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Short communication

Effect of interfacial structure on the thermal conductivity of carbon nanofibers reinforced aluminum nitride composites

Zhongqi Shi*, Wanli Yang, Jiping Wang, Guiwu Liu, Guanjun Qiao*, Zhihao Jin

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

The interface in carbon nanofilaments/ceramic–matrix composites significantly affects the interfacial thermal transfer characteristics. In this work, the effect of interfacial structure on the thermal conductivities of carbon nanofibers (CNFs)/aluminum nitride (AlN) composites with and without sintering aids (Y_2O_3 and CaF_2) were studied. For the composites sintered with aids, the interfacial amorphous glass phases originated from the aids and Al_2O_3 layer in AlN powders surrounded the CNFs, which acted as elongated pores for deteriorating the thermal conductivity. However, a clean interface was obtained in the composites without aids because the amorphous carbon and the Al_2O_3 layers in the CNF–AlN system were removed by their interreaction to form volatile products such as Al_2O and CO, resulting in the enhanced thermal conductivity. Moreover, theoretical analysis was also employed to investigate the effect of the interfacial structure on the thermal conductivity of the CNFs/AlN composites.

Keywords: C. Thermal conductivity; Aluminum nitride; Carbon nanofibers; High-resolution transmission electron microscopy

1. Introduction

Carbon nanofibers (CNFs) are very promising reinforcing or functionalizing elements to endow ceramic composites with multifunctional characteristics due to their excellent physical properties [1,2]. It has been confirmed that the incorporation of CNFs into ceramic–matrix composites can strongly improve the mechanical and electrical properties [3–7]. However, few efforts have been achieved to obtain CNFs/ceramic composites with enhanced thermophysical properties [8]. One of the major problems is the large interface thermal resistance between carbon nanofilaments and the ceramic–matrix, which drastically increases the phonon scattering, and thus decreases the interfacial thermal transfer in the composites [9]. Therefore, to tailor the interfacial structure of the CNFs/ceramic composites for decreasing the interface thermal resistance has become an urgent issue.

Aluminum nitride (AlN) is considered to be a promising substrate, heat sink and package material for high power integrated circuits because of its excellent thermal conductivity, high electrical resistivity, low dielectric constant and low thermal expansion coefficient [10]. AlN powder is always covered with a thin amorphous oxide layers (Al_2O_3) due to its oxidizable characteristic [11]. The addition of sintering aids (such as Y_2O_3, CaF_2 and Li_2O) is an effective route to purify the grain interfaces by formation of Al_2O_3-contained glass phases [12,13], which could decrease the interface thermal resistance. In addition, recent work indicated that the interfacial reactions between carbon nanotubes and Al_2O_3 ceramic–matrix can improve the interfacial bonding [14]. These results may give a hint to tailor the interfacial structure of the CNFs/ceramic composites to achieve high thermophysical properties. In this work, high-density CNFs/AlN composites were fabricated by plasma activated sintering (PAS) with and without aids (Y_2O_3 and CaF_2) in vacuum, and the effect of the

*Corresponding authors. Tel.: +86 29 82665221; fax: +86 29 82663453.
E-mail addresses: szqxjtu@gmail.com (Z. Shi), gjqiao@xjtu.edu.cn (G. Qiao).

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interfacial structure on the thermal conductivity of the CNFs/AlN composites was also investigated.

2. Experimental procedure

High purity AlN (type H, $>99.9\%$ purity, $\sim 0.5\ \mu m$) and CNFs ($\sim 99\%$ purity, ~ 150 nm in diameter and 4–5 μm in length) powders were used as the starting materials. 2 wt.% of CaF_2 ($>98.5\%$ purity, $\sim 2\ \mu m$) and 1 wt% of Y_2O_3 (99.8% purity, $<1\ \mu m$) were added as sintering aids. The amount of CNFs ranged from 0 to 5 wt%. The surface of the CNF was covered with amorphous carbon layer with a few nanometers thick [15]. The fabrication process of the CNFs/AlN composites with and without sintering aids was described similarly in our previous work [7]. The bulk density ρ of the specimens was measured by the Archimedes immersion technique with ethanol, and the theoretical density was determined by the rule of mixtures. Hence, the relative density was calculated by dividing the bulk density to the theoretical density. The fracture microstructures were characterized by a field emission scanning electron microscopy (FE-SEM; JEOL JSM-7000F). The interfacial structure were characterized by a high-resolution transmission electron microscopy (HR-TEM; JEOL JEM-2100F) coupled with energy-dispersive spectroscopy (EDS) using the Cu-grid as sample holder. The thermal conductivity K was calculated by the equation $K=\rho C_p \alpha$, where thermal diffusivity α and specific heat C_p were measured in the direction parallel to the PAS compression axis at the room temperature using the laser-flash technique (LFA457; NETZSCH). At least five specimens were tested for the average thermal conductivity.

