



**HAL**  
open science

# Thermal expansion coefficient and thermal fatigue of discontinuous carbon fiber-reinforced copper and aluminum matrix composites without interfacial chemical bond

Grégory Lalet, Hiroki Kurita, Jean-Marc Heintz, Guillaume Lacombe, Akira Kawasaki, Jean-François Silvain

## ► To cite this version:

Grégory Lalet, Hiroki Kurita, Jean-Marc Heintz, Guillaume Lacombe, Akira Kawasaki, et al.. Thermal expansion coefficient and thermal fatigue of discontinuous carbon fiber-reinforced copper and aluminum matrix composites without interfacial chemical bond. *Journal of Materials Science*, 2014, 49 (1), pp.397-402. 10.1007/s10853-013-7717-7. hal-00949254

**HAL Id: hal-00949254**

**<https://hal.science/hal-00949254>**

Submitted on 8 Jun 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Thermal expansion coefficient and thermal fatigue of discontinuous carbon fiber-reinforced copper and aluminum matrix composites without interfacial chemical bond

Grégory Lalet · Hiroki Kurita · Jean-Marc Heintz · Guillaume Lacombe · Akira Kawasaki · Jean-François Silvain

**Abstract** Fully dense carbon fiber-reinforced copper and aluminum matrix (Cu–CF and Al–CF) composites were fabricated by hot press without the need for an interfacial chemical compound. With 30 vol% carbon fiber, the thermal expansion coefficients (TECs) of pure Cu and Al were decreased to  $13.5 \times 10^{-6}$  and  $15.5 \times 10^{-6}/\text{K}$ , respectively. These improved TECs of Cu–CF and Al–CF composites were maintained after 16 thermal cycles; moreover, the TEC of the 30 vol% Cu–CF composite was stable after 2500 thermal cycles between  $-40$  and  $150$  °C. The thermal strain caused by the TEC mismatch between the matrix and the carbon fiber enables mechanical enhancement at the matrix/carbon fiber interface and allows conservation of the improved TECs of Cu–CF and Al–CF composites after thermal cycles.

## Introduction

Thermomechanical stress management is an important consideration in the design of high performance reliable multichip module-based electronic devices [1–4]. There is thus a significant requirement for development of novel materials and methods to increase the efficiency and reliability of each component [5–12]. The heat sink (or base

plate) should dissipate the heat produced in the electronic chip and also give some mechanical resistance to the electronic packaging. Materials with high thermal conductivity and a thermal expansion coefficient (TEC) compatible with that of the bonded ceramic materials (e.g., alumina or aluminum nitride) are required to maintain the chip in a stress-free, low-temperature state [13–20]. However, pure copper and aluminum, with TECs of  $17.0 \times 10^{-6}$  and  $23.0 \times 10^{-6}/\text{K}$ , respectively [21], are not useful as heat sink materials due to the TEC mismatch with the TEC of ceramic materials, around  $8.0 \times 10^{-6}/\text{K}$  [22]. Here, carbon fiber has a TEC of  $-1.0 \times 10^{-6}/\text{K}$  in the longitudinal direction [23], and it, therefore, appears that the combination of carbon fiber and metal matrices can lead to low TEC composite materials.

In metal matrix composites, interfacial chemical reactions should be carefully considered. A small quantity of an interfacial chemical compound can help to reinforce interfacial strength by chemical bonding; however, many chemical reactions cause degradation of this reinforcement, decreasing the desirable characteristics of composites. In addition, it is likely that TEC improvement for composite materials, in which the interface is enhanced by chemical bonds, is lost during thermal cycles due to the bond breaking attributed to the thermal mismatch between the matrix and the reinforcement, even if the interfacial chemical bond has a high initial TEC for a composite.

In this paper, we present our carbon fiber-reinforced copper (Cu) and aluminum (Al) matrix (Cu–CF and Al–CF) composites, fabricated by hot press with no interfacial chemical compounds. We considered that the TEC mismatch between Cu or Al and carbon fibers explains the thermal strain that exists inside Cu–CF and Al–CF composites, and this thermal strain can enhance metal matrix/carbon fiber interfaces. We investigated the TEC variations

---

G. Lalet · H. Kurita (✉) · J.-M. Heintz · G. Lacombe · J.-F. Silvain  
Institut de Chimie de la Matière Condensée de Bordeaux,  
ICMCB-CNRS, Université de Bordeaux, 87 Avenue du Docteur  
Albert Schweitzer, 33608 Pessac Cedex, France  
e-mail: h.kurita0319@gmail.com

G. Lalet · A. Kawasaki  
Department of Materials Processing, Graduate School of  
Engineering, Tohoku University, Sendai 980-8579, Japan

of Cu–CF and Al–CF composites, and evaluated the long-term reliability of Cu–CF and Al–CF composites as heat sink materials.

