Fabrication, interface characterization and modeling of oriented graphite flakes/Si/Al composites for thermal management applications

Cong Zhou a, Gang Ji b,c, Zhe Chen a,⇑, Mingliang Wang a, Ahmed Addad b, Dominique Schryvers c, Haowei Wang a

a State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China
b Unité Matériaux et Transformations, UMR CNRS 8207, Bâtiment C6, Université Lille 1, 59655 Villeneuve d’Ascq, France
c Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

Article info
Article history:
Received 15 May 2014
Accepted 5 July 2014
Available online 17 July 2014

Keywords:
Composites
Graphite flake
Thermal conductivity
Interface structure
Amorphous

Abstract
Highly thermally conductive graphite flakes (Gf)/Si/Al composites have been fabricated using Gf, Si powder and an AlSi7Mg0.3 alloy by an optimized pressure infiltration process for thermal management applications. In the composites, the layers of Gf were spaced apart by Si particles and oriented perpendicular to the pressing direction, which offered the opportunity to tailor the thermal conductivity (TC) and coefficient of thermal expansion (CTE) of the composites. Microstructural characterization revealed that the formation of a clean and tightly-adhered interface at the nanoscale between the side surface of the Gf and Al matrix, devoid of a detrimental Al4C3 phase and a reacted amorphous Al–Si–O–C layer, contributed to excellent thermal performance along the alignment direction. With increasing volume fraction of Gf from 13.7 to 71.1 vol.%, the longitudinal (i.e. parallel to the graphite layers) TC of the composites increased from 179 to 526 W/m K, while the longitudinal CTE decreased from 12.1 to 7.3 ppm/K (matching the values of electronic components). Furthermore, the modified layers-in-parallel model better fitted the longitudinal TC data than the layers-in-parallel model and confirmed that the clean and tightly-adhered interface is favorable for the enhanced longitudinal TC.

1. Introduction

In the microelectronics industry, the ever-increasing power density and continuing miniaturization of semiconductor and optoelectronic devices lead to mounting thermal management challenges [1,2]. In order to realize high performance, long life and high reliability, it is imperative to develop very efficient electronic packaging materials with high thermal conductivity (TC) and low coefficient of thermal expansion (CTE). The TC should be as high as possible to effectively dissipate heat generated from electronic components, while the CTE needs to be lower than 10 ppm/K in order to minimize thermal stress due to the CTE mismatch between electronic components (4–7 ppm/K) and packaging materials [3–10]. Towards this goal, both single phase and composite systems have been investigated. Pure metals including Cu and Al have relatively high TCs, but their CTEs are much higher than those of electronic components [2,10]. Mo and W reinforced Cu matrix composite candidates, despite their low CTEs of 6–7 ppm/K being compatible with those of electronic components, have relatively low TCs of around 200 W/m K [10–13]. Two other composites have been considered, but they also failed to meet expectations. One is SiC/Al composites where the main drawback is again its insufficient TC of 170–250 W/m K [2,8,14]. The other one is diamond/metal (Al, Cu or Ag) composites which exhibits excellent thermal properties with TCs approaching 600 W/m K [12,15,16]. However, application of the latter has been limited to niche markets due to the high price of diamond particles; moreover, poor machinability of the diamond/metal composites has been an additional limitation [8].

To date, several further carbon-based materials (e.g., carbon fibers [17,18], carbon nanotubes (CNT) [19–22], graphite particles [18,23,24], porous graphite foams [25,26], graphite foam [18,27], graphene [28,29] etc.) have been considered and integrated in metal matrices via various fabrication techniques. Graphite flakes (Gf), in particular, have attracted significant recent attention for thermal management applications due to their superior thermal properties, low cost and ease of machining [1,18,30,31]. However, stacking of Gf leaves almost no space between the flakes, which makes liquid metal infiltration under pressure an almost unfeasible technique for fabrication of, for
example, Gf/Al composites [18]. To address this issue, Prieto et al. [31] introduced a small proportion of SiC particles which acted as spacers between the layers of Gf. As a result, the produced Gf/SiC/AlSi12 composites exhibited alternating layers of Gf and had TC in the range of 294–390 W/mK.

