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Iron foams created by directional freeze casting of iron oxide, reduction and sintering

Amelia A. Plunk *, David C. Dunand

Department of Materials Science and Engineering, Northwestern University, 2220 Campus Dr., Evanston, IL 60208, USA

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ABSTRACT

Iron foams with aligned, lamellar channels were created by directionally freeze-casting slurries of water and Fe_2O_3 nanopowders, sublimating the ice, and reducing and sintering under hydrogen the powders accumulated in the interdendritic spaces. Foam porosity decreases from 85 to 50% with Fe_2O_3 slurry fractions increasing from 14 to 23 vol.%. For foams created from 18.5 vol.% Fe_2O_3 slurries, with increasing sintering temperature from 900 to 1100 °C, a decrease in porosity from 71 to 61% and an increase in unidirectional compression strength from 8 to 20 MPa are observed.

1. Introduction

Directional freeze-casting is a bottom-up templating technique that has seen extensive use over the past decade to create ceramic foams with aligned, elongated channels tens to hundreds of micrometers in width, and millimeters to centimeters in length [1–3]. Micropores within channel walls can occur due to incomplete sintering, increasing surface area of the foams. Directional freeze-casting is based on the following steps: (i) slurry is created with fine ceramic powders in suspension in liquid; (ii) suspension is frozen directionally; ice dendrites grow along the temperature gradient and push the suspended powder in the interdendritic space; (iii) ice is sublimated, leaving aligned, lamellar channels replicating the ice dendrites, surrounded by ceramic powder walls; (iv) powder walls are sintered into the dense walls of a strong ceramic foam. For metallic foams, the same method can be used with metallic powders as demonstrated for Ti [4,5], or with oxide powders which are reduced before or during sintering, as demonstrated recently for Cu [6,7], Ni [8], and W [9]. This latter method overcomes difficulties associated with suspending fine metallic powders in water, i.e., powder rapid settling in the suspension and premature engulfment by ice dendrites due to higher densities of metals as compared to oxides, and oxidation of submicron powders required to prevent engulfment. Recent work [10] has shown the ability to freeze-cast nanometric hematite Fe_2O_3 powders in liquid camphene to create hematite foams, displaying cylindrical pores with high aspect ratio; hydrogen reduction to iron was also demonstrated. In the present work, we demonstrate for the first time the combination of directional freeze-casting of nanometric Fe_2O_3 powders in water, creating aligned, lamellar ice dendrites with nanopowders rejected to the interdendritic space, and reduction and sintering in a hydrogen atmosphere to create iron foams with aligned, lamellar channels and micropores within channel walls. Parameters controlling the freeze-casting, reduction and sintering process are explored and discussed. These directional iron foams could be used for structural applications [11] and for redox cycling in iron-air batteries. In the latter application, freeze-cast iron foams are expected to show a unique combination of permeability, high surface area and resistance to sintering, superior to current iron powder beds [12–15].

2. Experimental

Slurries were prepared for freeze-casting by dissolving 4.5 vol.% poly(ethylene glycol) binder (PEG, Sigma–Aldrich, avg. M_n: 400) into deionized water together with 2 vol.% of a commercial dispersant. Mixture was stirred for 30 min. Subsequently, 14, 18.5 or 23 vol.% Fe_2O_3 nanopowders (40–60 nm, from US Nano LLC) were added; slurry was stirred for 30 min more. Slurries were poured into cylindrical Teflon molds and sealed on the bottom by thin copper foil. The filled mold was placed on a copper rod cooled to −17 °C. The sides and top of the mold were insulated using polystyrene foam to prioritize the vertical temperature gradient.

* Corresponding author.
E-mail address: aplunk@u.northwestern.edu (A.A. Plunk).

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Slurries were left to freeze on the copper rod for ~90 min until solidified. Frozen samples were removed from the mold and transferred to a freeze dryer (Labconco Corp.). Here, samples were held at 0.133 mbar and a collector temperature of −40 °C for 24 h for ice sublimation.

After sublimation, green bodies were subjected to a three-step heat-treatment in a tube furnace under pure flowing H_2: (1) 300 °C, 1 h: dispersant and binder burnout, (2) 600 °C, 4 h: chemical reduction, (3) 900, 1000 or 1100 °C, 3 h: sintering. Full reduction from Fe_2O_3 to Fe was confirmed through weight loss comparison to theoretical values and through X-ray diffraction (XRD). Longitudinal and radial cross-sections were cut and examined using scanning electron microscopy (SEM), and were also impregnated with resin and polished for examination using optical microscopy.