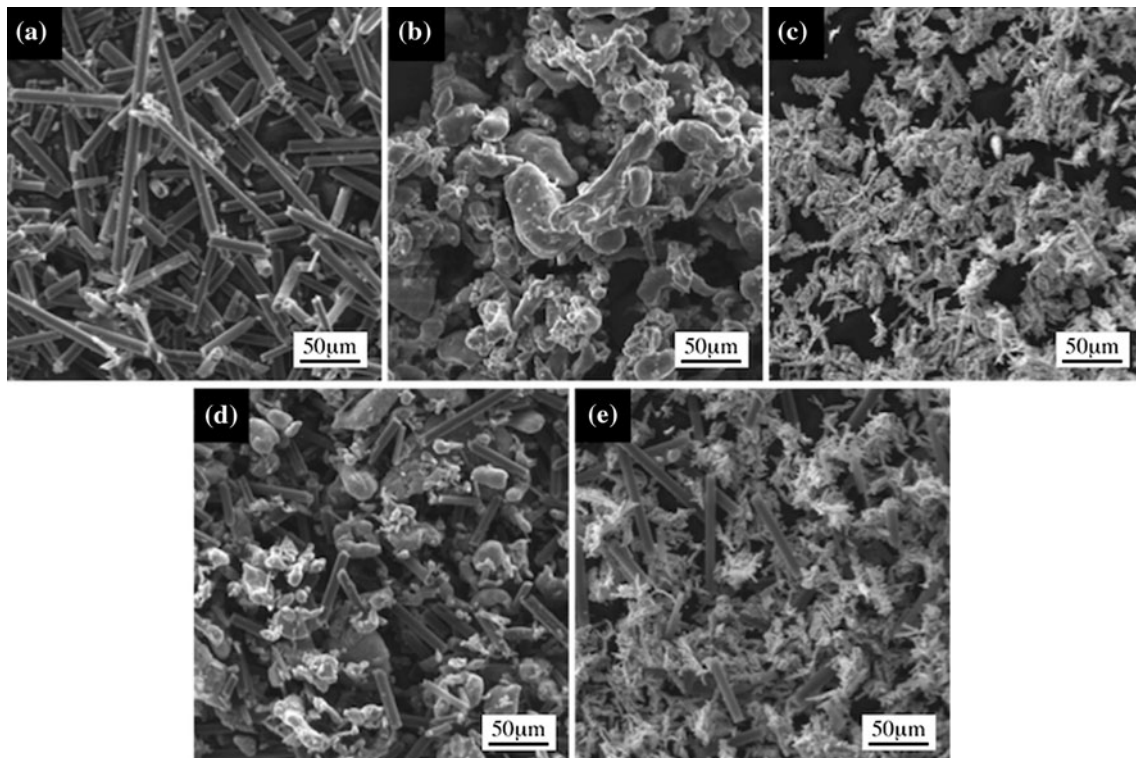
## Materials and methods

As a starting material, carbon fibers (CN80C, Nippon Graphite Corporation), which had a diameter of 10  $\mu\text{m}$  and TECs of  $-1.0 \times 10^{-6}$  and  $12.0 \times 10^{-6}/\text{K}$  in the longitudinal and transverse directions, respectively, were prepared [23]. They were annealed at 400  $^{\circ}\text{C}$  for 1 h in air to remove the polymer coating from their surface. The annealed carbon fibers were chopped using a blade mixer to obtain discontinuous carbon fibers, which had lengths between 50 and 200  $\mu\text{m}$  (see Fig. 1a). To obtain the matrix powder, Cu powder (CH-L10, Ecka Copper, 99.75 wt%) was prepared by an electroless process and spherical Al powder (Al F3731 Poudres Hermillon, 99.97 wt%) was obtained using an atomization process. The particle sizes of Cu and Al powders were around 35 and 25  $\mu\text{m}$ , respectively (see Fig. 1b, c).