Highly crystalline graphite has extremely high TC and near-zero CTE along the basal plane of its crystal lattice [17,32]. Considering this high anisotropy in thermal properties parallel and perpendicular to the basal plane of Gf, control of the preferred orientation of Gf is crucial since it is one of the main factors enhancing the TC of Gf/Al composites [1]. A further concern is the graphite/Al interface configurations, which should facilitate thermal exchange across the interface by providing good adhesion and minimum thermal boundary resistance. However, the influence of interface formation and diffusion on the interface conductance is still not fully understood. It has been well documented that the excessive formation of aluminum carbide (Al4C3) phase at the interface hinders thermal transfer and degrades mechanical properties [26]. In this work, we report fabrication and interface characterization of oriented Gf/Si/Al composites by room-temperature mixing and pressing followed by an optimized pressure infiltration process. The microstructure of the composites is characterized at length scales from the macro to the nanoscale to investigate presence of Al4C3 in particular and more generally the detailed graphite/Al interface assembly configuration. The effect of the volume fractions of Gf on thermal properties (TC and CTE) of the composites is also investigated and discussed. Furthermore, efforts are devoted to present predictive models for fitting experimental TC values of the oriented Gf/Si/Al composites by considering the interfacial features revealed at the nanoscale.

2. Experimental details

2.1. Fabrication of the oriented Gf/Si/Al composites

The raw materials consisted of Gf, Si particles and Al alloy (AlSi7, Mg0.3) ingots. The Gf was acquired from Shandong Graphite Co., Ltd., China. The Si particles (99.9% purity) were supplied by Jiangsu Maoyuan Co., Ltd., China. The thermo-physical properties of these raw materials are given in Table 1. The main reasons for using Si instead of SiC particles are (i) Si particles are more easily machinable and have a lower density of 2.33 g/cm3 than SiC (3.2 g/cm3) and (ii) SiC suffers from its severe reactivity with molten Al [33]. AlSi7Mg0.3 alloy was used for infiltration due to its good fluidity as compared to pure Al.

Fig. 1 illustrates the typical fabrication process of the Gf/Si/Al composites used in this work. The three key steps were: (1) mixing of Gf with Si particles; (2) pressing the mixture into a block and (3) pressure infiltration. In particular, Gf and Si particles with volume ratios of 1:4, 1:2, 1:1, 2:1 and 4:1 were mixed by mechanical stirring for 30 min. The mixtures were then loaded in a steel mould and uniaxially pressed to obtain a block in a pressing apparatus using a pressure of 50 MPa. As will be illustrated by Optical Microscopy (OM) images below, this step can space and orient the layers of Gf. The block was then heated up to 400 °C. The AlSi7Mg0.3 alloy (melting temperature of around 581 °C) was heated to 760 °C, degassed and cleaned in a graphite crucible. Subsequently, the molten Al alloy was poured onto the block, and a pressure of 100 MPa was applied for 60 s to force the molten Al alloy to fill the pores inside the block.

It has been reported that a relatively low infiltration temperature and a high cooling rate can suppress the formation of the interfacial Al4C3 phase [25,26,35]. This is what led us to use the moderate 760 °C as an optimal temperature preventing Al4C3 formation on the one hand, yet facilitating infiltration of the AlSi7, Mg0.3 alloy on the other hand. At this temperature, better fluidity of the AlSi7Mg0.3 alloy with respect to pure Al (melting temperature of around 660 °C versus 581 °C for the alloy) can be correlated with the lower melting temperature of the former. It is well known that an external pressure is usually applied to facilitate infiltration of molten Al alloy into the pores inside the block [23]. Too high a pressure however can hinder infiltration by making the infiltration channels too small, while too low a pressure requires longer infiltration times at high temperature which may favor Al4C3 formation. Thus, in order to maximize infiltration and prevent Al4C3 formation, an optimized infiltration pressure of 100 MPa was employed based on our experience with our homemade facility.

2.2. Microstructural characterization

The microstructure was examined using OM and Scanning Electron Microscopy (SEM, JEOL JSM-7600F). The formed Gf/Si/Al composites were cut and mechanically polished. The volume fraction of Gf (Vg) was determined with image analysis software (Image-Pro Plus 6.0) based on a grey-scale threshold criterion. Table 2 displays thermo-physical properties of the Gf/Si/Al composites with different Vg. The volume fraction of Si particles (Vs) in the Si/Al matrix is also listed in Table 2.

