Experimental and computational studies on the thermal behavior and fire retardant properties of composite metal foams

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A comprehensive experimental and computational evaluation of thermal behavior and fire retardant properties of composite metal foams (CMFs) is reported in this study. Thermal behavior characterizations were carried out through specific heat, effective thermal conductivity, and coefficient of thermal expansion analyses using differential scanning calorimetry, high temperature guarded-comparative-longitudinal heat flow technique, and thermomechanical analyzer (TMA), respectively. The experimental results were compared with analytical results obtained from respectively rule of mixture, Brailsford and Major's model, and modified Turner's model for verification. United States Nuclear Regulatory Commission (USNRC) standard were employed as regulatory standard and criteria for fire retardant property study. The results revealed a superior thermal resistance and fire survivability of CMFs compared to 304L stainless steel. A physics-based three-dimensional model accounting for heat conduction was built using Finite Element Analysis to validate the reliability of the experimental results. The model led to a good reproduction of the experimentally measured data when comparing CMF to bulk stainless steel. This research indicates that one of the potential applications of lightweight CMFs can be in nuclear spent fuel casks replacing conventional structural and radiation shielding materials with demonstrated benefits of excellent thermal isolation, fire retardant, light weight and energy absorption capabilities.

1. Introduction

Spent fuel nuclear transportation casks are commonly used as containers for transporting radioactive waste materials from nuclear power plants to fuel reprocessing plants or disposal sites. A typical nuclear cask uses forged 304L steel as an outer shielding layer to attenuate gamma rays, and beech or spruce encased in stainless steel shells as an impact limiter to absorb impact energy. The increasing need for lightweight, radiation shielding, high-energy absorption, and heat resistance nuclear casks has sparked an interest towards multifunctional materials. *Composite Metal Foam (CMF)* is a new type of metal foam that can be produced by filling the vacancies around a random loose collection of preformed metallic hollow spheres with a solid metallic matrix either by casting or powder metallurgy (PM) techniques with the aim of increasing the foam's strength and energy absorption. The presence of the matrix strengthens and stabilizes the sphere walls, reducing the possibility of their buckling under loading and resulting in a stronger material with a much greater energy absorbing capability. The properties of composite metal foams can be altered by their processing technique, variation of the size and wall thickness of the hollow spheres as well as the matrix and sphere materials. This new metallic foam has shown up to 7-8 times higher energy absorption compared to any other metal foam made from similar materials and almost two orders of magnitude higher energy absorption under loading compared to the bulk materials that they have been made of (Vendra et al., 2009; Brown et al., 2010).

Composite metal foam (CMF) fulfills the requirements needed to replace the current cask designs as characterized by its low density, high specific stiffness and strength, extraordinary radiation attenuation efficiency, and good energy absorption capability (Chen et al., 2015, 2014; Garcia-Avila et al., 2014; Neville and Rabiei, 2008; Rabiei and Vendra, 2009; Vendra and Rabiei, 2007). However, thermal behavior and heat transfer mechanisms for CMF and its actual

performance under fire exposure have not been studied before. Such information is critical to provide guidance to determine the feasibility of application of CMFs in many structures with potential heat and fire exposure such as nuclear cask. In order to address these requirements, thermal characterizations including specific heat, effective thermal conductivity (ETC), and coefficient of thermal expansion (CTE) of CMFs were investigated in this work. Specific heat of CMFs was tested by Differential Scanning Calorimetry, and compared with theoretically calculated values obtained through rule-of-mixture. The ETC was measured by means of high temperature guarded-comparative-longitudinal heat flow technique, and verified by Brailsford and Major's model. The CTE was experimentally studied using thermomechanical analyzer (TMA), and validated via modified Turner's model. Flame test was also performed in accordance with United States Nuclear Regulatory Commission (USNRC) standard [49 CFR 173.398(d)] (Walton and Blackburn, 2012), in which CMF was subjected to a fully engulfing fire with an average flame temperature of 800°C for a period of 30 minutes. A physics-based three-dimensional model was carried out using Finite Element Analysis to secure the credibility of the experimental results.