The Cu–CF and Al–CF mixed composite powders were prepared using individual and uniform dispersions of carbon fibers (see Fig. 1d, e), by dry propeller mixing for 5 min under argon gas flow. The volume fraction of carbon fibers

was controlled to achieve 30 vol%. Columnar Cu–CF and Al–CF 30 vol% compacts ( $\phi 10 \times 8 \text{ mm}^3$ ) were fabricated under vacuum, under compressive stress below 50 MPa by hot press. Hot pressing conditions were 650  $^{\circ}\text{C}$  for 20 min for the Cu–CF 30 vol% composite, or at 600  $^{\circ}\text{C}$  for 40 min for the Al–CF 30 vol% composite. To compare the Al/CF interfacial aspect, the Al–CF 30 vol% composite was also fabricated by spark plasma sintering (SPS). SPS was conducted at 600  $^{\circ}\text{C}$  for 20 min, with pulse conditions of 3:3 (ON:OFF ratio). Temperature was monitored using a K-type thermocouple positioned in a graphite mold, 5 mm from the sample. Carbon fibers were mostly oriented in-plane (two-dimensional random) to the perpendicular direction of the applied compressive axis after hot pressing [23]. The fabricated Cu–CF and Al–CF 30 vol% columns were vertically machined to  $\phi 6 \times 5 \text{ mm}^3$  using a drill press, in-plane with the carbon fiber orientation, to prepare the specimens for TEC investigation. The top and bottom surfaces of specimens were carefully polished to ensure they were parallel, using waterproof abrasive SiC paper (#800).

The relative densities of Cu–CF and Al–CF 30 vol% composites were measured using Archimedes principle. The TECs of Cu–CF and Al–CF 30 vol% composites were measured 32 times during 16 thermal cycles using a differential dilatometer (NETZSCH DIL 402 PC) with a heating/cooling rate of 2  $^{\circ}\text{C}/\text{min}$  under argon gas flow. The



**Fig. 1** SEM micrographs of: **a** carbon fibers after heat treatment and chopping, **b** copper powder, **c** aluminum powder, **d** aluminum + carbon fibers 30 vol% composite powder, and **e** copper + carbon fibers 30 vol% composite powder

temperature ranged between 50 and 150 °C for the Al–30 vol% composite, or 50 and 300 °C for the Cu–CF and Al–CF 30 vol% composites. To reduce measurement error, the displacement of specimens was measured using an alumina rod, which was placed on the top of the specimens, and measured between 75 and 135 °C or 75 and 200 °C, respectively, for the cases outlined above. After measuring the TEC of the alumina reference (also  $\phi 6 \times 5 \text{ mm}^3$ ), the TECs of Cu–CF and Al–CF 30 vol% composites were estimated from the average measured displacements with respect to each thermal cycle, after deduction of the measured alumina reference value. Furthermore, the thermal fatigue of the Cu–CF 30 vol% composite was evaluated by a longer thermal cycling test (up to 2500 times) between –40 and 150 °C, with a heating/cooling rate of 5 °C/min. The TEC of the Cu–CF 30 vol% composite was estimated from the average measured values four times (during two thermal cycles), during each 500th thermal cycle.

The microstructure of Cu–CF and Al–CF 30 vol% composites were observed by scanning electron microscopy (SEM, Tescan VEGA) and transmission electron microscopy (TEM, Hitachi). For the TEM observation, thin specimens of Cu–CF and Al–CF 30 vol% composites were prepared by using focused ion beam (FIB) system (SMI2050, Seiko Instruments), after polishing using waterproof abrasive SiC paper (#800, #1000, #2000) to be less than 50  $\mu\text{m}$  thick.

## Results and discussion

### Density and carbon fiber orientation of Cu–CF and Al–CF composites

The relative densities of Cu–CF and Al–CF 30 vol% composites were close to 98 %. Figure 2 shows the SEM micrographs of Cu–CF and Al–CF 30 vol% composites. No serious degradation of carbon fibers occurred, and the tight Cu/CF and Al/CF interfaces were observed. Carbon fibers were individually and uniformly dispersed in the Cu or Al matrices. The white arrow on the illustration at the lower left of the figure indicates the applied stress axis in the hot press; these SEM micrographs reveal that carbon fibers tended to be oriented in-plane (two-dimensional random) to the direction perpendicular to the applied compressive axis in the hot press. However, the fiber orientation shows imperfections and it appeared that a few inclinations of the fibers existed (approximately  $\pm 10^\circ$ ) [23].

