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Fabrication of Carbon Nanotube - Chromium Carbide Composite Through Laser Sintering

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Abstract Ceramics often have high hardness and strength, and good wear and corrosion resistance, and hence have many important applications, which, however, are often limited by their poor fracture toughness. Carbon nanotubes (CNTs) may enhance ceramic fracture toughness, but hot pressing (which is one typical approach of fabricating CNT-ceramic composites) is difficult to apply for applications that require localized heat input, such as fabricating composites as surface coatings. Laser beam may realize localized material sintering with little thermal effect on the surrounding regions. However, for the typical ceramics for hard coating applications (as listed in Ref.[1]), previous work on laser sintering of CNT-ceramic composites with mechanical property characterizations has been very limited. In this paper, research work has been reported on the fabrication and characterization of CNT-ceramic composites through laser sintering of mixtures of CNTs and chromium carbide powders. Under the studied conditions, it has been found that laser-sintered composites have a much higher hardness than that for plasma-sprayed composites reported in the literature. It has also been found that the composites obtained by laser sintering of CNTs and chromium

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carbide powder mixtures have a fracture toughness that is ~23 % higher than the material obtained by laser sintering of chromium carbide powders without CNTs.

Keywords Laser sintering · Ceramic composite · Carbon nanotube

Introduction

Ceramic materials often have high strength and hardness, and good resistance to wear and corrosion, and hence have many important applications, such as wear or corrosion-resistant surface coatings [1–4]. However, on the other hand ceramics are often brittle and have low fracture toughness, which may negatively affect many related applications [3].

Carbon nanotubes (CNTs) have many unique properties, and hence lots of research work has been performed on CNT-reinforced composite materials, including CNT-ceramic composites (although the reported work in this area is much less than those on CNT-reinforced polymer composites) [3]. It has been found that CNT-reinforced ceramic composites may have enhanced fracture toughness [3]. One of the major fabrication technologies for CNT-ceramic composites is hot pressing [3, 5]. However, this technology is difficult to apply for many applications that require localized heat input, such as fabricating CNT-ceramic composites as surface coatings with no obvious thermal effects on or damages to the substrate.

A laser beam is a unique energy source, which can deliver high power densities to a localized area with little thermal effect on the surrounding regions. This is desirable for many critical applications, such as fabricating CNT-ceramic composites as surface coatings. Tables 1 to 3 of Ref. [1] list many typical ceramics for hard coating applications (e.g., chromium carbide). However, for the listed ceramics, the previous work on laser sintering of CNT-ceramic composites with mechanical property characterizations has been very limited.

This paper reports the work on laser sintering and characterizations of CNT-chromium carbide composites, which has been rarely reported in the literature. CNT-chromium carbide ceramic composites are fabricated through laser sintering of CNT and chromium carbide powder mixtures. The fabricated composites are characterized through scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD). The mechanical properties (such as hardness and fracture toughness) have also been measured. It has been found that under the studied conditions, laser sintering can produce CNT-chromium carbide composites with good hardness (which is much higher than the hardness of plasma-sprayed composites reported in [4]), and the addition of CNTs has obviously enhanced the material indentation fracture toughness.

Experiments

Figure 1 shows the experimental setup. The laser used in the experiment is the SPI redPOWER R4 RS fiber laser, which has a wavelength of ~1070 nm (http://www.spilasers.com/Products/redPOWER_R4.aspx?) and is operated in the continuous mode at the power of ~120 W in this work. The laser beam has a diameter of ~6 mm. A laser

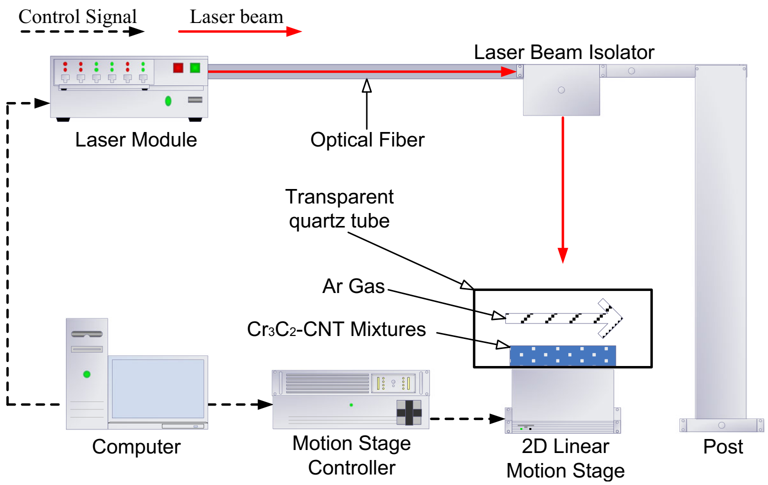

Fig. 1 Schematic diagram of the experimental setup (some components are not shown)