X-Ray Diffraction (XRD) measurements were performed on a D8 ADVANCE X-Ray diffractometer, operating at 40 kV/40 mA and using Cu Kα radiation (λ = 0.15406 nm). 2θ scans were performed between 20° and 70° with a scan speed of 5°/min. Particular care was taken in checking for the presence of Al4C3 (JCPDS file 65-9731). For this, careful scanning was performed in the angle ranges of 30.5–33.0° and 39.5–41.0° with a step size of 0.005°. The scan time was 5 s per increment. Degree of graphitization of initial Gf was determined by the JSPS method [36] where standard silicon (200 Mesh, 99.99%, Soekawa Chemical Co., Japan) was used for calibration.

The Gf/Si/Al composite (55.3% in Vg), see Table 2) was further analyzed by (High-Resolution) Transmission Electron Microscopy (HRTEM) in order to examine the graphite/Al interfaces, being parallel and perpendicular to the alignment direction along the xy-plane of Gf. TEM thin foils were cut parallel to the alignment direction, mechanically polished and finally thinned using a Gatan Model 691 precision ion polishing system. A FEI Tecnai G2-20 Twin microscope operated at 200 kV and equipped with a Gatan Energy-Dispersive X-ray Spectroscopy (EDX) analyzer was used for HRTEM examination. Selected Area Electron Diffraction (SAED) was performed for phase identification. Scanning TEM mode with a probe size of a few nanometers was used for EDX analyses. For HRTEM, significant sample tilting was avoided in order not to overlap the lattice contrasts from Gf and Al matrix at the interface.

2.3. Measurements of the thermo-physical properties

The TC (κ) of the composites was calculated from the thermal diffusivity (α), density (ρ) and specific heat capacity (Cp) using Eq. (1) [1]:

\[
\kappa = \alpha \cdot C_p \cdot \rho
\]
The laser-flash diffusivity instrument (Nano-Flash-Apparatus, LFA 447, NETZSCH) was used to determine the thermal diffusivity of the cylindrical specimen ($\phi \times 12.6 \times 2 \text{ mm}$) at room temperature. The specific heat capacity of the composites was calculated by the linear rule of mixtures (ROM) using the specific heat capacity values of the components (i.e. Gf, Si particles, and Al alloy) [31]. The CTE values of the specimens ($\phi \times 5 \times 25 \text{ mm}$) were characterized with a dilatometer (DIL 402C, NETZSCH) from room temperature up to 300 °C. As shown in Table 2, the CTE values perpendicular to the $xy$-plane of the prepared samples No. 4 and No. 5 were not measured due to sample size limitations.

2.4. Modeling approaches

Layers-in-parallel [37] and layers-in-series models [38] were used to calculate longitudinal (i.e. along the $xy$-plane, see Fig. 1) and transversal (i.e. along the $z$-axis) TC of the oriented Gf/Si/Al composites, respectively. The layers-in-parallel model considers heat-transfer characteristics parallel to the major heat flow direction of layered composites, while the layers-in-series model considers those perpendicular to the major heat flow direction. The models are described as follows:

Layers-in-parallel model:

$$K_L^c = fK_L + (1 - f)K_m$$

Layers-in-series model:

$$\frac{1}{K_T^c} = \frac{f}{K_L} + \frac{1 - f}{K_m}$$

where $K_L^c$, $K$, and $K_m$ refer to the TC of composites, Gf, and matrix, respectively; the subscripts $L$, $T$ denote the longitudinal and transversal directions, and $f$ is the volume fraction of Gf. It should be noted that in reality both simple models could yield a certain degree of overestimation as the important effect of interfacial thermal resistance on TC is not taken into account. Thus, as will be detailed below, we modified the models in order to improve their predictive capacity.