### Microstructure of Cu–CF and Al–CF composites

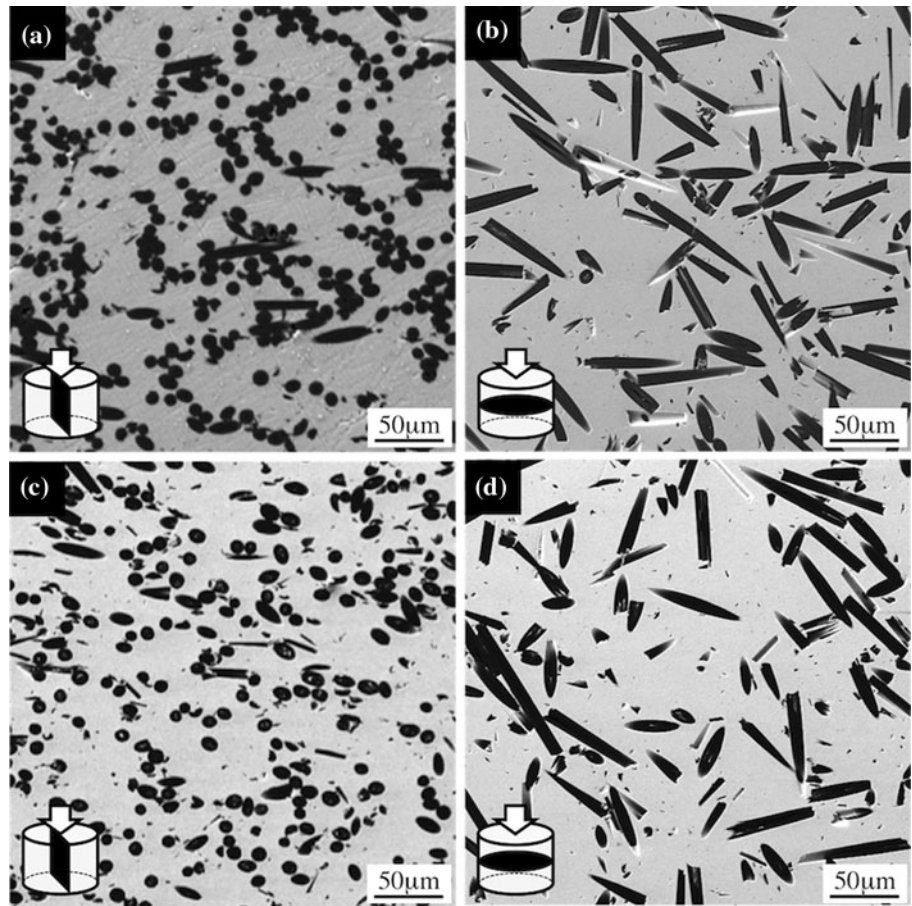
Figure 3 shows TEM micrographs of Cu/CF and Al/CF interfaces in Cu–CF and Al–CF 30 vol% composites

fabricated by hot press. Cu was directly and tightly in contact with the carbon fiber surface (see Fig. 3a). On the other hand, it was observed that a thin alumina ( $\text{Al}_2\text{O}_3$ ) layer (5–10 nm) occurs at the Al/CF interface in Al–CF 30 vol% composites fabricated by hot press (see Fig. 3b). This alumina layer was continuous, and prohibited direct contact between Al and the carbon fiber surface. No aluminum carbide ( $\text{Al}_4\text{C}_3$ ) crystals were observed in the Al–CF 30 vol% composite fabricated by hot press, although needle-like  $\text{Al}_4\text{C}_3$  crystals were observed at the direct-contact Al/CF interface in the Al–CF 30 vol% composite fabricated by SPS (see Fig. 3c). Furthermore, an  $\text{Al}_2\text{O}_3$  layer was not observed in the Al–CF 30 vol% composite fabricated by SPS. This needle-like  $\text{Al}_4\text{C}_3$  formation in the Al–CF 30 vol% composite fabricated by SPS agreed with the result reported by Kurita et al. [24], and the disappearance of the  $\text{Al}_2\text{O}_3$  layer corroborated the surface cleaning effect in SPS [25].

