Laser sintering of carbon nanotube-reinforced ceramic nanocomposites

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The fabrication of carbon nanotube (CNT)-reinforced ceramic nanocomposites through laser sintering has been rarely studied, and the fabrication feasibility has been rarely tested. Laser sintering is a flexible, localized and high-precision process, which can also potentially produce coatings or parts with complicated shapes and/or spatially controlled compositions. Therefore, compared with other technologies laser sintering has its own advantages. Experimental investigations reported in this paper have confirmed the feasibility of fabricating CNT-reinforced ceramic nanocomposites through laser sintering of ceramic nanoparticles and CNTs. The studies show that laser sintering can induce the agglomeration of ceramic nanoparticles into a relatively more continuous ceramic phase, and during the sintering process CNTs are well preserved without any obvious quality degradation, and they are also bonded with the ceramic phase after laser sintering.

Keywords: laser sintering; carbon nanotube reinforcement; ceramic nanocomposite

1. Introduction

The potential energy crisis the world is facing has led to a growing need to enhance the energy efficiency of engines, such as gas turbines. The energy efficiency can be improved by increasing the working temperatures inside the engine, which may result in larger thermal stresses and hence higher mechanical property requirements on thermal barrier coating (TBC) materials. Ceramics, due to their good high-temperature performance, are very common TBC materials [1]. They are also widely used in aerospace, biomedical, automotive, and many other areas as wear or corrosion resistance coatings due to their good wear and corrosion resistance. However, ceramics often have low fracture toughness, which has seriously limited their performance and capability to meet the higher mechanical property requirements on TBC materials due to the need for higher energy efficiency of engines.

The mechanical properties of ceramics can be potentially improved by adding carbon nanotubes (CNTs) as reinforcing materials. Studies have been performed on CNT-reinforced ceramic nanocomposites [2–7] and also polymer nanocomposites [8,9].

However, research on the fabrication of CNT-reinforced ceramic nanocomposites through the laser sintering process has been rarely reported, and the fabrication feasibility

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has been rarely tested. Compared with other technologies, laser sintering has many potential advantages [10–13], such as good flexibility, localized heating, and the capability of manufacturing parts with very complicated geometries, and coatings or parts with controlled spatial distributions of material compositions. Composite fabrication through laser sintering has been studied [14], but the previously studied composites were not CNT-reinforced.

In this paper, experimental studies are reported that tested the feasibility of fabricating CNT-reinforced ceramic nanocomposite through laser sintering. The major question to answer was whether or not laser sintering can induce the agglomeration of ceramic nanoparticles into a relatively continuous ceramic phase, and produce CNT–ceramic bonding, without damaging the CNT structure or degrading its quality. The employed composite fabrication process consists of two steps: (i) paper making, i.e. manufacturing of carbon nanotube paper (CNTP), which consists of ceramic nanoparticles and CNTs; (ii) laser sintering of CNTP to fabricate ceramic nanocomposite materials. The paper-making step is required to realize a good dispersion of CNTs in ceramic nanoparticles. The fabricated nanocomposites were comprehensively characterized through scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and Raman spectroscopy.

2. Experimental procedures

Figure 1 shows a schematic diagram of the nanocomposite fabrication process, which consists of two steps: (i) paper-making to realize a good dispersion of CNTs in ceramic nanoparticles (the produced paper will be called carbon nanotube paper (CNTP)), and (ii) laser sintering of CNTP to produce the composites. The paper-making process involves four stages: (1) dispersing CNTs into water using high energy sonication; (2) dispersing ceramic nanoparticles into water by sonication; (3) mixing the two solutions together to create a uniform suspension of CNTs and ceramic nanoparticles; and (4) infiltrating the suspension through a filter paper to make a hybrid CNT/ceramic nanoparticle paper (called CNTP for simplicity). The paper-making process can realize a good dispersion of the CNTs with a controlled concentration in the composite paper. In this study, TiO$_2$ ceramic nanoparticles with an average size of around 300 nm were used in the paper-making process. Multi-walled carbon nanotubes (MWCNTs) were received from Nanolab, Inc. (length: 5–20 µm) and used as received.

Laser sintering of the CNTP was performed using a SPI G3.0 laser system, which can be operated in both the continuous mode and the pulsed mode with adjustable pulse durations. In this study, it was operated in a mode with a full pulse duration of 200 ns. The laser beam has a wavelength of 1064 nm. It is delivered and focused through a laser scan head (ScanLab, HurryScan 14) onto the surface of the CNTP that is positioned by three linear motion stages (Newport ILS 100PP) in X, Y and Z directions. The scan head has a lens with a 100 mm focal length, and the focused laser beam has a spot diameter of ~30 µm on the CNTP surface. To avoid chemical reactions with the ambient air, argon gas was applied to protect the CNTP surface during laser sintering.

