In-situ Deposition of Diamond on Functionally Graded Copper Scaffold for Improved Thermal Conductivity and Mechanical Properties

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Abstract: A novel functionally graded structure of diamond was developed with significantly enhanced thermal conductivity and compressive strength, based on synergistic effects combining chemical vapor deposition (CVD) and selective laser melting (SLM). *In-situ* diamond growth was achieved without conventionally complex pretreatment steps thanks to the high surface roughness of as-printed graded copper scaffold. The continuous diamond film coated on graded copper scaffold forms a monolith with interconnected network, acting as an effective layer for heat conduction with an exceptional increase (459 %) in thermal conductivity compared with copper counterpart. The functionally graded structure also demonstrates a progressive mechanical response to loading compared with the uniform structure. This work opens a new avenue for realizing three-dimensional diamond structure and proves its multifunctionalities, especially for high-power electronics applications.

Keywords: *Additive manufacturing; Carbon materials; Functionality; Chemical vapour deposition; Porous materials; Thermal properties*

1. Introduction

With the increasing trend of miniaturization in portable electronic devices, it is of great necessity to efficiently dissipate the heat generated to ensure their high reliability and durability. Every 10 °C increase in the chip temperature could lead to an increased risk of device failure by an order of magnitude [1]. Diamond has attracted significant attention to applications in such devices due to its extremely high thermal conductivity (2200 $W \cdot m^{-1}K^{-1}$) [2] and hardness (100 GPa) [3]. Impact protection is another key design criterion considering the mobility of these portable electronic devices. Porous metals (e.g., copper) exhibit high specific surface area and lightweight. Copper porous scaffold with thermal conductivity (400 $W \cdot m^{-1}K^{-1}$), good machinability and energy absorption capability, could function as impact protection component. The reinforced diamond film on copper scaffold to form a three-dimensional (3D) diamond network monolith is therefore highly promising for electronic devices where effective pathway for heat conduction and impact protection are greatly required [4-5]. Although most of the porous metal templates prepared by foaming or de-alloy are restricted by the challenges of porosity control, selective laser melting (SLM) possesses great advantages in fabricating complex geometrical structures (macro- to micro-scales). The high surface roughness from unmolten powders of SLM part could also improve the adhesion of diamond layer deposition. So far, few studies devoted in constructing complex diamond structures using SLM and CVD for such applications.

Herein, we creatively leverage up the as-printed SLM copper scaffold template for *in-situ* diamond growth to form a functionally graded diamond/copper (dCu) composite. Microstructures, thermal and mechanical properties are investigated and explored.

2. Experimental

Copper (purity >99.9 %) with rod gradient from the bottom to the top (getting thicker from 0.15 to 0.70 mm) were fabricated at the optimized parameters [6], using a SISMA MYSINT100 SLM system. Control samples were polished by abrasive flow (smks-6290) with loading of 90 kg for 12 minutes. Diamond growth on the SLM copper was performed under the CH_4 and H_2 with volume ratio of 0.5%, filament temperature of ~2000 °C and substrate temperature of ~800 °C. The deposition process lasted for 5 hours with the growth rate of 0.6 μm/h (Beijing Technol-HF650).

The microstructure was characterized by a scanning electron microscope with an energy dispersive spectroscopy (Hitachi-Su8010). Structural information of the diamond was verified by Raman spectroscopy (SENTERRA, Bruker) at excitation laser of 532 nm wavelength, with power of 6.25 mW and resolution of 1.5 cm^{-1}. Thermal conductivity was measured by hot disk (Hot Disk-TPS2500S) from thicker to thinner end and infrared images were obtained by infrared thermal camera (FLIR T540). All sample surfaces were sprayed thin graphite to avoid effect of different emissivity. Compressive tests were conducted parallel to the gradient direction by a universal tester (SANS-CMT5105, according to ASTM D695-15) with the compression rate of 1 $mm \cdot min^{-1}$. Energy absorption was calculated according to ISO 13314:2011.

