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Loic Constantin,[1,2] Lisha Fan,[1] Mael Pontoreau,[2] Fei Wang,[3] Bai Cui,[3] Jean-Luc Battaglia,[4] Jean-François Silvain,[1,2] and Yong Feng Lu,[1]**

[1] Department of Electrical and Computer Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588-0511.

[2]CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UPMR 5026, F-33608 Pessac, France

[3] Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588-0526.

[4]CNRS, University of Bordeaux, I2M, UMR 5295, F-33400 Talence, France

*Correspondence :

Dr. Jean-François Silvain; Address: Institut de Chimie de la Matière Condensée de Bordeaux – ICMCB-CNRS 87, Avenue du Docteur Albert Schweitzer, F-33608 Pessac Cedex, France; Email: jean-françois.silvain@icmcb.cnrs.fr

Prof. Yongfeng Lu; Address: Electrical and Computer Engineering Department, University of Nebraska-Lincoln, E430P Nebraska Hall, Lincoln, NE 68588-0511; Tel: 402-472-8323; Fax: 402-472-4732; Email: ylu2@unl.edu.

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ABSTRACT: Copper (Cu)/diamond (D) composites have been extensively studied as the next-generation thermal management materials due to its excellent thermal property. However, the presence of D particles makes processing these composites difficult. Additive manufacturing (AM) provides an intriguing method to overcome this issue because of its high degree of freedom to fabricate complex shapes. In this letter, we demonstrated the feasibility to additively manufacture structures using Cu/D composite materials. D particles were coated with a graded TiO_2-TiC interphase using a molten salt process to enhance its wettability with molten Cu. A dense Cu/coated-D composite was printed (96%) at an optimized energy density of 1200 J/mm^3. Strong bonding between the matrix and reinforcement was observed, leading to a highly thermally conductive composite (330 W/m.K). Furthermore, the quality of the coated-D remained unchanged after being exposed to the high laser power, thus making AM a suitable approach to manufacturing Cu/D composites.

INTRODUCTION

The fabrication of components with high thermal conductivity (TC), a low coefficient of thermal expansion (CTE), and intricate shapes is crucial for the development of highly efficient heat-exchanging components for microelectronic industries [1,2]. Creating a composite material consisting of two highly thermally conductive elements, such as copper (Cu) and diamond (D), may fulfill these unmet needs [3]. However, the lack of chemical affinity between Cu and D together with the difficulty of processing D-based materials into complex shape present significant challenges [4,5].

Extensive research has been devoted to achieving highly thermally conductive metal matrix composites (MMCs) by promoting interfacial bonding between Cu and D. Cu/D composites with a low CTE and a high TC were reported resulting from a synergic effect [6–8]. However, conventional processing methods (e.g., sintering and infiltration) impose several limitations when sophisticated geometries are required. The recent development of laser additive manufacturing (AM) has attracted attention due to the ability to fabricate sophisticated shapes of metal and alloy parts with properties similar to bulks [9–13]. Nevertheless, to our best knowledge, AM of Cu/D composites remains less explored.

In this letter, the feasibility of additive manufacture using Cu/D composites was investigated by laser engineering net shaping (LENS), as illustrated in **Figure 1 (c)**. The Cu/D composites were printed using a composite powder mixture of 95 vol.% Cu, and 5 vol.% D coated with a graded TiO_2-TiC layer. It was shown that an energy density of 1200 J/mm^3 led to the formation of dense Cu/coated-D composites (96%) with a strong bonding throughout the Ti-based interphase. Additionally, the printed composites with Ti-based interphase show a 10% enhancement of the TC compared to the same composite processed by conventional powder metallurgy.