2. Materials Processing and Sample Preparations

2.1. Materials Processing

The hollow spheres used in this study were produced by Hollomet in Germany, using a powder metallurgy process. All spheres were made of 316 stainless steel (except that the carbon content is slightly higher than 316 stainless steel) and have two major nominal outer diameter sizes of 2 and 4 mm. The average outer diameter, wall thickness and porosity percentage of all spheres are presented in Table 1. The spheres are designed in a way to maintain a constant ratio of sphere wall thickness to outer diameter in all spheres and have a low percentage of porosities within the sphere walls. This was to make sure the samples were all uniform and that the resulting data would be repeatable and reliable. Aluminum A356 casting alloy (TriAlCo, Inc), and 316L stainless steel powder (North American Hoganas High Alloys LLC) with particle size sieved to -325 mesh (95%) and -200/+325 mesh (5%) were used as the matrix material in manufacturing CMFs. The chemical compositions of hollow spheres is given in Table 2 while that of Aluminum A356 alloy, and 316L stainless steel are given in Table 3. Aluminum-steel composite metal foams (Al-S CMFs) consisting of steel hollow spheres and a solid aluminum A356 alloy matrix were processed through gravity casting technique, whereas steel-steel composite metal foams (S-S CMFs) comprised of steel hollow spheres closely packed in 316L stainless steel powder were manufactured through powder metallurgy technique. More details of manufacturing procedures of CMFs can be found elsewhere (Neville and Rabiei, 2008; Vendra and Rabiei, 2007).

2.2. Sample Preparations

2.2.1. Samples for Specific Heat Analysis

Specific heat was studied on (4mm sphere) S-S CMFs and (4mm sphere) Al-S CMFs. 50 mg metal filings from each sample was obtained through milling the sample surface without using any lubricant in order to keep the filings clean and dry.

2.2.2. *Samples for Effective Thermal Conductivity Analysis*

Three CMF samples were selected to study the effect of sphere size and matrix material on thermal conductivity and compared with the properties of 316L stainless steel and Aluminum A356 available in literature:

- Composite metal foams with 2mm steel hollow spheres and 316L stainless steel matrix [(2mm sphere) S-S CMF]
- Composite metal foams with 4mm steel hollow spheres and 316L stainless steel matrix [(4mm sphere) S-S CMF]
- Composite metal foams with 4mm steel hollow spheres and Aluminum A356 matrix [(4mm sphere) Al-S CMF]

These samples were cut using a Buehler Isomet 4000 linear precision saw to nominal dimensions of 2.54 x 2.54 x 2.54cm. The specimen ends (top and bottom surfaces as illustrated in Figure 1) were prepared to be flat and parallel to each other, and perpendicular to the sides within 25µm per 25mm accuracy. Both surfaces were finished using a progression of 240, 600, and 1200 grit papers at a wheel speed of 90rpm for S-S CMFs and 70rpm for Al-S CMFs in order to improve the flatness, parallelism and thickness uniformity of the samples. Physical properties of the CMF samples are summarized in Table 4.

2.2.3. *Samples for Coefficient of Thermal Expansion Analysis*

Two S-S CMF samples with respectively sphere sizes of (2mm sphere) and (4mm sphere) were used to evaluate the coefficient of thermal expansion (CTE):

- (2mm sphere) S-S CMF
- (4mm sphere) S-S CMF

The sample dimension was designed to have a length of 20mm and cross-section of 8mm by 8mm. Specimen contact areas (top and bottom surfaces) were cut to be parallel, following by surface finishing using a progression of 240, 600, and 1200 grit papers at a wheel speed of 90rpm.

2.2.4. *Samples for Flame Test*

A typical nuclear cask uses forged 304L stainless steel (SS) as an outer shielding layer (19.05mm thick). Therefore, 304L SS was selected as control sample in the flame test study. Figure 2 shows the digital image of flame test samples:

- 304L stainless steel (control sample)
- (2mm sphere) S-S CMFs

Due to the size limitations of existing furnaces and high cost of full-scale nuclear cask flame test, a small-sized horizontal propane fired burner with an opening of 15.2 x 15.2cm and accommodating samples of 6.35 x 6.35 x 1.91cm were used to carry out the flame test. Physical properties of the samples are presented in Table 4.

3. Experimental Methods

3.1. Specific Heat Measurements

The determination of specific heat was performed in according to the ASTM E1269 by means of differential scanning calorimeter (DSC) technique (NETZSCH 204 F1 Phoenix). DSC measurements of 12-15mg of powdered CMF were carried out in opened alumina crucibles

under a nitrogen atmosphere in the temperature range between -130°C and 400°C with a heating rate of 10°C/minute.

