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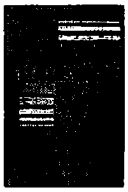

Photoacoustic thermal characterization of Al_2O_3–Ag ceramic nanocomposites

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ABSTRACT

Laser-induced nondestructive photoacoustic (PA) technique has been employed to determine the thermal diffusivity of nanometal (Ag) dispersed ceramic alumina matrix sintered at different temperatures. The thermal diffusivity values are evaluated by knowing the transition frequency from the amplitude spectrum of PA signal using the one-dimensional heat flow model of Rosencwaig and Gersho. Analysis of the data shows that heat transport and hence the thermal diffusivity value is greatly affected by the influence of incorporation of foreign atom. It is also seen that sintering temperature affects the thermal diffusivity value in a substantial manner. The results are interpreted in terms of variation in porosity and carrier-assisted heat transport mechanism in nanometal dispersed ceramics.

1. Introduction

The functional nanocomposites involving ceramic matrix and nanosized particles of transition metals are known to exhibit multifunctional and attractive properties and are identified as potential candidate for structural [1], mechanical [2], catalytic [3], thermal [4], optical [5], magnetic [6] and electrical [7] applications. Alumina is considered to be an important material in adsorption and catalysis and it is widely used as a substrate material in evolving technologies such as optoelectronics, magnetic, optical devices and protective coatings. The thermal properties of this material merits close scrutiny from device fabrication point of view. The heat diffusion in such materials is essentially determined by thermal diffusivity value [8–10], the inverse of which is a measure of the time required to establish thermal equilibrium in the specimen after a transient temperature change has occurred [11,12]. Thermal properties of ceramics are essentially determined by composition and structure which is governed by constituent phases and processing conditions. As the nanometal dispersed ceramics are reported to exhibit enhanced toughness, chemical inertness, good oxidation resistance as compared to bulk specimen, present investigation on thermal parameters of nanocomposites doped with metallic atom has great physical and practical significance.

In recent years, thermal wave physics has been emerging as an effective research and analytical tool for the characterization of thermal, transport and optical properties of matter, in all its different forms [13,14]. Laser-induced nondestructive and nonintrusive photothermal methods are widely used for the thermal characterization of materials, particularly for the evaluation of thermal diffusivity value [15]. All the photothermal methods are based on the detection, by one means or other, of a transient temperature change that characterizes the thermal waves generated in the sample after illumination with a chopped optical radiation [16]. In spite of a variety of photothermal methods used for the characterization of material, the photoacoustic (PA) technique is the most popular technique due to its simple and elegant experimental set-up

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nd its capability to provide material parameters with great accu- acy [17]. Depending upon the mode of excitation and the specimen nder investigation PA signal can be detected using a microphone r piezoelectric transducer [17,18].

Research towards a better understanding of the physical prop- erties of heterogeneous solids has both scientific and technological mportance. In this paper we describe the thermal characterization f nanosized Ag metal dispersed ceramic alumina matrix prepared y sol–gel method with varying weight concentration of Ag and sin- ered at different sintering temperatures, using microphone version f PA technique. In the case of composites as in the present case, he thermal diffusivity is a measure of rate at which a tempera- ure disturbance at one point in a body travels to other point and higher thermal diffusivity value indicate more rapid heat prop- gation and vice versa. Hence the present investigations where e focus is made on the influence of sintering temperature and clusion of foreign atom on the thermal diffusivity of the porous umina matrix have great importance.

2. Preparation of nanocomposite

The composite precursor was prepared from a mixture of oehmite (Al–O–OH) and silver nitrate. In a typical experiment, 000 ml of boehmite (Al–O–OH) sol was prepared by hydrolyz- ng 250 g of $Al(NO3)_3{\cdot}9H_2O$ (S.D. Fine Chemicals, India) dissolved n 500 ml of double-distilled water followed by peptisation using itric acid. Details of the method are reported elsewhere [19]. Silver itrate (Glaxo Laboratories, India, Purity—99%) in aqueous solution 5 g in 100 ml) is added in different weight proportions (0%, 1% and % with respect to aluminum oxide) to the boehmite sol in sepa- ate batches and subjected to mechanical stirring for a period of h. The sol was first evaporated on a water bath and finally was ried at ∼100 °C in an electric oven. The precursor gel was further alcined at 450 °C for a period of 3 h. The nanocomposite samples ere prepared by uniaxial consolidation to disc pellets of size 10- m diameter and 1-mm thickness applying a force of 4 tons for min using hydraulic press. Care was taken to pelletize all the sam- es at identical experimental conditions. The thicknesses of the pecimen used in the present investigation were further reduced ∼500 µm. The pelletized samples were sintered at 700 °C, 800 °C d 900 °C with a soaking period of 3 h to study the influence of intering temperature on thermal diffusivity.

