Exploring Mechanical Properties of SiO$_2$ Elastic Micro-Nano Ceramic Fibres Aerogels

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Abstract. With the development of hypersonic vehicles and the military, SiO$_2$ elastic nano-fibre ceramic aerogel becomes a preferred and potential material due to its ultralight, thermal super-insulation, and superelasticity properties. Compared with traditional ceramic materials which are brittle and easily degraded, SiO$_2$ elastic nano-fibre aerogel shows up with its outstanding characteristics under extreme conditions. Facing a major demand in the national strategy of thermal insulation materials, this study will keep an eye on these growing and famous novel materials. Summarizing current studies and research at home and abroad. And explaining the evolution from traditional SiO$_2$ aerogels to elastic aerogels to new SiO$_2$ nano-fibre aerogels with flexible elastic bonds. Finally, providing regulation factors that can be improved and employed in future experiments. Giving prospects and focus for future research.

1. Introduction
With the rapid development of aerospace and missile, the hypersonic vehicle needs to withstand super-high temperatures from prolonged aerodynamic heating of surfaces, severe mechanical shocks, and high heat fluxes. Under harsh environments, it requires heat sealing materials to withstand reversible compression with large circle strains and high-temperature oxidative environments (>800°C). Ceramic materials have been well studied and researched with wide applications in aerospace, military, machinery, environment, and energy consumption, because of ceramic intrinsically high thermal resistance, anti-corrosion, chemical inertness, and good thermal insulation properties. However, deconstruction will occur to ceramics due to their brittle and rigid characteristics under external forces and repeated thermal shocks[21]. Meanwhile, aerogel is an outstanding kind of ultralight thermal insulation material, which possesses low thermal conductivity commonly used in thermal insulation fields. Facing major national strategic needs, ceramic aerogels with ultralight, super-elastic, high-temperature resistance (1100°C) and low thermal conductivity are in demand, which has meaningful prospects in the thermal insulation area. Therefore, it is urgent to solve the problems and challenges that under high-temperature use for a long time this material will break and collapse[15].

To improve the mechanical properties of ceramic aerogel, the approach of narrowing diameters of fibres is gaining more and more attention, which can fabricate micro-nano ceramic fibres with less than five $\mu$m, also helps lower the thermal conductivity of fibres. Additionally, fibre-reinforced granular aerogels (nanoarrays), 1D micro-nano fibres assembled networks, nanobelts, and 2D nanolayer stacked structures have been tried and made to improve ceramic aerogels’ thermal and mechanical properties. In this review, the current study and research progress of SiO$_2$ nano-fibre aerogel are examined. The
mechanical characteristics and improvement of the micro-nano fibres with their elastic aerogel are introduced systematically. Furthermore, influence factors are reviewed. Finally, the challenges and issues at present are analysed, and the future growth of micro-nano ceramic aerogel has been prospected.

2. Building Blocks and Performance

The microstructure of ceramic aerogels including porosity, pore sizes, interactions between fibres, fibre-aerogel interactions, interconnections between fibres, diameters of fibres and length of fibres dominates the macro performance of ceramic aerogel network hierarchy for its mechanical and thermal properties. 1D and 2D unit blocks are popular in building 3D porous networks of ceramic aerogel owing to their excellent performance in overcoming brittleness and improving recoverable compressibility. For 1D fibre-reinforced ceramic aerogel such as nanotube, nanofibre, nanowire and so forth, it has been widely used over the whole world possessing excellent comprehensive performance. There is a series of aerogel built by 1D blocks via layer-by-layer stacking, template, direct spinning and self-assembly like SiO$_2$ nano-fibre aerogel[1], SiO$_2$ nano-fibre aerogel, oxide ceramics nano-fibre sponge (ZrO$_2$, TiO$_2$, Y$_2$O$_3$), and BN nanobelt aerogel[2]. They can bear large cyclic compressive strain up to 99% compressive strain and tremendous deformation. But it is observed that they have poor structural adjustability and bad mechanical and thermal performance due to weak connections between fibres and weak interactions between fibre and particles.

![Figure 1. CVD fabrication of SiC aerogel stacked by nanofibre firms](image1)

![Figure 2. SEM photo of aerogels built by Al$_2$O$_3$ nanotubes[3]](image2)

![Figure 3. SEM photo of aerogel built by BN nanobelt](image3)

![Figure 4. Fabrication of SiO$_2$ aerogel](image4)
3. SiO₂ Micro-Nano Ceramic Fibre Aerogel
SiO₂ aerogel is a bulk material composed of nanoscale SiO₂ particle skeleton and tortuous nanopores inside the skeleton[4]. SiO₂ micro-nano ceramic fibre aerogel has high porosity, super fine holes, ultralow density, and low thermal conductivity compared with traditional ones, so it is used most in practical applications and interindustry. However, there are shortages in this material because the necklace-like shape with poor continuity brings high brittleness and the risk of collapse dropping powders. It is becoming increasingly popular since Ding et al. had made SiO₂/PAN composite fibre aerogel successfully. So, it is an urgent demand to produce a new elastic SiO₂ micro-nano ceramic fibre aerogel[19].

3.1. Fabrication of SiO₂ Aerogel
Dou et al. have successfully made SiO₂ aerogel early. For producing the precursor, initially, the silicon precursor undergoes a series of hydrolysis and polycondensation reactions under the action of a catalyst (one-step or two-step method) to form a wet gel with a nano-network structure and a pore structure filled with a liquid medium. Then, ageing under a certain temperature, and supercritical drying is used to eliminate H₂O in the wet gel to get the same structure of SiO₂ aerogel as shown in Figure 5 and Figure 6. However, the nanoparticles in the skeleton network structure are only connected by the neck contact so the contact area is small, and the connection effect is weak. The brittle particle skeleton structure of SiO₂ aerogel makes it prone to structural damage and fragmentation during use, thus losing the application performance. Therefore, enhancement strategies following are employed to improve its mechanical properties: First, change the new precursor of Si, and introduce soft organic groups to the aerogel[5][6]. Secondly, wrap the whole aerogel structure with polymers to improve its mechanical property[7]. Lastly, add second phase materials with good continuity such as 1D fibre, 2D or 3D fibre precursor[8][9].