Uniaxial compression tests were conducted using a servo-hydraulic mechanical testing system with a 50kN load cell on iron foams cut into $5 \times 5 \times 10\ mm^3$ rectangular prisms using a low-speed diamond saw. The samples were loaded parallel to the alignment of channels.

3. Results and discussion

Fig. 1a-b show optical micrographs of polished cross-sections of a representative Fe foam in the planes parallel and perpendicular to the temperature gradient. Foams display colonies of parallel walls surrounding aligned, lamellar channels. These lamellar channels extend from the base to the top of the sample, as illustrated in Fig. 1a. A similar channel and wall structure was reported in Cu, Ni and W foams created by through similar pathways [6–9].

Two processing parameters were studied: (i) sintering temperature; (ii) volume fraction of Fe_2O_3 in slurry. As shown in Fig. 2a, porosity of the sintered foams decreases with increasing sintering temperature (from ~70% at 900 °C to ~60% porosity at 1100 °C) for a constant Fe_2O_3 slurry fraction of 18.5 vol%; this decrease in porosity is also shown in channel thickness measurements, which decrease from ~46 µm at 900 °C to ~40 µm at 1100 °C, while wall thickness is ~36 µm for all three samples. Fig. 2b shows that for a constant sintering temperature of 1100 °C, varying the Fe_2O_3 slurry fraction from 14 to 23 vol.% decreases foam porosity from ~85 to ~50% porosity, a result consistent with the decreasing channel width from ~49 µm to ~37 µm and increasing wall thicknesses from ~27 µm to ~46 µm. A recent study on directional freeze-cast tungsten foams shows similar trends [9].

Fig. 1. Optical micrograph of iron foam reduced and sintered from 20 vol.% Fe_2O_3 slurry. Cross-sections are (a) longitudinal, showing short-range lamellar channel structure consistent with conventional unidirectional freeze-casting [3] separated by Fe walls, and (b) radial, showing lamellar channels parallel to each other within colonies of consistent size.

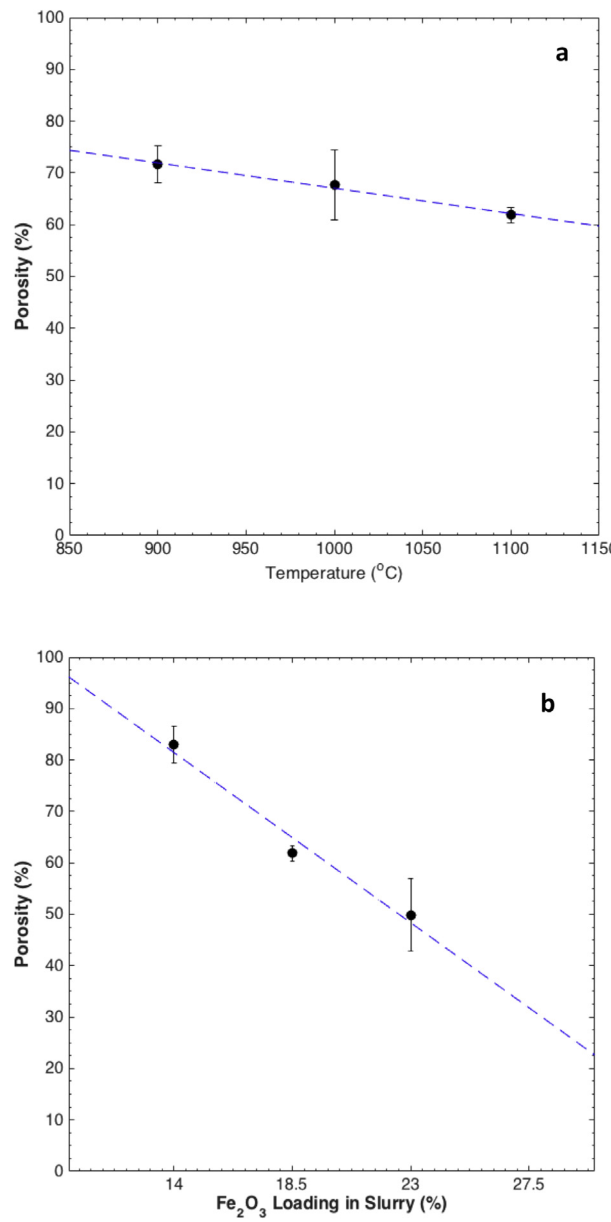

Fig. 2. Effect on foam porosity of (a) sintering temperature at constant Fe_2O_3 slurry fraction of 18.5 vol.%, and (b) Fe_2O_3 slurry fraction at constant sintering temperature of 1100 °C.

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