

CELLULAR FOAMS: A POTENTIAL INNOVATIVE SOLID BREEDER MATERIAL FOR FUSION APPLICATIONS

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Ceramic foam and cellular materials are being used in a wide variety of industries and are finding ever growing number of applications. Over the past decade advances in manufacturing of cellular materials have resulted in ceramics with highly uniform interconnected porosities ranging in size from a few μm to several mm. These relatively new ceramic foam materials have a unique set of thermo-mechanical properties, such as excellent thermal shock resistance and high surface to volume ratios. Based on new advances in processing ceramic foams, we suggest the development of ceramic foams or cellular ceramics for solid breeders in fusion reactor blankets. A cellular breeder material has a number of thermo-mechanical advantages over pebble beds, which can enhance blanket performance, improve operational stability, and reduce overall blanket costs.

I. INTRODUCTION

Ceramic foams have an interesting combination of properties, such as low weight, high temperature stability, high permeability, high porosity, low thermal conductivity, and low heat capacity. These properties have lead to a diverse range of applications, such as metal melt filtration, ion-exchange filtration, heat exchangers, catalyst support, refractory linings, thermal protection systems, diesel soot traps, flame rectifiers, and solar radiation collectors.¹⁻¹⁰ Recently, the bio-technology and biomedical industries are employing ceramic foams made of hydroxyapatite, which can simulate bone and bio-implants.^{11, 12} Most of the new applications have been made possible because of advances in manufacturing ceramic foams with highly tailored pore morphologies.

Characteristic dimensions of solid breeder packed beds are driven by operation limits, such as maximum breeder temperature and low thermal conductance at the breeder wall interfaces. These limitations are further exasperated by uncertainties in thermo-mechanical properties, caused by pebble movement, sintering, and potential pebble fracture or disintegration during operation. However, ceramic breeder foam or cellular breeder materials could have a number of thermo-mechanical advantages over pebble beds: higher thermal conductivity, higher heat convection, higher wall-bed thermal conductivity, structural rigidity, and lack of sintering. Furthermore, cellular ceramic materials are not limited in density as packed beds are to packing fractions.

Increase in breeder density, higher thermal conductivity, and improved breeder-wall contact would result in a reduction of blanket multiplier and structure volume fractions, which would not only improve performance but also reduce design complexities and blanket costs.

Some of the more recent manufacturing techniques and applications of ceramic foams are summarized. Typical thermo-mechanical properties are briefly outlined and a brief discussion regarding potential advantages of solid breeder foams over pebble beds is given.

II. CERAMIC FOAM APPLICATIONS

Engineered foams have cellular structures which are categorized as either open cell or closed cell foams. Foam consists of an assembly of irregularly shaped prismatic or polyhedral cells connected to each other with solid edges (open cell) or faces (closed cell). Engineered foams have been manufactures from polymers, metals, glasses, and ceramics. Ceramic foams are porous brittle materials with closed, fully open, or partially interconnected porosity. First, some of ceramic foam applications are highlighted followed by a discussion of various manufacturing processes.

Ceramic foams offer a unique combination of properties, such as low density, high surface area to volume ratio, high stiffness to weight ratio, low thermal and electrical conductivity, and highly localized strain and fracture characteristics.^{1,2} Ceramic foams have a very high thermal shock resistance and thus open cell foam is used to spread flames, fuels, or coolants uniformly.^{9,10} Closed cell ceramic foams are mostly used for fire protection and thermal insulation materials.

Open cell ceramic foams are used for a very wide range of applications. The excellent thermal shock resistance facilitates their use for metal melt filtration¹³ and Diesel engine exhaust filters.^{3,4} Ceramic foam filters improve molten metal casting quality by removing non metallic inclusions. These filters must withstand thermal shock and be stable against chemically reactive metals at elevated temperatures. Combustion in porous media is an intense area of research because of flame stabilization, improved burning velocity, and reduction in NO_x emission.^{5,6} Ceramic foams are employed in catalytic combustion devices and in a variety of catalysis reactors.⁸ Ceramic foams are also being developed and employed for solar based processes, either direct CO₂-CH₄

reforming⁹ or volumetric receivers for concentrated solar radiation.¹⁰ More recently porous ceramic materials are finding applications as bio-resorbable macroporous scaffolds for bone tissue engineering. The high interconnectivity of porous ceramics ensures the transport of nutrients and metabolic waste, as well as large surface areas for tissue attachment and growth.^{11,13,14}

III. CERAMIC FOAM MANUFACTURING

Ceramic foam manufacturing techniques can be classified into three general categories: sponge-replication, foaming agents, or space holder method.