The microstructure of the sample is analyzed using transmission ectron microscopy (JEOL 3000 EX; JAPAN) with an acceleration ltage 300 kV and a resolution of less than 0.2 nm and it is seen at Ag particles are almost uniformly dispersed [20] and the particle size in the dispersed phase ranges between 5 and 20 nm. The microstructure observed for Al_2O_3–5% Ag composition is given in Fig. 1 whereas Figs. 2 and 3 show the fracture surfaces of nanocomposite containing 5 wt% Ag sintered at 700 °C and 900 °C, observed using scanning electron microscopy (Hitachi, Japan). The sintering temperature is limited to a maximum value of 900 C in view of possible agglomeration, which may be caused by preferential melting of dispersed silver particles (melting point of is ∼960 °C).

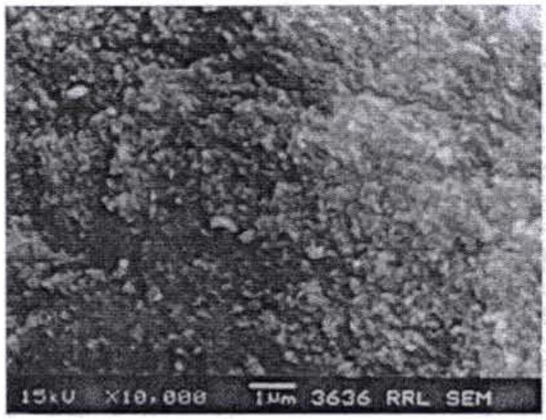

Fig. 2. SEM fractograph of 5% Ag-doped sample sintered at 700 °C.

The density of the composite is determined by water displacement method. The measured density is divided by a corresponding theoretical density measured using rule of mixtures, which gives the volume fraction or relative density (x) of the specimen [21]. Then the porosity of the material is given by $p = 1 - x$ [22]. The values of porosities of the specimen under study are presented in Table 1. The samples used for the present investigation are ceramic alumina dispersed with various weight fraction of (0%, 1% and 5%) nano Ag metal and all these specimens are sintered at different temperatures (700, 800 and 900 °C).

3. Experimental

A detailed account of the present experimental set-up is explained elsewhere [23]. Continuous optical radiation at 2.54 eV from an Argon ion laser (Liconix 5300), which is mechanically chopped (Stanford Research Systems SR 540) is used as the source of excitation. Optical radiation directly irradiates on the sample surface (PA cell in the reflective configuration) and consequent periodic nonradiatve de-excitation causes density fluctuations in sample as well as in the coupling medium. The corresponding pressure fluctuations generated in the PA cell cavity is detected

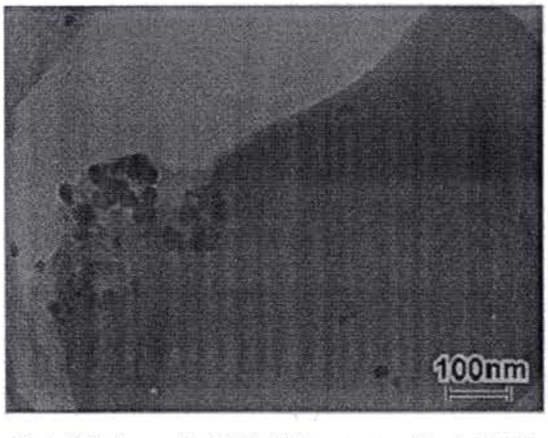

Fig. 1. TEM micrograph of Al_2O_3–5% Ag precursor calcined at 450 °C.

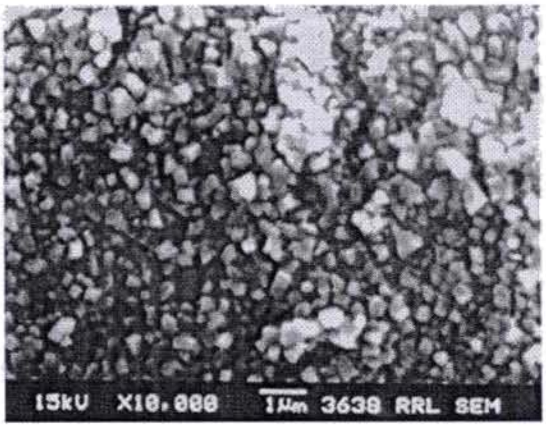

Fig. 3. SEM fractograph of 5% Ag-doped sample sintered at 900 °C.

