THERMAL CONDUCTIVITY PROPERTIES OF CARBON NANOTUBE-GOBU NATURAL BENTONITE CERAMIC COMPOSITES AT HIGH TEMPERATURES

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For the first time, the thermal conductivity properties of the natural Azerbaijani Gobu bentonite/x Multi-Walled Carbon Nanotube (x MW-CNT)(x = 1%, 2%, 4%, 8%, and 16%) ceramic composites were studied at high temperature ranges for investigation of their application abilities in the fabrication of new generation nanodevices. A laser flash technique was used to measure the thermal conductivity of the prepared nanocomposites. The nanocomposites were prepared by an irreversible dispersion method that was developed by our research group. The highest thermal conductivity was observed for 16% MWCNT-containing nanocomposites, as expected. The highest value of thermal conductivity is k = 1,04 W/(m*K) at T = 348^0C for Gobu bentonite/x MWCNT (x = 16%) nanocomposite and the lowest thermal conductivity for Gobu bentonite is k = 0,27 W/(m*K) and k = 0,31 W/(m*K) at T = 325^0C for Gobu bentonite/xMWCNT (x = 1%) nanocomposite. A sharp thermal conductivity drop was observed at 352^0C for Gobu bentonite without MW-CNTs as well as for nanocomposites containing low concentrations of xMW-CNTs (x = 1%). The main goal of this research is the investigation of the application abilities of these novel-type, cost-effective composites as substrates like coolers for electronic devices with less heat release, as heating elements apartments, and as novel-type thermoelectrics.

Keywords: Multi-walled carbon nanotubes, Aerosol-Chemical Vapor Deposition, irreversible dispersion method, thermal conductivity, natural Gobu Azerbaijani bentonite clay, nanocomposites.
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1. Introduction

In the last few decades, tremendous improvements have been made in electronic devices; in particular, they have become faster, cheaper, and more powerful along with continually decreasing size and ever-increasing device density. The heat generated in a device is directly transported or indirectly through a heat spreader to a heat sink. The effective thermal management of these devices is essential and quite urgent; otherwise, the performance, reliability, and lifetime of devices would be decreased [1]. To avoid heat breakdown, integrated circuits of this small scale need to be efficiently cooled. As ceramics can withstand high temperatures, they are very useful for this application. However, the fabrication process of sintering ceramics are very expensive and demand high temperature which in the end impact the price of the product. Therefore, currently, mostly natural bentonites based ceramics are becoming more popular and useful. Thus in this research work ceramic composites were prepared based on natural Gobu bentonite clay. As additive material, we have used MW-CNTs due to their high thermal conductivity (2000-3000W/m*K) as well as other unique properties [2–4]. However, a lot of parameters impact the thermal conductivity. For example, the thermal conductivity of a single CNT is related to its microstructure including defects, crystallinity, diameter, and the number of walls. Several theoretical studies showed that a small number of defects such as vacancies, and isotopic impurities drastically decrease the thermal conductivity of CNTs due to enhanced scattering, and damping of phonon modes [5-8].

Higher defect density in CNTs leads to worse thermal conductivity. A general trend that the thermal conductivity of CNTs decreased with increasing tube diameter was verified by experimental work. The effect of the number of walls on the thermal conductivity of CNTs is still unclear. In addition, we have listed above the interfaces formed between MW-CNTs and bentonites as well as the MW-CNT network forms formed inside bentonite will affect the thermal conductivity. Therefore, in this research work, we have solved some problems which are very relevant from a scientific and practical point of view.