3.2. Effective Thermal Conductivity Measurements

The effective thermal conductivities of (2mm sphere) S-S CMF, (4mm sphere) S-S CMF, and (4mm sphere) Al-S CMF were measured by means of high temperature guarded-comparative-longitudinal heat flow technique (Testing service provided by Precision Measurements and Instruments Corporation (PMIC)). The measurement system design was adapted from the American Society of Testing and Materials (ASTM) E1225-04 as shown schematically in Figure 3. In this technique, CMFs of unknown thermal conductivity was inserted between two stainless steel meter bars of known thermal conductivity forming a sample stack. 3.18mm thick copper shims were placed between the specimen and meter bars to act as lateral heat spreaders. 0.51mm diameter metal-sheathed K-type thermocouples were used for temperature measurement. Six thermocouples were embedded in the appropriate holes at specific locations to record the temperature along the axial direction during the heating process. As indicated in Figure 3a, the thermocouples were located 2.54mm apart from the top and bottom surfaces of specimen and meter bars. The temperature values were continuously recorded as a function of time using a Labview-based program on a PC workstation. A small quantity of thermal grease was applied to the tip of each thermocouple to improve thermal grounding to the specimen or meter bars. A thin film of thermal grease was also applied at each interface, between the specimen, copper shims, meter bars and hot and cold plates to reduce or eliminate the thermal resistance. During the measurement, a uniform compressive pressure of 0.7Mpa was applied on the specimen stack to ensure good contact between each interface. A temperature gradient is established using a heater on one end and a cold sink on the other end. The test apparatus was ramped to the desired temperatures and held for sufficient time to reach steady state. The total temperature difference between the upper and lower plates was maintained at 40°C. At equilibrium conditions, the thermal conductivity is derived from the measured temperature gradients in the respective specimens and the thermal conductivity of the reference materials, two stainless steel meter bars. The tests were performed in vacuum (<200mTorr, 27Pa). Heat losses were minimized by use of a longitudinal insulation guard having approximately the same temperature gradient. The thermal conductivity-testing apparatus was verified with NIST SRM 1462 Stainless Steel. The data supplied with the SRM were used for the verification. With the reference material in place of the specimen, a test was run under identical conditions. Measurements on (2mm sphere) and (4mm sphere) S-S CMFs were performed from 300°C up to 600°C at increments of 100°C, while (4mm sphere) Al-S CMF was tested from 300°C up to 500°C at increments of 100°C.

3.3. Coefficient of Thermal Expansion Measurements

Linear thermal expansions of (2mm sphere) and (4mm sphere) S-S CMF were measured from 0°C to 400°C at 5°C/min using a commercial thermomechanical analysis equipment (TMA 202, NETZSCH-GERÄTEBAU GMBH) at Advanced Materials and Processing Branch at NASA Langley Research Center. The measurement system design was adapted from the American Society of Testing and Materials (ASTM) E831, in which the sample was placed in a furnace enclosure, which can be maintained within a few tenths of a degree using closed-loop

temperature control. The sample is positioned on a fused quartz platform and a moveable probe is placed on the top of the sample. The dimensional changes occurring as a function of time and temperature were monitored by a linear variable differential transformer (LVDT) attached to the probe. The position of the probe was set to zero on the platform. Following by raising the probe, placing the sample on the platform, lowering the probe on the sample, and starting the temperature program. The resulting record showed the linear thermal expansion of the CMFs samples with changing temperature. Each sample was tested twice, and the average of the two was used for calculation and comparison.

3.4. Flame Test

3.4.1 Flame test experimental measurements

Flame test was performed at the Center for Research on Textile Protection and Comfort (T-PACC) at North Carolina State University. A schematic of the test setup is shown in Figure 4, the burner with a square tray size of 152.4 x152.4mm was operated with propane based typical low-calorific value fuels. The installation of the burner was performed in accordance with ASTM F2700 guidelines. The horizontal position of the samples, with the lower surface exposed to the fire, represents a fully engulfing fire with an advantage of a more homogeneous temperature distribution on the fireside of the samples. Two mineral fiber insulation boards (Figure 5) were cut and used to insulate the sample, mimicking an adiabatic boundary condition on the sample periphery, preventing heat and mass loss through the borders of the investigated assembly. Figure 6 shows the sample assembly in fiber insulation materials. This assembly was supported on an adjustable ring clamp fastened on the pole of a metal support stand. The height of the ring clamp was adjusted to be 18cm above the burner surface so that an average flame temperature of 800°C reaches the center bottom of the sample. Temperature measurement was performed by Type-K (chromel alumel) probe-style thermocouples, which was connected to a computer and LabVIEW interface via a data acquisition control unit (Agilent 34970A). Three thermocouples were installed, one for measuring the temperature of the flame reaching the bottom of the sample, the other two for determining the temperature from the upper and lower surfaces of the sample. The probes of the thermocouples are held horizontally with the tip reaching the centerline. The junctions were fixed in intimate contact with the specimen by means of high temperature cement (Omegabond 600") that was cured at room temperature 24 hours before commencing the measurements. An infrared thermo-camera (FLIR A325sc), featuring 320 by 240 pixels, with detector pitch of 25um, and recording 30 frames per second, was implemented to further explore the sample and flame temperature. The camera was positioned on a tripod with the imaging field of view just above the supporting ring, capturing one of the side cross section of the sample. The camera lens was placed 25cm from the centerline of the sample to perform accurate quantitative temperature measurements.