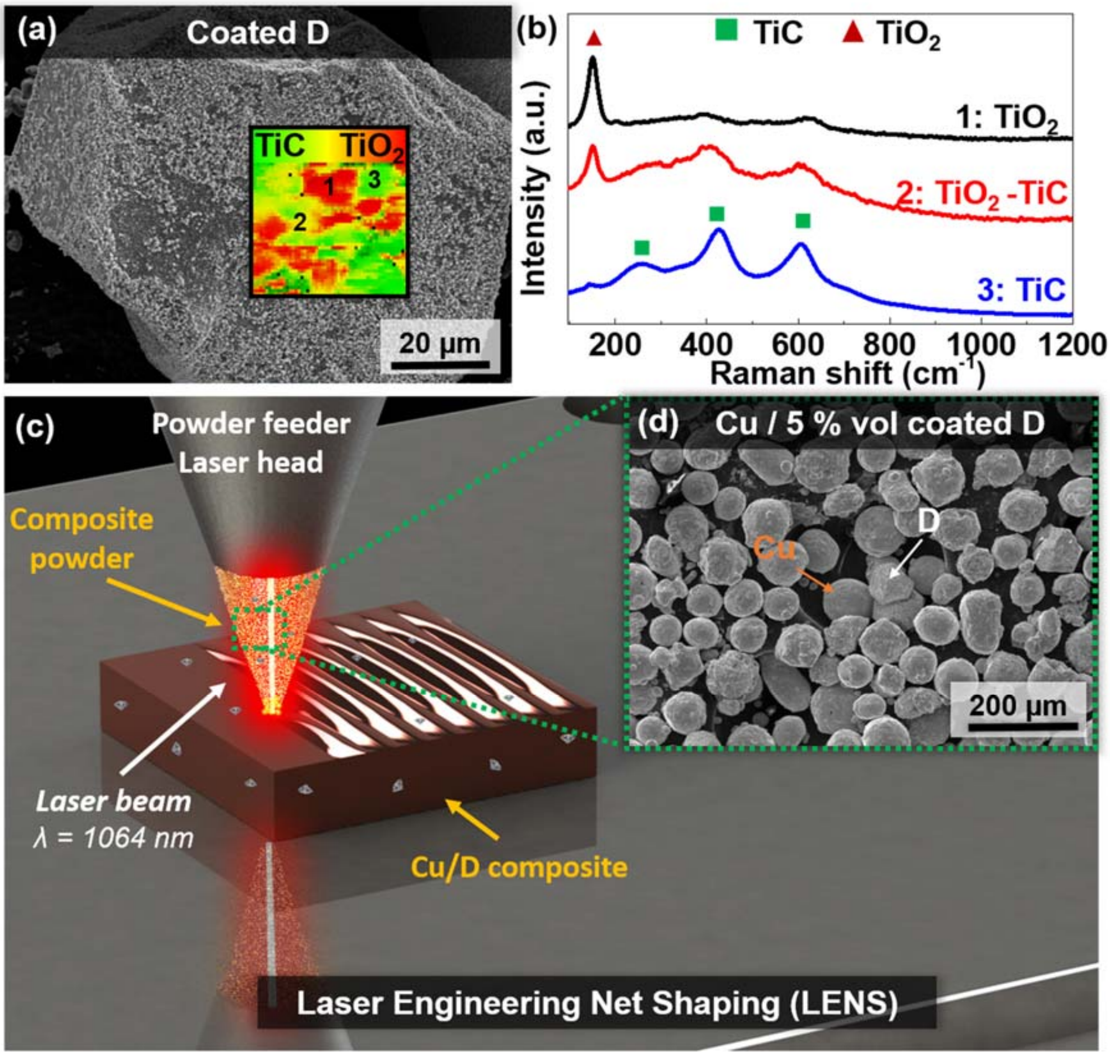

Figure 1. **(a)** SEM micrograph of a D particle coated with a TiO_2-TiC layer, with a Raman mapping in the insert; **(b)** Raman spectra of TiO_2, TiC, and a TiO_2-TiC mixture from the Raman mapping; **(c)** Schematic of the LENS process; and **(d)** SEM micrograph of the Cu/D powder mixture.

MATERIALS AND METHODS

Diamond powders with a mean diameter of 105 μm (Eastwind Diamond Abrasives) were coated with a graded TiO_2-TiC layer using a molten salt process (details are provided in the supplementary information (SI)). A 5 vol.% of coated D was mixed with spherical Cu powder with a mean diameter of 93 μm (99.5% US Research Nanomaterials, Inc.). AM was performed using an Optomec, Inc., LENS 3D Hybrid Machine Tool System. The laser power and scan speed were varied between 700 and 1000 W, 4.25 and 21.2 mm/s, and the layer thickness and hatch distance were kept constant to 0.2 and 0.3 mm respectively (details in the SI).

