Boron carbide particle fabrication by pulsed laser irradiation of boron particle dispersed in organic solvent with various wavelengths

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B₄C spherical particles were fabricated by laser irradiation at various wavelengths (355, 532, and 1064 nm) of B dispersed in organic solvents. Obtained B₄C yields were 78, 90, and 84% in ethanol and 68, 82 and 65% in ethyl acetate by irradiation at 355, 532 and 1064 nm. The highest B₄C yield was obtained at 532 nm in each solvent. Important factors for large B₄C yield were considered to be laser irradiation at long wavelength and large absorbance.

Key words: laser processing, boron carbide, nanoparticles

1. INTRODUCTION

Boron carbide (B₄C) is widely used for abrasive material in polishing and grinding media, and ideal control and shielding media in nuclear industry, due to the extreme hardness and large neutron absorption cross-section of ¹⁰B. Especially B₄C particle is expected for boron neutron capture therapy (BNCT) agent application [1,2]. BNCT is based on tumor destruction by α particles produced from nuclear division of ¹⁰B ingested in the tumor cells [3,4]. The energy of the released α particle is deposited within 10 μ m of the site of neutron capture in tissue, resulting in the selective destruction of tumor cells of equivalent size.

Boron carbide can typically be produced by carbothermal reduction of boric acid or boron oxide at temperature above 1000 °C [5,6]. However, obtained products are generally contaminated with carbon compounds. Moreover, these products are ordinarily large grains in micrometer size, and consequently need a further milling process, which possibly contaminates the products from the grinding media, to produce small particles [6]. Chemical vapor deposition (CVD) is also employed for boron carbide particle fabrication, although BCl₃ and borane gases with strong toxicity have to be used as a boron source [7]. *closo*-C₂B₁₀H₂ (dicarbo-closo-decaborane(12)) is also a raw material for B₄C fabrication in CVD method [8], although *closo*-C₂B₁₀H₂ is generally very expensive. Therefore, a simple, harmless, and low-cost technique for the preparation of highly pure B₄C particles is required.

We have reported B₄C particle fabrication by laser irradiation of B powder dispersed in liquid phase under atmospheric pressure and room temperature [9]. The technique of laser irradiation onto dispersed powder or a plate placed in liquid has been attractively investigated to fabricate small particles. Various particles prepared by this technique have already been reported for noble metal and metal oxide [10-13]. This technique has several advantages over conventional nanoparticle

preparation in liquid phase [9,14,15]; (1) highly pure nanoparticles with less use of surfactant molecules mostly toxic in biological system, (2) crystallized nanoparticle formation due to the transient high-temperature process induced by pulsed laser irradiation, and (3) fabrication of particles that are difficult to be chemically processed in liquid. In this paper, we report the effect of irradiation laser wavelength on the yield of obtained B₄C particles. Because production yield increase is generally an important challenge in laser materials processing, this study may be helpful for BNCT agent application of B₄C particle produced by this technique.

2. EXPERIMENTAL

Boron powder (99.995%, Aldrich Chemical Company, Inc.) of 0.24 mg was dispersed in 6 ml organic solvent, ethanol (99.5%, Wako Pure chemical Industries, Ltd.) or ethyl acetate (99.5%, Wako Pure chemical Industries, Ltd.), in a glass vessel. The B powder in organic solvent was then irradiated for 180 min at the wavelength of 355, 532, or 1064 nm from Nd:YAG (yttrium aluminum garnet) laser operated at 10 Hz with 1.5 J cm⁻² with a pulse width of 7 ns. The laser beam was focused 2 mm below the suspension surface using a lens with the focal length of 50 mm. The suspension was agitated using a magnetic stirrer during irradiation. The particles obtained by laser irradiation of B in organic solvent were treated with HNO₃ by the following procedures to remove unreacted raw B and by-product H₃BO₃. First, organic solvent was completely evaporated using a centrifugal evaporator and the obtained particles were dispersed in 6.2 M HNO₃ for 24 h. Next, B and H₃BO₃ were completely dissolved in HNO₃, whereas B₄C particles remained undissolved. After the dissolution process, B₄C particles were separated from the supernatant by centrifugation. The B concentration of the supernatant was then analyzed by inductively coupled plasma optical emission spectrometry

(ICP-OES) measurement for B_4C yield evaluation. At the same time, collected B_4C particles were repeatedly rinsed with de-ionized water by centrifugation to remove HNO_3 . The as-prepared suspension and suspension after the HNO_3 treatment were dropped onto Si substrate and dried in air for x-ray powder diffraction analysis (XRD) (Rigaku RAD-C system) with $Cu\ K\alpha$ radiation. Morphology observation of the particles was performed by a field emission scanning electron microscope (SEM) (Hitachi S4800). The particles treated with HNO_3 were also mounted onto a carbon-coated grid for transmission electron microscope (TEM) (JEOL JEM 2010) observation.

Absorbance of B powder dispersed in organic solvent was evaluated by measuring optical transmittance spectra of sufficiently diluted suspension (7.9×10^{-4} M) to suppress multiple scattering effect.