4. Flame Test Model

A physics-based three-dimensional model accounting for the conduction of materials was carried out using finite element analysis in ANSYS WorkBench. The sphere packing arrangement in (2mm sphere) S-S CMF is represented through body-centered cubic (BCC). The boundary conditions implemented in the thermal model are based on the experimental setup, where the top and side faces are thermally insulated. The model is subjected to a 25.4mm diameter heat source held at a constant temperature of 800°C at the bottom to mimic the heat

input from the flame. The heat convection and radiation through the sphere pores are neglected since their outer diameters are only 2 mm. It has been shown that the convection has negligible effects in hollow spheres with diameters less than 4 mm (Kulesa and Robinson, 2015). In addition, the flux due to radiation typically does not control heat transfer in composite foams (Jablonski and Ogden, 2008). As such, this study only considers conduction to model the flame retardant behavior of CMF. In order to fully compare the model with bulk stainless steel, custom inputs for the three-dimensional model include an input of density, specific heat, and thermal conductivity, taken from the experimental results. The geometry was created by introduction of porosities arranged in BCC structure with an inner diameter of 1.9 mm in the matrix. Both spheres and matrix are considered as one material, assuming uniform chemical composition, grain structure, and microporosities. A representation of the model built in SolidWorks can be seen in Figure 7.

5. Results and Discussions

5.1. Specific heat results and discussions

5.1.1. Specific heat experimental results and discussions

Figure 8 presents the evolution of the specific heat of CMFs during the heating process in the temperature ranging from 0°C to 400°C. A linear variation can be seen in the specific heat of both Al-S CMF and S-S CMF samples at various temperatures. A positive deviation from linear behavior is observed in Al-S CMF samples beginning around 200°C, which is an indication of dissolution of Si precipitation in the Al matrix during the heating process according to the Neumann-Kopp rule (Zahra et. al, 1995). As indicated in Figure 8, (4mm sphere) Al-S CMF has a higher specific heat than (4mm sphere) S-S CMF, which is due to the fact that the specific heat of Al is higher than that of steel. Comparing CMF with its matrix materials, it was found that, at room temperature (4mm sphere) Al-S CMF ($C_p=0.790 \text{ J/(g-}^\circ\text{C)}$) has lower specific heat as compared with bulk Aluminum A356 ($C_p=0.900 \text{ J/(g-}^\circ\text{C)}$), this may be attributed to the existence of the stainless steel sphere wall material with lower specific heat inside an Al matrix. Compared with bulk 316L stainless steel ($C_p=0.444 \text{ J/(g-}^\circ\text{C)}$), (4mm sphere) S-S CMFs ($C_p=0.551 \text{ J/(g-}^\circ\text{C)}$) exhibits a higher measured specific heat, which can be attributed to the higher carbon content in the sphere walls (0.58 wt%) compared to 316L stainless steel (0.03 wt%), as listed in Table 2 and Table 3.

5.1.2. Theoretical model to predict specific heat

The model used for predicting specific heat (C_p) is based on the general rule-of-mixture is shown in Equation (1) (Kate, 2012):

$$C_p = \sum_i x_i (C_p)_i \quad (1)$$

where x_i is the weight fraction and $(C_p)_i$ is the specific heat of the i^{th} element.

The hollow sphere packing density of CMFs was reported to be 59 vol% (Rabiei and Vendra, 2009). The percentages of matrix porosities were calculated using image analysis techniques to

be 6.7 vol% in (4mm sphere) Al-S CMFs (Chen et al., 2015) and 50.1 vol% in (4mm sphere) S-S CMFs (Garcia-Avila and Rabiei, 2015). By using the densities of hollow spheres (Table 1) and matrix (Table 5), as well as their corresponding volume fraction as input, the weight fractions of matrix materials in the (4mm sphere) Al-S CMF and (4mm sphere) S-S CMF were calculated to be 51.7 wt% and 63.2 wt%, respectively (Table 5). Chemical compositions of (4mm) Al-S CMF and (4mm) S-S CMF were then derived through Table 2 and Table 3, and summarized in Table 6, along with the specific heat of each element at 25°C. The theoretical heat capacities of CMFs were obtained (Equation (1)) to be 0.670 J/(g·°C) for (4mm) Al-S CMF and 0.443 J/(g·°C) for (4mm) S-S CMF (Table 7). They are in reasonable agreement with the experimental results considering the uncertainty in the exact percentages of spheres, matrix material voids and impurities in CMFs as well as the uncertainty in accuracy of experimental procedure.