The crystalline phases and chemical structures of the coated D were analyzed both by X-ray diffraction (XRD, Bruker-AXS D8 DISCOVER Diffractometer, Cu Kα = 0.154 nm) and micro-Raman (inVia™, Renishaw). The volume percentage of D in the printed composites was estimated by image analyses using ImageJ. The density of the printed samples was measured using the Archimedes method (METTLER TOLEDO AT201). The microstructures of the parts printed were characterized using a scanning electron microscope (ESEM™, FEI Quanta™ 200 Environmental SEM) and a high-resolution transmission electron microscope (HRTEM, FEI Tecnai Osiris™, 200 kV). The TC was measured via the periodic photothermal radiometry method (details in the SI and elsewhere [14]).

RESULTS AND DISCUSSION

The realization of dense Cu/D composites with high TC requires the formation of strong interphase between the Cu and D because of their incompatibility [5,15]. Our previous study on titanium (Ti)-based coating on carbon fibers via a molten salt process has demonstrated an enhanced wettability of molten Cu on a graded TiO_2-TiC layer compared to a pure TiC layer. The same process has been applied on D particles [16]. The formation of a graded layer was confirmed by Raman spectroscopy mapping, as shown in **Figure 1 (a)** and **(b)**, where the yellow and red colors represent TiC and TiO_2, respectively, and by XRD of the coated D, as shown in **Figure S3** [17,18].

Coated D particles were then mixed with Cu powder (**Figure 1(d)**). The printing parameters were explored to form a dense Cu/D composite. It was observed that scan speeds between 8.7 and 21.7 mm/s and laser power levels between 700 and 1000 W, mainly resulted in parts with rough surfaces (**Figure 2 (a)** and **(d)**). The poor surface finish has arisen because the Cu powder was insufficiently melted which inhibits its ability to fuse completely[19]. Nevertheless, a narrow processing window was identified for obtaining parts with smooth surface finish: a scan speed of 12.7 mm/s and laser powers ranging from 900 to 925 W (**Figure 2 (b)** and **(d)**). At a low scan speed (4.3 mm/s) and high laser powers (800 to 1000 W), the printed parts exhibit a spherical shape, not a designed cubic shape (**Figure 2 (c)** and **(d)**). The deformation of the printed cube is due to the elevated temperature during the printing process.