The sponge replication was first developed in the early 1960s.¹⁵ It consists of using a natural sponge or polyurethane foam as a form, which is infiltrated with ceramic slurry. The ceramic slurry is then fired to form ceramic foam.^{2, 13, 16} Fig. 1 shows an example of a TiO₂ foam made by sponge replication.¹⁷ Chemical vapor deposition has also been used as a sponge replication method to create ceramic foams with high density struts.⁷

The second technique is based on gas bubbles in preceramic melts.^{2, 12, 13, 18} Gas evolving constituents are added to the melt. During the treatment bubbles are generated, causing the material to foam. This process was introduced in 1973 by Sunderman.¹⁹ Foaming uniformity and cell geometry can be adjusted by careful selection of surfactants and foaming agents.²⁰⁻²²

The third technique is based on a space holder concept. For example, sodium chloride is sintered and compacted to form a porous space holder, which is infiltrated with polycarbosilane. The salt is then dissolved and a polymer foam remains, which is then pyrolyzed to form the SiC foam.^{23, 24} Qian²⁵ made highly porous SiC ceramic with wood-like microstructure and porosity by infiltrating wood with silica sol-gel. The resulting porous SiC morphology resembles a wood microstructure.

IV. CERAMIC FOAM PROPERTIES

Typically, open cell ceramic foams exhibit high porosities (70–90%) with non uniform spherical-like cells connected to each other by ligaments. The tortuosity of the foam is characterized in terms of the pore diameter, d_p , or pore per inch (PPI) density. Typical pore diameters range between 0.01 to 2 mm, although recently open cell microcellular SiOC foams with cell sizes ranging from about 1 to 100 microns have been manufactured.²⁶ In isotropic foams, typical pore densities range between 10 to 100 ppi. Fig.1 shows an example of a sponge replicated 40-PPI TiO₂ foam.

The tetracadehedron is the most common unit cell structure of open-cell foams, consisting of 14 faces, 36 edges and 24 vertices. Table I lists the geometric constants of a tetrakaidecahedron unit cell. The interconnecting struts provide an enormous surface area per unit volume, S_v . In 10 to 65 PPI pore densities, S_v varies from 1.71×10^4 to 6.84×10^4 m²/m(solid)³, which is

equivalent to that of spherical packed beds with diameters ranging 0.05 to 0.34 mm.⁸

TABLE I: Constants of the tetrakaidecahedron unit cell.^{2,8}

Property	Symbol	Formula
Pore diameter	d_p	Measured
Solid porosity	p	Measured
Hexagonal side	l	$0.5498d_p/[1-0.97(1-p)^{0.5}]$
Strut thickness	t_s	$0.971(1-p)^{0.5}l$
Cell volume	V_c	$11.31 \times l^3$
Strut surface area	S_s	$36t_s \times l$
Surface area/vol.	S_v	$S_s/[V_c(1-p)]$

An important property of any cellular solid is its relative density, ρ^*/ρ_s ; where ρ^* is the density of the cellular solid and ρ_s is the density of the solid from which the foam is made. In general, a relative density of 0.3 is the cut-off value between cellular solids (foams) and porous materials. For low density foams the relative density can be expressed in terms of unit cell geometric constants given in Table I.

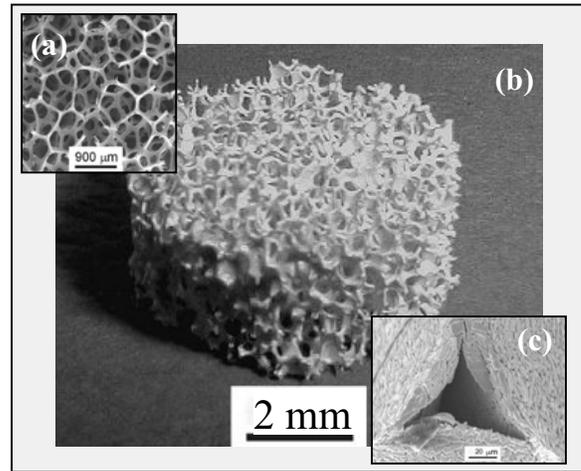


Fig. 1: TiO₂ ceramic foam: (a) fully reticulated polyester polyurethane foam with 45 ppi; (b) TiO₂ foam, (c) hollow TiO₂ foam ligament: polyurethane is removed during sintering resulting in hollow ceramic struts.¹⁷

