



# Physical properties and formation mechanism of carbon nanotubes–ultrafine nanocrystals reinforced laser 3D print microlaminates

Jianing Li<sup>a,c,\*</sup>, Kegao Liu<sup>a</sup>, Werner Craeghs<sup>b</sup>, Yuanbin Zhang<sup>a</sup>, Xingdong Yuan<sup>a</sup>, Peng Liu<sup>a</sup>, Guocheng Ren<sup>a</sup>

<sup>a</sup> School of Materials Science and Engineering, Shandong Jianzhu University, Jinan 250101, PR China

<sup>b</sup> Fraunhofer Institute for Laser Technology ILT/Chair for Laser Technology LLT, RWTH Aachen, Steinbachstraße 15, D-52074 Aachen, Germany

<sup>c</sup> Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, PR China

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## ABSTRACT

Rapid prototyping based on laser alloying by the pre-placed mixed powders has been used to produce the nanocrystals reinforced three-dimensional microlaminates in this study. Such microlaminates were fabricated on a TA7 titanium alloy by laser rapid prototyping (LRP) of the Stellite SF12-CNTs (carbon nanotubes)–Cu/Stellite SF12-CNTs laminate pre-placed powders. Through experimental work, it was confirmed that when laser power was not high enough, a portion of CNTs can be retained in bottom-layer of such LRP microlaminates; the Cu addition was able to refine the microstructures, also favoring the formations of ultrafine nanocrystals (UN). When laser power increased to a certain value, the boundary of such microlaminates became indistinguishable, and a great number of the coarse precipitates were also produced.

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## 1. Introduction

CNTs have recently emerged as materials with exceptional properties exceeding those of any conventional material [1]. LRP (laser 3D print) is a technology which can directly fabricate three-dimensional solid models from computer aided design (CAD) data [2]. Nanocrystalline-amorphous composites have become very popular because of their high toughness and stiffness along with their superior hardness [3]. The microlaminates comprised of alternating layers of the intermetallics, ductile metal and ceramics are the particularly attractive composite architectures. One major advantage of the microlaminates is the availability of attractive manufacturing routes based on Additive Manufacturing (AM) technique [4].

Laser technique has been used to modify the surface of these alloys by melting alloying materials, while less work has been carried out on the LRP CNTs reinforced microlaminates. Through experimental work, it was confirmed that when the laser power was not high enough, a portion of CNTs can be retained in bottom-layer of such microlaminates; the Cu addition refined the

microstructures, also favoring formations of UN. In this study, the physical properties, microstructures and formation mechanism of the CNTs reinforced LRP microlaminates on a TA7 titanium alloy were discussed. This research provides the essential experimental and theoretical basis to promote the applications of the laser 3D print nano technologies in the modern industry.

## 2. Experiments

The TA7 titanium alloy samples,  $10 \times 10 \times 10 \text{ mm}^3$  in size, were abraded with SiC grit paper prior to the operation. Chemical compositions (wt%) of TA7 alloy: 5.00Al, 2.50Sn, 0.5Fe, 0.08C, 0.05N, 0.015H, 0.20 and balance Ti. Alloy powders of Stellite SF12 (20–150  $\mu\text{m}$ ,  $\geq 99.5\%$  purity), single-walled CNTs with a diameter of 1.2–2.5 nm, and Cu (3–100  $\mu\text{m}$ ,  $\geq 98.5\%$  purity) were used for LRP. A LRP technique was conducted on the YAG (HL 3006D) laser materials processing system equipped with four-axis computer numerical controlled laser materials processing machine under a vacuum environment, to melt the samples' surfaces at the same time.

The powders of CNTs ( $\geq 99.5\%$  purity), Stellite SF12 ( $\geq 99.5\%$  purity, 50–150  $\mu\text{m}$ ), and Cu ( $\geq 99.5\%$  purity, 20–100  $\mu\text{m}$ ) were used for LRP, chemical compositions (wt%) of Stellite SF12: 1.00C, 19.00Cr, 2.80Si, 9.00W, 3.00Fe, 13.00Ni, and balance Co. Alloying powders (wt%): 97Stellite SF12-3CNTs mixed powders were pre-

\* Corresponding authors at: School of Materials Science and Engineering, Shandong Jianzhu University, Jinan 250101, PR China.  
Tel.: +86 15865289824; fax: +86 531 88393538.

E-mail address: [jn2369@163.com](mailto:jn2369@163.com) (J. Li).

placed on a TA7 alloy by water-glass ( $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ ) to form a bottom-layer; 94Stellite SF12-3CNTs-3Cu mixed powders were pre-placed on such bottom-layer to form an upper-layer, forming