3. Results and discussion

Table 1 shows the relative density of the CNFs/AlN composites with and without sintering aids, noted as ρ_{as} and ρ_s, respectively. Both the ρ_{as} and ρ_s values decreased with the CNFs content increasing from 0 to 5 wt%. The ρ_{as} was a little higher than the corresponding ρ_s, suggesting that the aids promoted the densification of the composites. However, even if the addition of CNFs was up to 5 wt%, the relative density of the composites with and without aids could still attain 98.3% and 96.1%, respectively, indicating that the CNFs content of ≤ 5 wt% had no remarkable deleterious effect on the densification of the composites.

Fig. 1 shows the measured thermal conductivities of the CNFs/AlN composites with and without sintering aids (solid lines). The measured results showed the different variation tendency for the two series of composites. For the composites sintered with aids, the thermal conductivity of the monolithic AlN reached the high value of about 117.9 W m^{-1} K^{-1}, which was much higher than that of the monolithic sample without aids (82.6 W m^{-1} K^{-1}). With the addition of the CNFs, the value dramatically decreased to less than 90 W m^{-1} K^{-1}. Surprisingly, the thermal conductivity of the composites without aids firstly increased and then decreased. The highest value (91.2 W m^{-1} K^{-1}) was obtained when using 2 wt% CNFs (3.33 vol%), with an increase of about 10 W m^{-1} K^{-1} for the matrix. The above results indicated that the thermal conductivity of the AlN matrix can be improved by incorporating CNFs as a reinforcement phase, however, the CNFs seemed not to be the main factor. In addition, although the porosity increased with the CNFs content increasing (indicated in Table 1), the thermal conductivity of the composites without aids was not decreased monotonically. This suggested that the deterioration of the thermal conductivity by pores was compensated effectively by any other reason. As we know the interface thermal resistance between matrix and reinforcement plays

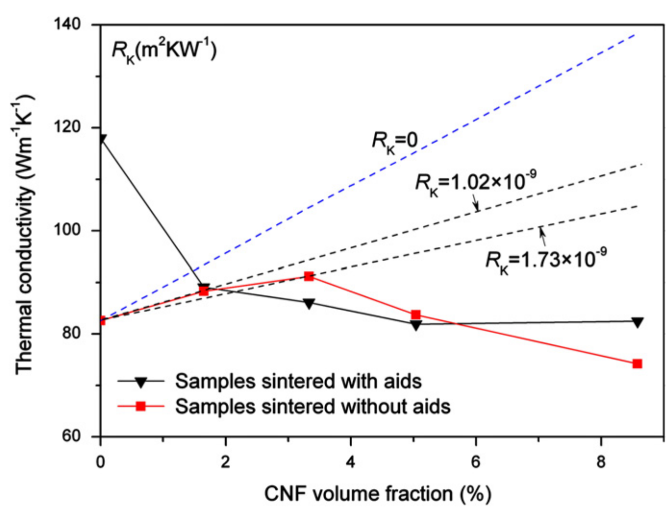

Fig. 1. Thermal conductivities of the CNFs/AlN composites with and without sintering aids. The solid lines represent the measured data, while the dashed lines are the calculated values.

Table 1
Relative density of the CNFs/AlN composites with and without sintering aids.

Samples	CNFs content (wt%)				
	0	1	2	3	5
ρ_{as}	99.7	99.5	98.6	97.6	98.3
ρ_s	98.9	98.6	98.4	96.9	96.1

