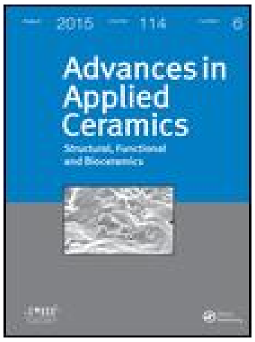

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Effects of optical absorbance with ablation characteristics in femtosecond laser irradiation of carbon reinforced Al_2O_3 composites

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The thresholds and depths of ablation of carbon [carbon nanotubes (CNTs) or graphene nanoplatelets (GNPs)] reinforced Al_2O_3 composites were compared and correlated with those of monolithic Al_2O_3 using femtosecond pulsed laser irradiation ($\lambda = 1027$ nm, $\tau_P = 380$ fs). These composites were processed using a spark plasma sintering method ($T_s = 1500°C$, $\tau_s = 10$ min and $P=40$ MPa) through which highly densified (more than 97%) composites were fabricated. The optical absorbance of each composite improved in the wavelength range from ultraviolet to near infrared. Compared with the corresponding values for monolithic Al_2O_3, the ablation thresholds of CNT/Al_2O_3 and GNP/Al_2O_3 were 50 and 75% lower respectively, and their ablation depths were two to three times deeper.

Keywords: Ceramic composites, Carbon reinforcements, Optical absorbance, Femtosecond laser, Ablation characteristics

Introduction

Carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs), which were originally discovered as byproducts of fullerene research, have been attracting increasing interest as constituents of novel materials for a wide range of applications. In particular, CNTs should be ideal for reinforcing fibres, and GNPs are also ideal for reinforcement in applications of toughened and strengthened composites, such as field emission displays, radiation sources, sensors, probes, interconnects, energy storage and conversion devices, hydrogen storage media, nanometre sized semiconductor devices and high strength conductive composites.[1,2] Thus, these carbon materials may be used for reinforcement in order to simultaneously improve the mechanical, electrical and thermal properties of metals,[3] ceramics[4,5] and polymers.[6]

Peigney *et al.*[7] reported decreased bending strength and fracture toughness in Al_2O_3 ceramic nanocomposites reinforced with multiwalled CNTs for the first time. However, Zhan *et al.*[8] successfully realised the possibility of using CNTs to significantly reinforce ceramic nanocomposites, resulting in a 194% increase in fracture toughness over that of pure alumina. Liu *et al.*[9] achieved a 30.75% increase in flexural strength and a 27.20% increase in fracture toughness in Al_2O_3 ceramic composites by adding grapheme platelets. Recently, Sikder *et al.*[10] fabricated hard sintered multiwalled CNT/Al_2O_3 nanocomposites, resulting in a yield 18% higher than that of monolithic Al_2O_3. Previous papers have focused on mechanical, electrical and thermal properties, while this paper focuses on another useful property: improved optical absorbance.

Despite the advantages of CNTs and GNPs, more extensive use in reinforced composites has been limited due to their high inherent hardness and brittleness, which combine to cause machining difficulties and high processing costs. It is thought that ultrashort pulsed laser micromachining could potentially overcome these issues because the intense laser light from an ultrashort pulsed laser can induce non-linear processes such as multiphoton absorption. This ability implies that the fine micromachining of high band gap materials like ceramics can be readily achieved with minimal thermal and mechanical defects on the substrate; accordingly, the use of ultrashort laser pulses in the structuring and drilling of ceramics has been actively researched in recent years.[11,12]

In this investigation, we fabricated monolithic Al_2O_3 and CNT reinforced Al_2O_3 (CNT/Al_2O_3) and GNP reinforced Al_2O_3 (GNP/Al_2O_3) composites using a spark plasma sintering method and investigated the optical absorbance of each bulk material over the wavelength range from ultraviolet (UV) to near infrared. Furthermore, the ablation characteristics, such as threshold and depth, were investigated as functions of pulse energy for monolithic Al_2O_3 and the CNT/Al_2O_3 and GNP/Al_2O_3 composites using femtosecond laser ablation. In this

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paper, the relationships between the ablation characteristics and optical absorbance following CNT or GNP reinforcement will be discussed.