### Thermal expansion coefficient (TEC)

Figure 4 shows the TECs of Cu–CF and Al–CF 30 vol% composites in the direction in-plane to the carbon fiber orientation. With carbon fiber content of 30 vol%, the TECs of pure Cu and Al were decreased to  $13.5 \times 10^{-6}$  and  $15.5 \times 10^{-6}/\text{K}$ , respectively. This low TEC was achieved without any interfacial chemical compound (i.e., chemical bond) in Cu–CF and Al–CF 30 vol% composites, despite the necessary strong interfacial link required to develop the remarkable TEC of carbon fibers in a matrix. Here, the TECs of pure Cu and Al are higher than that of carbon fiber in any direction (longitudinal and transverse); this indicates that the shrinkage level of Cu and Al matrices is higher than that of carbon fiber during the cooling process of hot pressing. In addition, there is free stress at the fabrication temperature, 650 °C (Cu–CF composite) or 600 °C (Al–CF composite). It can, therefore, be observed that there is compressive stress (i.e., thermal strain) at Cu/CF or Al/CF interfaces at room temperature. This thermal strain achieves mechanical interfacial enhancements, such as interfacial friction and the anchor effect. Silvain et al. [26] have shown that dislocations are due to the thermal mismatch induced by the large difference in TEC at the Cu/carbon nanotube (CNT) interface in Cu–CNT composites. The different families of dislocations act to reduce the different types of stresses (e.g., shear and normal) and prevent delamination at the interfaces. In our case, it seems that a high density of dislocations can be obtained in Cu–CF and Al–CF composites due to the large TEC difference between the Cu or Al matrix and the carbon fibers. Consequently, it seems that these interfacial mechanical enhancements develop the remarkable TEC of carbon fibers in Cu and Al matrices. Indeed, Estili et al. [27] have

**Fig. 2** SEM micrographs of: **a** the cross section and **b** the parallel section of the Cu–CF 30 vol% composite; and **c** the cross section and **d** the parallel section of Al–CF 30 vol% composite



reported effective load transfer from shrunk ceramic matrices to CNTs in alumina–CNT composites.

The TEC of the Cu–CF 30 vol% composite was, for the most part, maintained during 16 thermal cycles between 50 and 300 °C. However, the TEC of the Al–CF 30 vol% composite increased to  $19.0 \times 10^{-6}/\text{K}$  after two thermal cycles over the same range. The TEC of the Al–CF 30 vol% composite was, however, maintained during 16 thermal cycles in the lower temperature range. Furthermore, the TEC of the Al–CF 30 vol% composite gradually decreased during thermal cycles between 50 and 300 °C, and the TEC improvement achieved by the addition of carbon fiber was lost, as the TEC tended toward that of pure Al ( $24.0 \times 10^{-6}/\text{K}$ ) after ten thermal cycles. Here, our Al–CF composite has a thin alumina layer at the Al/CF interface; this alumina layer is formed by oxidation of Al particles. This indicates that there is a chemical bond at the Al/alumina interface, and no chemical bond at the alumina/CF interface. However, the chemical bond at the Al/alumina interface should detach due to the high TEC mismatch between Al ( $24.0 \times 10^{-6}/\text{K}$ ) and alumina ( $6.7 \times 10^{-6}/\text{K}$ ) in subsequent thermal cycles. It is, therefore, inferred that the TEC of the Al–CF composite is degraded in thermal cycles between 50 and 300 °C because the Al/alumina interface is detached and broken due to the