The fabricated nanocomposite was characterized through high-resolution SEM, TEM, EDS, and Raman spectroscopy. The instrument (LEO Gemini 1525) used for SEM has a Schottky field emission gun for high resolution (1.5 nm at 20 kV and 3.5 nm at 1 kV). The instrument used for TEM imagining is the JEOL JEM-2100F FAST TEM, which has high brightness Schottky emitter operated at 200 kV. The Raman spectroscopy measurement was performed using a Renishaw® Ramascope with an excitation wavelength of 532 nm, and the spectra were accumulated in 120 seconds.
Figure 1. Schematic diagram of the ceramic nanocomposite fabrication process: (a) the paper-making process to produce the carbon nanotube paper (CNTP), which consists of ceramic nanoparticles and well dispersed carbon nanotubes; (b) laser sintering of CNTP to fabricate the CNT-reinforced ceramic nanocomposites.
3. Results and discussions

To test and confirm the feasibility of fabricating CNT-reinforced ceramic nanocomposites through laser sintering, there are three questions that need to be answered:

(1) Has the laser sintering process induced the agglomeration of ceramic nanoparticles into relatively continuous ceramic phase?
(2) Have the CNTs survived the sintering process?
(3) Will CNTs be bonded with the ceramic phase after laser sintering?

The above questions were answered through comprehensive experimental work by combining SEM, TEM, EDS and Raman spectroscopy techniques. SEM and TEM images of the CNTP samples before laser sintering are shown in Figures 2 and 4, respectively, whereas SEM and TEM images of laser-sintered samples are shown in Figures 3 and 5, respectively. The EDS result is given in Figure 6, and the Raman spectroscopy results are given in Figures 7–9.

3.1. Agglomeration of ceramic nanoparticles into relatively continuous ceramic phase

The SEM images in Figure 2 show that before laser sintering the TiO$_2$ nanoparticles are separated and are roughly spherical in shape. Separated nanoparticles can also be clearly observed in the TEM images in Figure 4, where the samples underwent sonication treatment before the TEM images are taken, and hence the nanotubes and nanoparticles are more separated. As shown in Figure 7a, before laser sintering three major Raman peaks are present at $\sim$240 cm$^{-1}$, $\sim$445 cm$^{-1}$ and $\sim$610 cm$^{-1}$ that originate from the TiO$_2$ nanoparticles. These Raman features are intrinsic to the TiO$_2$ nanoparticles [15].

After the CNTP sample was sintered using 1064 nm, 200 ns laser pulses at a fluence of 1.9 J/cm$^2$ per pulse, SEM images were taken in the middle of the sintered region, and are shown in the first row of Figure 3. It can be seen that no spherically shaped nanoparticles can be observed, and instead the nanoparticles agglomerate into relatively continuous ceramic phase. The sintered TiO$_2$ phase shown in Figure 3 (the first row) is also relatively dense. Similarly, in the TEM images in Figure 5, unlike Figure 4, no spherical dark region can be seen, which also indicates the agglomeration of nanoparticles in the sintering

![Figure 2. SEM images of CNTP before laser sintering (CNTP is a mixture of carbon nanotubes and TiO$_2$ nanoparticles. The images clearly show separated nanoparticles, which are not bonded with nanotubes).](image-url)
process. Finally, in the Raman spectroscopy results in Figure 7a, the peaks at ∼240 cm\(^{-1}\) and ∼610 cm\(^{-1}\) have diminished completely, while the peak at ∼445 cm\(^{-1}\) remains visible with much lower intensity. This indicates a phase change and a modified TiO\(_2\) crystal structure after laser sintering, which provides supporting evidence for the creation of a more continuous phase of TiO\(_2\).

In summary, the SEM, TEM and Raman spectroscopy results all show that the laser sintering process has induced the agglomeration of ceramic nanoparticles into a relatively more continuous ceramic phase.

3.2. Preservation of CNTs during laser sintering

A very critical issue about the fabrication of CNT-ceramic nanocomposite through laser sintering is whether or not CNTs can survive the sintering process. For the CNTP samples after laser sintering, the SEM images in Figure 3 clearly show well-preserved CNTs, which are also relatively even dispersed. CNTs can also be clearly observed in Figure 5, which is the TEM image of laser-sintered CNTP. The Raman spectroscopy results also indicate the CNTs have retained their structure after laser sintering. In Figure 7b, the presence of intact MWCNTs is supported by the intensity increase of both the G and G’ bands after sintering, while the D band intensity remains about the same. G and G’ are both intrinsic features of the MWCNT, while the D band is a disorder-induced Raman feature [16,17].
Figure 4. TEM images of CNTP samples (which are the mixtures of MWCNT and TiO$_2$ nanoparticle) before laser sintering: (a) low-magnification TEM image, scale bar: 200 nm; (b) high-magnification image, scale bar: 20 nm (the samples go through sonication treatment before the TEM images are taken).