Experimental

Preparation and characterisation of CNT/Al_2O_3 and GNP/Al_2O_3 composites

An α-alumina powder (Sumitomo Chemical, Osaka, Japan) with a purity of 99.9%, an average particle size of 500 nm and 0.1 wt-%MgO was used as a sintering aid in this work. In addition, CNTs (CNT90, Applied Carbon Nano Technology Co. Ltd, Pohang, Korea) and GNPs (M5, XG-Science, Lansing, MI, USA) were added to an Al_2O_3 matrix with 5% volume fractions for reinforcement and to increase the material properties. The composites were sintered using a spark plasma sintering method (Dr Sinter, SPS, Syntex Inc., Japan). The sintering process was conducted under a vacuum of 5 Pa. A uniaxial pressure P of 40 MPa was applied during sintering. The sintering temperature T_s was increased to 1500°C at a rate of 100°C min^{-1}, and a 10 min holding time τ_s was used during the sintering. The bulk densities of the sintered samples were measured using Archimedes' principle. The rule of mixtures was followed to calculate the theoretical densities of the composites. The optical absorbance of each composite as a function of wavelength from 200 to 1500 nm was measured using a UV–visible–near infrared spectrophotometer (V-670, JASCO, Japan) in order to cover all wavelengths commonly used in laser machining. The samples were prepared for optical absorbance measurements by spark plasma sintering under the same conditions. To measure the optical absorbances, the materials were required to be very thin so that they would be transmitted by the laser beam. The samples were cut in 50 μm using a diamond wire saw. The faces of the samples were polished to decrease the effects of surface roughness, such as scattering and reflecting. A schematic of an optical absorption enhancement mechanism involving carbon reinforcement is shown in Fig. 1. Figure 1 illustrates the van Hove singularities of CNTs. The energies between the van Hove singularities depend on the nanotubes' structure. Thus, by varying this structure, it is possible to tune the optoelectronic properties of CNTs. Such fine tuning has been experimentally demonstrated using UV illumination of polymer dispersed CNTs.[13] The new energy level between valence band and conduction band could cause optical absorption to occur more easily. To improve the reliability of the observations and accuracies of the ablation threshold and depth measurements, ablation targets with polished surfaces (R_a, <100 nm) were used.

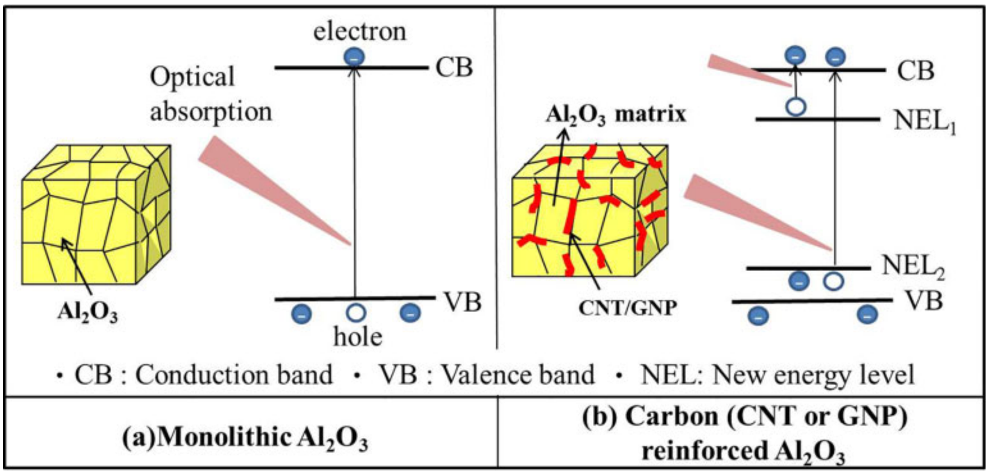
Ablation tests using femtosecond laser irradiation