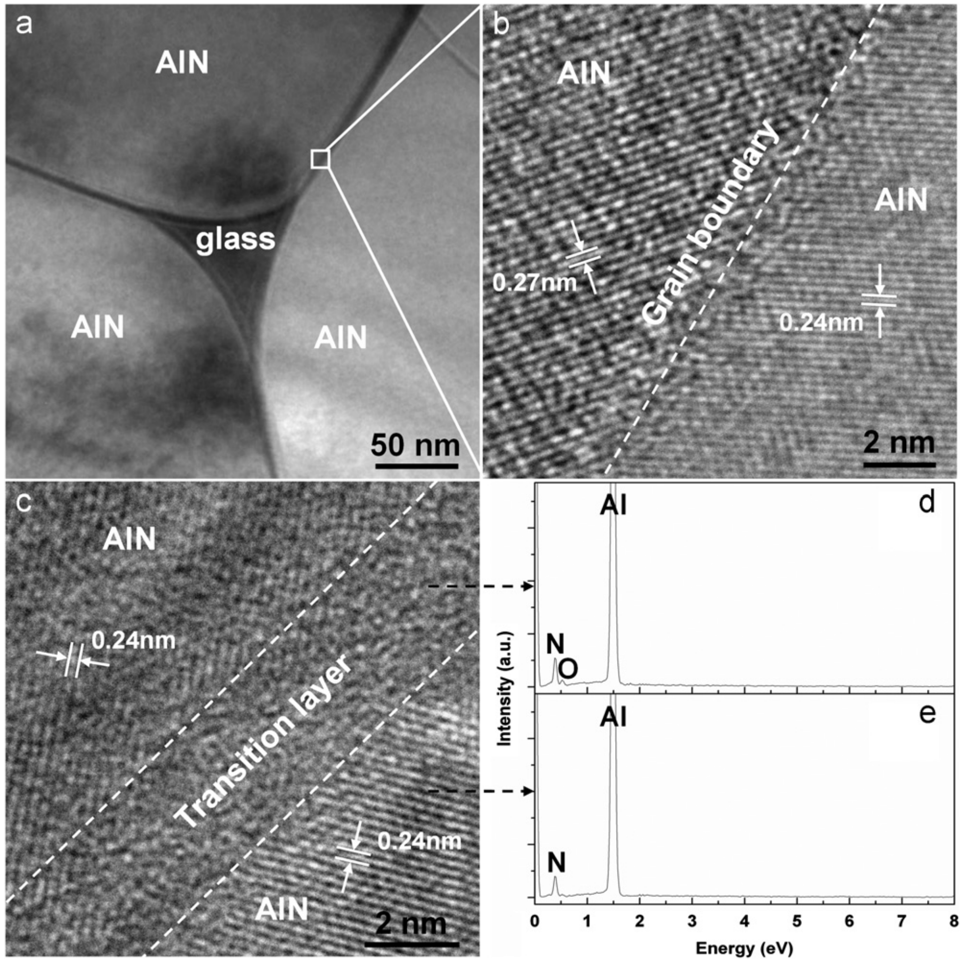

Fig. 2. TEM and HR-TEM images of the monolithic AlN ceramics with and without sintering aids. (a) TEM image of the triple grain junction of AlN sample sintered with aids and (b) HR-TEM image of the grain boundary in the rectangle area of (a); (c) HR-TEM image of the transition layer between two AlN grains for the monolith sample without aids, and the corresponding EDS patterns for the transition layer (d) and AlN grain (e).

a crucial role in determining the effective thermal conductivity of the composites [16,17]. So the effect of the interfacial structure on the thermal conductivity of the CNFs/AlN composites with and without sintering aids are analyzed and discussed as follows.

Fig. 2(a) shows a typical TEM image of the triple grain junction of the monolithic AlN ceramic sample sintered with aids. It can be seen that the glass phases were trapped at the triple point of the AlN grains, and a clean grain boundary was formed in the sample (Fig. 2(b)), indicating that the Al_2O_3 layer on the AlN powder was removed by the sintering aids. Furthermore, the glass phases were composed of $CaYAlO_4$ and $Y_4Al_2O_9$, which has been confirmed in our previous study [7]. The AlN grains in Fig. 2(b) can be identified by the fringe spacing of 0.27 nm and 0.24 nm corresponding to the (100) and (101) planes, respectively. However, for the AlN ceramic sintered without aids, a transition layer of ~3 nm width was found between the AlN grains (Fig. 2(c)). The further EDS analysis (Fig. 2(d)) revealed that the transition layer consisted of Al, nitrogen and a trace of oxygen while no oxygen was detected in the AlN grain (Fig. 2(e)), indicating that the Al_2O_3 layer may react with the adjacent part of AlN grains to form the thin Al–O–N transition layer as a thermal barrier. Hence, the purification of grain boundary by the glass phases could be the main reason for the higher thermal conductivity of the monolithic AlN sample with aids, which was good agreement with other literatures [12,13].