IV.A. Mechanical and Thermal Properties

The mechanical properties of open cell foams, e.g., stiffness (E^*), the elastic collapse stress (σ_{ei}^*), the plastic collapse stress (σ_{pi}^*), the crush strength (σ_f^*), and the fracture toughness (K_{IC}^*) are summarized in Table II. Foams made of engineering ceramics such as alumina offer comparatively high strengths – up to 80 MPa crush strength and 25 MPa modulus of rupture.²⁷

IV.B. Creep Rate and Time to Failure

Compressive creep of open-cell Al₂O₃ foam was measured for temperatures between 1200°C and 1500°C³⁰.

TABLE II: Mechanical and thermal properties of low density open cell foam.^{2,28}

Property	Formula
Density	$\frac{\rho^*}{\rho_s} = C_1 \left(\frac{t}{l}\right)^2$
Stiffness	$\frac{E^*}{E_s} \approx 1.0 \left(\frac{\rho^*}{\rho_s}\right)^2$
Elastic Collapse Stress	$\frac{\sigma_{el}^*}{E_s} \approx 0.05 \left(\frac{\rho^*}{\rho_s}\right)^2$
Plastic Collapse Stress	$\frac{\sigma_{pl}^*}{\sigma_y} \approx 0.3 \left(\frac{\rho^*}{\rho_s}\right)^{3/2}$
Crushing Strength	$\frac{\sigma_f^*}{\sigma_{fs}} \approx 0.2 \left(\frac{\rho^*}{\rho_s}\right)^{3/2}$
Fracture Toughness	$\frac{K_{IC}^*}{\sigma_{fs}} \approx 0.65 \sqrt{\pi l} \left(\frac{\rho^*}{\rho_s}\right)^{3/2}$
Creep	$\frac{\dot{\epsilon}_f^*}{\dot{\epsilon}_0} \approx \frac{0.6}{(n+2)} \left(\frac{1.7(2n+1)\sigma^*}{n\sigma_0}\right) \left(\frac{\rho_s}{\rho^*}\right)^{(3n+1)/2}$
Thermal Conductivity	$\frac{\kappa^*}{\kappa_s} \approx 0.35 \left(\frac{\rho^*}{\rho_s}\right)$

C₁ is a foam material dependent constant.

The creep behavior of the ceramic foam was very similar to that of dense alumina except at much lower stresses. For strain rates between 10⁻⁸ and 10⁻⁶ s⁻¹ creep occurred by diffusional flow for stresses in the range 20-100 kPa. The activation energy for steady state creep was 504 kJ/mol, which is typical for creep of dense alumina. The onset of tertiary creep was associated with the formation of creep cracks in the struts subjected to bending. For diffusional flow the parameter n of the creep equation (Table II) is unity and the steady state creep then becomes²⁹:

$$\dot{\epsilon}_f^* \approx A \frac{\sigma^*}{\sigma_s} \left(\frac{\rho_s}{\rho^*}\right)^2 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where ε_f^{*} is the foam steady state creep rate, σ^{*} is the foam crushing strength, ρ^{*} is foam density, and Q is the foam activation energy; and σ_s, ρ_s are solid material values. Open cell foam is thus expected to have the same stress dependence and activation energy as the dense material, with the difference of a -2 power of the relative density (ρ^{*}/ρ_s)⁻². For alumina foam with densities less than 30% the steady state creep rate at strain rates between 10⁻⁸ and 10⁻⁶ s⁻¹ in a temperature range of 1200-1500°C was found to be:

$$\dot{\epsilon}_f^* = A \sigma^{1\pm 0.1} \exp\left(-\frac{504 \pm 20 \text{ kJ mol}^{-1}}{RT}\right) \left(\frac{\rho_s}{\rho^*}\right)^{1.8} \quad (3)$$

Creep rates larger than 6% to 9% resulted in accelerated creep that caused creep cracks in individual ligaments. The analysis showed that the primary deformation mode in these ceramic foams was consistent with strut bending. In a review of creep in cellular solids, Andrews et al.,³⁰ examined the behavior of metallic aluminum foams. The failure times of ceramic foams is well described with the Monkman-Grant relationship²⁹:

$$\log t_r + m \log \dot{\epsilon} = B \quad (4)$$

where B and m are density dependent constants. Thus lifetime predictions become possible for known creep rates.

