Acta Materialia 127 (2017) 450–462

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Cast-in-place, ambiently-dried, silica-based, high-temperature insulation

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ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form
29 January 2017
Accepted 30 January 2017
Available online 3 February 2017

Keywords:
Silica gel
Cast-in-place
Ambiently-dried
High-temperature insulation
Thermoelectric generator

ABSTRACT

A novel sol-gel chemistry approach was developed to enable the simple integration of a cast-in-place, ambiently-dried insulation into high temperature applications. The insulation was silica-based and synthesized using methyltrimethoxysilane (MTMS) as the precursor. MTMS created a unique silica microstructure that was mechanically robust, macroporous, and superhydrophobic. To allow for casting into and around small, orthogonal features, zirconia fibers were added to increase stiffness and minimize contraction that could otherwise cause cracking during drying. Nano-sized titania powder was incorporated as an opacifier to reduce radiative heat transport. To assess relevance to high temperature thermoelectric generator technology, a comprehensive set of materials characterization experiments were conducted. The silica gel was thermally stable, retained superhydrophobicity with a water contact angle >150°, and showed a high electrical resistance >1 GΩ, regardless of heating temperature (up to 600 °C in Ar for 4 h). In addition, The silica-based thermal insulation exhibited a Young's modulus ~3.7 MPa and a low thermal conductivity <0.08 W/(m.K) at room temperature before and after heat treatment (up to 600 °C in Ar for 4 h). Thus, based on the simplicity of the manufacturing process and the optimized material properties, we believe this technology can act as an effective cast-in-place thermal insulation (CTI) for thermoelectric generators and myriad other applications requiring improved thermal efficiency.

1. Introduction

Diminishing fossil fuel supplies require improved energy efficiency [1]. In the United States, approximately 60% of the energy converted from fossil fuels is currently rejected as waste heat while only 40% is serviceable [2]. Clearly, there is a compelling need for waste heat recovery technology. One approach involves the development of thermoelectric generators (TEGs) to convert waste heat from combustion directly to electrical energy [3]. For example, efforts are underway to integrate TEG technology into internal combustion engine (ICE) exhaust systems to convert waste heat in the exhaust gas into electricity. The electricity could then be used to improve fuel efficiency by reducing the load on or eliminating the need for an alternator, which requires mechanical energy from the ICE.

TEG technology typically consists of semiconducting elements, which convert a heat flux into a DC voltage that can be used to drive an external load, and a heat management system whereby thermal insulation is needed to reduce parasitic heat loss [3,4]. At present, aerogel-based insulation is under development for space TEG technology [5]. Aerogel was first produced in the 1930s [6], and is a unique class of materials exhibiting high specific surface area (200–1200 m^2/g), high porosity (80–99%), low density (<0.05 g/cm^3) and low thermal conductivity (<0.02 W/(m.K)) [7–11]. When prepared using silica or carbon, aerogel can achieve the lowest thermal conductivity (<0.01 W/(m.K) at 298 K) of any material, making it an appealing candidate for thermal insulation [7]. However, to achieve aggressive cost targets for industrial and

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http://dx.doi.org/10.1016/j.actamat.2017.01.060
1359-6454/

automotive applications requiring high temperature insulation, an alternative material approach to aerogel is required for several reasons: 1) aerogel is typically prepared using a supercritical drying process which can complicate and/or prohibit large volume production of bulk insulation and/or integration into TEG technology, 2) aerogel is inherently brittle, thus it may not survive applications involving vibrations and shock, 3) infrared radiation (IR) is the dominant heat transport mechanism in high porosity ceramic materials, and 4) typically high surface area materials absorb substantial amounts of water, causing corrosion upon thermal cycling in ambient air. In short, developing a low-cost insulation material is the subject of much research worldwide with many different strategies having been proposed, but to date none have had widespread success.

The purpose of this study is to address the challenges listed above for aerogel-based thermal insulation by developing an alternative material approach and tailoring the material specifically for integration into TEG technology. To simplify and reduce cost of aerogel-based insulation production, one approach is to synthesize a porous, silica-based gel using an ambient drying process. The most common approach to ambiently dry porous silica involves a combination of exchanging the pore fluid with a low-tension solvent and treating the surface with a silylating agent to reduce surface tension. Such a route has been systematically explored by A. Venkateswara Rao and A. Parvathy Rao et al., who reported the effects of various solvents and surface modifications on ambiently-dried silica gels [12,13]. Such methods can produce high quality monoliths, but a few challenges remain. First, the additional processing steps involved in exchanging the pore fluid and chemically modifying the surface can add significant time and cost. This has been somewhat alleviated by Schwertfeger et al. who developed a single-step process for surface treatment and solvent exchange using a mixture of hexamethyldisiloxane (HMDSO) and trimethylchlorosilane (TMCS) [14]. The second issue is that such drying techniques typically rely on the so-called “spring-back” effect, where >40% contraction of the gel's initial wet volume occurs before expanding back to near its original volume [8,15,16]. While such a technique is perfectly suitable for monoliths, reliance on spring-back precludes the use of ambiently-dried silica gel as a cast-in-place insulation material in applications with complex geometries or rigid inclusions. In such instances, the gel will crack and break apart during the initial high-shrinkage phase of drying before spring-back occurs. Another strategy is to reinforce the gel network with short fibers, or to react a cross-linked polymer on the silica surface [17–19]. However, both approaches still depend on some degree of spring-back effect, and the polymeric coating is not stable at high temperatures (>500 °C).