5.2. Effective thermal conductivity results and discussions

5.2.1. *Effective thermal conductivity experimental results and discussions*

Thermal conductivity data for control materials: 316L stainless steel, Aluminum A356, and air are available in literature as a source of comparison (Bakhtiyarov et al., 2001). Table 8 and Table 9 summarize effective thermal conductivity values of CMFs and control materials, respectively. Figure 9 shows temperature-dependent thermal conductivities of CMFs, and two control materials. Both Al-S CMF and S-S CMF exhibit much lower thermal conductivity than their matrix materials (control samples). This is due to the presence of porosities within the sample. In thermal conductivity studies, voids play an important role due to the low thermal conductivity of air within (Tien Chih Lin, 2009). Thus, the high air content inside CMFs offers extremely good thermal insulation performance as compared to the commercially available nuclear structural materials such as Aluminum and stainless steel. It is well-known that Aluminum exhibits very high heat conductivity, which is governed by valence electrons (Totten and MacKenzie, 2003). As shown in Table 9, thermal conductivity of Aluminum A356 is about fourteen times higher than that of 316L stainless steel. However, the difference between S-S CMF and Al-S CMF is relatively small, where the thermal conductivity of Al-S CMF is only seven times higher than that of S-S CMF. This is attributed to the placement of hollow steel spheres within Al matrix in Al-S CMF, the sphere wall material and air inside sphere core have lower thermal conductivity compared to Al.

(2mm sphere) and (4mm sphere) S-S CMFs have shown similar thermal conductivity at a given temperature (Table 8). This is due to the fact that the sphere wall thickness to its diameter ratio is the same in both sphere sizes and as such there is the same amount of sphere and matrix materials in both samples. All of these can be translated into a similar volume fraction of spheres wall and matrix material in all samples (Table 10). Therefore, the thermal conductivity of S-S CMF is relatively independent of sphere size as long as the sphere wall thickness to outer diameter is kept constant.

It should be noted that the variation of thermal conductivity of S-S CMFs is relatively small under the measured temperature range when compared with solid stainless steel. This can be attributed to the presence of air in the porosities. Stable thermal conductivity of CMFs under various temperatures is important for their practical application.

5.2.2. *Theoretical model to predict effective thermal conductivity*

Brailsford and Major (Brailsford and Major, 1964) developed a model to predict the effective thermal conductivity of monodisperse homogeneous particles made of two different

materials randomly distributed in a continuous matrix. They compared the experimental results with the relation derived from their study, and a good agreement was obtained. The effective thermal conductivity (k_{eff}) of three-component media is given by (Brailsford and Major, 1964):

$$k_{eff} = \frac{k_m \phi_m + k_{sc} \phi_{sc} \frac{3k_m}{(2k_m + k_c)} + k_{sw} \phi_{sw} \frac{3k_m}{(2k_m + k_c)}}{\phi_m + \phi_{sc} \frac{3k_m}{(2k_m + k_c)} + \phi_{sw} \frac{3k_m}{(2k_m + k_c)}} \quad (1)$$

where k_m , k_{sw} , and k_{sc} are the thermal conductivities of the matrix, sphere wall, and sphere core materials (air), respectively. Similarly, ϕ_m , ϕ_{sw} , and ϕ_{sc} are the volume fractions of the matrix, sphere wall, and sphere core materials, respectively.

The theoretical effective thermal conductivity was obtained by using Brailsford and Major's model and compared with experimental results in Table 8. A 20% average difference between the experimental results and model prediction can be seen in this table. Considering the complexity of the structure of CMFs and simplifications proposed in order to construct Brailsford and Major's model, the analytical results show a good agreement with the experimentally measured thermal conductivity.

5.3. Coefficient of thermal expansion results and discussions

5.3.1. Coefficient of thermal expansion experimental results and discussions

The thermal strain of (2mm sphere) S-S CMF and (4mm sphere) S-S CMF were measured in temperature range of 0-400°C and presented in Figure 10. It was observed that (2mm sphere) and (4mm sphere) S-S CMFs exhibit very similar behavior. The thermal strains increase linearly with increasing temperature, which may be attributed to the similar matrix and spheres wall material since both sphere wall and matrix are made of stainless steel. Therefore, there is no induced thermal stress during the heating process resulting from any mismatch of coefficient of thermal expansion of components. The sphere size effect on coefficient of thermal expansion (CTE) is relatively small, which may be resulted from their similar volume fraction of sphere wall material, matrix material, and air (Table 10).