2. Experimental methods and characterization:
2.1. Characterization techniques

Electron microscopy investigations of the prepared nanocomposites were carried out using scanning electron microscopy (SEM) JEOL JSM6610LV Oxford microscope. The typical magnification used for the SEM was 5μm and is denoted at the bottom of each image as a 30 kV electron beam. Thermal conductivity measurements were performed using the laser flash using the Light

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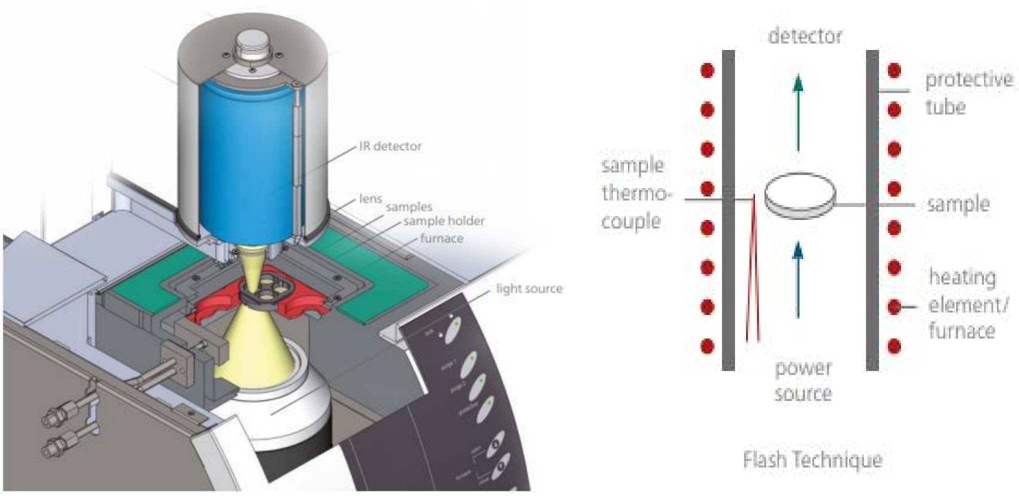
Flash (LFA 467 Hyper Flash-NETZSCH) technique in a 300–400^{0}C range. Complete set of thermophysical properties such as thermal diffusivity (a), specific heat capacity (cp), and thermal conductivity (k) as input data for numerical simulations. In this technique, one face of the sample is irradiated by a short (1 ms) laser pulse. An IR detector monitors the temperature rise on the opposite side of the samples. The thermal diffusivity is calculated from the temperature rise versus the time profile. The thermal conductivity is related to the thermal diffusivity, $D=k/d*C_p$, where d is the density and C_p is the heat capacity. The visual image and the scheme of the laser flash technique are shown in Figure 1.



a) b)

Fig. 1. The Visual image (a) and scheme (b) of the laser flash technique.

Combining these thermophysical properties with the density value results in the thermal conductivity as follows:

$$k (T) = a (T) \cdot c_{\rho}(T) \cdot \rho (T) \qquad (1)$$

where k = thermal conductivity [W/(m*K)]; a = thermal diffusivity [mm^2/s]; c_p = specific heat [J/(g*K)]; ρ = bulk density [g/cm^3]. Then, thermal conductivity is determined from the measured thermal diffusivity, specific heat, and bulk density of the sample using a special equation.

3. RESULTS

For obtaining information about the surface morphology of the prepared nanocomposites, Gobu/Xylene-MWCNT (4%) ceramic composite was measured using SEM. The SEM image of this composite shows that inside Gobu bentonite, MWCNTs were distributed in parallel bundles or in a horizontally oriented direction, which will directly impact their thermal conductivity properties. Thus, the form and shape of MW-CNT's network influence the thermal conductivity of nanocomposites.

