

Research on Ceramic Nanofiber Assembled Aerogel

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Abstract: With the accelerated advancement of science and technology, the traditional textiles material has been unable to meet the specific functional and performance requirements. Meanwhile, the special structure of aerogel exhibits the drawback of limited thermal stability. The high surface energy of the particles makes it susceptible in high-temperature environments, which can lead to a reduction in specific surface area and even collapse of the porous structure. Aerogel assembled from ceramic nanofibers could be a solution. When the fiber size is reduced from micron to nanometer, the special properties brought by the small size effect and the high specific surface area effect will give the nanofibers new properties such as in light, electricity and sound. This paper provides a comprehensive general introduction of the structure, capability, preparation, and modification techniques employed in ceramic nanofiber aerogel research. The sol-gel electrospinning method can produce nanofiber aerogel with excellent properties. The paper reveals the excellent thermal insulation properties of ceramic grains that is located on ceramic fibers such as ZrO₂, SiO₂ and Al₂O₃, combined with the porous structure of aerogel can lock gas molecules, so that they can be used in high temperature environments.

Keywords: electrostatic spinning, ceramic nanofibers, aerogel, insulation

1. Introduction

Aerogel is a solid nano-porous material with a 3D mesh structure, which is composed of nanoparticles or polymer molecules. It is the product obtained by replacing the liquid in the pores with air on the basis of keeping the pores and space network structure undamaged [1]. The nano-porous structure of aerogel gives it the characteristics of high porosity, low dielectric coefficient, high specific surface area, low thermal conductivity and low density. With these properties, aerogels have been widely used in various fields such as thermal insulation, adsorption, catalytic action, separation and percolation. However, the traditional synthetic aerogels have poor thermal and mechanical stability. Advanced ceramics can be divided into functional ceramics and structural ceramics based on their performance and application. Structural ceramics have high hardness, high temperature resistance, and oxidation resistance, while functional ceramics have thermal/piezoelectric properties, magnetic properties, and optical properties. However, the characteristics of both structural ceramics and functional ceramics are fundamentally due to the strong covalent and ionic bonds between the atoms in the ceramic composition [2]. In addition, both covalent and ionic bonds are beneficial to enhance the mechanical strength and fire resistance.

However, both covalent and ionic bonds are oriented, thus limiting the slipping of atoms, which results in brittleness in their macroscopic state and limits the behavior of toughness and flexibility at the macroscopic level, severely hindering their application in more complex environments. To this end, the researchers found that one-dimensional ceramic fibers with extremely high length-to-diameter ratios and good continuity can withstand large bending deformations by axially accumulating smaller local deformations, resulting in significantly improved flexibility [3-5]. In recent years, the new electrospinning technology has realized the continuous synthesis of ceramic nanofiber aerogels [6,7]. The micro/nano pores formed by the interlacing of nanofibers make them have low mass density and morphological structure similar to that of traditional granular ceramic aerogels. Ceramic nanofiber aerogel combines the fire resistance of ceramic material itself with the unique porous network structure of aerogel, which has excellent thermal insulation performance and good flexibility.

Through theoretical analysis and research status, the objective of this study is to elaborate the preparation strategy of flexible ceramic nanofibers and the ceramic nanofiber aerogel produced by stacking ceramic nanofibers. In this paper, the definition of the flexibility of ceramic nanofibers is explained, and the factors that influence flexibility of oxidized ceramic materials are analyzed in detail. The excellent fire and heat insulation performance of ceramic nanofibers aerogel is also theoretically analyzed and demonstrated. The author hopes to have a deeper understanding of the law of the excellent thermal insulation properties of ceramic nanofiber aerogel and put forward new insights.

2. Ceramic nanofiber aerogels

2.1. Overview of ceramic nanofiber aerogel

As a new research focus in inorganic materials, ceramic aerogel can lock gas molecules due to its unique 3D interconnected porous network structure, showing a fast heat transfer path and extremely low thermal conductivity[8]. The researchers have demonstrated the remarkable effect of ceramic aerogels in blocking the runaway propagation of heat. In addition, the lightweight ceramic aerogels have less effect on reducing the energy density of the battery pack [9]. Ceramic aerogels are mainly composed of granular powders, and the production process involves sol-gel, aging, modification and drying. The drying process is very important for the synthesis of aerogels. The main drying processes include supercritical drying and atmospheric drying. By slowly drying the liquid components without degrading the solid skeleton structure, ceramic aerogels with low density, high specific surface area and extremely high porosity can be formed. This kind of ceramic aerogel has high fire and thermal insulation properties, but its pearl nain-like microstructure is prone to structural fracture or sliding under very small tensile strain, resulting in poor mechanical properties[10-13]. In addition, since the supercritical manufacturing method is discontinuous, it is difficult to achieve large-scale processing.