IV.C. Pressure Drop

Richardson et al.,⁸ compared the pressure drop of a bed of glass spheres to that of alumina foam for catalytic reactor applications. Both had similar geometric surface areas. The glass spheres had a diameter of 0.5 mm, a porosity of 0.416, and a surface area of 0.582x10⁴ m²/m³. Equivalent alumina foam was chosen with a pore density of 30 PPI, which translates into a porosity of about 0.874 with a bed equivalent geometric surface area of 0.423x10⁴ m²/m³. Although surface areas are similar between the sphere packed bed and the foam, the larger porosity of the foam results in a reduction in pressure drop of about a factor of 16 at high velocities. Fig. 2 demonstrates the reduced pressure drop of ceramic foam catalyst structures compared with sphere packed beds.

V. ADVANTAGES OF “BREEDER FOAM”

Ceramic foams or cellular ceramic materials have a number of features and/or properties, which make them a promising candidate material for solid breeder applications. These include:

1. Densities are not limited to packing fractions.
2. Higher thermal conductivity due to a continuous strut network, instead of sphere-to-sphere point contacts.
3. Increased breeder density and better thermal performance of foam reduces structure volume fractions and multiplier.
4. No sintering; beginning-of-life and end-of-life configuration changes are primarily creep and swelling driven; reduced shifting of material.
5. Foam-to-wall contact using brazing technology replaces low-conductivity sphere-to-wall point contacts of packed beds.
6. Capability of tailoring pore morphology, could accommodate swelling
7. Anisotropic foam: porosity gradient to achieve uniform heating and tritium release in blanket.

8. Self supporting structure, no shift of material during operation.
9. Potential for improved performance at a lower blanket cost.

Higher densities are beneficial for higher breeding ratios, because structural and multiplier (Be) volume fractions could be reduced. The higher thermal conductivities would increase the spacing between coolant channels in a SB blanket. Foams are self supporting structures, and as such can be machined, cut, and shaped into desired geometries. For foams, the concern of breeder material movement is reduced compared with changes that can occur in packed beds due to sintering or pebble shifting.

A stand alone foam structure can be attached to the coolant wall using one of several adhesion techniques, such as high temperature brazing or CVD.⁷ A well defined and reliable coolant structure wall-to-foam contact can thus be established.

Colombo²⁶ and Zeschky¹⁸ have recently developed the technology to create foams with density gradients. Porosity gradients decreasing from the front of the blanket (close to the first wall) towards the back of the blanket could be used to achieve more uniform temperature distributions through the blanket thickness. A uniform temperature distribution would result in uniform tritium release throughout the blanket.

The foam porosity can be anisotropic. For example, foam with elongated porosity perpendicular to the direction of streaming neutrons can be manufactured similar to the wood-like ceramics developed by Qian et al.²⁵ Such pore morphology could decrease the overall blanket thickness because of reduced porosity along the direction of streaming neutron.

The cost of manufacturing ceramic cellular materials could eventually be substantially lower than that of spherical breeder pebbles. The reason is that ceramic foam manufacturing is becoming a well established industry. Furthermore, the tight sphericity requirements and the narrow size distribution needed for packed beds would no longer be cost driving factors. For example, gel-casting technology, in essence is a casting process that can be developed to produce all forms of shapes of breeder foam materials.

Tritium inventory and tritium release are major issues for solid breeder materials. Tritium release depends on breeder material microstructure, pebble diameter, surface constituents, purge gas chemistry, and operating temperature. In developing a foam-based solid breeder it is critical that the breeder material microstructure is optimized for maximum tritium release and the ligament diameters not to exceed the optimized pebble diameters. Surface modifications and purge gas chemistry could both be adopted from sphere-packed beds. As for the operating temperature, the foam-based breeder could have an

advantage over the sphere-packed beds, in that the temperature across the foam can be made more uniform compared with sphere packed beds, by tailoring foam densities for maximum tritium release.