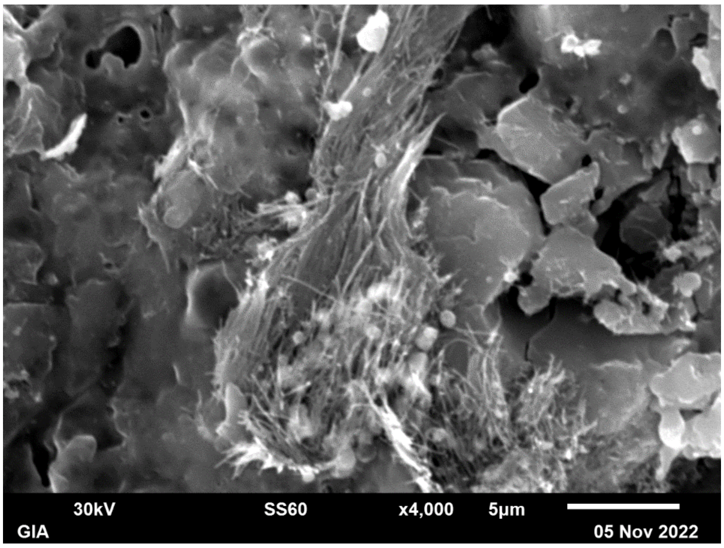


Fig. 2. SEM image of Gobu /x MWCNT (x=4%) ceramic composite at 5 μm scale.

The thermal conductivity properties of the prepared Gobu/xMWCNT (x = 1%, 2%, 4%, 8%, and 16%) nanocomposites were investigated to determine the role of mixed MWCNTs inside bentonite matrices for increasing their thermal conductivity, as the thermal conductivity of individual MW-CNTs is very high. Due to literature results, the thermal conductivity properties of nanocomposites can be impacted by different parameters: the structure and type of MWCNTs, their length, MWCNT distribution inside matrices, phonon scattering, alignment, interfacial resistance between MWCNT and matrices, CNT-CNT contacts, etc. The literature results showed that the thermal conductivity of different types of natural bentonite clays is very low, even when filled with different types of carbon fillers like CNT, expanded graphite, etc. For example, in research work [9], the thermal conductivity of capric acid, expanded perlite, and expanded graphite are 0,49 W/(m*K). For organic montmorillonite, paraffin, or grafted multi-walled nanotubes, the value is 0.30 W/(m*K) [10]. Therefore, our main goal is to increase the thermal conductivity of MWCNT containing natural bentonites and prepare novel-type, cost-effective composites [11,12]. First of all, we used mixed MWCNTs as nano-fillers in the beginning, as it is the easiest way to prepare nanocomposites. Depending on the results, the shape of the CNT network will change. The measured results of thermal conductivity are given in Figure 3 for all nanocomposites. For comparison, first of all, Gobu bentonite clays were measured in argon and air.

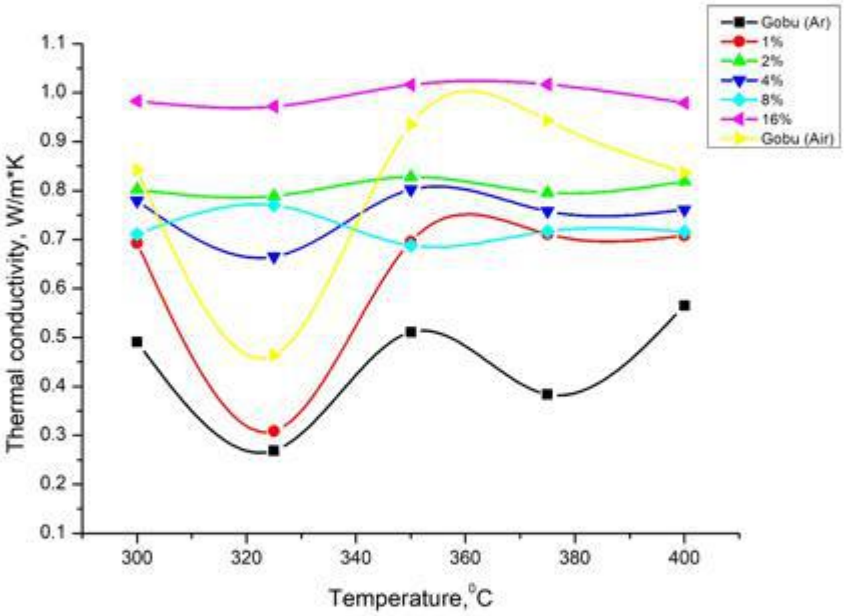


Fig. 3. Thermal conductivity of Gobu/ x MWCNT (x=1% ; 2%; 4%; 8%; 16 %) nanocomposites.