Electrospinning technology, which has emerged in recent years, enables continuous synthesis of ceramic nanofiber sponge aerogels[14,15], which have low density and adiabatic properties due to micro/nano-scale pores formed by the interleaved nanofibers, just like ceramic particle aerogels. For instance, Yang et al. prepared a flexible composite ceramic NF sponge of strawberry structure, in which porous silica nanoparticles are used as insulation fill[16]. The addition of porous silica nanoparticles changes the heat transfer path in the aerogel from continuous NFs to a discontinuous irregular path, thus giving the sponge a low thermal conductivity[17].

2.2. Preparation of ceramic nanofiber aerogels

Different from the traditional aerogel preparation, ceramic nano fiber aerogel is prepared by the sol-gel electrospinning method, which is formed by stacking and sintering of the nano-fibers ejected by

electrostatic spinning. The sol-gel method is a wet chemical process used to prepare porous materials. The method involves hydrolyzing a solute (usually a metal alkoxide or metallic inorganic salt) in a solvent to form a sol that is subsequently formed by polycondensation reaction to form a gel. In the confinement of polymer template, the competitive growth of ceramic grains will effectively reduce the crystal particle size to tens of nanometers. For example, Feng proposes a self-template spinning stacking strategy and coaxial electrospinning method to synthesize silica/alumina ceramic micro/nano-fiber sponges with both high mechanical strength and high thermal capability of insulation[18].

In addition, the physical and chemical properties of polymers and precursor salts, electric field, air humidity strength have a significant impact on the formation of continuous precursor or MNFs (Micro/Nano Fiber). Yan et al. developed a novel ball milling and bending stretching-based crosslinked electrospinning technology, which constructs a crosslinked sol-gel system through the ball milling process and uses it to prepare a range of flexible oxide ceramic MNF crystal materials with binary to multi-component (including tri- and tetra-component mixtures), allowing the metal salt precursors to undergo sufficient reactions beforehand, reducing the nucleation force during crystallization, thus significantly reducing impurity phases and effectively reducing particle size. Moreover, ball-milling the sol can reduce colloidal particles, thereby reducing the crystalline particles after sintering. Where after, it was further discovered that bending and stretching the electrospun precursor MNFs can substantially reduce the porous flaws, induce grain orderly assemble, and form long-range ordered amorphous or twin boundaries. Long-range boundary sorting plays a significant role in consuming bending energy, making MNFs sufficient toughness to prevent breakage[19].

Additionally, scholars have found that the phase transition and the growth of oxide crystals can be inhibited by adding rare earth oxides such as Y_2O_3 and Yn_3O_9 , amorphous oxides such as silica and Al_2O_3 , or metal compound or metals such as magnesium sulfate or sodium, magnesium, and aluminum, thereby improving their thermal insulation properties. Finally, by using low-temperature sintering, dense oxide ceramic MNFs are formed in the aerogel[20].

2.2.1. The Mechanism of 2D Transforming into 3D

In 3D cases, the jet bends closer to the nozzle because the stronger the electrical conductivity of the solution, the stronger the electrostatic force generated, which enhances instability. The solution ejection not only forms helices in the direction perpendicular to the nozzle, but in the direction parallel to the electric field, primarily due to the redistribution charges. Dong et al. used $Y(NO_3)_3$ as an example, where the ions carry a charge, namely NO_3^- , AcO^- , and Y^{3+} . These charges diffuse through the liquid phase and are lopsidedly distributed within the solution jet. These ions are subject to static electricity forces in the direction of the electric field or opposite to it (F_E). This uneven force changes the conformation of the jet and causes additional helices to be generated in the initial stage of the curved instability region[21].

In traditional two-dimensional electrospinning, the spun fibers fall horizontally onto the collector to form a dense pile. However, in 3D electrospinning, the fiber segments fall vertically onto the collector surface when they reach the collector. This can be explained by electrostatic induced polarization, where the fiber carries unevenly distributed positive and negative ion charges as it approaches the substrate. At the same time, the positive high voltage induces negative charges on the top of the already collected fiber pile, making it another collector that induces negative charges to apply uneven electrostatic force (F_S) to the fiber segments, causing them to reorient and fall vertically onto the already deposited fibers. Due to the deposition of fibers being negatively polarized subsequently, the Coulomb repulsion (F_R) between adjacent fibers helps to sustain a larger distance between fiber and fiber. Additionally, the attractive force between the polarized fiber and the metal nozzle also stabilizes the three-dimension structure.

