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ScienceDirect
Ceramics International 35 (2009) 747–753
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Pore geometry of 3D-C_f/SiC composites by mercury intrusion porosimetry

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Received 27 August 2007; received in revised form 15 November 2007; accepted 8 February 2008
Available online 4 June 2008

Abstract

The 3D-C_f/SiC composites fabricated via precursor infiltration and pyrolysis (PIP) are porous inside due to their specific processing. To evaluate the porosity of 3D-C_f/SiC, a novel procedure of mercury intrusion porosimetry (MIP) was adopted to extract information from the hysteresis and entrapment. This method is able to eliminate the temporarily retained Hg at atmospheric pressure from the real entrapment due to topological reasons. From the interpretation of the MIP primary and secondary intrusion–extrusion data, accompanied by scanning electron microscopy (SEM) analysis and bubble point measurement, the pore geometry of 3D-C_f/SiC is supposed to be a 3D network originating from the architecture of braided carbon fabrics. This network is composed of hundreds of micron-sized large chambers between bundles, micro-cracks below 0.1 μm and medium-sized channels about 20–4 μm that bridge the former two and provide passages for fluids permeating the material.

Keywords: B. Porosity; CMCs; 3-Dimensional reinforcement; Analytical model; Mercury intrusion

1. Introduction

Precursor infiltration and pyrolysis (PIP) is one of the most important fabrication processes for 3-dimensional carbon fabric reinforced SiC (3D-C_f/SiC) composites. However, due to the pyrolysis gas escape and incomplete precursor infiltration, there are inevitably some voids and cracks in the 3D-C_f/SiC even after successive infiltration–pyrolysis cycles. Thus, the 3D-C_f/SiC composites are not totally dense but actually porous. This specific microstructure has critical influence on C_f/SiC mechanical and thermal properties [1,2], thus its evaluation is attractive and valuable undoubtedly. For fibers reinforced composites (FRC), scanning electron microscopy (SEM) is prevalently used to characterize the inner morphology [3,4], however, it is difficult to evaluate the porosities of the composites by SEM only, for its 2-dimensional, limited sight-fields.

For porous media, especially solids, mercury intrusion porosimetry (MIP) and isothermal N_2 sorption (INS) are the two classic methods to characterize the porosity, specific surface area, pore size distribution (PSD), and the surface roughness/surface fractal dimensions etc. [5,6]. Examples of the characterization of FRC by MIP are also reported [7,8]. The interpretation of MIP results is based on the Washburn equation [9], under the assumption that the pores are bundles of capillaries with various sizes which are equally accessible to the exterior mercury reservoir. The deviation of real cases from the above simplified model results in the intrusion–extrusion hysteresis and mercury entrapment. Several explanations have been offered to account for these phenomena, the most accepted one is the so-called ''ink-bottle'' effect [10] i.e., the pores' chambers are surrounded by smaller pore throats and access to the outside via them. Due to the shielding of throats on chambers, intrusion hysteresis occurs and the calculated PSD will be biased towards smaller than actual status, thus is also called the pore throat size distribution (PTSD). With the MIP becoming popular in many fields, this throat-chamber model faces increasing challenges and some new concepts have been raised to describe the complicated experimental results, e.g., the hysteresis of MIP is separated to ''structural hysteresis'' and the ''parametric hysteresis'' [11], according to their sources. The former is caused by the connectivity of pore network and

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0272-8842/$34.00
doi:10.1016/j.ceramint.2008.02.011

the inter-shielding status of the large and small pores, reflecting the media's topological characters [12], while the latter is referred to the ones caused by the variation in contact angles, surface tensions during mercury advancing or retreating from the samples, and can be eliminated by adjusting the extrusion contact angles carefully [13]. The permanent mercury entrapment is believed to occur in the large pores shielded by the small ones, caused by the snap-off of mercury flow at the pore throats when retreating from the chambers [14], which is more likely to happen if the chamber/throat size ratio reaches 6 or higher [15].

MIP is an indirect characterization and the interpretation of the experimental data needs some theories and well-established models. Moreover, to extract more useful porosity information, specific operations are often applied during usual MIP procedure, among which applying secondary intrusion–extrusion after the primary cycle is the most familiar. This application can help to estimate the contribution of the shielded pores to mercury entrapment, evaluate the structures' damage of the samples induced by high pressures during intrusion, and distinguish the continuous, accessible parts of all the pore network that is crucial to permeability [16–18]. According to the previous literature, during MIP procedure, the re-intrusion started immediately as soon as the pressures reduced to a low level where the primary extrusion came to an end. However, to avoid dangers and damages upon apparatus, the primary/1st extrusion can only be carried out in the high-pressure ports, which determines the end pressure is higher than atmospheric pressure, e.g., 29 psia [18], or 250 psia [16]. Obviously, these pressures are not low enough to let the mercury retreat thoroughly, and mercury droplets will still retain in the large pores, which is immingled with the ''real'' entrapment.