Table 1
Thermal diffusivity of samples sintered at different temperatures

Sintering temperature	Amount of Ag (wt%)	Porosity $(1-x)$	Thermal diffusivity value ($cm^2\,s^{-1}$)	Calculated value of thermal diffusivity using Eq. (1) in $cm^2\,s^{-1}$
700 °C	0	0.488	0.210 ± 0.002	0.210
	1	0.450	0.220 ± 0.003	0.220
	5	0.349	0.242 ± 0.003	0.240
800 °C	0	0.481	0.240 ± 0.003	0.240
	1	0.418	0.280 ± 0.004	0.280
	5	0.234	0.360 ± 0.004	0.362
900 °C	0	0.450	0.280 ± 0.002	0.279
	1	0.410	0.312 ± 0.003	0.311
	5	0.216	0.400 ± 0.004	0.397

using a sensitive electret microphone (Knowles BT 1754) having flat frequency response for the entire experimental frequency range and the output of microphone is measured using a dual phase lock-in amplifier. The laser power used for the present studies is 50 mW with a stability of ±0.5%.

4. Results and discussions

The theoretical background for the evaluation of thermal diffusivity from amplitude spectrum of PA signal is explained elsewhere [24]. As the thermal diffusion length is function of chopping frequency, by varying the chopping frequency of optical radiation and consequently amplitude of thermal waves, the transition frequency at which sample changes from thermally thin to thermally thick regime can be known from the amplitude spectrum of the PA signal. By knowing the transition frequency and the thickness of the specimen under investigation, the thermal diffusivity value can be evaluated using the expression $k_c(p) = l_s^2 f_c$ [24]. The present experimental set-up is standardized by evaluating the thermal diffusivity value of copper and aluminum, of which thermal diffusivity value is well known. It is seen that the measured thermal diffusivity values (1.176 ± 0.003 and $0.976 \pm 0.003\,cm^2\,s^{-1}$, respectively) agree well with earlier reported thermal diffusivity values of these samples [9]. Fig. 4 shows the log–log plot of PA amplitude as function of modulating frequency for the intrinsic alumina sintered at 700 °C. All the specimens under investigation show similar nature (not shown). The evaluated effective thermal diffusivity values of all the samples under investigation are tabulated in Table 1. It is clear that the sintering temperature and the inclusion of nano Ag metal content in alumina host and the concentration nano Ag metal content have great influence on the effective thermal diffusivity value of all the samples investigated under the present study. The observed result can be understood in terms of carrier-assisted heat transport mechanism in porous nanocomposites.

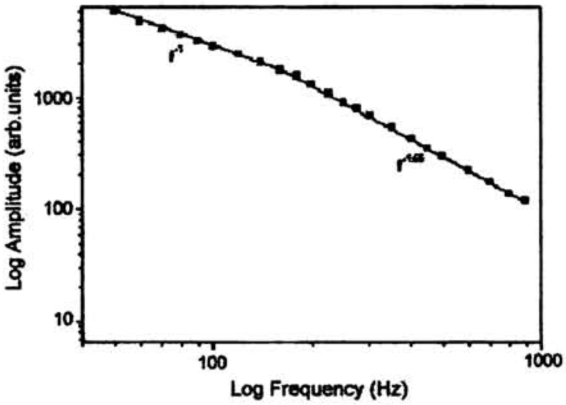

Fig. 4. Log–log plot of PA amplitude against frequency for pure alumina sintered at 700 C.

In general, ceramics are composed of a mixture of one or more phases such as porosity, impurities, etc. Hence the measured thermal diffusivity value is an effective parameter with a contribution from different heat diffusion mechanisms. The samples under investigation can be considered as a two-phase mixture of regular shaped particles embedded in continuous matrix. The heat diffusion through the two-phase mixture, where one phase (the air interfaces) is randomly dispersed in a continuous ceramic matrix is essentially characterized by Leob equation, according to which; the thermal conductivity of a specimen having porosity 'p' is given by the expression $K_c(p) = K_0(1-p)$. Here K_0 is the thermal conductivity of the specimen having zero porosity. However, the propagation of thermal energy carriers is greatly affected by scattering mechanism. As the scattering mechanisms essentially determine the mean free path of thermal energy carriers, it can affect the measured thermal diffusivity value in a substantial manner. In order to incorporate the influence of pores in the propagation of thermal waves and hence the thermal diffusivity value, Sanchez et. al. [22] modified the Leob equation for the evaluation of thermal diffusivity values as

$$k_c(p) = k_0 \frac{1-\gamma p}{1-p} \tag{1}$$

where γ is an empirical constant which essentially determines the significance of pores on thermal diffusion processes. The evaluated values of γ are 1.264, 1.472 and 1.450 for the specimens sintered at 700 °C, 800 °C and 900 °C, respectively. The value of $\gamma > 1$ also implies the fact that the effect of porosity on heat conduction processes is not a mere density effect (air holes in the bulk volume) but it is also related to the structure of the material [9].