3. Results and Discussion

Fine graded copper scaffolds were successfully fabricated by SLM without broken struts using optimized processing parameters. The adhered unmolten Cu particles on the surface, a major drawback of SLM techniques, aggravated the surface roughness **(Fig. 1 b-1, b-3)**. To investigate the effect of roughness on diamond growth, surfaces of some samples were polished **(Fig. 1 b-2, b-4).** Diamond was then *in-situ* grown on the as-printed and polished copper substrates via CVD. A continuous and dense diamond interconnected network successfully grew with well-faceted grains on as-printed template. The diamond crystalline grains (ranging from 1 to 3 μm) were close to thermal equilibrium shape (i.e., octahedron or truncated octahedron) with compact distribution **(Fig. 1e)**. Without traditional seeding or scratching, the 3D interconnected diamond network was successfully fabricated because the enhanced surface roughness from the unmolten powder benefited nucleation. Similar results were obtained by J.C. Arnault [7] and found that diamond tended to nucleate at the grooves or protrusions. On the other hand, the polished surface of copper template hindered the nucleation and deposition of diamond due to poor adhesion **(Fig. 1 h-i)**. The Raman spectra of all the samples revealed typical diamond peaks around 1336 cm^{-1}, slightly shifting to higher frequency compared with the stress-free diamond peak at 1332cm^{-1}, which was attributed to high compressive stress [8] (**Fig. 1c**). The sharp diamond peak related to well-development of diamond crystalline, while the G peak (1580 cm^{-1}) originates from amorphous carbon situated at the grain boundaries of polycrystalline diamond. The strong Raman signal from as-printed dCu confirms high density of diamond growth, in contrast to the polished sample with rather weak signals. This agreed with the SEM observations.