3. Results and discussion

3.1. Microstructures of the starting materials and the oriented Gf/Si/Al composites

Fig. 2 illustrates the morphologies of Gf, Si, and Gf/Si/Al composites used to calculate longitudinal (i.e. along the $xy$-plane, see Fig. 1) and transversal (i.e. along the $z$-axis) TC of the oriented Gf/Si/Al composites, respectively. The layers-in-parallel model considers heat-transfer characteristics parallel to the major heat flow direction of layered composites, while the layers-in-series model considers those perpendicular to the major heat flow direction. The models are described as follows:

$$K_L^c = fK_L + (1 - f)K_m$$

$$\frac{1}{K_T^c} = \frac{f}{K_L} + \frac{1 - f}{K_m}$$

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_Gf$ (%)</th>
<th>$V_{Si}$ (%)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$C_p$ (J/g/K)</th>
<th>$a$ (mm$^2$/s)</th>
<th>TC (W/mK)</th>
<th>CTE (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.7</td>
<td>66.1</td>
<td>2.43</td>
<td>0.767</td>
<td>96$^a$</td>
<td>179$^a$</td>
<td>12.1$^a$</td>
</tr>
<tr>
<td>2</td>
<td>24.0</td>
<td>65.7</td>
<td>2.41</td>
<td>0.761</td>
<td>40$^b$</td>
<td>266$^a$</td>
<td>11.5$^b$</td>
</tr>
<tr>
<td>3</td>
<td>38.5</td>
<td>65.2</td>
<td>2.38</td>
<td>0.753</td>
<td>45$^b$</td>
<td>350$^a$</td>
<td>11.4$^b$</td>
</tr>
<tr>
<td>4</td>
<td>55.3</td>
<td>64.6</td>
<td>2.35</td>
<td>0.742</td>
<td>40$^b$</td>
<td>475$^a$</td>
<td>9.1$^b$</td>
</tr>
<tr>
<td>5</td>
<td>71.1</td>
<td>64.3</td>
<td>2.32</td>
<td>0.731</td>
<td>26$^b$</td>
<td>526$^a$</td>
<td>7.3$^b$</td>
</tr>
</tbody>
</table>

$^a$ Parallel to the graphite layers.
$^b$ Perpendicular to the graphite layers.

The laser-flash diffusivity instrument (Nano-Flash-Apparatus, LFA 447, NETZSCH) was used to determine the thermal diffusivity of the cylindrical specimen ($\phi \times 12.6 \times 2 \text{ mm}$) at room temperature. The specific heat capacity of the composites was calculated by the linear rule of mixtures (ROM) using the specific heat capacity values of the components (i.e. Gf, Si particles, and Al alloy) [31]. The CTE values of the specimens ($\phi \times 5 \times 25 \text{ mm}$) were characterized with a dilatometer (DIL 402C, NETZSCH) from room temperature up to 300 °C. As shown in Table 2, the CTE values perpendicular to the $xy$-plane of the prepared samples No. 4 and No. 5 were not measured due to sample size limitations.

3.1. Microstructures of the starting materials and the oriented Gf/Si/Al composites

Fig. 2 illustrates the morphologies of Gf, Si, and Gf/Si/Al composites used in this work. The Gf displays neat platelet morphology with an average diameter of a plate of about 500 μm (see Fig. 2a) and a mean thickness of about 20 μm (see inset in Fig. 2a). The Si particles have irregular shape with a mean particle size of 10 μm (see Fig. 2b). The degree of graphitization of the initial Gf is estimated to be higher than 99% by the JSPS method from Fig. 3a [36]. As is well known, a well arrayed graphite structure is especially important for a high TC of the graphite materials [30]. Such a high degree of graphitization indicates that the Gf are highly crystalline and have a very high TC along the basal plane of the crystal lattice.

As shown by the OM images of the obtained Gf/Si/Al composites in Fig. 4a–c, the elongated dark regions represent the Gf while the light ones are the Si/Al matrix. No pores are visible, indicating a...
fully densified assembly. The layers of Gf are stacked mostly parallel to each other and oriented perpendicular to the pressing direction (i.e. the z-axis, see Fig. 1). Bending of the Gf is more pronounced in the sample with high Gf volume (Fig. 4e). Fig. 4f is a SEM micrograph showing the Al alloy, the Si particles and the sharp interface between the graphite and the Si/Al matrix.