The ablation tests of the monolithic Al_2O_3 and of the CNT/Al_2O_3 and GNP/Al_2O_3 composites were performed under normal atmospheric conditions using a femtosecond laser system (JenLas-D2.fs, Jenoptik, Germany; repetition rate = 100 kHz, wavelength $\lambda = 1027$ nm, pulse duration $\tau_P = 380$ fs). The laser system specifications are listed in Table 1. A Gaussian shaped and linearly polarised laser beam was used in this experiment, and a stage that could move in the X, Y and Z directions was used as part of the ablation tests in order to more suitably represent micromachining. A charge coupled device camera was installed with an objective lens inline, and the laser beam was focused using the charge coupled device camera view during femtosecond laser machining. The ablation thresholds and depths of the machined lines that formed during the scribing process were measured using a confocal scanning microscope (NS-3000, Nanoscope, Korea) because of its ability to produce three-dimensional images of thick objects. Cross-sectional views of the ablation craters were obtained using a field emission scanning electron microscope (FE-SEM, S4800, Hitachi, Japan). Each depth measurement was repeated a number of times in order to minimise measurement errors.

Results and discussion

Fabrication and characterisation of CNT/Al_2O_3 and GNP/Al_2O_3composites

The monolithic Al_2O_3 and the CNT/Al_2O_3 and GNP/Al_2O_3 composites were fabricated using a spark plasma sintering machine and were highly densified, as shown in Table 2. The relative densities of the monolithic Al_2O_3 and of the CNT/Al_2O_3 and GNP/Al_2O_3



1 Schematic of optical absorption enhancement mechanism by adding carbon reinforcements

Table 1 Specifications of femtosecond laser system

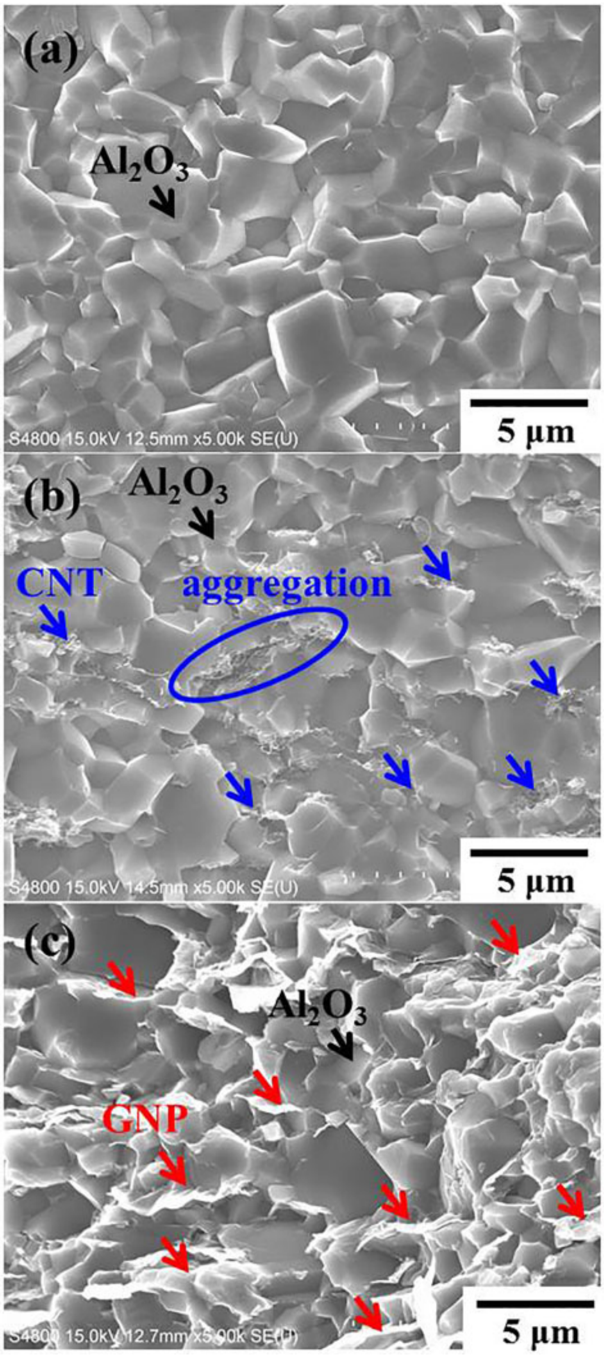
Wavelength	1027 nm
Pulse width	~380 fs
Max pulse energy	38 μJ @ 100 kHz
Beam diameter	4 mm
Company	Jenoptik, Germany
Spatial mode	TEM_{00} (M^2<1.3), Gaussian