2.3. Modification of ceramic nanofiber aerogels

The modification methods of ceramic nanofiber aerogel mainly include solid phase modification, liquid phase modification and gas phase modification. By introducing different functional substances or changing the microstructure of the aerogel, these methods enhance its mechanical properties, thermal insulation properties, catalytic properties and so on.

2.3.1. Solid phase modification

Solid phase modification occurs mostly in the formation process of nanofiber aerogel precursors. By adding functional materials to the precursors, the nanofiber aerogel can be enhanced or given specific properties. For example, the research team of Donghua University prepared ceramic nanofiber aerogel with super elastic layered structure by combining SiO₂ nanofibers with aluminum borosilicate matrix. This method successfully assembled randomly deposited SiO₂ nanofibers into elastic ceramic aerogel with low density[22], CNFAs(Ceramic Nano Fiber) can recover quickly from 80% strain, Poisson's ratio is zero at 1100 °C, and it has super elasticity that does not change with temperature. In addition, the overall ceramic characteristics provide CNFAs with strong fire resistance and thermal insulation properties.

2.3.2. Liquid phase modification

Liquid phase modification usually involves placing the aerogels in a solution containing functional substances, and introducing functional substances into the aerogels through impregnation, adsorption or chemical reaction. Specific metal ions or organic compounds can be introduced into the liquid phase to form new functional groups on the surface or inside the aerogel through chemical reactions, thus giving the aerogel new properties.

Electro spun fibers are ideal absorption materials. Both two-dimension and three-dimension structures have high absorption ability for water and all kind of organic solvents. Nevertheless, the maximum liquid absorption capacity of two-dimensional structures is limited by its volume. On the contrary, three-dimensional structures not only have 2-3 times higher absorption capacity than 2D structures, but also can absorb large amounts of liquid. Dong et al. further applied the aerogel material to the cleanup of oil spills in natural environments by fluorinating the surface of the previously developed TS-3D aerogel to make it selectively absorbent that is hydrophobic and lipophilic. The resulting TS-3D aerogel has a contact angle of 127°, and its non-wetting surface appears as a mirror reflection and has high organic liquid absorption capacity. Based on this, bTF-3D aerogel can separate multifarious organic solution from water, showing supernormal application potential in environmental remediation [21].

2.3.3. Gas phase modification

Aerogel gas modification refers to the introduction of new chemical components on the surface or inside the aerogel material through the vapor chemical reaction to change its original physical and chemical properties, so as to expand the application field of aerogel. This modification method usually involves chemical vapor deposition, physical vapor deposition and other technologies, which can significantly improve the mechanical strength, thermal stability, corrosion resistance and specific surface functionality of aerogel.

For example, the Institute of Metal Research, Chinese Academy of Sciences, has obtained a patent that involves a method of preparing carbon aerogel composite materials by modifying carbon fibers using a chemical vapor infiltration process[23]. This technology optimizes the fiber/matrix interface structure by depositing a new dense pyrolytic carbon layer on the surface of the carbon fibers,

improving the carbon fibers' antioxidant activity and improving the uniformity of the matrix particle distribution. As a result, high-strength and high-toughness carbon aerogel composite materials are obtained. The photocatalytic performance of the aerogel is also improved. A research by the Swiss Federal Institute of Technology at Zurich shows that the light absorption range of TiO₂ nanoparticle aerogel can be broadened by a gas phase nitrogen doping method, enabling it to utilize more visible light and thus improve the efficiency of photocatalytic hydrogen production[24]. This modified aerogel exhibits higher activity and stability in photocatalytic hydrogen production reactions.

3. Conclusion

In this paper, the application of ceramic fiber in the aerogel and the modification of ceramic nanofiber aerogel are summarized. The defects of thermal and mechanical properties of conventional aerogels and also the special coupling properties of ceramic nanofiber aerogels were introduced. This study provides a systematic theoretical analysis about the ceramic nanofiber aerogel, which provides a useful foundation for further research in related fields. For example, the modification research with different phase modifications can be combined by reducing the time cycle of electrospinning ceramic nanofibers. On the basis of this paper, readers can further study the more complicated cases such as the transformation of electrospinning products from 2 to 3 dimensions well, so as to deepen the understanding of fabrication mechanism. To conclude, this work should be a suitable reference for the readers in this field.

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