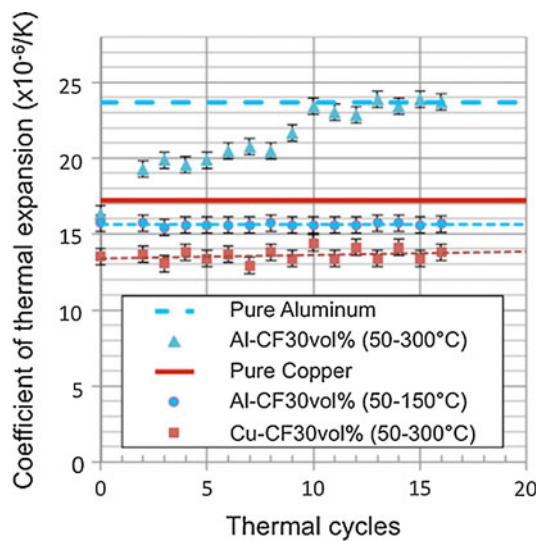
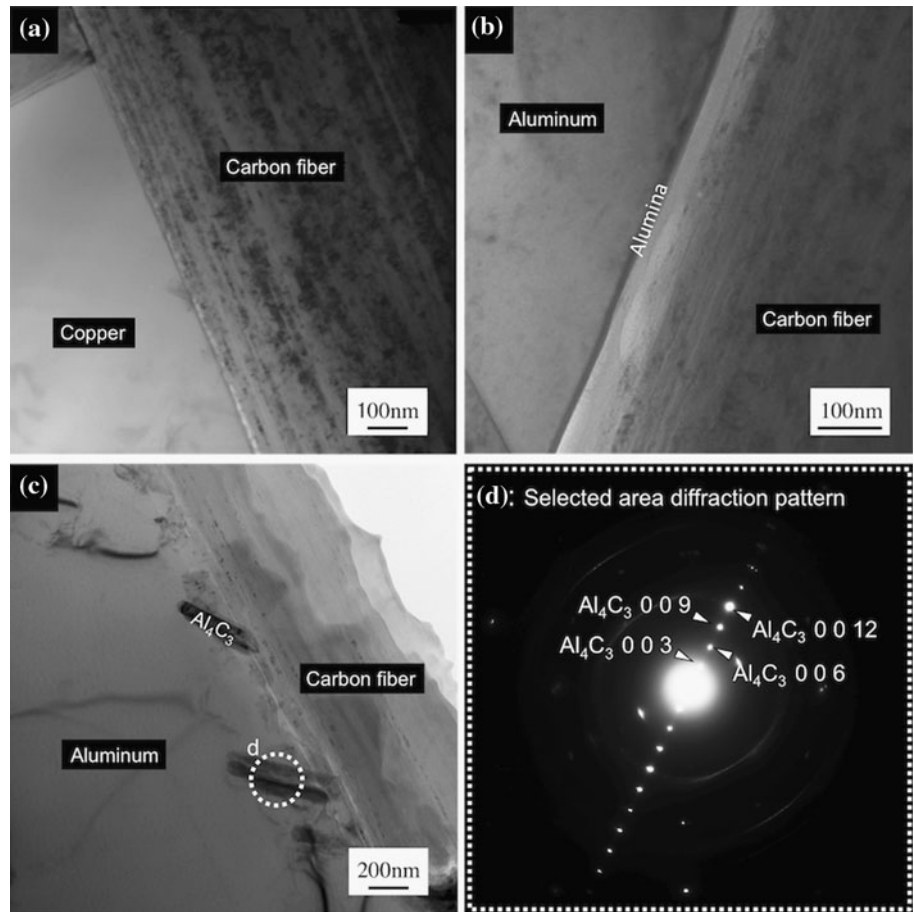
high thermal mismatch and detached alumina particles at the Al/CF interface, which interrupt the effective TEC development of carbon fibers.

Figure 5 shows the TEC of the Cu–CF 30 vol% composite over longer thermal cycling tests. The TEC of the Cu–CF 30 vol% composite slightly decreased to  $12.4 \times 10^{-6}/\text{K}$  after 2500 thermal cycles, although it gradually increased and reached  $15.5 \times 10^{-6}/\text{K}$  after 1000 thermal cycles. In subsequent thermal cycles, the TEC mismatch between the matrix and the reinforcement generally caused breaking of an interfacial chemical bond, and the TEC improvement in composite materials was gradually lost while the initial TEC of the composite was low. However, in our case, the Cu–CF composite, which has a mechanically enhanced interface, maintained its TEC and was stable after 2500 thermal cycles. This result implies that mechanical enhancement can be achieved repeatedly by reshrinkage of the Cu matrix, even if this mechanical enhancement is weak at high temperatures due to the release of thermal strain in the Cu–CF composite.