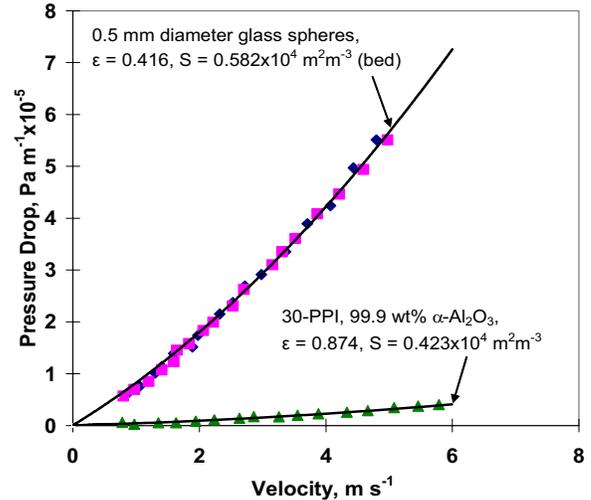


Fig. 2: Pressure drop of a sphere packed bed (glass beads ~0.5 mm diam.) and a 30-PPI, 99.5 wt% alpha-Al₂O₃ foam with comparable geometric surface areas.⁸

VI. CONCLUSIONS

Lithium based solid breeder materials in the form of cellular foam are suggested as an innovative ceramic breeder material. Various manufacturing techniques exist, which could be employed to develop such lithium ceramic foams. To date, lithium ceramic foams have not been manufactured, instead other ceramic foams made of alumina, zirconia, SiC, Si₃N₄, TiO₂, mullite, and glass were investigated. Thermo-mechanical properties of foam structures were listed and specific examples of typical foam behavior were given.

Potential advantages of a lithium-based cellular solid breeder compared with sphere-packed bed are based on potentially higher densities and thermal conductivities along with controllable wall-foam interface conductance. Enhanced thermo-mechanical ceramic breeder foam properties would result in reducing multiplier and structural material volume fractions. This would lead to an increase in tritium breeding ratio and a significant reduction in blanket cost. Rapidly evolving new processing techniques and the ever growing range of ceramic foam applications provide a venue for leveraging required R&D efforts for developing lithium based ceramic breeder foam or macro-porous cellular breeder materials.