Table 2 Material properties and ablation thresholds of monolithic Al_2O_3 and carbon (CNT or GNP) reinforced Al_2O_3 with wavelength

	Monolithic Al_2O_3	CNT/Al_2O_3	GNP/Al_2O_3
Relative density/%	99.7	97.5	98.3
Surface roughness/nm	⩽100	⩽100	⩽100
Absorbance (at 1027 nm)	0.06	0.59	0.78
Ablation threshold/μJ	2.03	1.12	0.57

composites were found to be 99.7, 97.5 and 98.3% respectively. The CNT/Al_2O_3 composite had the lowest relative density because of its aggregation in the matrix. The fracture surface is shown in Fig. 2. Figure 2*b* and *c* shows the CNTs and GNPs dispersed between Al_2O_3 grains, and as can be seen in Fig. 2*b*, aggregation of CNTs is partially evident in the CNT/Al_2O_3 composite. Homogeneous dispersion of the CNTs into the ceramic matrix is very difficult due to the hard agglomeration that occurs during the process of synthesising the CNTs into the matrix. The presence of aggregation is believed to affect the mechanical properties of composite materials. Otherwise, as shown in Fig. 2*c*, the GNPs are well dispersed in the matrix, which could improve the optical absorbance and other properties, such as the mechanical, electrical and thermal properties.[14,15]

The variations of the absorbances of each of the composites with wavelength are shown in Fig. 3. From this figure, it is apparent that the absorbance tends to increase with increasing wavelength and that the GNP and CNT reinforcements caused absorbance increases, which may be due to a new energy level between the valence and conduction bands.[16] In particular, the absorbances of themonolithic Al_2O_3 and of the CNT/Al_2O_3 and GNP/Al_2O_3 composites were found to be 0.06, 0.59 and 0.78 respectively, at a wavelength of 1027 nm (the installed laser wavelength). It is thought that monolithic Al_2O_3 has a high band gap but that GNP and CNT reinforced Al_2O_3 could have a new energy level that would facilitate laser beam absorption and would also make multiphoton absorption more prevalent than in the case of monolithic Al_2O_3.



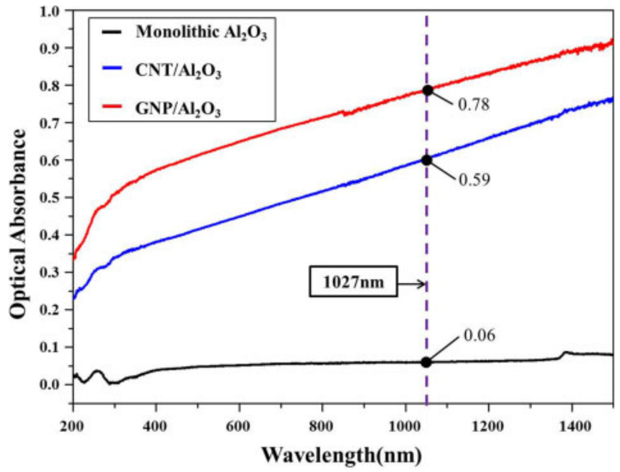
a monolithic Al_2O_3; *b* CNT/Al_2O_3composite; *c* GNP/Al_2O_3 composite