beam isolator is used to block back-reflected laser light. Mixtures of CNT and chromium carbide (Cr_3C_2) powders are placed on a metal plate (not drawn in the figure) inside a transparent quartz tube, which is positioned on a two-dimensional (2D) motorized linear motion stage that slowly moves the sample during laser sintering. The laser and the motion stage are controlled using a computer. The metal plate inside the tube is only for the purpose of supporting the sample being sintered, and it is not the goal of the work in this paper to coat CNT-ceramic composites onto a metal substrate, which may be a good topic in the future.

Argon gas is flowed through the quartz tube during the sintering process, which is to effectively remove air in the tube to generate a high-purity argon environment to avoid or minimize possible chemical reactions of the sample with the ambient environment. The CNTs used in the experiments are multi-wall carbon nanotubes with a purity higher than 99.9 % (from NanoLab Inc., Waltham, MA, USA; outside diameter: typically around 30±15 nm, and length: typically around 5 to 20 μm). The chromium carbide powders have typical sizes of a few microns. The mixtures of CNTs and chromium carbide powders are obtained through the following approach: CNTs are dispersed and sonicated in distilled water to create a stable suspension with an aid of surfactant. Next, Cr_3C_2 powders are added to the created suspension and further mixed through a high shear mixer. The filtration of the solution through a filter paper yields the mixtures of Cr_3C_2 powders and CNTs. The mixtures obtained are dried in a vacuum oven in order to remove water and the surfactant.

Laser-sintered samples are characterized through SEM (Zeiss Ultra-55 FEG SEM), X-ray diffraction (Bruker D2 Phaser with the LynxEye detector), and a Raman system that has a confocal Raman spectrometer (Voyage™, B&W Tek) and an Olympus BX51 microscope [6, 7]. For the Raman spectrometer, the excitation laser has a wavelength of 532 nm, and is focused using a 50× objective lens (LMPLFLN 50×, NA=0.5) [6, 7].

The hardness of sintered samples has been measured using a Vickers hardness tester. The Young's modulus of the sintered samples is measured using a Micro materials nano indentation system, which is equipped with a diamond indenter in the pyramid shape. The maximum indentation load selected for the measurements is 200mN. For each measured laser-sintered sample, typically around 20 measurements have been performed over multiple areas. Utilizing the measured hardness and Young's modulus, the indentation fracture toughness of sintered samples has been determined based on the crack lengths induced by a Vickers hardness indenter on the samples [3, 8].

Results and Discussions

One important question in fabricating CNT-ceramic composites through laser sintering is whether or not CNTs can survive the high temperature induced during the laser sintering process. Figure 2 shows SEM images for fractured cross sections of composite samples produced by laser sintering of CNTs and chromium carbide powders. The images show that after laser sintering, CNTs can still be clearly observed. Also, the CNTs shown in the image appear to be encapsulated by and bonded with the matrix material (a good topic for the future is to study the nature of the bonding). In the un-sintered samples, CNTs and chromium carbide powders are not bonded with each other. Hence, the bonding is obviously formed due to the laser sintering process. It may be good topic in the future to study how the matrix material encapsulates CNTs, which is expected to be due to the matrix material melting/re-solidification and/or mass diffusion, etc.

Figure 2 shows that CNTs still exist after the laser sintering process, and the next natural question is whether or not the quality of CNTs in the samples has been significantly changed by laser sintering. Figure 3 shows the Raman spectrum of an un-sintered mixture sample of CNTs and chromium carbide powders and the Raman spectrum of a laser-sintered composite sample. For the un-sintered sample, the spectrum has a clear G-peak, which is a characteristic Raman spectrum peak for CNTs [9–12]. The G peak still exists for the laser-sintered sample. In addition, it can be seen that compared with the un-sintered sample, the G over D intensity ratio for the sintered sample is much higher. Because the D-band intensity is associated with the structural defects in CNTs [9], the increase of the G over D ratio suggests that the CNT quality