The formation of Al4C3 at the graphite/Al interface is thermodynamically favorable (e.g. -168 kJ/mol at 750 °C [39]) and is often observed in graphite/Al composites produced by gas pressure infiltration [26]. Thus, in order to further test for its presence as well as that of other interfacial reaction products, the composites were also examined at the macroscopic scale by XRD (see Fig. 3b) and at the nanoscale by (HR)TEM (see Fig. 5 and 6). The XRD patterns of all the obtained composites look similar. A representative one in Fig. 3b shows only the diffraction peaks of Al, Si and graphite. No evidence of Al4C3 indicates that this phase was not formed to any significant extent at the interface. What is revealed by (HR)TEM (Fig. 5) is an interfacial layer homogeneously distributed along the Gf/Al interface, evidently binding the graphite and the Al matrix. This layer has a thickness of 40–50 nm (Fig. 5a) and is rich in the elements C, O, Al and Si (Fig. 5f). An SAED pattern from the layer is shown in Fig. 5b. The central diffuse ring provides evidence of an amorphous phase, with as of yet unindexed crystals (evidenced by the two accompanying sharp rings shown in Fig. 5b) embedded within the amorphous phase. The 0.20 reflection (d₀₂₀ spacing of around 0.2 nm) of the indexed [105] Zone Axis Pattern (ZAP) of Al is located on one of the arrowed rings. This ring can hence be attributed to graphite since the d₁₀₁ spacing of graphite is also around 0.2 nm. The HRTEM image of graphite in Fig. 5c shows the (002) basal planes (d₀₀₂ spacing of around 0.34 nm), which are buckled with clearly visible dislocation-like defects. The morphology of the interfacial layer is shown with higher resolution in Fig. 5d. The nanocrystals are less than 5 nm in nominal size and tend to distribute themselves adjacent to the interfaces with the Al matrix and the Gf. One examined nanocrystal (pointed by an arrow in Fig. 5e) exhibits lattice fringes with a d-spacing of roughly 0.19 nm (the resolution limit of the microscope).

The interface between the side surface of Gf and Al matrix (i.e. side surface of Gf/Al interface) is represented in Fig. 6. As Gf only presents very high TC along its basal plane, this interface configuration is thus the key to determine the overall thermal properties of the oriented composites. Two interfaces nearly located at the tip of a graphite layer, as indicated in Fig. 6a, were characterized by HRTEM shown in Fig. 6b–e. Completely different from the Gf/Al interface previously revealed in Fig. 5, no reaction products are detected along the whole interfaces. Only the amorphous carbon layers of Gf, confirmed by the corresponding FFT (inset in Fig. 6c) and with a thickness of around 5–8 nm, are observed to tightly adhere to the Al matrix (highlighted by dotted lines in Fig. 6b and c). Structural evolution is also visible in the layer of graphite, generally from the crystalline areas slightly away from the interfaces (Fig. 6d and e) to the poorly crystalline areas adjacent to the amorphous layers (low parts of Fig. 6b and c). An entirely turbostratic characteristic shown in Fig. 6d and e is produced by bending, buckling and breaking of the (002) basal planes. Comparatively, only a few basal planes can be very locally identified in Fig. 6b and c.
3.2. Thermal properties and modeling

As shown in Table 2, the measured longitudinal TC of the oriented composites increases from 179 to 526 W/m K with an increase of the VGf from 13.7 to 71.1 vol.%, while the transversal TC decreases from 90 to 41 W/m K. Theoretical predictions of the longitudinal and transversal TC, by means of the layers-in-parallel and the layers-in-series models, are plotted versus the experimental data in Fig. 7a and b, respectively. The layers-in-parallel model increasingly overestimates the TC of the Gf/Si/Al composites with increasing volume fraction of Gf (see Fig. 7a). In order to take into account the effect of interfacial thermal resistance, the Gf can be considered to be coated with a very thin interfacial thermal barrier layer [40]. Analytically, it can be solved by replacing the inclusion with a non-ideal interface by an "effective" inclusion having an effective TC, $K_{\text{eff}}$, and can be expressed as

$$K_{\text{eff}} = \frac{K_i}{1 + \frac{2hD}{tD}}$$

(4)

where $h$ is the interface thermal conductance (i.e. the reciprocal of the interfacial thermal resistance), $t$ and $D$ denote the thickness and diameter of the inclusion. The value of $h$ can be calculated by the acoustic mismatch model (AMM) [41], which treats the interface heat transfer in terms of continuum mechanics by calculating the probability of an incident phonon traversing the interface [42]. $h$ is calculated to be:

$$h = \frac{1}{2} \rho_m C_m \frac{v_m^2}{v_i^2} \frac{\rho_m v_m - \rho_i v_i}{(\rho_m v_m + \rho_i v_i)^2}$$

(6)

where $\rho$, $C$, $v$ are the density, the specific heat capacity, and the phonon velocity, respectively; subscripts $m$, $i$ denote the matrix and the inclusion, respectively.