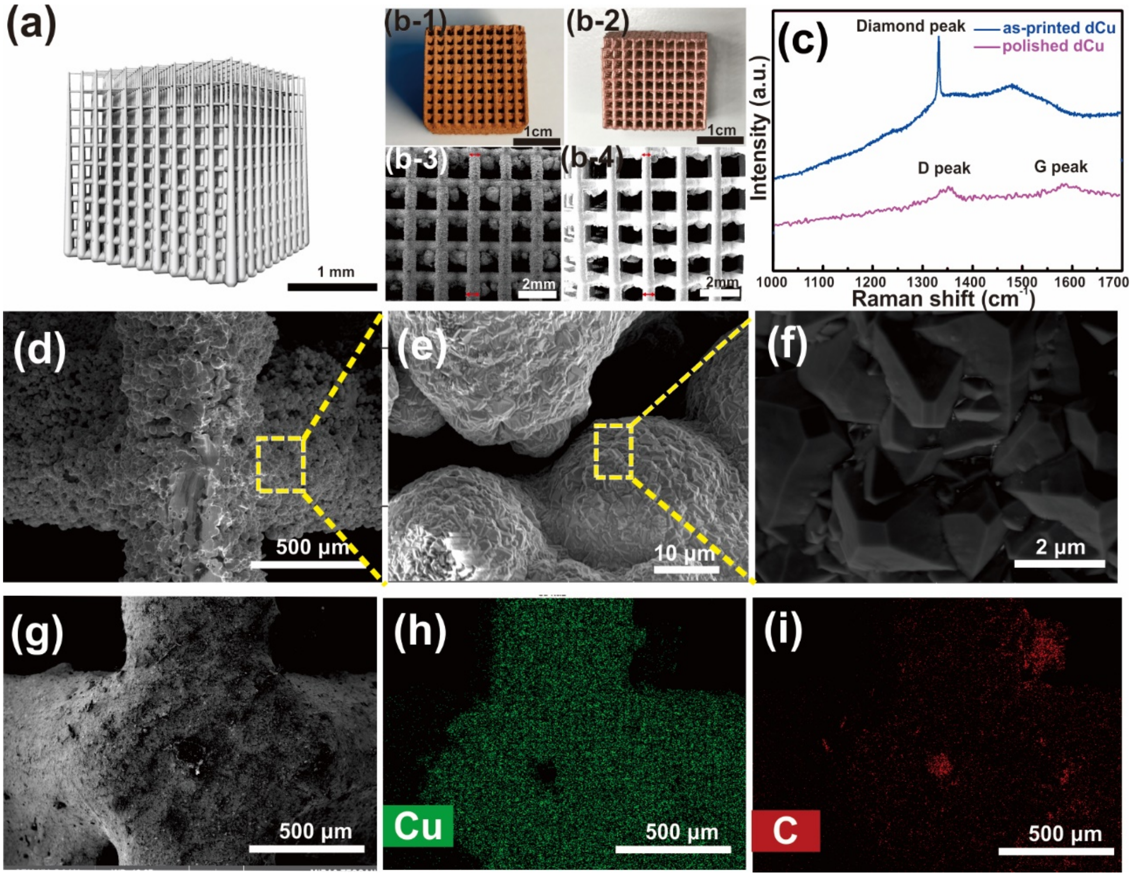

Fig. 1 (a) CAD model of graded Cu scaffold; Optical and SEM images of (b-1, 3) as-printed and (b-2, 4) polished samples; (c) Raman spectroscopy of diamond on different Cu scaffolds; SEM images of (d-f) as-printed and (g) polished Cu after *in-situ* growth of diamond, with (h-i) element mapping.

The average temperatures of the top and side surfaces were recorded **(Fig. 2a-c)** to measure the heat transfer of graded structures. The graded dCu exhibited quicker heat transfer than the uncoated graded Cu (**Fig. 2d)**. At contact time 500 s, the coated and uncoated graded dCu reached 42.3 °C and 36.8 °C, respectively. Excellent thermal conductivity was achieved in all dCu specimens (**Fig. 2e**). The as-printed (unpolished) graded dCu shows a value of thermal conductivity 10.91 $W \cdot m^{-1}K^{-1}$, 459 % higher than that of the primitive Cu (1.95 $W \cdot m^{-1}K^{-1}$). The high thermal conductivity of graded dCu further confirmed a higher loading of diamond on Cu substrate (in line with SEM result). With the diamond growing on the polished Cu scaffold, the thermal conductivity was only 6.50 $W \cdot m^{-1}K^{-1}$, due to a less effective deposition on its smooth surface. The thermal conductivity of the graded dCu was the highest among the reported metal-based porous structures [4, 9-10].