CTE values were calculated to be $3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for both S-S CMFs. These experimental results are listed in Table 11, and plotted in Figure 11 in comparison with 316L stainless steel control material. It is interesting to observe that S-S CMF display superior thermal stability as its CTE stayed constant over the testing temperature range (0-400°C). As compared to 316L stainless steel, it can be clearly seen that the addition of hollow spheres in S-S CMF resulted in a decrease of CTE by about 80%. This is attributed to the presence of microporosities in the matrix and sphere wall as well as the macro porosities of the hollow spheres. These porosities accommodate local thermal expansion, keeping the bulk CTE constant. For various structures such as those used in nuclear applications, high degree of dimensional stability with temperature fluctuations is very essential in order to minimize the possibility of failure induced by thermal stress.

5.3.2. Theoretical model to predict coefficient of thermal expansion

The CTE of CMFs is relatively difficult to predict precisely because it is influenced by several factors including the microporosity content and microstructure of both sphere walls and

matrix material. Turner's model, based on the rule of mixture is a common model to predict CTE of composite materials (Turner, 1946):

$$\alpha_{CTE} = \frac{\alpha_m \phi_m K_m + \alpha_s \phi_s K_s}{\phi_m K_m + \phi_s K_s} \quad (1)$$

where α_m and α_s are the CTE of the bulk matrix and sphere, respectively. Similarly, ϕ_m and ϕ_s are volume fraction of the matrix and sphere, respectively, while K_m and K_s are the bulk moduli of the matrix and sphere, respectively.

The bulk modulus can be estimated from the Young's modulus (E) of the constituents as:

$$K = \frac{E}{3(1-2\nu)} \quad (1)$$

where (ν) is the Poisson's ratio of the respective constituents

Turner's model is mainly applicable to composites containing solid fillers and do not include hollow particles, which is an additional parameter available for variation in CMFs. In order to determine the effective steel hollow sphere modulus, the radial displacement at the outer surface of the two systems are compared and the effective modulus (E^*) as a function of the hollow sphere radius ratio is found as (Nji and Li, 2008):

$$E^* = \frac{E_{sw}(1-2\nu)(1-\eta^3)}{(1-2\nu) + \frac{(1+\nu)\eta^3}{2}} \quad (1)$$

where (E_{sw}) is the modulus of the sphere wall material and it can be found in Table 12.

The values of (η) is defined as radius ratio (Gupta et al., 2010):

$$\eta = \frac{r_i}{r_o} \quad (1)$$

where r_i and r_o are the inner and outer radii of the hollow sphere. The calculated values of (η) are listed in Table 10.

The modified Turner's model for CTE with hollow spheres is given by substituting Equation (4) and Equation (5), into Equation (3) as (Shunmugasamy et al., 2012):

$$\alpha_{CTE} = \frac{\alpha_m \phi_m E_m \left[(1-2\nu_{sw}) + \frac{(1+\nu_{sw})\eta^3}{2} \right] + \alpha_s \phi_s E_{sw} (1-2\nu_m)(1-\eta^3)}{\phi_m E_m \left[(1-2\nu_{sw}) + \frac{(1+\nu_{sw})\eta^3}{2} \right] + \phi_s E_{sw} (1-2\nu_m)(1-\eta^3)} \quad (1)$$

The comparison of theoretical and experimental values for CTE of CMFs at various temperatures is shown in Table 11. Good matching between theoretical and experimental results can be observed. Considering the complexity of the microstructure of CMFs and the simplicity

of proposed model, the theoretical results show a good agreement with the experimental measurements.

5.4. Flame test results and discussions

5.4.1. *Flame test experimental results and discussions*

Sequential IR images of (2mm sphere) S-S CMF and 304L stainless steel are both displayed in Figure 12. As can be seen, 304L stainless steel reached its thermal steady state in about 4mins, while it took 8mins for S-S CMF to reach its equilibrium condition. The main reason for flame retardant function of CMF is associated with the high percentage of porosity (about 60%) filled with low heat permeability air, which restrict fire and prevent the heat transfer. Whereas in solid 304L stainless steel, there is no air and the heat spreads quickly. As such the S-S CMF seems to perform better under nuclear waste flame test conditions.

5.4.2. *Finite element analysis modeling for flame test*

A side view of the model for the flame test of (2mm) S-S CMF and 304L stainless steel is shown in Figure 13. Although not visually compiled in ANSYS, the sphere BCC structure is spread through the entirety of the model as seen in Figure 7. The model is in good agreement with the experimental results. Variation between the model and the experiment can be attributed to initial assumptions made when creating the model such as the perfect bonding between spheres and matrix and a uniform distribution of chemical composition, uniform grain sizes and porosity content in sphere walls and matrix as well as the assumed heat source size and shape. The model can be further expanded upon future analysis by differentiating the sphere and matrix.