Considering the fact that no reactions occurred at the side surface of Gf/Al interface, we assume that the influence of the amorphous carbon layer on the TC of the composites is negligible.

Fig. 4. OM micrographs (magnification of 100×) of the Gf/Si/Al composites with different Gf volume fractions: (a) 13.7%, (b) 24%, (c) 38.5%, (d) 55.3%, (e) 71.1%; and (f) a typical SEM micrograph of the graphite/Al interface.
since the layer thickness is much smaller (5–8 nm, see Fig. 6b and c) than the diameter of $G_f$ (500 $\mu$m, see Fig. 2a). Thus, the side surface of $G_f$/Al interface can be regarded as the simple $G_f$/AlSi$_7$Mg$_{0.3}$ one and the interface thermal conductance can be calculated using Eq. (6). Given the lack of data for AlSi$_7$Mg$_{0.3}$, pure Al is considered here for theoretical calculations. The material parameters for the calculation are given in Table 3. We obtain $h = 4.5 \times 10^7$ W/m$^2$ K, which is very close to the experimental data ($\sim 5 \times 10^7$ W/m$^2$ K) measured by Chen et al. [45]. The effective TCs of the $G_f$ parallel and perpendicular to the basal plane are calculated from
Eqs. (4) and (5) to be 918 and 35 W/m K, respectively. Hence, we replace $K$ in layers-in-parallel model and layers-in-series model by $K^{\text{eff}}$. The modified layers-in-parallel model and modified layers-in-series model are expressed as:

$$K^{\text{eff}}_c L = fK^{\text{eff}}_c L + \left(1 - f \right)K_m$$

(7)

$$\frac{1}{K^{\text{eff}}_c} = \frac{f}{K^{\text{eff}}_c} + \frac{1 - f}{K_m}$$

(8)
as evidenced by the CTE values parallel to the xy-plane always being higher than those perpendicular to the xy-plane. Considering the intrinsic CTE values of the G\textsubscript{f} (−1.5 ppm/K parallel, versus 25 ppm/K perpendicular to the basal plane, see Table 1), the results seem counterintuitive. All efforts to fit the data using, for example, the ROM [32], Turner model [46], Kerner model [47], and Schapery model [48] have failed. In the literature, Pireto et al. [31] also reported the same difficulties in modeling the experimental CTE values of the G\textsubscript{f}/SiC/AlSi\textsubscript{12} composites. The underlying reason for the unusual thermal expansion behaviour of the composites requires further investigation but is out of the scope of this paper.

3.3. Discussion of thermal properties and interface configurations

Based on the microstructures (see Figs. 2–6), the obtained enhanced longitudinal TC of the G\textsubscript{f}/Si/Al composites can originate from the following reasons. On the one hand, the oriented arrangement along the basal plane of highly crystalline G\textsubscript{f} is very favorable for global thermal transfer along the alignment direction. Additionally, we find that G\textsubscript{f} stack, upon packing, with their basal planes parallel to each other and simple mixing with Si particles suffices for inducing requisite separations between the flakes (see Fig. 1). On the other hand, at the nanoscale the clean and tightly-adhered interface (see Fig. 6) between the side surface of G\textsubscript{f} and Al matrix, instead of the reacted amorphous layer (see Fig. 5) and detrimental Al\textsubscript{4}C\textsubscript{3} [26] is also favorable. As described above, the optimized pressure infiltration processing conditions of moderate temperature and pressure used in this work effectively suppress the formation of Al\textsubscript{4}C\textsubscript{3}. The segregation of Si along the graphite/Al interface (see Fig. 5f), originating from the Al alloy with 7 wt% Si, is beneficial since small quantities of Si hinder C solubility in the Al matrix hence limiting Al\textsubscript{4}C\textsubscript{3} formation by interfacial reaction [26,49]. Use of G\textsubscript{f} with a high degree of graphitization (Fig. 3a) is an additional factor for hindering the nucleation of Al\textsubscript{4}C\textsubscript{3} due to a lack of surface defects [26]. Interfacial amorphous layers have been previously characterized by (HR)TEM in squeeze cast diamond/Al [50], spark
plasma sintered CNT/Cu [51,52] and hot-pressed vapor grown carbon fiber/Al composites [53]. In our case, decomposition and transformation of graphite surfaces into amorphous carbon layers can occur at the high temperature of our experiments. Incorporation of O, Si and Al, most probably due to oxidation and interfacial reaction, tend to promote amorphous aluminosilicon oxy carbide (Al–Si–O–C) formation [54]. It was reported that the formed amorphous phase may also act as the nucleation site for Al4C3 [50]. Essentially, energy transfer between electrons in aluminum and phonons in graphite dominates heat conduction across the graphite/Al interface. The presence of the reacted interfacial amorphous layer cannot facilitate this energy exchange due to strong phonon scattering in the amorphous phase. This process may further be dissipated by the presence of interfacial oxygen atoms leading to degradation of the TC of the composites [55]. Nevertheless, as this type of interface is parallel to the alignment direction of the composites, it only contributes to the transversal TC. Theoretical calculations by means of the (modified) layers-in-series models also indicate that the effect of the amorphous layer on the transversal TC is very limited.