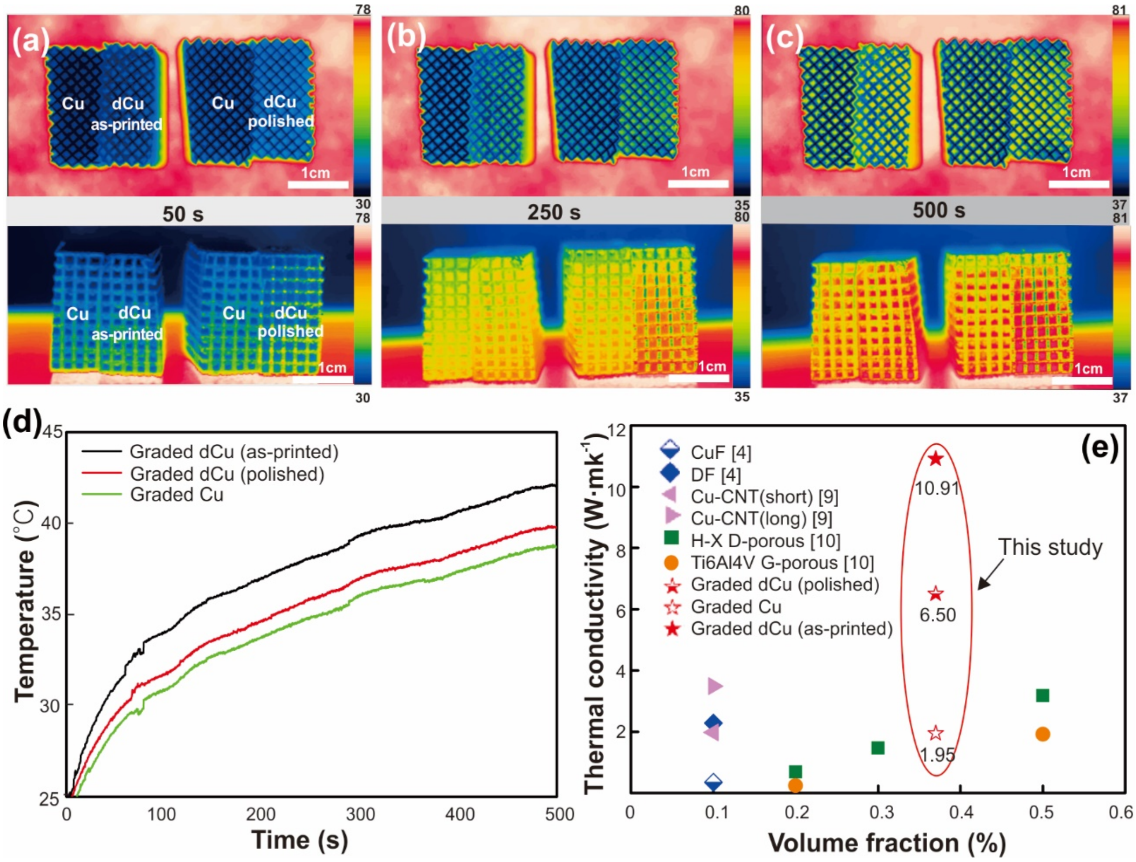

Fig. 2 (a)-(c) Infrared images of graded Cu and dCu with top (above) and side view (below) at different time; (d) Variations of average surface temperatures (top view) with heating time; (e) Comparison of thermal conductivities.

Outstanding mechanical property is necessary to resist external impacts in the practical applications. The compressive stress-strain curves are shown in **Fig 3a**. After reaching a certain stress value, the struts crushed to release the stress. This periodic yielding and crushing observation were due to the layer-by-layer collapses instead of abrupt shear failure of uniform samples [11]. As the strut diameter increased during loading, the stress-strain curves comprised linear rising (special feature of graded structure), and finally the graded Cu reached a compressive strength of 78 MPa before densification. Similar deformation was also observed on the graded dCu, indicating limited effects of deposited diamond layer on the mechanical behavior of the porous structure. Although the graded dCu presented a slightly lower modulus and compressive strength (attributed to partial embrittlement of Cu resulted from the high-temperature and hydrogen-rich environment during CVD process) compared with the graded Cu, the compressive strength obtained was still much higher than those of other Cu porous structures reported in [11-14] (**Fig. 3b**).

The absorbed energy efficiency (η) up to a given strain divided by that stress was calculated and the ε_D was determined as the peak value of strain before densification [12] **(Fig. 3c). Fig. 3d** shows the cumulative energy absorption per unit volume as a function of strain. Both graded Cu and dCu exhibited the superior energy absorption of 117.63 and 109.87 $MJ\cdot m^{-3}$, respectively. The increasingly higher energy absorption made this structure particularly appealing to impact protection, as the progressive mechanical response to external loading.