Figure 8a shows the D over G intensity ratio, $I(D/G)$, versus laser scanning speed at different laser fluences. It can be seen that $I(D/G)$ for sintered samples is smaller than that before laser sintering. This indicates the capability of the laser light to selectively remove amorphous carbon or other impurities from the sample material. This point has also been indicated by result in Figure 8b, which shows that the D over G’ intensity ratio, $I(D/G’)$, after sintering is also obviously lower than that before sintering. The values of $I(D/G)$ and $I(D/G’)$ change with the laser scanning speed during the sintering process, and the overall trend for most of the fluences in Figure 8 is that the intensity ratios increase with the scanning speed, except that at 2.2 J/cm$^2$, the ratio decreases with increased scanning speed. Future work is needed to study a wider range of laser conditions to further clarify and understand the dependence of $I(D/G)$ and $I(D/G’)$ on laser fluence and scanning speed.

Figure 6 shows the EDS-determined element weight percentage for CNTP before and after laser sintering. It can be seen that the percentage of each element changes very little, indicating that the laser sintering process has maintained the elemental composition of the material. In particular, the carbon element has very little weight percentage drop as
No CNTs are observed at locations away from the boundary of the sintered region. (b) CNTs (bonded with the sintered region)

Sintered TiO$_2$

Figure 5. TEM images of laser-sintered CNTP samples: (a) low-magnification TEM image, scale bar: 200 nm; (b) high-magnification image, scale bar: 20 nm (Even after a long sonication treatment before the TEM images are taken, still no CNTs can be observed at locations away from the boundary of the sintered region, indicating CNTs are bonded with the latter).

compared to the Ti and O element. This indicates that during laser sintering process, laser pulses have not caused any significant preferred removal of CNTs from the CNTP sample (otherwise the carbon element weight percentage will have a big drop).

In summary, the SEM, TEM, EDS and Raman spectroscopy results show that CNTs have been well preserved during the sintering process without any obvious quality degradation or relative mass loss (as compared to the ceramic phase). The decrease of $I(D/G)$ and $I(D/G')$ after laser sintering indicates that the laser beam may even have selectively removed amorphous carbon or other impurities from the sample material.
3.3. Bonding of CNTs with ceramic phase after laser sintering

The second row in Figure 3 shows SEM images of laser-sintered CNTP, taken near the boundary of laser-sintered region. A close look at the images (the locations pointed by the arrows) shows that CNTs are tightly connected with the sintered ceramic phase without observable gap in between. This implies that certain kind of bonding should be formed.
between CNTs and the sintered ceramic phase. This point has been further confirmed by the TEM results in Figures 4 and 5. The samples underwent sonication treatment before the TEM images were taken. Figure 4 shows that before laser sintering the CNTP sample can be easily broken into separated and dispersed nanoparticles and CNTs that are everywhere in the imaging field, indicating no bonding exists among nanoparticles or between nanoparticles and CNTs. However, after laser sintering, Figure 5 shows that even after a very long sonication treatment, the TiO$_2$ phase and CNTs still remain held together, and no separated CNTs be observed at locations away from the boundary of the sintered region. This indicates CNTs are bonded with the sintered TiO$_2$ phase.
The stress-sensitive G band for CNTs has been known to downshift under uniaxial load [18], as well as upshift under hydrostatic pressure [19]. Using a pseudo-Voigt based genetic algorithm adapted from a peak assignment by Osswald et al. [20], the G band’s peak position was measured to downshift as a function of laser fluence and scanning speed, as shown in Figure 9. It is expected that this downshifting should be caused by the encapsulation of TiO₂ around the MWCNT, presenting a transfer of stress into the MWCNT structure. The stress transfer into MWCNTs implies that they should be bonded with TiO₂. For the extreme fluence values of 1.9 and 2.5 J/cm² in Figure 9, the G band peak position and the scanning speed do not have a clear linear relationship. However, for the intermediate fluence values of 1.6 and 2.2 J/cm², a clear and approximately linear relationship has been observed between the G peak position and the scanning speed.

The Raman spectra offer the possibility of quantifying the bonding force between MWCNT and TiO₂ with the stress sensitive G band, and this kind of work will be performed in the future to quantify the bonding strength and understand its dependence on laser sintering conditions.

4. Conclusions
The experimental studies reported in this paper have confirmed the feasibility of fabricating CNT-reinforced ceramic nanocomposites through laser sintering. This kind of work has been rarely reported before in literature. First, carbon nanotube paper (CNTP) is produced through sonication and infiltration processes, which consists of ceramic nanoparticles and well dispersed carbon nanotubes (CNTs). Then, the CNTP is sintered by 200 ns, 1064 nm laser pulses under the protection of argon gas to fabricate the ceramic nanocomposite.

The experimental characterizations combining SEM, TEM, EDS and Raman spectroscopy techniques show that: (1) the laser sintering process has induced the agglomeration of ceramic nanoparticles into relatively more continuous ceramic phase; (2) CNTs
have been well preserved during the sintering process without any obvious quality degradation or relative mass loss (as compared to the ceramic phase); (3) CNTs are bonded with the ceramic phase after laser sintering. Therefore, the study has confirmed the feasibility of fabricating CNT-reinforced ceramic nanocomposites through laser sintering.

It would be good in the future to fundamentally understand the laser sintering mechanisms and the CNT-ceramic bonding nature, optimize the process conditions and test/improve the mechanical properties of the sintered nanocomposite.

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