2 Images (FE-SEM) of fracture surfaces

Ablation characteristics during femtosecond laser irradiation

Ablation threshold pulse energy

In order to determine the ablation thresholds for the monolithic Al_2O_3 and for the CNT/Al_2O_3 and GNP/Al_2O_3 composites, ablation tests were conducted at various laser pulse energies. The ablated surfaces of each of the composites at the threshold pulse energy are shown in Fig. 4. For these measurements, the crater shapes were approximated as circular, though the real craters did not appear fully circular due to cracking and exfoliation. As shown in Table 2, the ablation threshold pulse energies E_P of the monolithic Al_2O_3, CNT/Al_2O_3 and GNP/Al_2O_3 composites were determined to be 2.03, 1.12 and 0.57 μJ respectively. It is assumed that the reinforcements increased the free electron densities, that the composites became opaque and that large percentages of the absorbed laser energies were deposited. Hence, it can be assumed that the threshold damage fluencies are the minimum fluencies that yield the critical density. Similarly, the ablation depth is considered to be the maximum depth at which the free electron density is equal to the critical density.[16] As shown in Fig. 3, the optical absorbances of the



3 Variation of optical absorbance for monolithic Al_2O_3 and for CNT/Al_2O_3 and GNP/Al_2O_3 composites with wavelength

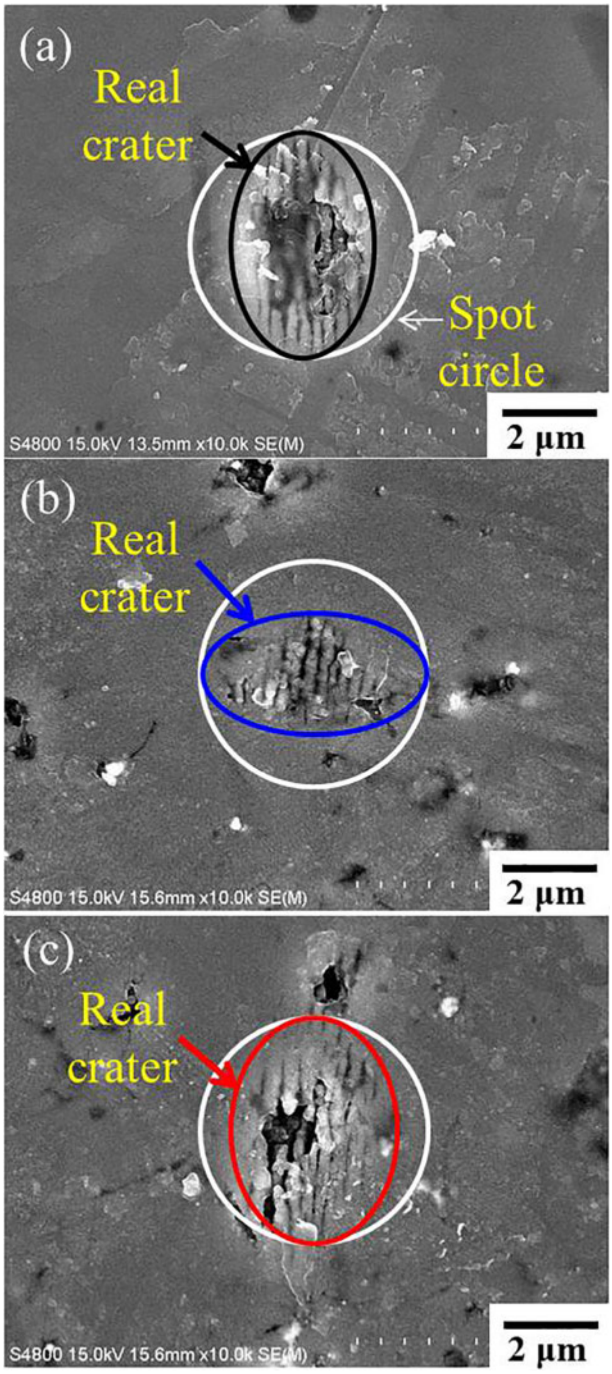
composites are significantly different from each other. It is therefore expected that the relatively higher optical absorbance of the GNP/Al_2O_3composite will result in a lower ablation threshold.