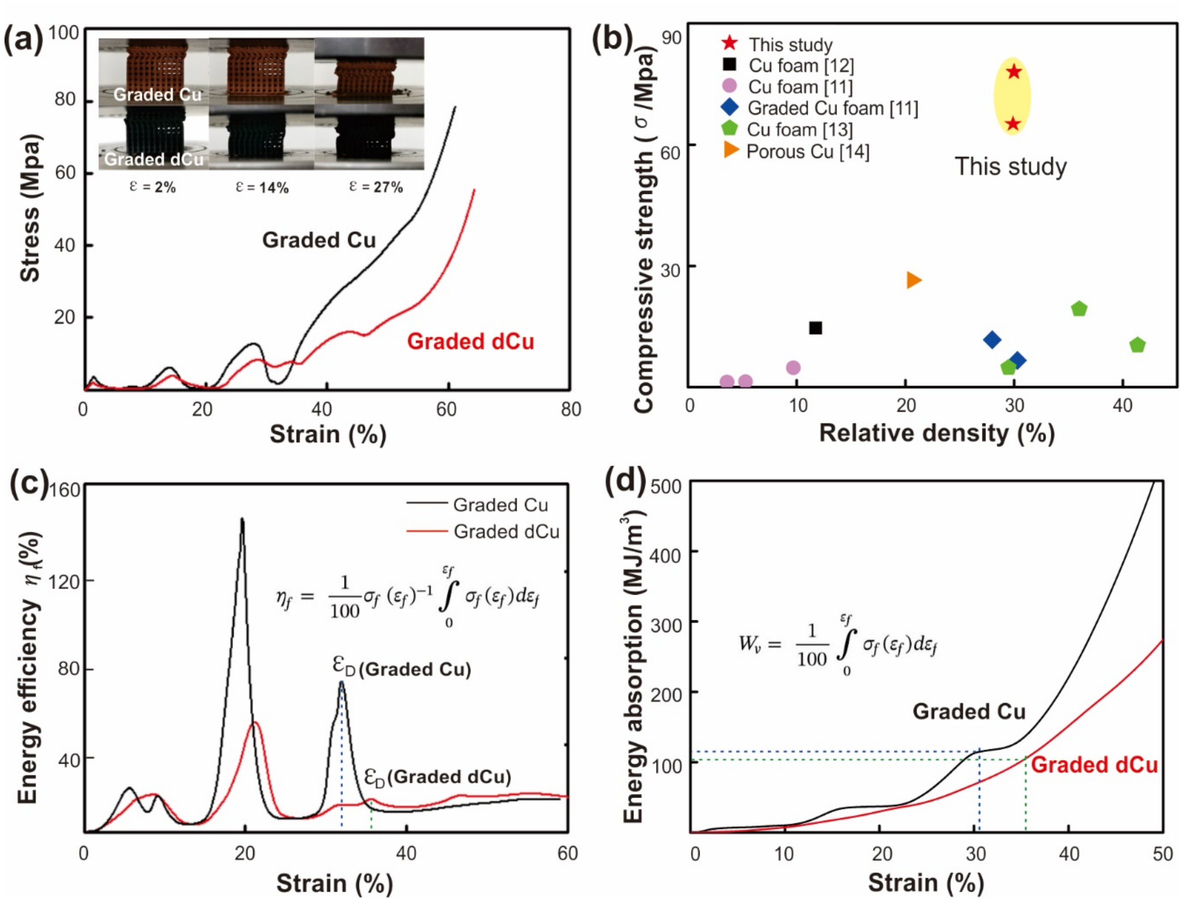

Fig. 3 (a) Strain–stress curves of as-printed graded Cu and dCu; (b) Comparisons of compressive strength versus relative density [11-14]; (c) Energy efficiency and (d) energy absorption of graded Cu and dCu.

4. Conclusions

A novel strategy to fabricate functionally graded dCu composite with porous scaffold has been successfully developed via a simple combination of SLM and CVD processes. Synergistic effect between relatively coarse Cu surface and *in-situ* CVD growth has been explored for an enhanced diamond deposition. The thermal conductivity of the graded dCu composite is significantly enhanced (459 %), while the graded porosity in Cu template also successfully eliminates the sudden failures with a compressive strength of 78 MPa.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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