6. Conclusions

The CMFs developed and discussed in this work offer extremely good thermal insulation, superior thermal stability, and excellent flame retardant performances as compared to commercially available materials such as stainless steel. Thermal conductivity and coefficient of thermal expansion of CMF is relatively independent of sphere size. It should be noted that the variation of thermal conductivity of S-S CMFs is relatively small under the measured temperature range comparing with solid stainless steel. The desirable characteristics of CMFs, along with other suitable properties such as lightweight, radiation shielding efficiency and energy absorption capability make them attractive materials for many structural applications such as nuclear spent fuel casks.

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Table 1: Geometrical characteristics of 2mm and 4mm stainless steel hollow spheres

Sphere diameter (mm)	Sphere wall porosity (%)	Sphere density (g/cm ³)	Sphere wall thickness t (mm)	Sphere outer radius R (mm)	t/R
2	8	2.03	0.104	1.02	0.1023
4	6	2.24	0.196	1.76	0.1111

Table 2: Chemical compositions of 2mm and 4mm stainless steel spheres used in processing CMFs (wt%)

	2mm diameter	4mm diameter
C	0.68	0.58
Mn	0.13	0.15
Si	0.82	1.14
Cr	16.11	17.34
Ni	11.53	12.28
Mo	2.34	2.28
P	--	0.009
S	--	<0.003
Cu	--	0.04
Co	--	0.02
Fe	balance	balance

Table 3: Chemical compositions of matrix materials used in processing CMFs (wt%)

Element	316L stainless steel	Aluminum A356
C	0.03	--
Mn	2.00	0.28
Si	1.00	7.01
Cr	16.00-18.00	0.02
Ni	10.00-14.00	--
Mo	2.00-3.00	--
Cu	--	0.11
Fe	balance	0.50
Mg	--	0.39
Ti	--	0.09
Zn	--	0.06
Al	--	balance

Table 4: Physical properties of CMFs and 304L stainless steel used to evaluate effective thermal conductivity and flame test

Samples		Thickness (cm)	Width (cm)	Length (cm)	Volumetric density (g/cm ³)
Effective Thermal Conductivity Samples	(2mm sphere) S-S CMF	2.54	2.54	2.54	2.7
	(4mm sphere) S-S CMF	2.54	2.54	2.54	2.6
	(2mm sphere) Al-S CMF	2.54	2.54	2.54	1.9
Flame Test Samples	304L stainless steel	1.91	6.35	6.35	8.03
	(2mm sphere) S-S CMFs	1.89	6.35	6.35	2.71

Table 5: Physical properties of matrix materials in (4mm sphere) Al-S CMFs and (4mm sphere) S-S CMFs

Samples	Matrix porosity (vol %)	Matrix density (g/cm ³)	Matrix weight fraction (wt%)
(4mm sphere) Al-S CMFs	6.7	2.5	51.7
(4mm sphere) S-S CMFs	50.1	4.0	63.2

Table 6: Percentage of various components in chemical composition of (4mm) Al-S CMF and (4mm) S-S CMF and their associated specific heat at 25°C (Lide, 2005)*

Element	Specific Heat at 25°C (J/(g-°C))*	(4mm sphere) Al-S CMF (wt %)	(4mm) S-S CMF (wt%)
C	0.709	0.280	0.232
Mn	0.480	0.217	1.319
Si	0.700	4.172	1.052
Cr	0.449	8.392	17.125
Ni	0.440	5.936	12.103
Mo	0.250	1.102	2.419
P	0.769	0.004	0.003
S	0.710	0.001	0.001
Cu	0.385	0.076	0.015
Co	0.421	0.010	0.007
Fe	0.444	32.239	65.723
Mg	1.020	0.201	--
Zn	0.388	0.031	--
Al	0.900	47.290	--
Ti	0.523	0.046	--

Table 7: Comparison of experimental and theoretical values of specific heat for (4mm sphere) Al-S CMF and (4mm sphere) S-S CMF

Material Description	Experimental specific heat J/(g-°C)	Rule – of – mixture model (J/(g-°C))	Difference between experimental and theoretical results (%)
(4mm sphere) Al-S CMF	0.790	0.670	15
(4mm sphere) S-S CMF	0.551	0.443	20

Table 8: Comparison of experimental and theoretical values of effective thermal conductivities for (2mm sphere) S-S CMF, (4mm sphere) S-S CMF, and (4mm sphere) Al-S CMF at various temperatures