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REFERENCES

- [1] M. R. NANGREJO, X. BAO, M. J. EDIRISINGHE, "Silicon carbide-titanium carbide composite foams produced using a polymeric precursor," *International Journal of Inorganic Materials* **3**, 37 (2001).
- [2] L.J. GIBSON, M.F. ASHBY, *Cellular Solids, Structures and Properties*, 2nd ed. Cambridge, Cambridge University Press, 1999.
- [3] L. MONTANARO, "Durability of ceramic filters in the presence of some diesel soot oxidation additives," *Ceramics International* **25**, 437 (1999).
- [4] T. INUI AND T. OTOWA, "Catalytic combustion of benzene-soot captured on ceramic foam matrix," *Applied Catalysis*, **14**, 83 (1985).
- [5] P. RUSSO, P. CIAMBELLI, V. PALMA AND S. VACCARO, "Simultaneous filtration and catalytic oxidation of carbonaceous particulates," *Topics in Catalysis* **22**, Nos. 1-2, 123 (2003).
- [6] F.A. LAMMERS, L.P.H. DE GOEY, "A numerical study of flash back of laminar premixed flames in ceramic-foam surface burners," *Combustion and Flame* **133**, 47 (2003).
- [7] A. J. SHERMAN, R. H. TUFFIAS, and R. B. Kaplan, "Refractory Ceramic Foams: A Novel High-Temperature Structure," *Am. Ceram. Soc. Bull.*, **70** [6] (1991) 1025-29.
- [8] J.T. RICHARDSON, Y. PENG, D. REMUE, "Properties of ceramic foam catalyst supports: pressure drop," *Applied Catalysis A: General* **204** (2000) 19-32.
- [9] J. F. Muir, R.E. Hogan, Jr., R. D. Skycypec, R. Buck, "The CAESAR project," Sandia Report, SAND92-2131, 1993.
- [10] T. FEND, R. AND P. PAAL, O. REUTTER, J. BAUER, B HOFFSCHMIDT, "Two novel high-porosity materials as volumetric receivers for concentrated solar radiation," *Solar Energy Materials & Solar Cells* **84** (2004) 291-304.
- [11] D. W. HUTMACHER, "Scaffolds in tissue engineering bone and cartilage," *Biomaterials* **21**, 2529 (2000).
- [12] P. SEPULVEDA, J. G. P. BINNER, "Processing of cellular ceramics by Foaming and in situ polymerisation of organic monomers," *J. Eur. Ceram. Soc.* **19**, 2059 (1999).
- [13] L. MONTANARO, Y. JORAND, G. FANTOZZI, A. NEGRO, "Ceramic foams by powder processing" *J. Eur. Ceram. Soc.* **18**, 1339 (1998).
- [14] A. ALMIRALLA, G. LARRECQA, J.A. DELGADOA, S. MARTINEZ, J.A. PLANELLA, M.P. GINEBRA, "Fabrication of low temperature macroporous hydroxyapatite scaffolds by foaming and hydrolysis of an α -TCP paste," *Biomaterials* **25**, 3671 (2004).
- [15] K. SCHWARTZWALDER, A. V. SONERS, Method of making porous ceramic articles, US 3.090,094 (May, 21, 1963).
- [16] J. SAGGIO-WOYANSKY, C.S> ACORR. W. P. MINNEAR, "Processing of porous ceramics," *Am. Ceram. Soc. Bul.* **71**, 1674 (1992).
- [17] H. HAUGEN, J. WILL, A. KOHLER, U. HOPFNER, J. AIGNER, E. WINTERMANTEL, "Ceramic TiO₂-foams: characteri sation of a potential scaffold," *J. Eur.Ceram. Soc.* **24**, 661 (2004).
- [18] J. ZESCHKY, F. GOETZ-NEUNHOEFFER, J. NEUBAUER, S.H. JASON LO, B. KUMMER, M. SCHEFFLER, P. GREIL, "Preceramic polymer derived cellular ceramics," *Composites Science and Technology* **63**, 2361 (2003)
- [19] E. SUNDERMAN AND J. VIEDT, Method of manufacturing ceramic foam bodies. US Pat no. US Pat no. 3 745 201, 1973.
- [20] P. COLOMBO AND M. MODESTI, *J. Am. Ceram. Soc.* **82** 573 (1999).
- [21] T. TAKAHASHI AND P. COLOMBO, "SiOC Ceramic Foams through Melt Foaming of a Methylsilicone Preceramic Polymer," *Journal of Porous Materials* **10**, 113 (2003).
- [22] M.R. NANGREJO AND M.J. EDIRISINGHE, "Porosity and Strength of Silicon Carbide Foams Prepared Using Preceramic Polymers," *Journal of Porous Materials* **9**, 131 (2002).
- [23] T. J. FITZGERALD AND A. MORTENSEN, "Processing of microcellular sic foams .1. Curing kinetics of polycarbosilane in air," *J. Mater Sci* **30** (4) , 1025 (1995).
- [24] T. J. FITZGERALD, V.J. MICHAUD, AND A. MORTENSEN, "Processing of microcellular sic foams .2. Ceramic foam production," *J. Mater Sci* **30** (4) 1037 (1995).
- [25] J.M. QIAN, J. P. WANG, G. J. QIAO, Z. H. JIN, "Preparation of porous SiC ceramic with a woodlike microstructure by sol-gel and carbothermal reduction processing," *J Euro Ceram Soc* **24**, 3251(2004).
- [26] P. COLOMBO, private communications, Sept. 2004.
- [27] J. BINNER AND R. SAMBROOK, "Break out the bubbly," *Mat World* **10** [2] 13 (2002).
- [28] S.K. MAITI, M.F. ASHBY AND L.J. GIBSON, "Fracture Toughness of Brittle Cellular Solids," *Sripta. Metall.* **18**, 213 (1984)
- [29] K. C. GORETTA, R. BREZNY, C. Q. DAM, D. J. GREEN, A. R. DE ARELLANO-LOPEZ AND A. DOMINGUEZ-RODRIGUEZ, "High Temperature Mechanical Behavior of Porous Open-cell Al2O3," *Materials Science and Engineering, A* **124**, 151 (1990).
- [30] E.W. ANDREWS, L.J. GIBSON, AND M.F. ASHBY, "OVERVIEW NO. 132: THE CREEP OF CELLULAR SOLIDS," *Acta Mater.* **47** [10], 2853 (1999).