3.2. Elastic and Soft SiO₂ Micro-Nano Fibre Aerogel
Electrospinning is the most common and effective way to produce nanofibres. The properties, number of constituents, and the design structure of the precursor are all important factors which influence fibre performance. Generally, the manufacturing process involves electrospinning and calcination (shown in Figure 7) to high temperatures (800°C -1000°C) to get desirable nanofibers finally (shown in Figure 9). Meanwhile, the fabrication process combines with freeze-drying and sol-gel method.

Using soft SiO₂ nanofibres as building blocks, Si et al. have fabricated cell elastic SiO₂ nanofibre aerogel by freeze-drying method. It finds that this aerogel has recoverable compression strain up to 80%, and even after 1000 cyclic compression the deformation is still low, which shows us a great elastic performance[10]. But it has poor bending behaviour, which limits its application. So, the Si group uses SiO₂ nanofibres with a high aspect ratio (400), and PEO polymers dispersed uniformly getting a well assembled and good continuity of interweaving cell structure. Testing results show that after 1000 cycles under a large bending strain of 85%, the maximum yield stress remains stable (Figure 8), and the structure is not damaged[14].
Initially, SiO$_2$ aerogels are prepared by the traditional sol-gel method with high brittleness, easy structure collapse, and nanoparticle powder falling off. Then, flexible SiO$_2$ nanofibers mixed with SiO$_2$ aerogels are produced by homogeneous dispersion-freeze-drying-high temperature calcination possessing better elastic properties but with weak bending performance. Finally, Si et al. have utilized the method of using high aspect ratio fibres to coat and freeze with liquid nitrogen. This research not only improves the bending performance but also builds a stable internal cell structure and improves mechanical properties. It is a successful leap from traditional aerogel to new nano-fibre ceramic aerogel which possesses outstanding elasticity and flexibility[17].

![Figure 7. Process of making nanofibers](image)

![Figure 8. Bulking stress versus bending cycles](image)

![Figure 9. SEM photos of SiO$_2$ nanofibre aerogel](image)

### 4. Factors of Regulating Material’s Mechanical Performance

#### 4.1. Precursor Solutions
The addition of a small amount of inorganic salt in the precursor solution increases the electron conductivity of the solution making the diameters of fibres thinner (shown in Figure 10). It finds that the amounts of NaCl nanoparticles influence the mechanical and structural performance of SiO$_2$ nano-fibre films (Figure 11). In the process of calcination, liquid phase NaCl between fibres makes SiO$_2$ particles easily move which creates a cohesion structure like welding points in the network. So, corresponding properties are affected by structure regulation. When amounts of NaCl particles are not very high, local cohesive joints form so that several fibres are under external forces together, which improves its mechanical property. Additionally, Almuhamed S et al. find that the amount of Na-MMT will also influence the electrospinning process resulting in an improvement in thermal stability[20].

#### 4.2. Calcination Temperature
The morphology and diameter of SiO$_2$ nanofibers change greatly with the increase in calcination temperature (shown in Figure 12). Different calcination temperature brings different specific surface area and interactions between fibres. At higher temperatures (1200°C), large shrinkage of fibres occurs along their length so that temperature influences the structure-property regulation. As temperature increases, the diameter of fibres grows gradually. At high temperatures, an integral cohesive structure
containing many cohesive joints forms. The fibre loses the ability to adjust the relative position because it cannot slip and cannot deform when the fibre membrane is subjected to external force, resulting in the macroscopically hard and brittle characteristics of the fibre membrane. The strength will decline correspondingly.

4.3. Other Factors
Ding employs Silica sol as connecting joints instead of rigid ceramic joints (between SiO₂ and borosilicate)[19]. Elasticity has improved and keeps stable undergoing one million compression tests[11]. Process parameter plays an important role in construction and regulation. Via electron spinning and directional freeze forming technology, Ding et al.[18]have fabricated cellular super-elastic aerogel. Additionally, Ding group has used the freeze-drying method to produce elastic nano-fibre aerogel[12][13][14].

5. Conclusions
To solve the brittleness and structure degradation problems of ceramic aerogels in the field of hypersonic vehicles and missiles, SiO₂ ceramic aerogels as the earliest research objects become a research hotspot year by year. At present, building an ultralight, elastic, low thermal conductivity, and thermal superinsulation SiO₂ ceramic aerogels is becoming the focus of the research. By 1D nano-fibre enforcement, adjusting processing parameters, precursor solution regulation and compounding second phase materials and so forth, some potential functions and improvement ideas emerge. Improving and designing building blocks of an aerogel network with good mechanical and thermal properties are the key to obtaining a desirable ceramic aerogel. Soft and elastic SiO₂ fibre with a high aspect ratio combined with aerogel can indicate a stable and robust mechanical property, which can be further
studied to improve production efficiency and simplicity. However, the rapid growth of ceramic grains under high-temperature conditions leads to material brittleness and failure, which limits the application in extreme situations[21]. The mechanism of soft fibres, ceramic aerogels, and thermal insulation is still waiting to be explored. More experiments and research need to be done under extreme high-temperature conditions to explore the response and performance of ceramic aerogels. More consideration and studies should focus on green, mass production, simple process and low-cost goals in the future.

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