Our preliminary work has shown that MIP is preferable to INS for characterization the porosity of 3D-C_f/SiC composites, because of the limited probing ranges and disability to macropores (>1 μm) of INS [19]. In this work, a novel secondary mercury intrusion–extrusion procedure was conducted to 3D-C_f/SiC besides the primary, to investigate the actual porosity of the composites. By interpreting the differences between these two MIP cycles, supported by SEM and bubble point method results, the pore geometry was analyzed and described.

2. Materials and methods

The 3D-C_f/SiC specimens were produced by subjecting the braided 3-dimensional carbon fiber fabrics (T300, Toray Inc., Japan) to some infiltration–pyrolysis cycles, using polycarbosilane (PCS) as the polymer precursor. To track the microstructural evolution of C_f/SiC, specimens underwent various fabricating cycles before finish were also chosen for characterization.

All MIP measurements were carried out with Micromeritics AutoporeIII 9420. Prior to characterization, the 3D-C_f/SiC specimens were sliced into segments about 4 cm × 4 cm to expose the inner pores. After repeated impregnation with ethanol, cleanout, and drying, some of these segments were loaded into the penetrometer, undergoing evacuation and pressurization at the low pressure port and the high one respectively, the pressures range from 1 to 55,000 psia ($6.9 \times 10^{-3} \sim 380$ MPa). Usually, the mercury extrusion begins as the pressure reaches the highest value and continues till the atmospheric pressure level (36 psia) reached. However, to make Hg withdraw from the samples as much as possible, a novel procedure was adopted. Firstly, the penetrometer was extracted from the high-pressure port when the 1st extrusion ended, then the sample segments were taken out carefully, loaded into another new penetrometer, evacuated to a very low pressure (5.3 Pa), and were subjected to the next intrusion–extrusion cycle. The raw data of 2nd MIP were adjusted by the original sample mass. The contact angle of Hg on the specimens during intrusion was assumed to be 130°, and its surface tension was 0.485 N/m. The equilibration time was 15 s both at intrusion and extrusion. The morphology of specimens cross-section was characterized by scanning electron microscope (JSM-5600LV, JEOL). The pore size and distribution was also characterized by the bubble point method according to the GB/T 5249-1985, GB/T 5250-1993 standards (PR China), applying ethanol as the saturation liquid.

3. Results and discussion

3.1. Capillary pressure curve

The primary and secondary MIP capillary pressure curves of 3D-C_f/SiC are plotted in Fig. 1. On the primary intrusion curve, there are several phases distinguished by different slopes. At the beginning of 1st extrusion, Hg does not retreat from the sample until the pressure reduces to the value of 0.2 μm-sized capillary, thus the extrusion branch lies above the intrusion one. With depressurization continuing, the extrusion's deviation from intrusion becomes wider and wider, till the pressure reaches the ambient level and retreating finishes. At the low capillary pressures below 20 μm, the 2nd intrusion curve is well consistent with the former one, but drops behind at higher

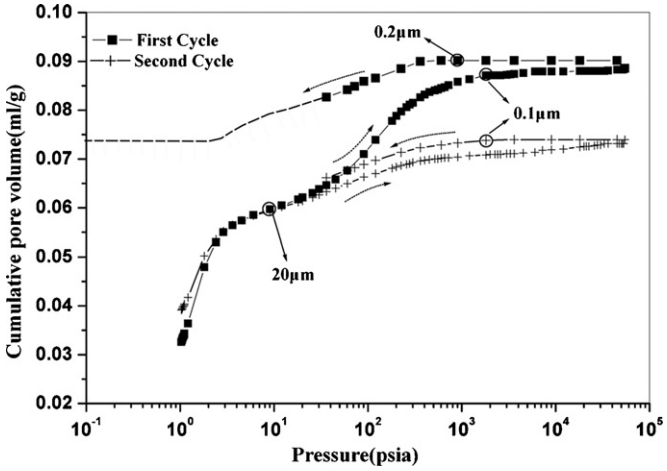

Fig. 1. Capillary pressure curves of 3D-C_f/SiC after primary and secondary MIP cycles, respectively. The dash line shows the possible trend of the 1st extrusion plot if the pressures keep reducing.