Ablation depth with pulse energy

The ablation depths and profiles of the monolithic Al_2O_3 and of the CNT/Al_2O_3 and GNP/Al_2O_3 composites at the maximum pulse energy (39.8 μJ) are shown in Fig. 5. These were measured using a confocal scanning microscope, and the greatest depth for each crater was determined using a ×50 objective lens. The measurement error is included so that the overall measurement uncertainty is ∼10% due to positioning uncertainties that occurred during target installation and removal. As shown in Fig. 5, the ablation depths of the monolithic Al_2O_3 and of the CNT/Al_2O_3 and GNP/Al_2O_3 composites are ∼2.4, 4.3 and 5.9 μm respectively at the maximum pulse energy. As shown in Fig. 5, the ablation depth of the GNP/Al_2O_3 composite was three times greater than that of the monolithic Al_2O_3. The relationships between ablation depth and laser pulse energy for the CNT/Al_2O_3 and GNP/Al_2O_3 composites are plotted, and cross-sectional FE-SEM images of the GNP/Al_2O_3 composite are shown in Fig. 6. In this graph, all of the ablation depths of the composites increase with increasing pulse energy. These results can be understood using an expression such as[17]

$$d_{ev} = \frac{l_s}{2} \ln \frac{F}{F_{th}} \quad \left(F = \frac{E_p}{A}\right) \tag{1}$$

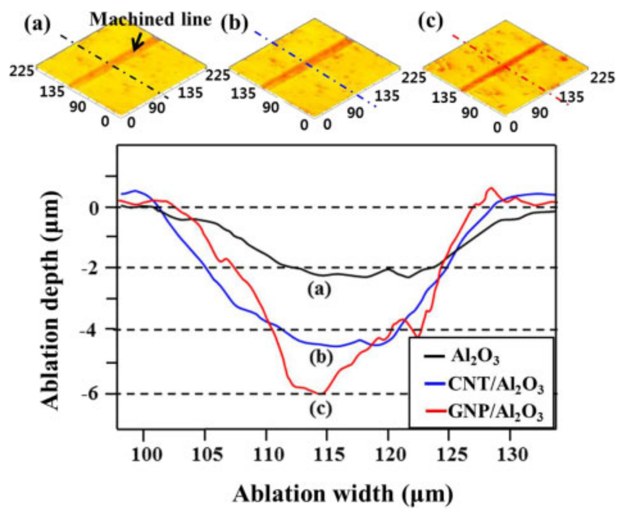
where l_s represents the electron heat penetration depth, F is the laser fluence, F_{th} is the laser fluence at threshold, E_p is the incident laser pulse energy and A is the spot size. For the different experiments, the spot size was constant, and the effects of l_s were not considered to differ significantly because the base materials were the same. Thus, based on the lower ablation threshold pulse energies of the CNT/Al_2O_3 (1.12 μJ) and GNP/Al_2O_3 (0.57 μJ) composites, the ablation depths increased two to three times compared to that of the monolithic