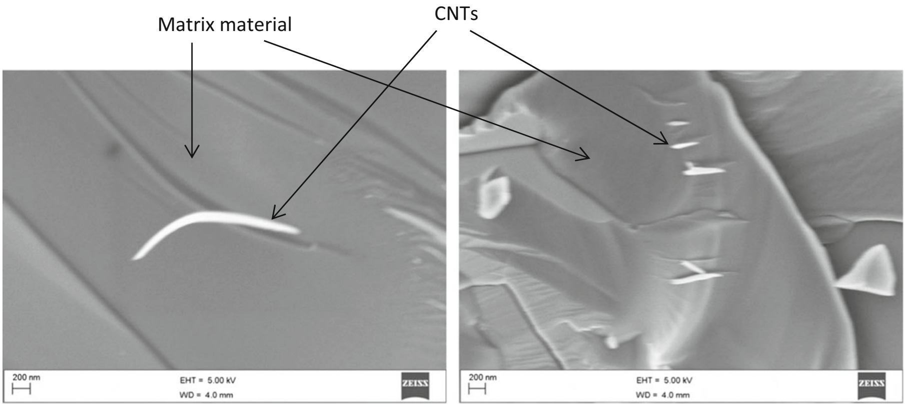

Fig. 2 SEM images of fractured cross sections of composite samples produced by laser sintering of chromium carbide powers and CNTs (0.5 wt.%)

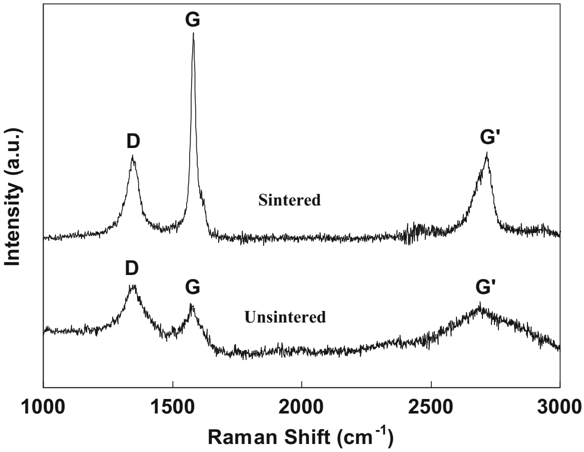

Fig. 3 Raman spectrum for an un-sintered mixture sample of CNTs (0.5 wt.%) and chromium carbide powders (*lower*), and for a laser-sintered composite sample (*upper*) (each spectrum clearly shows the G, D, and G' peaks [9–12])

has actually been enhanced by the laser sintering process. The exact underlying mechanism requires further work to completely understand.

In summary, Figs. 2 and 3 show that CNTs still exist after laser sintering process, and the CNTs in the laser-sintered composite have an enhanced quality with less defects. The next natural question will be whether or not there are significant phase differences between the chromium carbide in the sintered composites and the chromium carbide in the mixtures before laser sintering. Therefore, XRD measurements have been performed.

Figure 4 shows the x-ray diffraction (XRD) spectrum for an un-sintered mixture sample of CNTs and chromium carbide powders, and the XRD spectrum for a laser-sintered CNT-chromium carbide composite sample. XRD spectrum can provide useful information about material phase and crystalline structures [4, 12]. Due to the small fraction of CNTs in the un-sintered and sintered samples, XRD may not provide very clear information about the CNTs [12]. However, the spectrum can still provide very valuable information about chromium carbide. In Figure 4, the comparison of the spectrum peaks for the sintered sample and the peaks for the un-sintered sample suggests that the XRD measurement does not show significant phase differences between the chromium carbide in the sintered composite and the chromium carbide in the mixtures before laser sintering.

Figure 5 shows the measured hardness for composite samples obtained by laser sintering of mixtures of CNTs and chromium carbide powders, and the measured hardness for samples obtained by laser sintering of chromium carbide powders without CNTs. As a comparison, the hardness value for the plasma sprayed CNT-chromium carbide composite taken from [4] has also been shown. It can be seen that the hardness of laser-sintered samples with and without CNTs is very close. In other words, the addition of CNTs has not obviously changed the hardness of the sintered material under the studied conditions. However, the figure shows that the hardness value of laser-sintered samples is

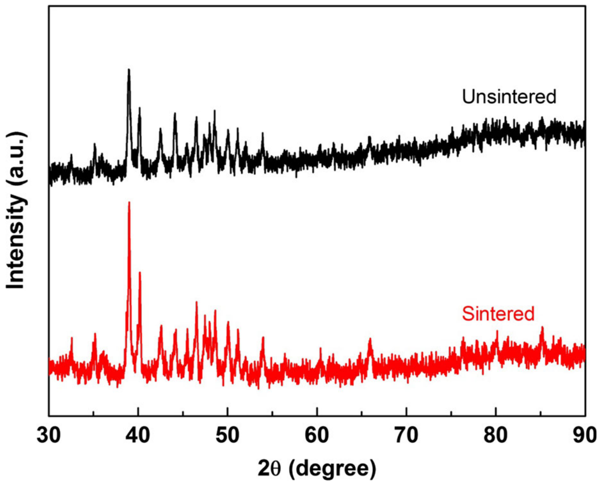

Fig. 4 XRD spectrum for an un-sintered mixture sample of CNTs (0.5 wt.%) and chromium carbide powders (*upper*), and for a laser-sintered composite sample (*lower*)

much higher than the plasma-sprayed samples by roughly more than ~65 %. It is expected that one of the likely major reasons is that the laser sintering process may yield a more significant powder coalescence and material densification than the plasma spray process. Certainly, future work is still needed to completely answer this question.

