Effect of metallic nanoparticle fillers on the thermal conductivity of diatomaceous earth

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Abstract

Thermal conductivity of solid nanoparticles (aluminum) in a nanoporous solid matrix (diatomaceous earth) is examined to understand the effect of conductive fillers on the thermal properties of a porous material. We find that thermal conductivity is strongly dependent on load applied to prepare the mixture compacts, while porosity is influenced by the composition of the mixture. The addition of nanoparticles contributes to limited increases in thermal conductivity of the mixture by (1) increasing contact area between the mixture constituents and (2) reduction of porosity that leads to enhanced solid-gas coupling contribution. Thermal conductivity increases exponentially with external gas pressures due to the coupling effect between the solid particles and the entrapped air.

Keywords

Aluminum nanoparticles, Diatomaceous earth, Thermal conductivity, Porosity

1. Introduction

Diatomaceous earth (DE) is a naturally occurring soft powdered material composed of fossilized remains of unicellular algae called diatoms; up to 100,000 species of diatoms can be found in a single sample¹⁻³. The diatom skeletons are primarily made of amorphous silica. Each of the different diatom species has a unique frustule structure, making DE an extremely heterogeneous material with notable variations in physical properties^{2, 4-6}. DE finds applications as filters, building material, abrasive, catalyst carrier, acoustic and thermal insulators, and even as ingredients in some medicines⁷⁻¹². DE has a low thermal conductivity (~ 0.1 W/mK) because of its nanoporous structure, and has recently received interest as a potential candidate for core insulation material in superior performance vacuum insulation panels (VIPs)^{8, 13-14}. The vacuum inside VIPs degrades with time due to pressure difference, ultimately resulting in gradual loss of thermal resistance. A major challenge is to increase the lifetime of VIPs for use in energy efficient buildings, and one possible solution is to tune the thermal conductivity of DE with fillers. While thermal conductivity (k) of pure DE has been reported in the literature^{7, 15}, the effect of impregnating the nanoscale pores with nanoparticles has not been explored. In particular, the presence of thermally conductive nanoscale fillers in the DE porous matrix can facilitate application-specific modification of k for insulation materials. Furthermore, DE has been traditionally used as a high temperature insulator ($>1000^\circ\text{C}$) whereby radiation heat transfer becomes especially pronounced in porous material^{3, 14}. Since metallic nanofillers could function as an opacifier without significantly increasing the thermal conductivity of the mixture, we examine the influence of Al nanoparticles (AlNPs) dispersed in bulk DE on the k of the mixture.

The thermal conductivity of porous materials depends, as obvious, on porosity¹⁶⁻²⁰. In addition, k of granular materials like DE is strongly influenced by the contact resistance between particles, leading to a significant change in k with gas pressure⁸. In this letter, we discuss the contribution of nanoparticles and porosity on the k of AlNP/DE mixture. The addition of AlNPs, as expected, increases the overall k of the mixture. However, as discussed below in details, this increment is only marginal even though a highly conductive material such as Al is used. Our results aid in understanding how the fillers influence k by modifying the contact between the mixture components.

2. Materials and Methods

AlNPs of ~ 800 nm diameter (US Research Nanomaterials, Inc) are mixed with DE having a pore size of ~ 1 μm (Perma-GuardTM, Inc) by shaking in a vibratory mill for 6 h, followed by dry pressing to form cylindrical compacts. The density of each compact is determined by measuring the mass and volume. In total, twenty-four samples are prepared each with varying AlNP mass fraction (0%, 10%, 20%, 30%, 40%, and 50%) and compaction load (0.45 MPa, 1.13 MPa, 1.70MPa, 2.26 MPa). k is measured by the transient plane source technique (Hot DiskTM TPS 1500) that employs a sensor acting as both a heat source and a resistance thermometer. The change in temperature is measured as a function of time, and subsequently k is obtained using the Gustafsson equation²¹. The microstructure of the samples is examined under a scanning electron microscope (SEM, JEOL JSM-6060LV). For two of the samples, viz., pure DE and 50% (w/w) AlNP/DE mixture, we measure k as a function of gas pressure between 27 Pa ($\sim$ vacuum) to 10^5 Pa (~ 1 atm.), by evacuating the sample in a bell jar (schematic shown in Figure 1).

3. Results and Discussion

Effect of nanoparticle concentration: Air occupying the nanopores in pure DE at atmospheric pressure contributes to the overall heat conduction²². With the addition of AlNPs, these air pockets are replaced by highly conductive metallic particles. We neglect the influence of nanoscale size effects since both the electron mean free path ($\lambda_{\text{electron}} \sim 22$ nm)²³ and the phonon mean free path ($\lambda_{\text{phonon}} \sim 8.1$ nm)²⁴ of Al are much smaller than the average particle diameter of 800 nm. Thus, k_{Al} for the nanoparticle used in this investigation is similar to the bulk Al thermal conductivity ($k_{\text{bulk}} = 237$ W/m.K).