Fig. 3(a) shows the TEM image of the 2 wt% CNFs/AlN composite sintered with aids. Some amorphous glass phases (bright layer) surrounded the CNF and existed at the grain boundary between the CNF and the AlN, which may be caused by the capillarity during sintering. From the HR-TEM of the CNF/glass/AlN interface (Fig. 3(b)), it can be seen that the glass bonded the CNF and the AlN tightly, and the width of the glass layer was about 10 nm. Fig. 3(c) shows the TEM images of the 2 wt% CNFs/AlN composite without sintering aids. A CNF with a diameter of 130 nm existed in the AlN grain boundary, and was closely attached to the AlN matrix without any gap or interlayer, as shown in Fig. 3(d). The clear interface could be caused by the reduction reaction between the active amorphous carbon layer and the Al_2O_3 layer in the

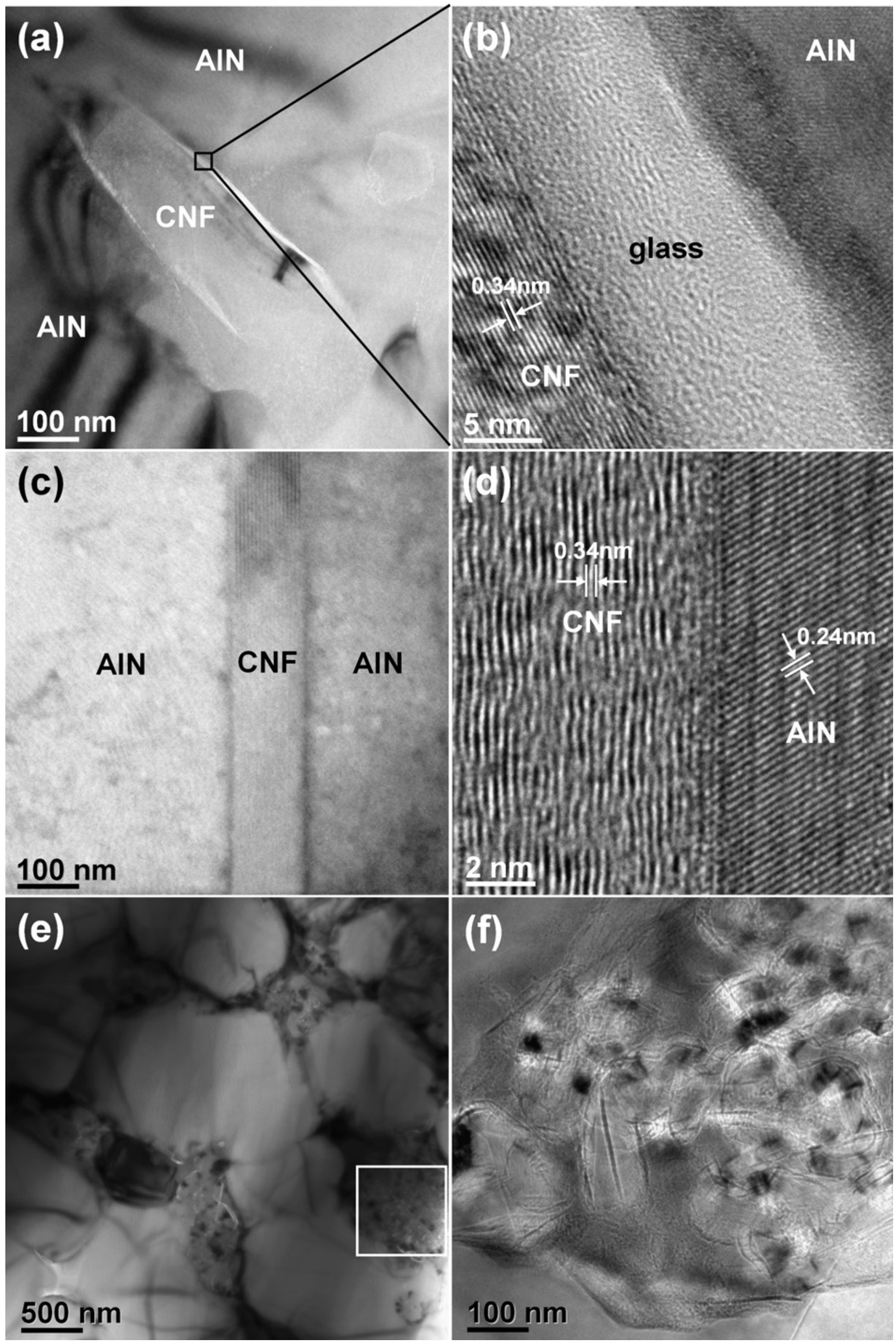

Fig. 3. TEM and HR-TEM images of the CNFs/AlN composites with and without sintering aids: (a) TEM image of the 2 wt% composite sintered with aids and (b) HR-TEM image of the CNF/glass/AlN interface in the rectangle area of (a); (c) TEM image of the 2 wt% composite sintered without aids and (d) a typical HR-TEM image of the CNF/AlN interface in (c); (e) TEM image of the 5 wt% composite sintered without aids and (f) CNFs clusters with higher magnification in the rectangle area of (e).