TEC estimation by Schneider's equation

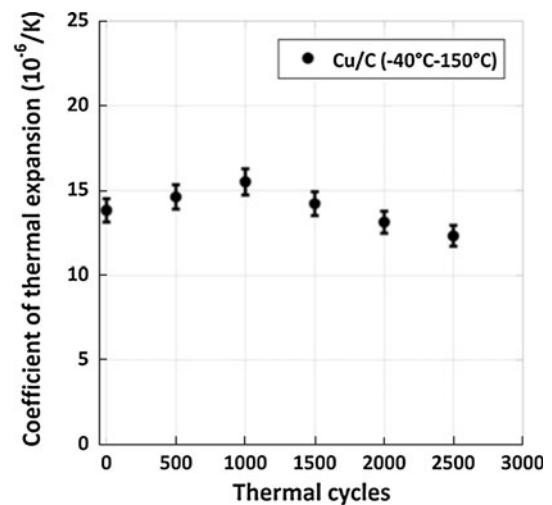
The TEC does not follow the rule of mixtures due to interfacial thermal stress [28]. As such, micromechanics

**Fig. 3** TEM micrographs of: **a** Cu/CF interface in Cu–CF 30 vol% composite and **b** Al/CF interface in Al–CF 30 vol% composite fabricated by hot press; and **c** Al/CF interface in Al–CF 30 vol% composite fabricated by SPS; with **d** the selected area diffraction pattern (within broken white circle in Fig. 5c)



**Fig. 4** TEC of Cu–CF 30 vol% and Al–CF 30 vol% composites versus thermal cycles with different temperature ranges

analysis has been carried out to calculate the accurate TEC of the composite in which discontinuous fibers are oriented in a 2-dimensional plane in the matrix [29]. However, it is also possible to roughly estimate the TEC in the in-plane



**Fig. 5** TEC of a Cu–CF 30 vol% composite after thermal cycling between  $-40$  and  $150$  °C for 2500 thermal cycles

direction of carbon fiber orientation from the average values calculated for the longitudinal and transverse directions of carbon fiber, by employing the conventional equations for a two-phase composite with unidirectionally oriented continuous fibers [28]. In this study, the TECs of Cu–CF

and Al–CF 30 vol% composites were estimated by Schneider’s equation, as follows [30]:

$$\alpha_1 = \frac{E_f \alpha_f V_f + E_m \alpha_m V_m}{E_f v_f + E_m v_m} \quad (1)$$

$$\alpha_2 = \alpha_m - (\alpha_m - \alpha_f) \left[ \frac{2(1 + v_m)(v_m^2 - 1)C}{\frac{1+1.1V_f}{1.1V_f-1} - v_m + 2v_m^2 C} - \frac{v_m \frac{E_f}{E_m}}{\frac{1}{C} + \frac{E_f}{E_m}} \right] \quad (2)$$

in which,

$$C = \frac{1.1V_f}{1 - 1.1V_f} \quad (3)$$

where  $\alpha_l$  and  $\alpha_2$  are the TEC values for the longitudinal and transverse directions of carbon fibers in a matrix, respectively;  $\alpha_f$  and  $\alpha_m$  are the TECs of carbon fiber and the matrices (Cu or Al);  $\alpha_f$  is  $-1.0 \times 10^{-6}$  or  $12.0 \times 10^{-6}/\text{K}$  for the longitudinal or transverse directions, respectively;  $\alpha_m$  is  $17.0 \times 10^{-6}/\text{K}$  for the Cu matrix and  $23.0 \times 10^{-6}/\text{K}$  for the Al matrix;  $E_f$  and  $E_m$  are Young’s moduli of carbon fiber and the Cu and Al matrices, which are 760, 129, and 70 GPa, respectively;  $V_f$  is the volume fraction of carbon fiber, 0.3; and  $v_m$  is Poisson’s ratio of matrices, 0.34 in the case of both Cu and Al matrices. The theoretical TECs of continuous carbon fiber-reinforced Cu and Al composites are estimated to be  $9.92 \times 10^{-6}$  and  $12.04 \times 10^{-6}/\text{K}$ , respectively. Here, taking account of the fact that the interfacial connection is assumed perfect in this theory, and the TEC of a discontinuous fiber-reinforced composite is normally higher than that of a continuous fiber-reinforced composite [21], our experimental TECs seem reasonable ( $13.5 \times 10^{-6}$  and  $15.5 \times 10^{-6}/\text{K}$  for discontinuous carbon fiber-reinforced Cu and Al matrix composites, respectively, which have no interfacial chemical compounds at the interface).