We present the change in effective k of the mixture with AlNP concentration in Fig. 2a. Though k_{Al} is significantly higher than that of pure DE, k for the mixture increases only by 15% even for 50% nanoparticle mass fraction under a compaction of 2.26 MPa. We conjecture that this small increase in k is due to impedance to heat transfer by interfacial thermal resistance arising from the increase in interfacial areas between dissimilar surfaces of Al and DE particles. Considering an interfacial thermal conductance $G = 120$ MW/m²K²⁵ between the Al nanoparticles and DE, the Kapitza length (L_K) calculated with the bulk thermal conductivity of Al, is ~ 1.975 μm . This L_K is much larger than the

average Al nanoparticle size (800 nm) employed here, suggesting that interfacial thermal resistance exerts a significant effect on heat conduction in the AlNP/DE mixture. The results also suggest that compaction has a more pronounced effect on k as compared against the influence of mixture composition. Increased load during dry pressing results in mixtures that are more compact with less voids between material particles, eliminating the air trapped within the interfacial areas, and thus increasing the effective k .

A higher compaction pressure creates structures with lower porosity. Porosity is related to both the gaseous molecules in the interfacial zones as well as the “coupling effect”. The coupling effect takes into account heat transfer between solid and gas phases when modeling the effective thermal conductivity of porous materials such as aerogels²⁶⁻²⁹. Effective thermal conductivity is typically determined by considering a combination of solid, gaseous and the coupling contributions to thermal conductivity. The coupling contribution is approximated as the composite of both solid and gas phases (proportional to their volume fractions) connected in series along the direction of heat flow, resulting in an intermediate k . Thus, lower porosity results in greater solid phase contribution to the coupling effect, which leads to higher measured thermal conductivity.

Accordingly, as shown in Figs. 2a and 2b, a lower porosity contributes to a relatively higher k . Porosities (Φ) are predicted from the densities of the mixtures as $\Phi = 1 - \frac{\rho_{avg}}{\rho_{effective}}$, where ρ_{avg} is the measured mean density and $\rho_{effective} = \rho_S(1 - x) + \rho_{Al}(x)$. ρ_S is density of silica, ρ_{Al} is density of bulk Al and x is concentration of AlNPs. Φ of the mixture is dependent on both the nanoparticle mass fraction and the compaction load used. An empirical fit of data presented in Fig. 2b gives $\Phi = 0.7594 - 0.1852 x - 0.02787 C_p$, where C_p is the compaction pressure. This dependence of Φ on x and C_p shows that, contrary to k , porosity is more sensitive to composition than compaction, and hence is only weakly correlated to the effective k of the mixture. Although the addition of AlNP leads to a larger change in the effective density of composite, the change in k is very small (Fig. 2c). On the other hand, despite the small increase in density with increasing compaction, we can observe a relatively large change in k for each of the AlNP concentrations considered.

Fig. 3a shows that k for both pure DE (with 0% AlNP) and DE containing 50% nanoparticles increases with increasing compaction but saturates above 1.70 MPa. The relative difference in k of the two samples widens with stronger compaction. The corresponding results measured under vacuum (27 Pa) presented in Fig. 3b, reveal a similar trend. Under vacuum conditions, conduction at the contact between solid particles is the predominant mechanism of thermal transport. The similarity between the two results suggests that the addition of AlNPs in DE increases the overall contact area, which increases k . Fig. 3c illustrates that the difference in k between the samples ($\Delta k = k_{50\% Al} - k_{pure DE}$) at 1 atm and at vacuum are comparable for lower compaction pressures but significantly differ as the applied load is increased. Δk at vacuum remains similar for the different compactions, implying that the contribution of AlNPs in increasing the inter-particle contact areas is consistent over the range of loads considered. The rise in Δk at 1 atm. with increasing compaction is due to the lower porosity and the coupling effect²⁹ in the presence of the pockets of air. Analyzing the microstructure of samples with different composition and compaction under SEM, as illustrated in Fig. 4, also confirms that nanoparticles do not undergo any noteworthy deformation.

Our results indicate that the addition of AlNPs does not significantly increase thermal conductivity of the material (Fig. 2a). These particles fill the pores of DE (Fig. 2b and Fig. 4), which is followed by an enhanced coupling effect (Fig. 3). High temperature insulation materials are typically more exposed to radiation heat transfer due to high porosity. Hence, the application of AlNP could lead to an improvement in the opacity of the material (by filling pores) without significantly increasing the overall thermal conductivity.