CNF–AlN system according to the equation $Al_2O_{3(s)}+2C_{(s)}\rightarrow Al_2O_{(g)}+2CO_{(g)}$ [14]. Both of the two gaseous products volatized during the PAS process, resulting in the clean interface. Therefore, the thermal conductivities for the CNF/AlN composites without aids were improved. However, for the 5 wt% CNFs/AlN composites without aids, some CNFs clusters existed at the grain boundaries of the AlN matrix (Fig. 3(e)). These tangled CNFs in the clusters (Fig. 3(f)) with highly thermal interfacial resistance may caused the thermal conductivity decrease (see Fig. 1).

In order to further understand the effect of interfacial structure on the thermal conductivity of the CNFs/AlN composites, theoretical prediction was also employed to compare with the experimental results. Nan et al. [17] proposed a model for predicting the thermal conductivity of carbon nanotubes (CNT)-reinforced composites in terms of a general effective medium theory. Assuming a random orientation of the dispersed CNTs within the matrix, the effective thermal conductivity of the composite (K_e) can be given by

$$\frac{K_e}{K_m} = 1 + \frac{fp}{3}\frac{K_c/K_m}{p + (2a_K/d)(K_c/K_m)} \quad (1)$$

where K_c and K_m denote respectively the thermal conductivities of the CNT and matrix; f is the volume fraction of the CNT; L and d ($p = L/d$) are the length and diameter of the CNT, respectively; and a_K is called the Kapitza radius and defined as

$$a_K = R_K K_m \quad (2)$$

where R_k represents the thermal contact resistance between the CNT and the matrix. Obviously, this model is also suitable for the present CNFs/AlN composites without sintering aids due to their enhanced thermal conductivities. For the CNFs/AlN composites, K_c and K_m were taken to be 1950 $W\,m^{-1}\,K^{-1}$ [18] and 82.6 $W\,m^{-1}\,K^{-1}$, respectively; L and d used in this calculation were 4.5 μm and 150 nm ($p = 30$). Given these parameters, we then took the two best samples of 1 wt% (1.65 vol%) and 2 wt% (3.33 vol%) CNFs/AlN composites without sintering aids to fit the theoretical calculations using Eqs. (1) and (2). The calculated curves are presented in Fig. 1 (dash lines). The value of R_k can be estimated to be $1.02\text{–}1.73 \times 10^{-9}$ $m^2\,KW^{-1}$, which was within the effective thermal conductivity enhancement region ($R_k < 10^{-7}\,m^2\,KW^{-1}$) [17], and also much lower than that ($R_k = 7.6 \times 10^{-6}\,m^2\,KW^{-1}$) in CNTs/$BaTiO_3$ composites [9]. Therefore, it can be deduced that the clean CNF–AlN interface significantly promoted the interfacial thermal transfer in the CNFs/AlN composites without aids, and the CNF may be more effective to improve the thermal conductivity of the composite than the CNT. However, from Fig. 1 the experimental values of the thermal conductivities for the CNFs/AlN composites were lower than the predictions without considering interface thermal resistance ($R_k = 0$), indicating that there still had an impact on interface phonon scattering between the CNF and the AlN though they had a clean interface. The reasons may be the lattice mismatch between the CNF and the AlN, and the residual pores existed in the composites. In addition, this model seemed inapplicable for the CNFs/AlN composites sintered with aids. This has not been fully understood. One reason could be considered for it. The amorphous glass phases with low thermal conductivity surrounded the CNFs (Fig. 3(a) and (b)), which can be regarded as elongated pores in the AlN matrix, and therefore deteriorated the heat transfer of the composites.

4. Conclusions

In summary, highly dense CNFs/AlN composites with and without sintering aids (Y_2O_3 and CaF_2) were fabricated by the PAS in vacuum, and the relationship between the interfacial structure and the thermal conductivity was investigated. It was found that the interfacial amorphous glass phases induced by the sintering aids improved the thermal conductivity of the monolithic AlN ceramic, while deteriorated the property of the CNFs/AlN composites since it covered the CNFs, which can be seen as elongated pores in the AlN matrix to deteriorate the heat transfer. However, for the CNFs/AlN composites without sintering aids, a clean interface was obtained due to the chemical reaction between the amorphous carbon layer from the CNF and the Al_2O_3 layer on the AlN powders to produce gaseous matters (Al_2O and CO), leading to the enhanced thermal conductivity with the CNFs content ≤ 2 wt%. Theoretical analysis indicated that the enhancement could be caused by the relatively low thermal contact resistance between the CNF and the AlN.

Acknowledgments

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