This work details the synthesis of a porous silica using MTMS as the sol-gel precursor. Preventing spring-back and reducing radiative heat transport were a specific focus for the reasons explained above. MTMS was first explored as an alkoxide for the synthesis of supercritically-dried aerogel by Hegde et al. [20], but an ambient drying technique was never reported. Bhagat et al. described the ambient drying of acid-base catalyzed MTMS gels, but reported that the gels underwent spring-back effect during drying [21].

In this study, the MTMS-derived silica network was robust and consisted of macropores. In addition, the incorporation of fibers and mineral powders effectively eliminated the spring-back effect.

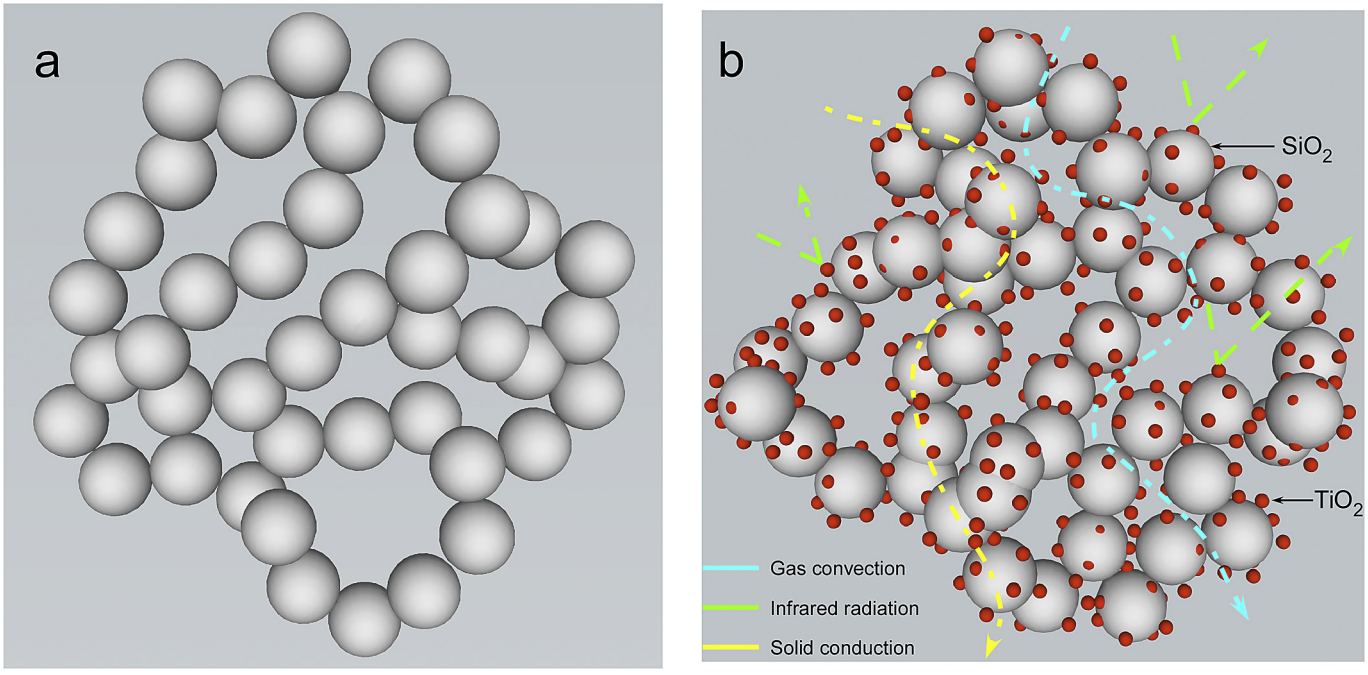

Fig. 1. 3D Illustrations of MTMS-derived silica network (a) pearl-necklace structure of silica gel, (b) heat transfer mechanisms in TiO_2 opacified silica gel.

Table 1
Nominal composition of silica gel.

Starting materials (ml)				Filler minerals (g)			
MTMS	Methanol	Water	Ammonia	Titania	Quartz	Fumed silica	ZrO_2 fiber
3.93	3.904	1.559	0.68	1	0.2	0.05	0.25