## Conclusions

Fully dense discontinuous carbon fiber-reinforced Al and Cu matrix composites were fabricated by hot press with no interfacial chemical compound. The TECs of pure Cu and Al were decreased to  $13.5 \times 10^{-6}$  and  $15.5 \times 10^{-6}/\text{K}$ , respectively, in the direction in-plane to the carbon fiber orientation, with a carbon fiber content of 30 vol%.

The TECs of Cu–CF and Al–CF 30 vol% composites, which had mechanical enhancement at the interface, were stable during 16 thermal cycles. In particular, the Cu–CF

30 vol% composite maintained its TEC after 2500 thermal cycles between  $-40$  and  $150$  °C.

This mechanical enhancement is not broken during thermal cycles and, unlike the case of a chemical bond, can be achieved by an increase of thermal strain. Therefore, the mechanical enhancement can be exploited for fabrication of reliable heat sinks in the long term.

**Acknowledgements** The authors would like to thank the “Délégation Générale pour l’Armement” and “Région Aquitaine” for financial support.

## References

1. Anandan SS, Ramalingam V (2008) *Therm Sci* 12:5
2. Ciappa M (2002) *Microelectron Reliab* 42:653
3. Schelling PK, Shi L, Goodson KE (2005) *Mater Today* 8:30
4. Schulz-Harder J (2003) *Microelectron Reliab* 43:359
5. Cho SH (2008) *Microelectron Reliab* 48:1696
6. He H, Fu R, Wang D, Song X, Jing M (2007) *Mater Lett* 61:4131
7. Johannessen R, Oldervoll F, Strisland F (2008) *Microelectron Reliab* 48:1711
8. Kim S, Kim KS, Kim SS, Sukanuma K, Izuta G (2009) *J Electron Mater* 38:2668
9. Ma H, Suhling JC (2009) *J Mater Sci* 44:1141
10. Mahdi H, Lopez P, Fuentes A, Jones R (2006) *Int J Energy Res* 30:851
11. Murali S, Srikanth N, Wong YM, Vath CJ III (2007) *J Mater Sci* 42:615
12. Xu H, Liu C, Silberschmidt VV, Chen Z (2010) *J Electron Mater* 39:124
13. Luedtke A (2004) *Adv Eng Mater* 6:142
14. Zweben C (1998) *J Miner Met Mater Soc* 50:47
15. Geffroy PM, Silvain JF (2007) *Mater Sci Forum* 534–536:1505
16. Mathias JD, Geffroy PM, Silvain JF (2009) *Appl Therm Eng* 29:2391
17. Herr E, Frey T, Schlegel R, Stuck A, Zehringer R (1997) *Microelectron Reliab* 37:1719
18. Huber T, Degischer HP, Lefranc G, Schmitt T (2006) *Compos Sci Technol* 66:2206
19. Rao VV, Krishna MV, Nagaraju J (2004) *Compos Sci Technol* 64:2459
20. Ruch PW, Beffort O, Kleiner S, Weber L, Uggowitzer PJ (2006) *Compos Sci Technol* 66:2677
21. Zweben C (1998) *J Miner Met Mater Soc* 50(6):47
22. Geffroy PM, Mathias JD, Silvain JF (2008) *Adv Eng Mater* 10:400
23. Veillère A, Heintz JM, Chandra N, Douin J, Lahaye M, Lalet G, Vincent C, Silvain JF (2012) *Mater Res Bull* 47:375
24. Kurita H, Kwon H, Estili M, Kawasaki A (2011) *Mater Trans* 52(10):1960
25. Omori M (2009) *Mater Sci Eng, A* 287:183
26. Silvain JF, Vincent C, Heintz JM, Chandra N (2009) *Compos Sci Technol* 69:2474
27. Estili M, Kawasaki A (2010) *Adv Mater* 22:607
28. Karadeniz ZH, Kumlutas D (2007) *Compos Struct* 78:1
29. Kataoka Y (2008) *Trans Jpn Soc Mech Eng A* 74(740):536
30. Sideridis E (1994) *Compos Sci Technol* 51:301