a number of Alumina (Al_2O_3) microfiltration membranes fabricated using a well-established large throughput thermal spray (TS) technique. In order to study the filtration characteristics and performance of the thermal spray membranes, a variety of microstructures were fabricated by the varying spray process, deposition parameters and the source materials. We characterized the prepared membranes using XRD (X-ray Diffraction), EDX (Energy dispersive X-ray Spectroscopy), SEM (Scanning Electron Microscopy), pore size analysis and dead end filtration tests. Permeability and rejection rate of the sprayed membranes were comparable to some of the commercially available inorganic membranes with the advantage of being highly scalable and potentially orders of magnitude cheaper than the commercially available ceramic membranes.

1. Introduction

Ceramic membranes are heavily used in filtration processes which not only demand high chemical and thermal stability but also extended durability. However, applications of these membranes are limited by a few major drawbacks, resulting in a much smaller market share as compared to that for polymeric membranes. These drawbacks include high manufacturing cost, stemming from expensive fabrication methods, complex processing, and higher operating costs [1]. Commercial membranes are generally produced via sol–gel, extrusion, and/or sintering methods [2]. While many methods have been explored to reduce the fabrication costs of the ceramic membranes [3], low scalability of membrane's dimensions remains an issue to overcome. Therefore, in order to expand the market for inorganic membranes, cost effective and scalable manufacturing methods need to be developed.

Thermal spray (TS) is a well-established technique for producing protective coatings which are extensively used in industries requiring thermal or surface protection of components, such as gas turbine, heavy machinery, etc. The process requires use of a high temperature and high velocity flame, such as plasma jet and oxy-fuel jet to melt the feedstock material and to deposit it onto a substrate surface (Fig. 1). The coating formation occurs with successive impingement of molten material in droplet forms on the substrate surface [4]. Due to layer-by-layer assemblage of individual particles, also referred to as 'splats', these coatings contain a myriad array of various kinds of defects, such as macro-pores, interlamellar pores, microcracks, oxide inclusion etc. (Fig. 1) [5]. The process can coat almost any non-volatile material including metals, ceramics and even polymers. There are several variants of this process, such as combustion flame spray (CFS), atmospheric plasma spray (APS), vacuum plasma spray (VPS), high-velocity oxygen fuel (HVOF) and others [6]. Among these methods, APS and CFS are the simplest and the most cost effective processes. For example, in such applications as fuel cells, APS provides significant cost and performance advantages as compared to that for the conventional wet casting process [7]. Given that the main focus of TS technology is to produce protective coatings, it would be also extremely encouraging to produce high quality porous membranes using a technique that is traditionally reserved for fabrication of coatings for thermal insulation. Over the last decade there have been several attempts to produce porous coatings using the TS APS method with a primary focus on such applications as gas separation and fuel cell electrodes [8]. However, there have been only a few attempts to use this technique to manufacture porous ceramic membranes for water filtration [9–11]. These attempts produced low porosity membranes, which exhibited limited water permeability. However, these published results for the water filtration membranes did not include optimization of the membrane

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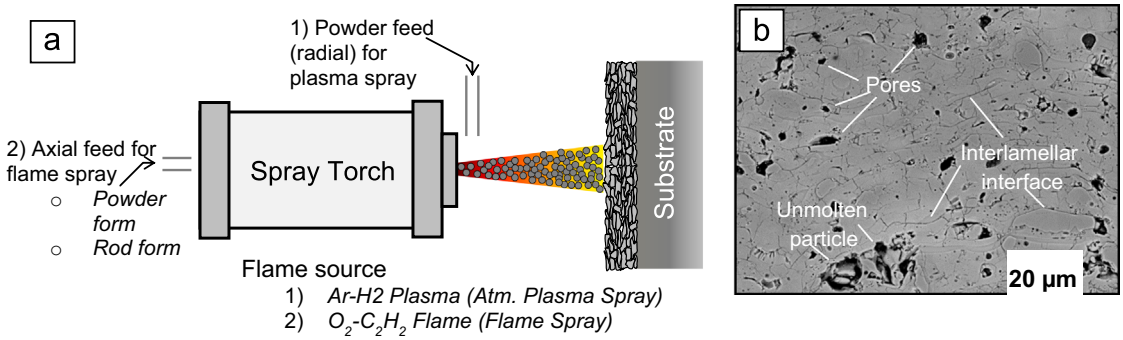

Fig. 1. Schematic of the plasma spray process (b) SEM image of spray cross section showing various features.

performance. In this paper, a systematic study of membrane performance was conducted by exploring the effects of different TS processes and process conditions as well as different types of feedstock materials on membranes permeability. For a given set of process parameters, the coating thickness was correlated to water flux and rejection. In addition to performance measurements, the membranes were characterized by XRD, EDX, SEM and pore size analysis.