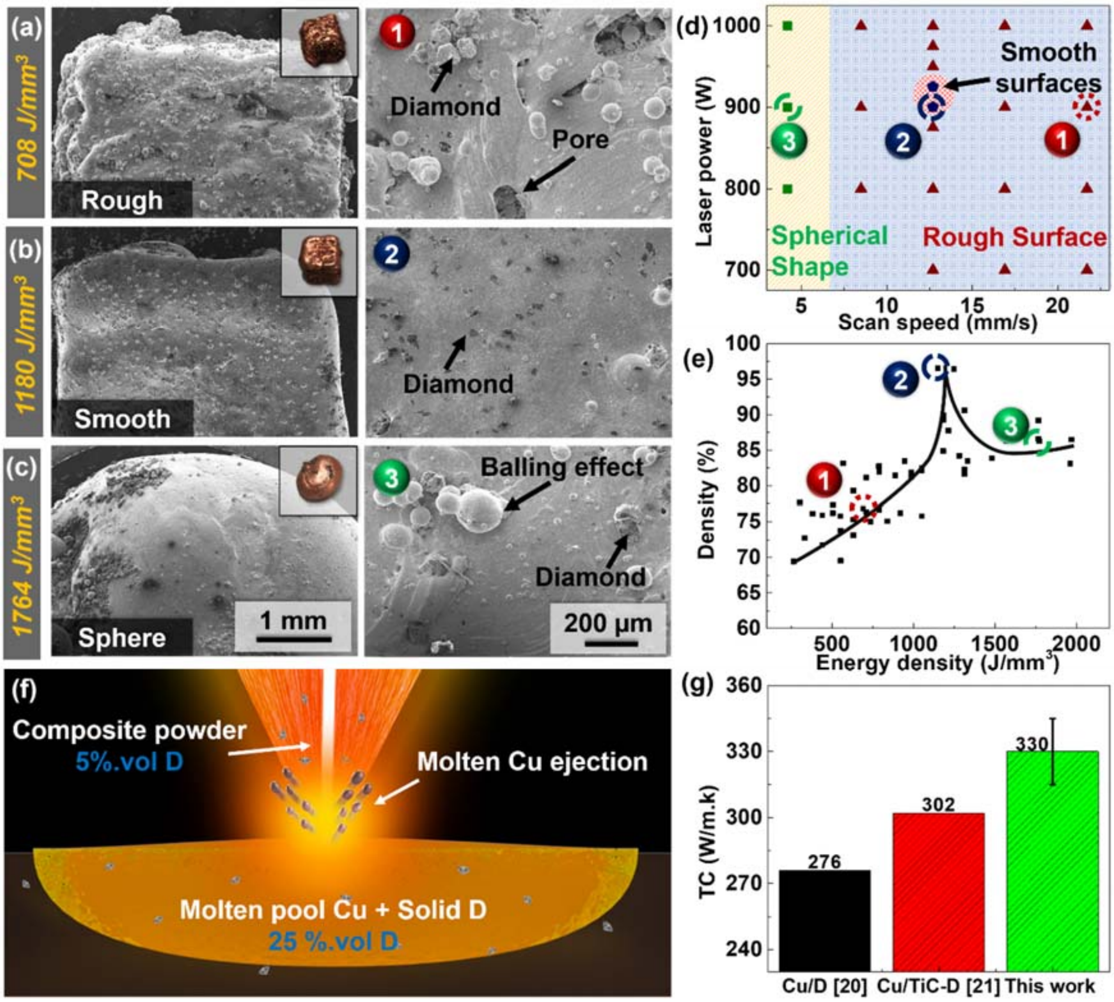

Figure 2. SEM micrographs of Cu/D composite surfaces printed at an energy density of **(a)** 708, **(b)** 1180, and **(c)** 1764 J/mm^3; **(d)** qualitative quality of Cu/D vs. printing parameters; **(e)** sample density vs. laser energy density; **(f)** illustration of particle ejection during LENS; and **(g)** thermal conductivities of Cu-D composites with no interphase [20], a TiC interphase [21], and a graded TiO_2-TiC interphase.

The diamond volume percentage in the Cu/coated-D composite printed was measured to be about 25 vol.%. compare to 5 vol.% in the powder feeding. A significant increase in the diamond volume percentage was found in the printed composites. One possible explanation is that during the lasermatter interaction, Cu particles were ejected or evaporated from the molten pool, leading to an increased concentration of coated-D in the final composites (**Figure 2 (f)**). **Figure 2 (e)** shows the relationship between the sample density and energy density [22]. It is noted that an energy density of about 1200 J/mm^3 yields a density of 96% with a TC of about 330 W/m.K. The TC of the Cu/TiO_2-TiC-D (330 W/mK) in this work is 10% and 20% higher than the TC reported for Cu/D (276 W/mK) [19] and Cu/TiC-D (302 W/mK) [20], respectively.

The interfacial bonding between the matrix and the reinforcement is the key to obtain dense and high TC composites. **Figure 3 (c)** shows a cross-sectional micrograph of the interface between Cu and D, where the coated-D was previously embedded in the Cu matrix (**Figure 3 (a)** and **(b))**. As shown in the SEM micrograph, an intimate contact between the Cu matrix and the coated-D particle was found, suggesting a strong connection. The HRTEM micrographs at the Cu-TiO_2 and TiO_2-TiC interfaces demonstrate a smooth transition between layers with no pores, confirming a strong bonding (**Figure 3 (d)** and **(e))**. Additionally, HRTEM of the Cu, TiO_2, and TiC layers in **Figure 3(f)–(h)** shows the crystalline structures of the (111) Cu, (101) TiO_2 and (111) TiC planes with an interlayer distance of 0.21, 0.35, and 0.25 nm, respectively [23,24].