Effect of vacuum: Measurements in vacuum eliminate the contributions of gas conduction and effectively isolate the role of the porous medium. Vacuum generation is also employed to reduce k in high efficiency insulators like VIPs³⁰⁻³⁵. Thermal conductivity measurements with varying gas pressures for pure DE and 50% AlNP/DE, both prepared at 2.26 MPa, are presented in Fig. 5. The difference between the two sets of measurements is attributed to the enhanced solid contact area due to the addition of AlNPs. The increase in k with rise in pressure for the two samples is qualitatively similar. This result is characteristic of conduction by coupling effect since it is strongly dependent

on the concentration of gas phase that varies with pressure. In vacuum, the mass of gas present in the mixture is minimal and hence its contribution to k is negligible. Heat transfer is predominantly due to conduction through the solid particles and across the contact areas between them. However, as the amount of air inside the porous material increases not only does the contribution due to gas conduction is enhanced but it also gives rise to coupling effect²⁹. The mean free path of the gas molecules, λ_{air} , is calculated to be in the range of 64 – 68 nm depending on the relative humidity³⁶. Although mercury porosimetry measurements reveal that DE contains pores of sizes comparable to the mean free path of gas molecules (<100 nm)¹⁴, these constitute less than 5% of the total porosity. The majority of the pores in DE are of microscopic dimensions. Hence the Knudsen effect associated with gas conduction is negligible in this case. It has been shown for glass fiber fleece with average pore size of 1 μm that the coupling effect initiates around 10^2 - 10^3 Pa²⁹. Here, as shown in Fig. 5 with a log-log distribution, we observe an exponential dependence of k on the external gas pressure.

4. Summary

We investigate the thermal conductivity k of mixtures of nanoporous DE and Al nanoparticles for different compaction loads, compositions and gas pressures using the transient plane source technique. k is strongly correlated to compaction while only slightly to nanoparticle mass fraction. In contrast, the filler concentration has a pronounced effect on porosity. Measurements in vacuum reveal that addition of AlNPs affects k by increasing the solid contact area rather than through its effect on porosity. Our SEM characterization illustrates no deformations in Al nanoparticles suggesting that solid contact area does not change with compaction. However, as the air content in the mixture increases, k increases exponentially with rising gas pressures aided by the solid-gas coupling effect. Our results contribute to improved understanding of the thermal properties of nanoscale solid dispersions in a porous matrix where the constituent species have significant differences in thermal conductivities. The mixture investigated in this work has potential applications for high temperature insulation materials where radiation heat transfer can become important.

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Figure 1: The experimental setup (a) comprises of a sample chamber placed inside an evacuated bell jar, as shown in the schematic (b). The chamber contains a Hot DiskTM thermal conductivity probe, which is sandwiched between the dry pressed cylindrical DE samples, as illustrated in (c), during thermal conductivity measurement.

Figure 2: (a) The thermal conductivity of AlNP/DE mixtures increase with increases in nanoparticle concentrations and compaction pressures. (b) The strong reduction in porosity with increasing AlNP concentration implies a weak dependence of the overall mixture thermal conductivity on porosity (c) Thermal conductivity variation with density is shown for all the samples. The cases with the same AlNP concentrations are connected by lines to aid data visualization. Despite the large increase in density with addition of AlNP, thermal conductivity is more sensitive to the compaction.

Figure 3: Thermal conductivity of pure DE and 50% AlNP/DE mixture is presented for different compaction loads at (a) 10^5 Pa (~ 1 atm.) and (b) 27 Pa (~ vacuum). (c) The difference between thermal conductivity of 50% AlNP/DE mixture and pure DE increases with compaction loads, especially at 1 atm., because of the decrease in porosity.

Figure 4: SEM characterization of the microstructure of the AlNP/DE mixtures at different compactions and nanoparticle concentrations: (a) 30% AlNP (w/w) at 0.45 MPa, (b) 30% AlNP (w/w) at 2.26 MPa, and (c) pure DE at 0.45 MPa. No non-negligible deformation in the nanoparticles is observed.

Figure 5: Thermal conductivity of both the pure DE and 50% AINP/DE mixture increases with increasing external gas pressure because the air content in the sample pores increases resulting in enhanced contribution of gas conduction to the overall effective thermal conductivity. Additionally, the gas molecules trapped between the DE frustules and nanoparticles induce a coupling effect ²⁹ due to presence of different material phases resulting in an exponential dependence of thermal conductivity on gas pressure. The difference between the two sets of results is attributed to the enhanced solid contact area due to the addition of AINP. The data are shown on a set of logarithmic scales.