2. Experimental details

2.1. Materials and methods

The Al_2O_3 ceramic membranes were prepared using APS (Ar–H_2 plasma, F4 MB, Oerlikon Metco, Westbury, NY, USA) and CFS (oxy-acetylene, TeraDyn™ 3000, and Rokide™, Saint Gobain, Worcester, MA, USA) spray processes. The feedstock introduction into the spray plume was radial and axial for APS and CFS process, respectively. Two types of alumina feedstock were used – powder (Micron abrasive, Westfield, MA, USA) and rod type (Saint Gobain Ceramic Materials, Worcester, MA, USA). The powders were used for both APS and CFS processes, while the rod feedstock was used only for the CFS process. When introduced to a flame, powder feedstock materials produced a higher degree of porosity as compared to that for rod feedstock due to significant number of unmolten particles trapped in the coating. While in rod-based CFS process, the feedstock is introduced axially to the plume and is melted locally in the hottest section of plume. The molten zone is then subjected to a high pressure N_2 jet, which first fragments and then carries out the molten particles to a substrate. This process fabricates a coating with almost no unmolten particle and relatively denser microstructure as compared to the powder type feedstock, since only fully molten particles can be carried out by N_2 jet. The process parameters details for the thermal spray processes are summarized in Table 1. All the membranes were deposited on 100×25 mm^2 porous stainless steel substrates of 2 mm thickness, procured from Mott Corp., Farmington, CT, USA, with an average pore size of 10 μm. In order to investigate the effect of membrane thickness on infiltration performance, three different thicknesses (~100, 200 and 300 μm) were sprayed for each set of the process and corresponding processing condition. The deposited membranes were cut into multiple pieces 25 mm × 25 mm, using high speed saw, (Buehler Inc., Chicago, IL, USA). These specimens were evaluated for clean water flux and rejection rate in a dead-end filtration module setup under 4.5 bar (450 kPa) pressure in the ambient conditions. The schematic of test method and an image of test cell is shown in the Fig. 2. Rejection rate was measured using 1 μm polystyrene spheres (Fisher Scientific Inc., Pittsburg, PA, USA). At least three measurements per specimens were measured.

Table 1
Processing conditions for the thermal spray samples.

Spray parameters	Plasma spray	Flame spray
Argon (slpm)/Oxygen (slph)	30 and 47.5	40
H_2 (slpm)/Acetylene (slph)	2 6	40
Current (A)	450	–
Plasma power (kW)	24 and 34	–
Feedstock	Powder	Powder and rod
Spray distance (cm)	10 and 15	15
Raster speed (mm/s)	500	500
Mean particle size (μm)	50	50
Feed rate (gm/min)	30	30

2.2. Characterization

Since the TS process involves melting and rapid solidification of material, there is always a possibility of phase change of material during the deposition process. Therefore, to ensure the presence of appropriate phases, the membranes were analyzed by X-Ray Diffraction (Philips PW 1720, Philips Analytical Systems, Mahwah, NJ, USA) with the following settings: working voltage and current of 35 kV and 25 mA, step size of 0.02° and scan 2-theta range from 20° to 70°. Scanning electron microscope (Hitachi TM3000, Angstrom Scientific Inc., Ramsey, NJ, USA) was used to obtain microstructures of polished cross-section of membranes under back-scattered electron mode. Standard image analysis (ImageJ software using Otsu algorithm) procedure was used to determine overall porosity of the membranes [12]. Pore size analysis was done using gray scale SEM images. Each of the membrane samples was sliced at the same depth before polishing and imaging to maintain consistency across the samples. Thickness measurements were done using a digital micrometer and verified using the image analysis software mentioned above. The flame sprayed membranes were designated as F1 and F2 based on the rod and powder feed stocks respectively. Likewise, plasma sprayed membranes were labeled based on the changes in the plasma power and spray distance with P1, P2 and P3, corresponding to 24 kW and 10 cm, 24 kW and 15 cm and 34 kW and 15 cm spray distance. Although we have not performed a direct coating adhesion test (ASTM C-633), the range for thermal sprayed ceramics can be from 10 MPa to 50 MPa, depending on substrate and coating material, substrate roughness and on processing conditions.

3. Results and discussion

3.1. XRD and EDAX analysis

The sprayed membranes were analyzed under XRD for phase transformations that could potentially occur during the spray and cooling process. The diffraction patterns obtained from the surfaces of the five