Material Description	Nominal temperature (°C)	Actual temperature (°C)	Experimental thermal conductivity (W/m-°C)	Brailsford and Major's model (W/m-°C)	Difference between experimental and theoretical results (%)
(2mm sphere) S-S CMF	300	301	3.9±0.20	4.5	16
	400	402	4.4±0.22	5.1	15
	500	503	5.0±0.25	5.6	12
	600	605	5.6±0.28	6.1	9
(4mm sphere) S-S CMF	300	302	3.8±0.19	4.7	22
	400	402	4.4±0.22	5.2	20
	500	503	5.0±0.25	5.8	16
	600	605	5.7±0.29	6.4	11
(4mm sphere) Al-S CMF	300	301	32.1±1.61	36.9	15
	400	402	30.7±1.84	38.9	27
	500	503	30.3±1.52	38.4	27

Table 9: Thermal conductivities of 316L stainless steel, Aluminum A356, and air at various temperatures (Lide, 2005)*

Material Description	Temperature (°C)	Thermal conductivity (W/m-°C)*
316L stainless steel	300	13.4
	400	15.2
	500	16.8
	600	18.4
Aluminum A356	300	205
	400	215
	500	210
Air	300	0.0451
	400	0.0510
	500	0.0564
	600	0.0615

Table10: Volume fraction of sphere wall material, matrix material, and air in CMFs

Samples	Volume fraction of matrix material (vol%)	Volume fraction of sphere wall material (vol%)	Volume fraction of air (vol%)	Radius ratio of steel hollow sphere (η)
(2mm sphere) S- S CMF	28.4	15.0	56.6	0.898
(4mm sphere) S- S CMF	25.4	16.5	58.0	0.873
(4mm sphere) Al-S CMF	23.2	16.5	60.2	0.873

Table 11: Experimental and theoretical values of coefficient of thermal expansions for (2mm sphere) S-S CMF and (4mm sphere) S-S CMF at various temperatures

Samples	Temperature (°C)	Experimental CTE (°C ⁻¹)	Theoretical CTE (°C ⁻¹)	Difference between experimental and theoretical results (%)
(2mm sphere) S-S CMF	0	3.00E-06 ±0.03E-06	2.47E-06	18
	100		2.50E-06	17
	200		2.57E-06	14
	300		2.63E-06	12
	400		2.78E-06	7
(4mm sphere) S-S CMF	0	3.00E-06 ±0.20E-06	2.52E-06	16
	100		2.58E-06	14
	200		2.63E-06	12
	300		2.79E-06	7
	400		2.83E-06	6

Table 12: Physical properties of 316L stainless steel used for prediction of thermal expansion of CMFs

Material Description	Temperature (°C)	Mean CTE (°C ⁻¹)*	Young's modules (GPa)*	Poisson's ratio*	Effective modulus of 2mm sphere (GPa)	Effective modulus of 4mm sphere (GPa)
316L stainless steel	0	1.55E-05	200	0.20	23.41	28.34
	100	1.60E-05	194	0.24	19.75	23.90
	200	1.65E-05	186	0.27	16.76	20.28
	300	1.70E-05	179	0.32	12.58	15.23
	400	1.75E-05	172	0.32	12.09	14.63

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Tips of the thermocouples reaching the samples' centerline

Figure 2: Digital images of flame test samples showing the location of thermocouples on the heat exposed surface with the tip reaching the centerline: (a) 304L stainless steel, and (b) (2mm sphere) S-S CMF

Figure 3: Schematic of guarded-comparative-longitudinal heat flow technique test setup

Figure 4: A schematic of the flame test setup

Figure 5: Mineral fiber insulation boards surrounded the sample

Figure 6: Sample enclosed in fiber insulation material: (a) 304L stainless steel and (b) (2mm sphere) S-S CMF. Dashed rectangular area indicates the area for IR imaging

Figure 7: (a) Isometric views of the CMF model built in SolidWorks and used in the ANSYS modeling software. (b) Section close up of the sample showing sphere voids. (c) Model shown imported into ANSYS.

Figure 8: A comparison of the specific heat of (4mm sphere) Al-S CMF and (4mm sphere) S-S CMF as a function of temperature

Figure 9: Thermal conductivity as a function of temperature for (a) all testing samples, and (b) zoomed in section related to CMFs and 316L stainless steel

Figure 10: Thermal strain of (2mm sphere) S-S CMF and (4mm sphere) S-S CMF as a function of temperature

Figure 11: Experimental coefficient of thermal expansion of CMFs as compared with 316L stainless steel

Figure 12: Sequential IR images of a) (2mm sphere) S-S CMF and b) 304L stainless steel during flame test showing temperature profile in the sample

Figure 13: Finite element analysis modeling with center section view of a) (2mm sphere) S-S CMF and b) 304L stainless steel exposed to an 800°C flame at the base.