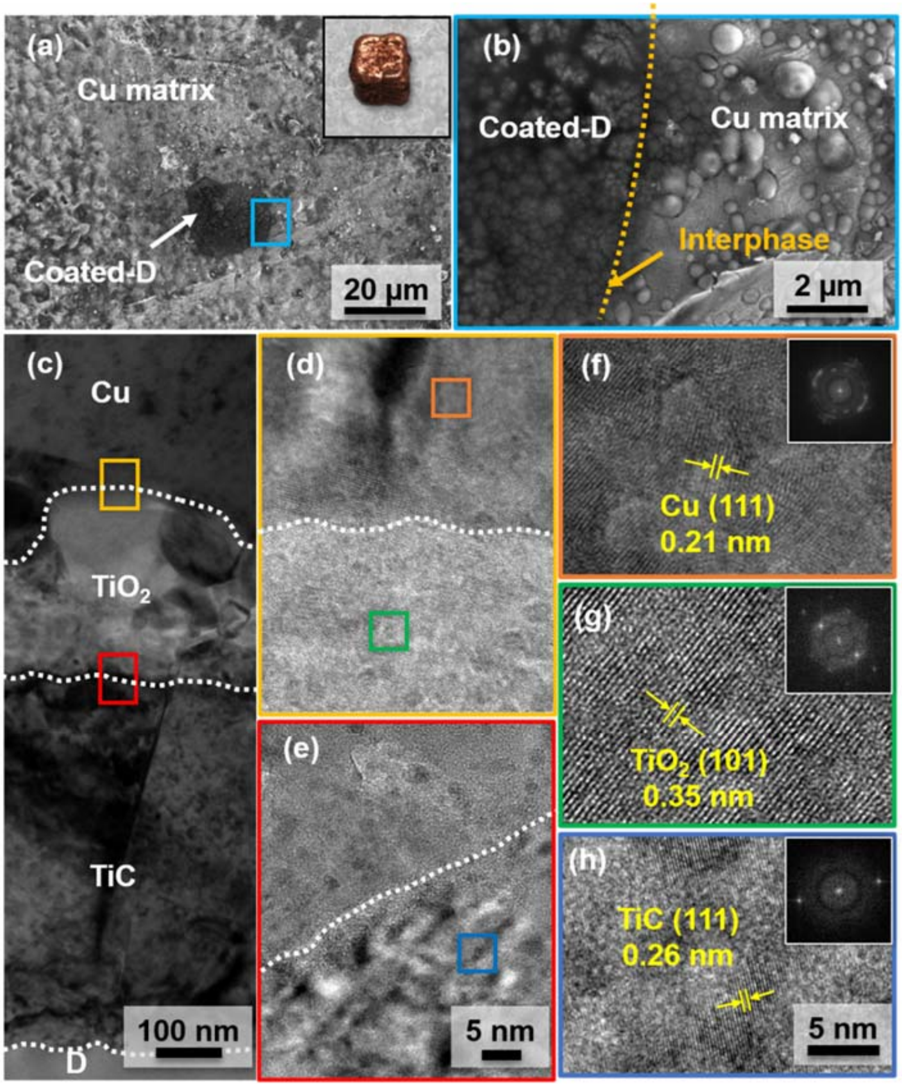

Figure 3. (a)–(b) SEM micrographs of the Cu/D surface. TEM micrographs of **(c)** cross-sectional view of Cu-(TiO_2-TiC)-D, **(d)** Cu/TiO_2 interface, and **(e)** TiO_2/TiC interface. **(f)–(h)** HRTEM micrographs of Cu, TiO_2, and TiC, respectively.