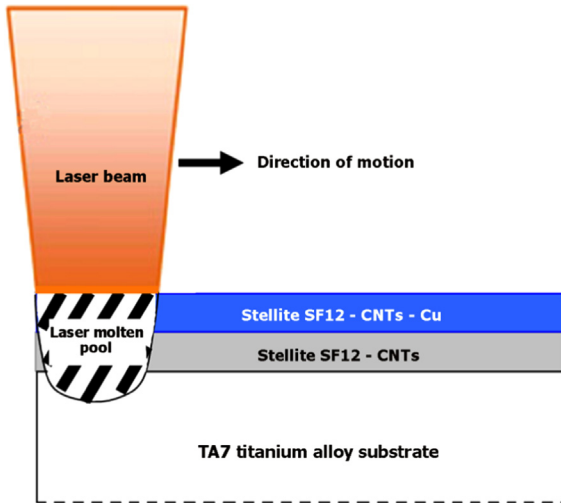


Fig. 1. Schematic diagram of the cross section of the LRP process.

the pre-placed laminates. Then such laminates were treated by a LRP process to produce the laser 3D print microlaminates. Process parameters of LRP: laser power  $P=1-0.72$  kW, scanning velocity  $V=7-10$  mm/s, laser beam diameter  $D=4.5$  mm. An overlap of 35% between successive tracks was selected. Cross-section of the whole LRP process is shown in Fig. 1 as follows.

A HV-1000 microsclerometer was used to test the microhardness distribution of such LRP microlaminates; microstructural morphologies of such microlaminates were analyzed by means of a LEO 1525 scanning electron microscope (SEM) and a Titan 80-300 High resolution transmission electron microscope (HRTEM); phase constitution was determined by a D/MAX-RC X-ray diffraction (XRD) equipment.

### 3. Results and analysis

As shown in Fig. 2a, the microlaminates were obtained after a LRP process with a metallurgical combination to a TA7 alloy substrate; a great number of unmelted CNTs were produced in bottom-layer attached to the TiC block-shape precipitates (see Fig. 2b). The fact that due to a high temperature of laser beam, lots of CNTs in bottom-layer were melted completely, delivering C to molten pool. Then, C reacted with Ti, forming TiC.

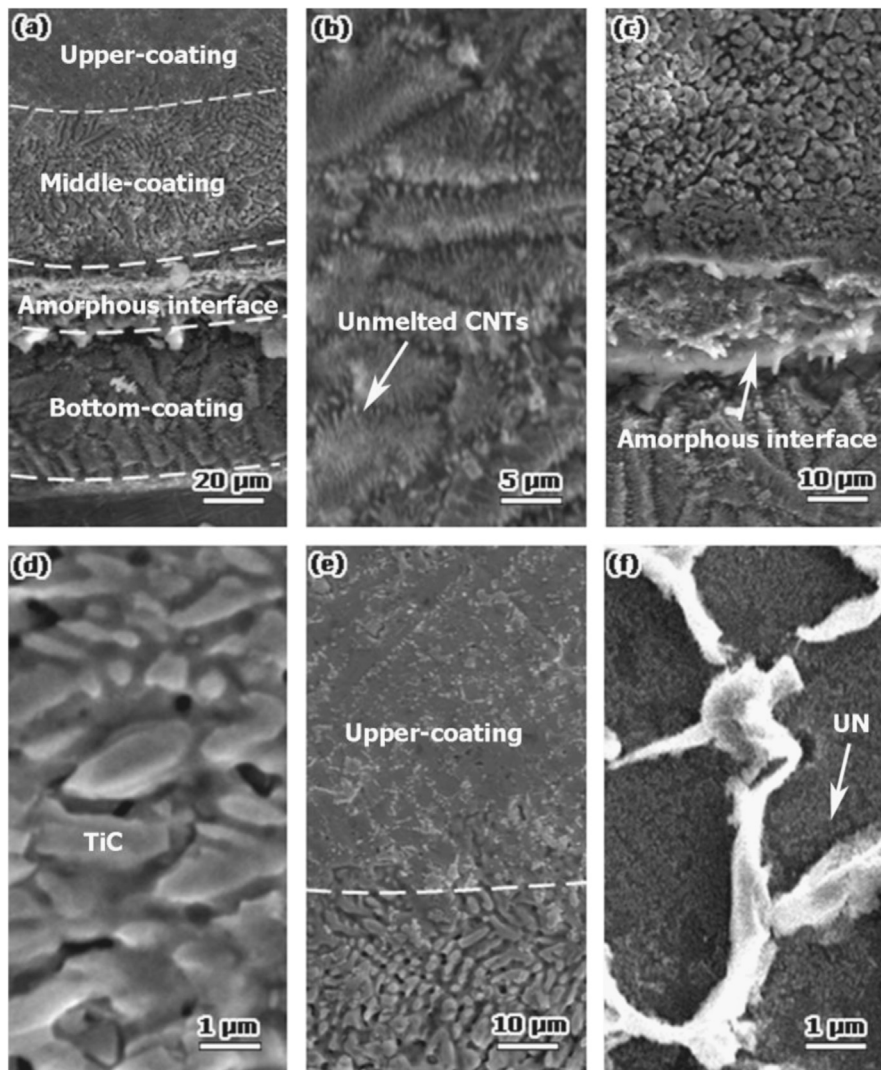


Fig. 2. SEM images of the microlaminates (720 W): (a) overview cross-section, (b) TiC and CNTs, (c) an amorphous interface, (d) TiC block-shape precipitates, (e) upper-layer, and (f) UN.

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