a monolithic Al_2O_3; *b* CNT/Al_2O_3composite; *c* GNP/Al_2O_3 composite

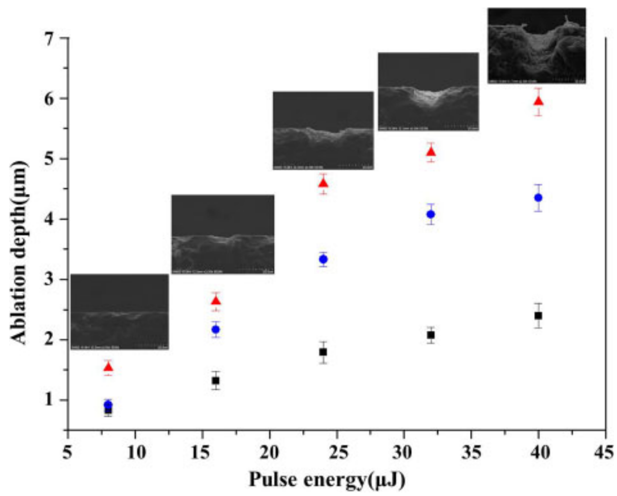
4 Images (FE-SEM) of ablated surface at threshold pulse energy

Al_2O_3 material. Optical microscopy images of the GNP/Al_2O_3 composite at various scan speeds, which is one of the parameters that most influences the thermal effects in laser micromachining, are shown in Fig. 7. In Fig. 7*a*, the machined line has no heat affected zone in which the composites experience thermal effects. In contrast to conventional laser processing, the minimal structure size that is achievable using femtosecond laser pulses is not limited by thermal or mechanical effects such as burr formation, melting or cracking.[18] Thus, these results are expected to apply to ultramicromachining.

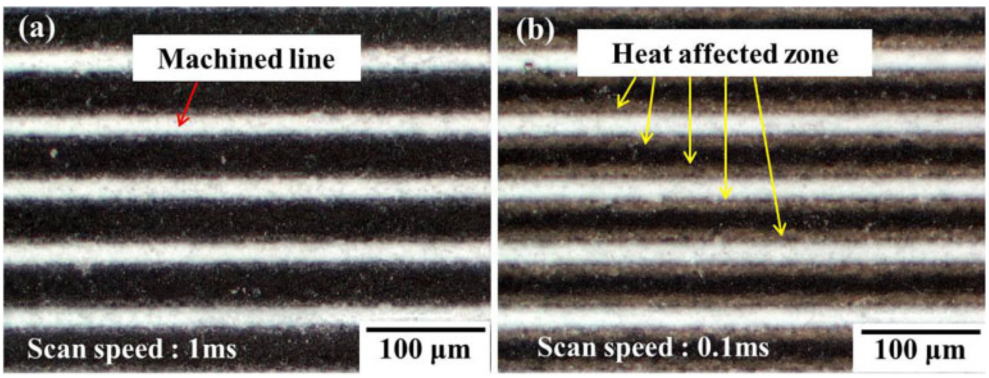


a monolithic Al_2O_3; *b* CNT/Al_2O_3composite; *c* GNP/Al_2O_3composite; *d* depth profile

5 Depth profile produced for laser pulses (E_p = 40 μJ)



6 Relationship between ablation depth and laser pulse energy for monolithic Al_2O_3 and for CNT/Al_2O_3 and GNP/Al_2O_3 composites



7 Optical images showing rear surface damage of GNP/Al_2O_3 after scribing process with scan speed by femtosecond laser irradiation of *a* 1 ms and *b* 0.1 ms

Conclusions

The thresholds, ablation depths and optical absorbance improvements in carbon reinforced Al_2O_3 composites were investigated. CNT/Al_2O_3 and GNP/Al_2O_3 composites were fabricated with high densities (more than 97%) by the spark plasma sintering method; these reinforcements caused higher optical absorbances. The optical absorbances of the CNT/Al_2O_3 and GNP/Al_2O_3 composites and of the monolithic Al_2O_3 were found to be 0.78, 0.56 and 0.06 respectively, at a wavelength of 1027 nm. In the ablation threshold measurement tests, the ablation thresholds of the CNT/Al_2O_3 and GNP/Al_2O_3 composites were 50 and 75% lower respectively than that of the monolithic Al_2O_3. The lower ablation thresholds resulted from the ablation depths of the CNT/Al_2O_3 and GNP/Al_2O_3 composites being two and three times deeper respectively than that of monolithic Al_2O_3.

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