The D quality is a crucial point to study the feasibility to laser print 3D Cu/D composites due to the potential D graphitization during the printing process. The D quality was evaluated after being immersed in a salt bath (coating process) and exposed to a high-power laser (printing process) as shown in **Figure 4 (a) – (c)**. The as-received diamond powder showed a sharp peak around 1331.5

cm^{-1}, with a full width at half maximum (FWHM) of 1.9 cm^{-1}, confirming its high degree of crystallinity (**Figure 4 (d)** and **(e)**) [25,26]. Diamond particles were recollected and reevaluated after the salt coating process and the printing process. As shown in **Figure 4 (d)** and **(e)**, the processed diamond particles still exhibit a sharp diamond peak, suggesting no graphitization occurred during the high-temperature coating and printing processes. The diamond peak position and FWHM values retrieved from the Raman spectra show no obvious peak broadening, confirming the multi-step processing did not degrade the crystallinity of the diamond particles.

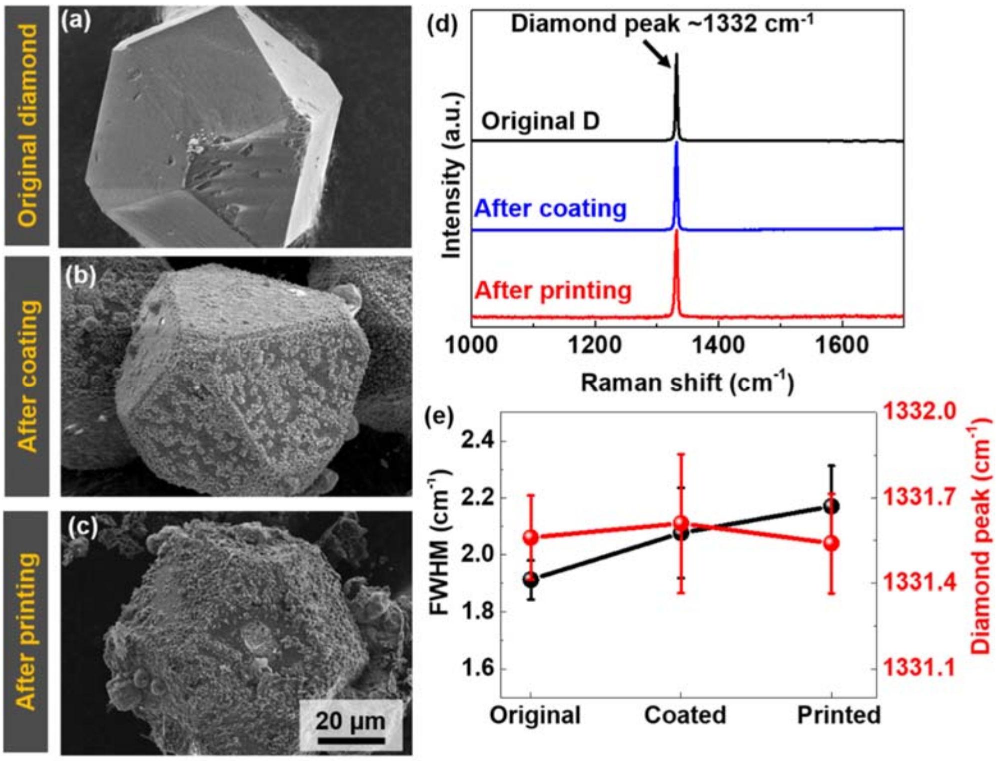

Figure 4. SEM micrographs of D particles at different stages of **(a)** as received, **(b)** after salt coating, and **(c)** after laser printing. **(d)** Raman spectra of an as-received D particle and D particles after salt coating and laser printing, and **(e)** FWHM and position of the diamond peaks measured from the D particles as-received, after salt coating, and after laser printing.

CONCLUSION

This work demonstrates the feasibility of additive manufacturing using Cu/D composites. An energy density of about 1200 J/mm^3 is necessary to make dense composites with smooth surfaces and high TC (330 W/m.K). The introduction of Ti-based coating on the diamond particles before printing enabled the formation of strong interphase between the matrix Cu and reinforcement D, facilitating the printing of dense Cu/D composites. In addition, the quality of the post-printing diamond was found to be close to the original one, making the process suitable for manufacturing high-TC materials.

AUTHOR INFORMATION

Corresponding Authors

*Jean-Francois Silvain: jean-francois.silvain@icmcb.cnrs.fr and Yong Feng Lu: ylu2@unl.edu

Author Contributions

All authors approved the final version.

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