The conduction of heat in disordered dielectric materials such as porous ceramics may be considered as the propagation of anharmonic elastic waves through a continuum and propagation occurs via interaction of the quanta of thermal energy called phonons. In the case of dielectrics, the frequency of lattice waves with velocity 'v' covers over a wide range and thermal conductivity $K(T)$ (consequently, thermal diffusivity $k(T) = K(T)/\rho C_p = (1/3)vl(T)$) is directly proportional to the phonon mean free path ($l(T)$) and transport velocity. However, the very weak dependence on temperature for ρ, C_p and v lead to the fact that mean free path of thermal energy carrier essentially determines the effective thermal diffusivity value. If the phonon mean free path is equal to the separation between the constituent atoms, the resulting conductivity is referred to as minimum thermal conductivity and it is the lower limit of dense materials at room temperature. This minimum thermal conductivity model [25] assumes that long wavelength phonons with long mean free path do not contribute significantly to heat transfer in disordered materials. However, the propagation of phonons through porous ceramic matrix and hence its mean free path is suffered by various scattering mechanisms such as phonon–phonon scattering (Umklapp processes), scattering from microvoids, microcracks, particles and pores. Sinring processes heals the microstructures, removes the cracks, icroporosity, and residual organics and causes the structure to ecome more uniform. Thus the phonon scattering due to the aforeentioned imperfections is reduced and consequently increases e phonon mean free path and results in the enhancement in ermal diffusivity value with sintering temperature. During the ocesses of sintering, there is the diffusion phenomenon of differ rent elements that compose the material, which provide mass ansport and give rise to better homogeneity in terms of pore disibution [26]. As it is obvious from Table 1, in the case of pure umina sintered at different temperatures, the density is increasg with sintering temperature which can be mainly attributed to ehydroxylation of alumina during the heating and sintering pross. Depending upon the increase in sintering temperature, the ain size of the alumina increases and thereby reduces the grainoundary resistance. Decrease in grain-boundary resistance offers se of diffusion of heat energy and results in enhanced thermal ffusivity value. More homogenized system allows the heat transort more effectively and thereby increase the thermal diffusivity alue.

Metal dispersed ceramics can be viewed as composite network here the effective thermal parameter depend upon the connecvity, area of contact between the particles, thermal conductivity metal as well as on the particle distribution. Previous investitions showed that alumina–silver composites exhibit enhanced echanical [27] and transport properties [28]. In the present case, e enhancement in relative density with the inclusion of metal to the ceramic matrix and consequent lowering of porosity of the ecimen results in decrease in scattering centers (pores) and a nsequent increase in the mean free path of thermal energy carris, which explains the observed increase in the thermal diffusivity lue. Besides that, in the case of metal dispersed ceramics, the terconnected metal network provides an efficient way to heat ansport processes across the composite by electron and therere enhances the thermal diffusivity value. During the calcinations, ver nitrate decomposes to form silver oxide at a temperature 444 °C and during the sintering processes agglomeration of silr particles take place. Increase in sintering temperature causes ore efficient agglomeration of silver particles and efficient heat ansport via both phonons and electrons through Ag network and sult in greater thermal diffusivity value. For specimen containg 5 wt% of Ag, this agglomeration effect is more compared to wt% of Ag incorporated ceramic alumina matrix. Consequently, ucture will have more density of thermal energy carriers and s interfacial thermal resistance. As a result, specimens conining 5 wt% of Ag exhibit higher value for thermal diffusivity. us, in the case of metal dispersed ceramic matrix heat is essenlly carried by both phonons and electrons. Such an increase in ermal diffusivity with the inclusion of Ag-doped zirconia comsites have already been reported [29]. An increased thermal ffusivity (thermal conductivity) reduces thermal accumulation in e specimen and a consequent increase in the resistance against ermally induced fracture enhances its applicability in the indusy.

5. Conclusion

In the present study, the thermal diffusivity value of pure alumina and nano Ag metal dispersed alumina ceramic matrix prepared by gel route is measured using laser-induced photoacoustic technique. From the analysis of data it is seen that incorporation of foreign atom into the ceramic host can affect the porosity of the specimen and consequently the thermal diffusivity value. It is also seen from the analysis that sintering temperature also can result in variation in porosity of the specimen and hence the thermal diffusivity value. The present investigation clearly shows that in a two-phase network as in the case of a nanometal dispersed ceramic alumina matrix, the heat transport and hence the thermal diffusivity value greatly depends on the propagation of thermal energy carriers through the composite and the scattering caused by pores of the specimen.

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