3. RESULTS AND DISCUSSION

Raw B particles and particles obtained by laser irradiation in ethanol at various wavelengths and subsequent HNO_3 treatment to eliminate by-product were observed by SEM measurement (Fig. 1). Connected irregular grains 50 to 100 nm in size were observed in particles before irradiation (Fig. 1(a)). In contrast, spherical particles 50 to 400 nm in diameter were formed by laser irradiation at all wavelengths we examined (Figs. 1(b)-(d)). Similar spherical particles were also obtained by laser irradiation at all wavelengths in ethyl acetate. The spherical morphology of the particles suggested that the raw B grains were melted by laser heating. Absorbed photon energy E_{abs} ($J\ mol^{-1}\ pulse^{-1}$) of irradiated particles in the region between the suspension surface and $1\ \mu m$ below the surface was calculated by the equation [16],

$$E_{abs} = \frac{I(1 - 10^{-A})}{C_B l_0}$$

where I , A , C_B , and l_0 are the laser fluence ($1.5\ J\ cm^{-2}\ pulse^{-1}$), absorbance at each wavelength, atomic mole number of B per unit volume in suspension ($3.7 \times 10^{-6}\ mol\ cm^{-3}$), and the optical path ($1 \times 10^{-4}\ cm$). The absorbance A in the suspension with $1\ \mu m$ optical path length was estimated by the Lambert-Beer equation using the absorbance measured from diluted suspension, and listed in Table I. E_{abs} at each wavelength in a solvent was also evaluated and demonstrated in Table I. Since the required energy for B fusion was calculated as $4.5 \times 10^5\ J\ mol^{-1}$ based on the method in Ref. 16, the estimated E_{abs} in any wavelength and solvent were sufficient to melt the B particles by laser irradiation.

The XRD patterns of B particles before and after laser

Fig. 1 SEM images of particles before and after laser irradiation in ethanol. (a) B particles before laser irradiation. Particles irradiated with (b) 355 nm, (c) 532 nm, and (d) 1064 nm, and subsequent HNO_3 treatment.

irradiation with 532 nm in ethyl acetate without subsequent HNO_3 treatment are presented in Fig. 2. Boron particles before laser irradiation were amorphous (Fig. 2(a)). In contrast, B_4C peaks and marginal H_3BO_3 peak were observed in particles obtained after laser irradiation with 532 nm in ethyl acetate (Fig. 2(b)), indicating that B_4C crystals and slight H_3BO_3 were formed by laser irradiation. The B_4C peaks were also observed in particles even after the HNO_3 treatment. Similar results were obtained by irradiation with any

Fig. 2 X-ray powder diffraction spectra of particles (a) before and (b) after laser irradiation with 532 nm in ethyl acetate.

Table I. Measured absorbance, estimated A and E_{abs} , and B_4C yield.

	355 nm		532 nm		1064 nm	
	Ethanol	Ethyl acetate	Ethanol	Ethyl acetate	Ethanol	Ethyl acetate
Measured absorbance	0.50	0.32	0.47	0.32	0.17	0.15
Estimated A	2.3×10^{-4}	1.5×10^{-4}	2.2×10^{-4}	1.5×10^{-4}	8.0×10^{-5}	7.1×10^{-5}
E_{abs} ($J\ mol^{-1}\ pulse^{-1}$)	2.2×10^6	1.4×10^6	2.0×10^6	1.4×10^6	7.4×10^5	6.6×10^5
B_4C yield (%)	78	68	90	82	84	65

wavelength and in both solvents. B_4C formation process was considered to proceed as follows. The B particles irradiated with laser absorbed photon energy, and formed B droplets by melting. Atomic C was formed from thermal decomposition of solvent molecules (ethanol or ethyl acetate) surrounding melted B with extremely high temperature or direct breakdown of these solvent molecule by laser energy. This atomic C probably dissolved into melted B, and finally B_4C formed after cooling.

B_4C yields obtained at each wavelength in solvent were displayed in Table 1. The highest yields were obtained by irradiation at 532 nm in both solvents. Surprisingly B_4C yields at 1064 nm were comparable to or over those at 355 nm even with low absorbance at 1064 nm. Figure 3 shows relationship between B_4C yield divided by absorbance and laser wavelength. The B_4C yield per absorbance increased with irradiation laser wavelength.

Fig. 3 Relationship between B_4C yield divided by absorbance and laser wavelength.

This result suggests that irradiation of laser light with longer wavelength is advantageous to B_4C production when optical absorption energy is the same in the wavelength range we tested. However, larger B_4C yield at 532 nm than that at 1064 nm was mainly due to the large absorbance at 532 nm. Therefore, we might be able to find optimal laser wavelength by using laser with different wavelength for large B_4C yield. However, further investigation is necessary to approach the large B_4C yield.

4. CONCLUSION

In conclusion, spherical B_4C particles were obtained by laser irradiation at various wavelengths (355, 532, or 1064 nm) of B dispersed in ethanol or ethyl acetate. Both the laser irradiation at long wavelength and the large absorbance were important for quantity synthesis of the B_4C particle. The highest B_4C yields (90 and 82% in ethanol and ethyl acetate) were obtained by laser irradiation at 532 nm in experimented wavelengths.

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