Furthermore, the side surface of Gf/Al interface configuration – a clean and well adhered interface – is beneficial for the improved TC along the alignment direction of the composites. The consistency of the experimental TC data and the predictive calculation by the modified layers-in-parallel model also confirms that the presence of an extremely thin carbon amorphous layer does not substantially degrade the longitudinal TC. Although it was reported that the TC of the amorphous carbon film is as low as about 0.2 W/m K [56], our results suggest that the negative effect of strong phonon scattering in the amorphous carbon layer on interfacial thermal resistance can be marginal when the layer is only of a few nanometers in thickness.

Finally, as revealed by OM and TEM in Figs. 4 and 6, the graphite flakes incorporated in the composites are not uniform in thickness. This thickness variation as well as the aspect ratio of the graphite flakes can have an effect on thermal conductivity of the composites and deserves a systematic study.

4. Conclusions

Gf/Si/Al composites with high TC and low CTE have been fabricated by a pressure infiltration process using optimized conditions. Microstructure and in particular the graphite/Al interface configurations, were characterized using XRD, OM, SEM and (HR)TEM. The evolution of the thermal properties of the composites as a function of the volume fraction of Gf was studied. The results allow us to draw the following conclusions:

(1) A successful processing route involved (i) mixing Gf with the Si particles and alignment of Gf under pressure at room temperature and (ii) infiltration of melted AlSiMg3 alloy at a moderate temperature of 760 °C and pressure of 100 MPa for 60 s.

(2) Enhanced longitudinal TC resulted from the following microstructural characteristics: (i) the Gf being stacked mostly parallel to each other and oriented parallel to the xy-plane and (ii) the clean and tightly-adhered side surface of Gf/Al interface, instead of the reacted C–O–Al–Si amorphous layer and detrimental Al4C3.

(3) The global TC increased from 179 to 526 W/m K correlated with an increase of the volume fraction of Gf from 13.7 to 71.1 vol.%, while the CTE in the directions parallel and perpendicular to the xy-plane decreased from 12.1 to 7.3 ppm/K and from 11.5 to 7.5 ppm/K, respectively. The fabricated Gf/Si/Al composites showed a TC in excess of 500 W/m K and a CTE compatible with those of electronic components (4–7 ppm/K). Thus this composite and its development show promise for low-cost thermal management applications.

(4) The modified layers-in-parallel model, which considered the interfacial thermal resistance introduced by the clean and tightly-adhered side surface Gf/Al interface, better predicted the longitudinal TC data than the original model. Nevertheless, based on the (modified) layers-in-series models, the Al–Si–O–C amorphous layer at the Gf/Al interface had a limited effect on the transversal TC.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Grant No. 51201099), China Postdoctoral Science Foundation (Grant No. 2012M520891), the foundation from the State Key Laboratory of Metal Matrix Composites, Shanghai jiao Tong University (China) and the FWO project of Belgium (No. U2 FA 070100/3506). Many thanks are also due to Dr. George Serghioiu, School of Engineering and Centre for Materials Science, University of Edinburgh, UK for revisions and discussions.

References