As a matrix, we have used natural Azerbaijani Gobu bentonite. Gobu bentonite shows very low thermal conductivity in air and in the argon atmosphere. With the addition of MWCNTs, thermal conductivity increased with increasing MWCNT concentration, from 1% to 16% (Figure 3). It is clear from Figure 3 that the highest thermal conductivity is observed for 16% MWCNT-containing nanocomposites. The highest value is k = 1,04 W/(m*K) at T = 348^{0}C for Gobu bentonite/xMWCNT (x = 16%) nanocomposite. A sharp thermal conductivity drop was observed for Gobu bentonite without MWCNTs as well as for low concentrations containing nanocomposites Gobu bentonite/xMWCNT (x = 1%) at 352^{0}C. This sharp decrease in thermal conductivity can be explained by the high porosity of bentonite, as bentonite is generally a porous material. With increasing concentrations of MWCNTs, they fill these porous places, and thermal conductivity increases. Another interesting result is that with increasing temperature from 350^{0}C, for Gobu bentonite/x MWCNT (x = 1%) nanocomposite, this sharp drop was eliminated, however for Gobu bentonite in Argon it is possible to observe them in another temperature (T=375^{0}C), but for Gobu bentonite in Air, the exact opposite was observed. This can be explained by many factors but mostly by the structure of Gobu bentonite clay in Ar atmosphere and in Air.

CONCLUSION

In this study, for the first time, the thermal conductivity properties of the prepared natural Azerbaijani bentonite (Gobu)/x MWCNT ceramic composites with different concentrations (x = 1%, 2%, 4%, 8%, and 16%) were investigated at high temperatures. The highest value of thermal conductivity is k = 1,04 W/(m*K) at T = 348^{0}C for Gobu bentonite/x MWCNT (x = 16%) nanocomposite. In comparison with the literature results, we could increase the thermal conductivity of the natural bentonite/MWCNT composite. Despite the fact that MWCNTs have a very high thermal conductivity on their own, the situation changes for nanocomposite materials. These results can be explained mostly by phonon scattering within the bundles of MWCNT, interfaces formed between natural bentonite ceramic matrix and MWCNTs, and the structure types of MWCNT networks. Based on these results, we can say that these nanocomposites made by mixing MWCNT networks inside bentonite matrices do not increase thermal conductivity significantly. Therefore, research in this field will continue. However, these nanocomposites can be potentially used as non-corrosive electrodes for electrolysis processes, as substrates like coolers (heat dissipation elements) for electronic devices with less heat release, and as heating elements for heating apartments.

[1] *L.S. Arden and L. Moore.* Mater. Today, 17, 2014,163–174.
[2] *Z. Han, A. Fina.* Prog. Polym. Sci. 36, 2011, 914.
[3] *P. Kim, L. Shi, A. Majumdar, P.L. McEuen,* Phys Rev Lett. 87, 215502, 2001.
[4] *C. Yu, L. Shi, Z. Yao, D. Li, A. Majumdar.* Nano Lett. 5, 1842, 2005.
[5] *A.M. Marconnet, M. A. Panzer, and K.E. Goodson.* Rev. Mod. Phys.85, 1295–1326, 2013.
[6] *J.W. Che, T. Cagin and W.A. Goddard.* Nanotechnology 11, 65–69, 2000.
[7] *C. Sevik, H. Sevincli, G. Cuniberti, and T. Cagin.* Nano Lett.11, 4971–4977, 2011.
[8] *W. Padgett and D.W. Brenner.* Nano Lett. 4, 1051–1053, 2004.
[9] *A. Sari, A. Karaipekli,* Materials Chemistry and Physics, 109, 459. 2008.
[10] *M. Li, Q.G. Guo, and S. Nutt.* Solar Energy, 146, 1, 2017.
[11] *A. Huseynov, S. Mammadova, E. Zeynalov* et al. Fullerens Nanotubes and Carbon Nanostructures, 1, 2022.
[12] *S. Mammadova, T. Baba, T. Mori, A. Huseynov, E. Zeynalov.* International Journal of ThermoPhysics, 44, 91-117, 2023.