Figure 6 shows the measured indentation fracture toughness of the composite material obtained by laser sintering of the mixtures of CNTs and chromium carbide powders, and the material obtained by laser sintering of chromium carbide powders without CNTs. It can be seen that the fracture toughness for the former is ~4.51 MPa·$m^{1/2}$ while it is ~3.65 MPa·$m^{1/2}$ for the latter. Under the studied conditions, CNTs have enhanced the fracture toughness by around ~23 %. The underlying mechanism for the observed fracture toughness enhancement still requires further work to completely understand, which may be CNT pull-out, crack bridging and/or other possible mechanisms [3].

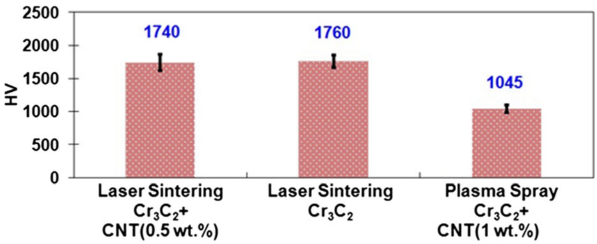

Fig. 5 (1) Hardness of composites produced by laser sintering of chromium carbide powders+CNTs (0.5 wt.%), (2) hardness of material produced by lase sintering of chromium carbide powders without CNTs, and (3) hardness of composites produced by plasma spraying of chromium carbide powders+CNTs (1 wt.%) taken from [4]

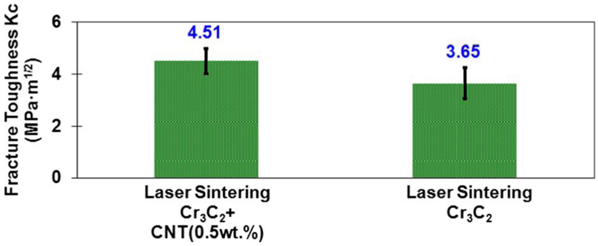

Fig. 6 Vickers indentation fracture toughness of (1) composites produced by laser sintering of chromium carbide powders+CNTs (0.5 wt.%), and (2) material produced by laser sintering of chromium carbide powders without CNTs

For the results on laser-sintered samples in Figs. 5 and 6, multiple measurements have been performed on multiple samples. It is normal that the measured hardness and fracture toughness values have certain standard deviations (as shown in the figures). However, one observation from Figs. 5 and 6 is that the mechanical property standard deviations for laser-sintered samples with CNTs are not significantly larger than the laser-sintered samples without CNTs (the samples with CNTs have a slightly larger standard deviation for hardness and a slightly smaller deviation for fracture toughness than the samples without CNTs). This indicates that for the laser-sintered samples measured for Figs. 5 and 6, the addition of CNTs has not significantly increased the inhomogeneity of mechanical properties under the experimental measurement conditions and scale.

Conclusions

Research work has been performed on the production and characterization of CNT - ceramic composites through laser sintering of mixtures of CNTs and chromium carbide powders. It has been found that under the studied conditions:

(1) CNTs can be clearly observed in SEM images of the laser-sintered composite material, which also show that the CNTs appear to be encapsulated by and bonded with the matrix material.
(2) The Raman spectrum of a CNT and chromium carbide mixture sample before sintering and the Raman spectrum of a laser-sintered composite sample suggest that the quality of CNTs has been enhanced by the laser sintering process.
(3) The performed XRD measurements do not show significant phase differences between the chromium carbide in the sintered composite and the chromium carbide in the mixtures before laser sintering.
(4) The composites obtained by laser sintering of mixtures of CNTs and chromium carbide powders have a hardness similar to the material produced by laser sintering of chromium carbide powders without CNTs, which is, however, much higher than the hardness taken from Ref. [4] for plasma-sprayed CNT- chromium carbide composites.
(5) Due to the addition of CNTs, the fracture toughness of laser-sintered composites with CNTs has been enhanced by around ~23 % compared with the material produced by laser sintering of chromium carbide powders without CNTs.

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